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Rendering complex colour inside 3D printed foods

**A thesis presented in partial fulfilment of the requirements for the degree of
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Sandra Kim

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Abstract

Three-dimensional (3D) printing refers to a group of digitally controlled, additive manufacturing technologies increasingly used to fabricate customised objects from a range of possible materials, including food ingredients, using a digital image file representing the object. A novel variation on 3D *food* printing is being developed to customise the appearance of foods with an embedded 3D colour image by the selective blending of primary colorants. This capability is beyond what is needed usually for the coloration of bulk, single food matrices.

In this thesis, non-food techniques of colorimetric matching (used in computer match prediction) and colour gamut mapping (from cross-media colour reproduction), were investigated as potential methods for dye recipe computation by the new 3D colour food printer. The aim was to develop a model for transforming image RGB data to dye recipe data, taking into account the variable effects of food properties. The two techniques were applied to the problem of matching a set of standard tile colours using a set of primary colorants in model food substrates. Kubelka-Munk (K-M) blending equations underlying both techniques were developed for blends of Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) food dyes when added to a microwave-baked cake and to four variants of a wheat starch gel. Validation of the model for the cake blends was shown by $\Delta E^*_{ab,10}$ differences between computed and measured $L^*_{10}a^*_{10}b^*_{10}$ colours falling within range of a visually acceptable match (three $\Delta E^*_{ab,10}$ units). For some of the gel blends, the $\Delta E^*_{ab,10}$ differences reached five units.

Dye recipes computed by a modified colorimetric matching algorithm to match target tile colours with cake colours at times called for negative quantities, or totals that exceeded the legal limits for foods containing dyes, indicating that the target colour was outside the range (gamut) of the cake-dye system. In these recipes, individual negative dye quantities were increased to zero, and totals scaled back to within the legal limit, retaining relative dye proportions. This resulted in close differences between tile and cake before scaling (with computed $\Delta E^*_{ab,10}$ values of less than three units for as many as eight of the twelve target colours) becoming much larger

after scaling (up to $39 \Delta E^*_{ab,10}$ units), though visual inspection of the colour pairs suggested that the matches might be closer.

The gamut of perceived colours from a coloured food is not only constrained by legal restrictions on dye addition, but dependent on the properties of the food itself, such as its background colour (seldom white) and the light-scattering effects of surface texture. Compared with colour images, foods are likely to have a more limited colour gamut, the size of which is expected to vary with changes in formulation and processing. Gamut mapping techniques were used to investigate the extent to which the target tile colours themselves needed to be scaled back before matching solutions and corresponding dye recipes could be computed. Using four samples of the gel that differed only in their level of (artificial) browning, including white, the impact of browning on the colour gamut was determined. Using the cake, solutions from gamut mapping were compared with those from colorimetric matching.

A gamut of discrete colours is treated as a continuous volume in colour space. In the absence of a published gamut calculation for coloured foods, a technique was developed to compute a mesh of points on the colour gamut boundary. Boundary colours were computed using dye blends not exceeding the legal limit, and spaced such that $\Delta E^*_{ab,10}$ did not exceed three units. This method was applied to the white (non-textured) gel containing dye blends, to generate a ‘base’ gamut. The absorption behaviour of each dye was found to be largely consistent among the white and browned gels which enabled quick computation of colour gamuts for the brown gels by substituting the absorption spectrum of a brown gel for that of the white in the K-M equation. The colour gamut was found to decrease in size and to shift position with increased gel browning. The dye blends that were used to compute the colour gamut boundary for the whitened gel were combined with the absorption spectrum for the cake to compute the gamut boundary for the cake colours. All colour gamuts were specific to the standard D65 illuminant and 10 degree standard observer.

In the investigation of the effects of browning, colour gamut mapping began with the initial replacement of each tile colour with a colour from the white gel gamut. All colours were replaced gradually by a darker, and often less chromatic, colour, as the level of browning in the gel was increased. As a result of the reduction in gamut size with increased gel browning, the difference between tile colours and their replacement targets in each of the reduced gamuts was smaller for tile colours having ‘brown’ characteristics (such as Orange, Red and Yellow) than they were for blue-, pink- and green- coloured tiles. Larger increases in total dye quantity with increased gel browning were needed for the latter group of colours than for the former. For most colours an increase in the relative proportion of the darkest dye in the recipe was also needed. The actual dye quantities computed for each replacement colour depended on the availability of mesh points in the region of colour space in which the tile was located.

Colour gamut mapping required a heavier computational load than the colorimetric matching technique to provide solutions for tile colours in the cake-dye gamut. Although not always giving solutions in the same angular region of colour space as the tile colours, colorimetric matching was able to produce similar $\Delta E^*_{ab,10}$ differences between tile colour and best cake match as did colour gamut mapping, for not necessarily more or less total dye.

Two forms of a generalised algorithm are proposed for the computation of dye recipes by the 3D colour food printer. One algorithm is modelled on a workflow for cross-media colour reproduction. A series of transformations that account progressively for the effect of individual characteristics of the food printing substrate on the achievable gamut from dye blends is incorporated into the main series of transformations that transcribes RGB image data to dye recipe data. In the other algorithm, modelled on colorimetric matching, it is the progressive effect of each individual characteristic on the light-absorption characteristics of the un-dyed food printing substrate that is accounted for, and incorporated into the main matching workflow.

Preface

This thesis is written in the style of (but not formally complying with) a submission based on publications, as described in the Handbook for Doctoral Study, Doctoral Research Committee, Massey University, Version 7, January 2011; each chapter following the Literature Review and preceding the final Overall Discussion is formatted as an extended research paper. Within research Chapters Four, Five and Six, the methods and results are described and discussed for each stage of the work, rather than in separate Methods and Results sections for the entire body of work. All research chapters (Chapters Four to Seven) have their own Introduction and General Discussion sections. Appendices follow each of these chapters. Due to the format of the thesis some of the detail that is covered in the Literature Review is repeated in the remaining chapters, which are presented in chronological order.

A shorter form of Chapter Four was published as an original research paper in the Journal of Food Science (Kim *et al.*, 2012). A copy is not included here. It is intended to use other chapters as the basis for future manuscripts.

Unless stated otherwise, the figures in this thesis are the work of the author.

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Chapter One: Introduction to 3D colour food printing

The concept of personalised or customised foods is one of foods produced to individual specifications for selected characteristics. Taste and flavor, convenience, and increasingly, nutritional functionality, are major considerations. The Innovative Food Solutions research platform of the Riddet Institute Future Foods programme is focused on the development of ‘personalised, high-quality food products’ based on novel products and concepts. One such concept, POSIFoods™, has been patented (Boland *et al.*, 2010), for point-of-sale individualised foods linking personalised nutrition with convenience and sensory preferences.

A follow-up concept being developed within the research platform is a new version of three-dimensional (3D) printed foods. Like its non-food counterpart, 3D food printing is designed to build objects in 3D, layer-by-layer, and differs from mass production methods in that objects can be produced on an ‘as-needs’ basis. 3D printing is a process that can provide considerable design freedom. Currently, 3D food printers range from concepts to prototypes to open-source or retail units. Printers differ also in the outputs offered, which range from new and unusual combinations of ingredients and new forms (a feature mainly of concepts), to more conventional food items which are printable (by extrusion) *per se* (such as chocolate), or have been modified to be printable (such as cookie dough, and meat and seafood pastes) (Lipton *et al.*, 2010), or are printable once ingredients have been reconstituted from powders (such as pizzas for long-distance space travel) (Souppouris, 2013).

The new 3D printer is being designed to offer outputs that are fully customised, in that they meet user specifications for shape, texture, flavour, nutrition and appearance. A raw food composition is rapidly formed then cooked into a solid matrix in a self-contained unit in which formation and cooking both take place. Outputs may not necessarily resemble conventional foods. Attention is being given to understanding the mechanisms of structure formation as a function of composition. This should enable the prediction of the likely textural outcomes when

users select ingredients to meet nutritional and sensory requirements. As well, the same compositions need to be extrudable in their raw state.

The way in which food appearance will be customised is a particularly novel aspect of the printer; the printer will have the capability to render a colour image or design in 3D within the food matrix. Each colour element of the image or design will be reproduced by the selective blending of primary food dyes. Dye blends will be positioned in the raw food composition to create a food comprised of 3D colour voxels (volume elements) upon cooking. This aspect of the new printer concept speaks to the role that coloration already plays in making foods attractive, but at a finer level of detail and control; it is also an advance on foods coloured manually in 3D and on the printing of colour images and designs on to food surfaces. Existing 3D food printing concepts either do not offer a coloration option, or if one is available, the number and types of colorants needed is not given, nor are the details of methods that are needed to compute the required quantities (Yang *et al.*, 2001; Inspix, 2014).

Developing the concept poses numerous technical challenges. The behaviours of (potentially a range of) matrix and colorant ingredients, and their interactions, under storage, forming and cooking conditions need to be understood so that structure setting and coloration can be a predictable and controllable process. Colour reproduction capability needs to be fast, built-in, and sensitive to changes in food matrix formulation in order to calculate the required quantities of colorants, which calls for a different approach than what is usual for food coloration. Because foods are hugely diverse in their physical and chemical characteristics, and in their processing, exact shades can be difficult to predict and colour blends need to be tested in the intended food application. Most solutions are based on visual assessment and provided by experienced colour formulators. Other considerations specific to the food printer, all of which will have an impact on the overall visual effect, include: controlling the diffusion of colorants within the matrix; the partitioning of colorants between matrix elements; expansion of the matrix (if it cooks to a solid foam structure); the background colour of the matrix; the

contribution of surface texture to light reflectance; the extent to which colour image data can be transcribed into colorant quantity data.

Automation of the coloration process may be possible using techniques from other industries such as computer match prediction used for paint, textiles, plastics and ceramics, and cross-media (e.g. screen to print) colour reproduction. Computer matching prediction algorithms draw on a database containing spectral information on colorants and substrates to select, quickly and accurately, the colorants and their quantities needed in a substrate to match target colours. In contrast to the food industry, industries using computer match prediction have high requirements for matching precision, and cater for a smaller range of well-defined substrates. The techniques seem not yet to have been adopted by the food industry, as a similar approach to food coloration would involve considerable time, effort and cost to develop relevant databases. However, as speed and automation are necessary for a 3D food printer, the applicability of computer match prediction to food systems needs to be investigated. An impediment to the adoption of cross-media colour reproduction techniques for food applications is, again, the complex nature of foods. In the transcribing of colour data from one medium (e.g. monitor display) to another (e.g. print) differences in the range of colours achievable in each medium is accounted for; if the second medium is a customisable food substrate, the range of colours possible from colorant addition is expected to be much more variable.

This thesis is focused on the development of a predictive colour matching toolbox for use by the new 3D food printer. This work is separate to the development of printer hardware and software, and of formulations for the food substrate, and to investigations of the rheological properties of the raw substrate and of colorant-substrate mixing, which are the subjects of other student theses in the research programme. The following Literature Review examines the novelty of the 3D colour food printing concept, the requirements for 3D colour food printing and to what extent existing coloration methods, both food and non-food, can meet these requirements. This leads to the aims and objectives of the thesis.

Chapter Two: Literature Review, Part 1 – Principles of colour and coloration

2.1. Scope of this Review

The purpose of this Review is to survey and examine existing methods and technologies relevant to the goal of developing a predictive coloration algorithm for a novel 3D colour food printer. The printer is being designed to produce customised foods within which complex colour images or designs are rendered in 3D, and for which the dye recipes needed for each voxel of colour are to be computed by the algorithm. This review will be (necessarily) wide-ranging in the topics that it covers, and may even be unique in bringing together relevant knowledge from the food and non-food areas in a way that has not been needed before.

Due to the need for digitally-controlled food coloration, this review encompasses *both* automated processes such as colour image reproduction and computer colour matching *and* currently used food coloration techniques. It also covers instrument-based methods for evaluating reproductions, and their relationship to visual assessments. These topics are the subject of **Part 1** of this Review (Thesis Chapter Two). As much of the theory and principles underlying these methods is already well covered in the literature, in a number of places this Review takes the form of summaries referencing key texts and key authors in their respective areas. Specific details of instrumentation are not included. Examples of applications are predominantly those containing synthetic colorants, but some reference to natural pigments is made, where useful. **Part 2** of the Review (Thesis Chapter Three), examines the novelty of the 3D colour food printing concept by exploring the current state of the customisation-3D printing-3D coloration ‘space’, and investigates in detail the properties of a food system which could be an ideal model substrate for the printer. Customised coloration requires an understanding of how the properties of materials impact coloration and how these effects can modelled and predicted; this is **covered in both Part 1** for food and non-food examples **and in Part 2** for an ideal food printing substrate. Finally, the **conclusions** from this Review aim to partner

coloration approaches (Part 1) with printer and substrate specifications (Part 2) in the form of a required experimental approach, and lead to the aims and objectives of the thesis.

2.2. Colour and Appearance

The sensation of colour occurs when light reaching an object is modified by the object and is then detected and processed by the eye and the brain, or human visual system. It follows that the sensation is very dependent on the properties of the light source, the material of the object and the observer (McClements, 2005), and that “colour exists only in the mind of the viewer” (Berns, 2000). This first section of the review provides an overview of these properties and how they contribute to perceptions of colour and appearance. The effects of light and object are considered together as the *stimulus*.

2.2.1. The stimulus: light and object

Colour and appearance, from the point of view of the stimulus, is due to the different directions in which light travels after it encounters the boundary between two media of differing refractive index, and the passage, directional changes and loss of light within the second medium. These phenomena are described below, according to surface effects (reflection and refraction) and subsurface effects (transmission, absorption and scatter), and illustrated later in Figure 2.3. Their contributions to various appearance attributes are given later in Table 2.1. For illustrative purposes the following descriptions use the examples of air and object as the first and second medium respectively.

2.2.1.1. Light and sources of light

Light is a visible form of electromagnetic radiation or energy. Within the electromagnetic spectrum, the visible spectrum occupies a relatively narrow region, from about 380nm to about 780nm (Berns, 2000), in between the shorter wavelength (higher frequency) gamma-ray, X-ray and ultraviolet regions, and the longer wavelength (shorter frequency) infrared, microwave and radio wave regions (Figure 2.1). Within the visible spectrum, light of different colours is produced by electromagnetic energy of different wavelengths (Figure 2.1), and collectively

energy of all wavelengths is perceived as white light. Sources of white or near-white light include the sun, filament bulbs and fluorescent lamps (Berns, 2000). Light sources are represented by their *spectral power distribution*, the spectrum of intensity as a function of wavelength (Berns, 2000; McClements, 2005). More specifically, intensity is expressed in terms of *relative power*, the power relative to that at 560nm; distributions are normalised with power at 560nm set to unity (Berns, 2000).

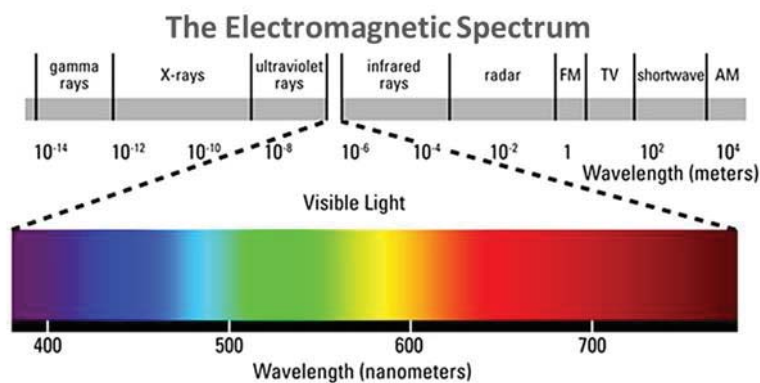


Figure 2.1 The Electromagnetic Spectrum (PhotovoltaicLightingGroup, 2013)

2.2.1.2. Refractive index

The difference in refractive index between two media contributes to the changes in the direction of light travel, both at the surface(s) of the object, and within the object. The **refractive index** of a material is equal to the speed of light in air, divided by the speed of light in the material; therefore the refractive index of air is (very close) to unity (Berns, 2000), and that of many common materials is near 1.5 (Berns, 2000). Effects other than refractive index differences also make a contribution to directional changes, as will be described below.

2.2.1.3. Reflection

At the surface of the object, a small amount of the incident light will be reflected back into the air. *Reflectance* is the ratio of reflected to incident light under a given set of conditions (Berns, 2000). The proportion of reflected light increases as the difference in refractive index between the two media increases (McClements, 2005), and as the **incidence angle**, the angle at which

light reaches the surface of the object, increases above 30° (Bridgeman, 1987). To give a general indication of the amount of light that can be reflected, 4% of incident light is reflected from the (smooth) surface of an object with a refractive index of 1.5, if the light hits the surface at **normal incidence** (i.e. perpendicular to the surface, at 0°) (Bridgeman, 1987; Berns, 2000). Reflected light is either **specular** or **diffuse**, depending on surface topography (McClements, 2005). ‘Specular’ refers to the mirror-like reflections from smooth surfaces; the angle of reflection and the angle of incidence (to the normal) are equal (Berns, 2000; McClements, 2005), and the reflected light is concentrated within a narrow region at this angle when specular reflectance is high (Bridgeman, 1987). The reflection of incident light in many different directions from rough surfaces, or from beneath smooth surfaces, is referred to as ‘diffuse’. Reflectance from objects is typically a combination of the two types (McClements, 2005). Using an appropriate measurement geometry, reflectance can be measured to either include or exclude specular reflections (‘SCI’ and ‘SCE’ modes respectively).

2.2.1.4. Refraction

Any light hitting the object at normal incidence that is not reflected at the surface continues in this direction as it enters the sample, while any light hitting the object at an angle that is not reflected changes direction as it enters the sample. The latter change in direction is referred to as **refraction**, and indicated by the **angle of refraction** (relative to the normal). The angle of refraction is not necessarily the same as the incidence angle; the degree to which light is refracted within an object is dependent on wavelength, which explains the spectrum of colours seen when white light passes through a glass prism (Bridgeman, 1987; Berns, 2000).

2.2.1.5. Transmission

Transmitted light is light that has passed directly through an object. If the object is clear and colourless all incident light is transmitted (Berns, 2000). **Transmittance** in these materials is equal to the ratio of the intensity of transmitted light to the intensity of the incident light wave, with adjustments made for light reflected at the front and inside surfaces.

2.2.1.6. Absorption

Visible light that penetrates the surface can be lost through the selective absorption of different wavelengths by colorants, which reduces the amount of light that is transmitted by clear objects, or that is otherwise produced from the sample. Transmittance decreases exponentially with increasing colorant concentration or path length (object thickness) (McClements, 2005). Light is absorbed by dyes that are dissolved in the medium, or by pigment particles so small that they are regarded as being effectively dissolved (Bridgeman, 1987). The absorption of light by **coloured, non-light scattering materials** is better expressed as **absorbance** rather than as transmittance, because it is directly proportional to colorant concentration and path length (McClements, 2005).

2.2.1.6.1. Molecular basis of light absorption (coloration)

The selective absorption of light by colorants is related to changes in energy within the colorant molecules. When light is absorbed, electrons transition from either π bonding or n non-bonding molecular orbitals, to the higher energy π^* anti-bonding orbitals. Bonding orbitals are so called because they contain electrons which contribute to a chemical bond, while the anti-bonding orbital does not contain electrons. Intermediate between these two is the non-bonding orbital, which contains electrons which are not part of a molecular bond, such as a lone pair of electrons from nitrogen. These mechanisms occur in compounds containing 'resonance structures' - conjugated double bonds (alternating double and single bonds) and atoms contributing lone pair electrons; these are common features of food colorants, which exist as both hydrocarbon chains and ring structures (Moss, 2002). The energy of the electron transitions decreases as the numbers of resonance structures increases, which causes the wavelengths of light that are absorbed to change (Moss, 2002). The *intensity* of the absorption can also change. These phenomena are described by an absorption spectrum, or a plot of absorbance versus wavelength (McClements, 2005). Relationships between absorbed and observed colours of colorants are given in Figure 2.2. The colour of an object will be a function of the shape of the curve and the

wavelength of maximum absorbance, while its intensity will be indicated by its height above the baseline (Bridgeman, 1987).

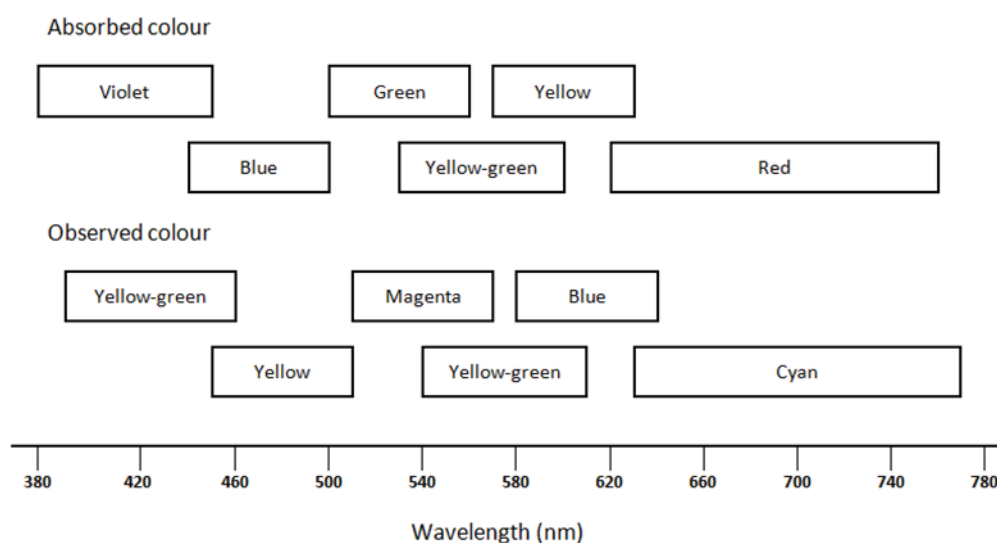


Figure 2.2 The relationship between the wavelengths of light absorbed by different colorants and the observed colours of the colorants. Adapted from Moss (2002).

2.2.1.6.2. Nomenclature

‘*Colorant*’ is an umbrella term used to describe compounds that absorb electromagnetic energy in the visible region that is, in the wavelength range between 380 nm and 750 nm. Within this group, a distinction is commonly made – from the point of view of colour chemistry - between colorants that are soluble in the medium in which they are dispersed, which are referred to as ‘*dyes*’, and those that are insoluble, which are termed ‘*pigments*’. However in a physiological sense, natural colorants of animal and plant origin are also referred to as pigments, and most are soluble (Moss, 2002). Natural colorants are included in the classification of food colorants according to their origin (synthetic, natural or nature-identical). Synthetic colorants do not occur in nature and are chemically synthesised; for this reason common food dyes (which are synthetic colorants) often evoke negative connotations, despite nature-identical colorants also being synthesised. Another classification for food colorants is that based on their chemical structure (Moss, 2002).

2.2.1.7. Scatter

The scattering of light (that has penetrated the object surface) by pigment and other particles contained within the medium depends on the size of the particles, and on the difference in refractive index between the particles and the surrounding medium. On the one hand, particle diameter needs to be at least ten times the wavelength of the light for scattering to occur (Bridgeman, 1987), though according to Berns (2000) scattering reaches a maximum when particles and wavelength are around the same size, and then decreases for larger particles. On the other hand, light will not be scattered unless the refractive indices of the particles and medium are different; when there is no difference light will be transmitted (Berns, 2000). Pigment particles which scatter light absorb any light which is not scattered; light emerging from particles after absorption is available to be scattered by other particles. Scattering results in a diffuse reflectance of light from the object, with light travelling from the object in all directions. The appearance of **coloured, light-scattering materials** can be expressed in terms of the **Kubelka-Munk absorption and scattering coefficients**, K and S respectively. These are described in more detail in Section 2.4.3.2.

Rayleigh scattering is the selective scattering of blue (shorter wavelength) light by small particles (Gibbs, 1997). Scattering by molecules of oxygen and nitrogen in the air is the reason that the day-time sky appears blue in clear, cloudless conditions. The opalescence of some gem stones is also the result of Rayleigh scattering.

2.2.1.8. Summary illustration

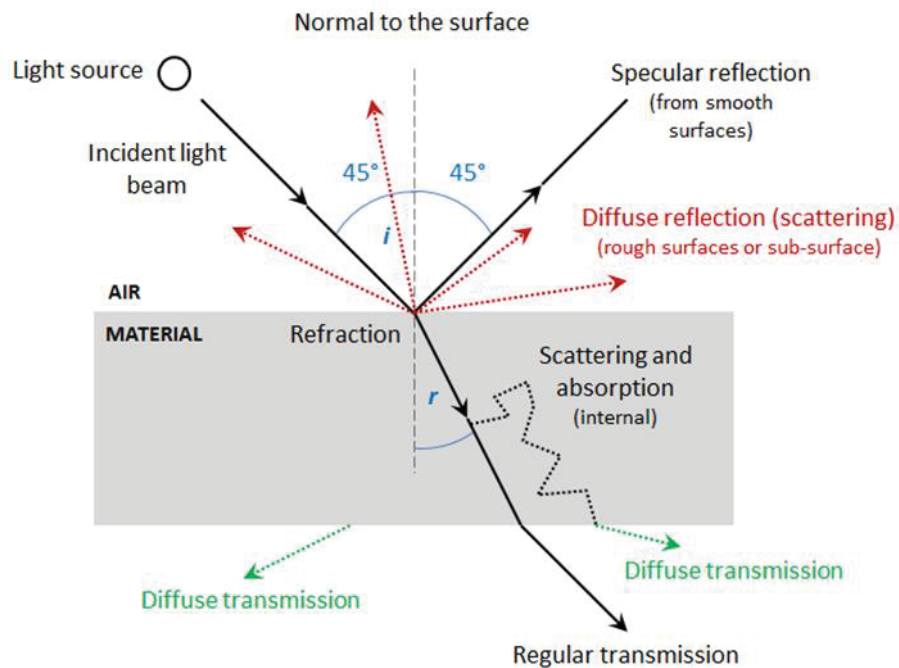


Figure 2.3 An illustration of the different phenomena (not including Rayleigh scattering) that can occur when visible light interacts with an object. The specific phenomena that occur depend on the physical properties of the object. The use of colour in this figure is not related to any object colour observed. Compiled using Bridgeman (1987), Hutchings (1999) and Berns (2000).

2.2.1.9. Effects on appearance

The degree to which light is modified in the ways described above depends on the material properties of the object. A general overview of the relationships between the surface and sub-surface effects of the object on incident light and the appearance of coloured objects is given in Table 2.1. Typically an object will modify light in a number of different ways simultaneously, as has been noted already for reflection at the surface (Section 2.2.1.3); in addition Table 2.1 lists the combined effects on appearance of sub-surface transmission, absorption and scattering of light. Reflected light, while not absorbed sub-surface (and therefore remaining the same colour as the incident white light) (Bridgeman, 1987), still impacts colour appearance; while smooth surfaces will appear more intensely coloured so long as viewing is adjusted to exclude the reflected light (a viewing condition represented in instrumental colour measurement by the SCE geometry), rough surfaces have will have dull, less intense colours because diffuse

reflection cannot be excluded from view, and will have a diluting effect (Bridgeman, 1987). Although rare, it is possible that under conditions of completely diffuse illumination that specular reflections of smooth and glossy surfaces will not be seen, but instead be included as uniform white light in the *visual perception* of the surface colour (Berns, 2000). (Reflectance *measurements* that include the specular component however are required for the derivation of Kubelka-Munk absorption and scattering coefficients as described later in Section 2.4.3.2.).

From the above, it follows that intentional changes to (colour) appearance of an object can be made by altering its physical properties, such as by the smoothing or abrading of the surface, or the control of scatter by selecting pigments with appropriate refractive index and particle size. The selection of pigments is not limited by the need to meet *both* refractive index and size criteria; particles can be effectively transparent if small enough, even if they differ in refractive index to the surrounding medium, and conversely, scatter is also possible when particles and medium have similar refractive index (Berns, 2000).

Table 2.1 Examples of the relationships between object appearance and the interaction of light with the object.

Appearance	Light-material interaction	Examples
Surface¹		
Glossy, intense colours	Specular reflection	Smooth surfaces such as paint films, also achieved by varnishing, waxing of other surfaces
Matte, less intense colours	Diffuse reflection (scattering)	Textured surfaces, also achieved by roughening
Sub-surface		
Transparent ('clear')	Transmission and absorption	Clear materials coloured by dissolved dyes, or by pigment particles which are very small ($<0.2\mu\text{m}^2$) AND/OR have similar refractive index to the surrounding medium; selective absorption of different wavelengths by dyes and pigment particles
Opaque ('solid')	Absorption and intense scattering, no light transmitted	Solids, concentrated emulsions; media containing inorganic pigments (e.g. titanium dioxide) with refractive index >2.0 (relative to medium of surface coating resin with typical refractive index of ~ 1.5) ² OR containing organic pigments having similar refractive index to medium, through control of pigment particle size; dependent also on particle or droplet concentration
Translucent ('cloudy')	Partial scattering and partial transmission; absorption	Dilute micellar dispersions such as low-fat and full-fat milk; full-fat milk is also a combined dispersion and emulsion

¹ Includes light absorption ² Bridgeman (1987)

2.2.1.10. Structural colour

The interaction of light with certain objects can produce colour without any dye or pigment being present. This is possible only when the structural dimensions of the object are in the order of the wavelengths of visible light. Objects having this property are referred to as (periodic) nanostructures. Table 2.2 lists only a few examples of naturally-occurring and fabricated nanostructures, and within each, the relationships between the physical dimensions and the colours that are produced; Xu *et al.* (2011) and Luiggi (2013) are useful starting points for further reading. In the metallic nanostructures, which are known as plasmonic nanostructures (Xu *et al.*, 2011), different geometries influence colour by changing the nature of the surface plasmons, which are the electron oscillations occurring at the surface; it is these plasmons that interact with incident light and control the interaction of the light (photons) with the metal surface. Photonic crystals are another type of periodic nanostructure capable of producing structural colour, but they will not be described in any detail here.

The distinct advantage of coloration based solely on structure is that it is chemically stable, compared to pigment- and dye- based colours which are subject to fading. Metallic nanostructures are particularly suitable for high-intensity or continuous illumination (Xu *et al.*, 2011). The fabrication of such structures however, is currently beyond the scope of 3D printing technologies being covered in this review.

Table 2.2 Examples of naturally-occurring and fabricated nanostructures, illustrating the relationships between physical dimensions and colour.

Type of nanostructure	Effect on incident light	Effect of physical dimensions	Purpose
Biological/natural			
Wing scales of the Indonesian male sub-species of <i>Papilio palinurus</i> ('Emerald Swallowtail') butterfly ¹	Iridescent, emerald green bands on each wing from the additive mixing of reflected yellow and blue light	Regular 2D array of concavities on surface of wing scales, ranging from 4-6 microns in diameter and between 0.5 – 3 microns at maximum depth; flat regions between and within each concavity appear yellow; double reflection of light (incident along the normal) from one side of the concavity inclined at 45°, to the opposite, orthogonal, side of the concavity, and back along the normal results in intense blue light; the surfaces of each side are multi-layered and have equal spectral reflectivity	Unclear
Berry-like fruits of the African perennial herb <i>Pollia condensata</i> ²	Selective reflection of blue light, intensely bright and iridescent, with some red, purple and green	Layers of cellulose microfibrils stacked in a helical manner within cell walls; helical pitch about the same as the wavelength of blue light; slight variations between cells in the spacing of the cellulose layers gives the other colours. Cellulose structures also highly reflective, reflecting about 30 percent of incident light.	Increase visibility and attractiveness of fruit to pollinating birds and other animals.
Synthetic/fabricated³			
Fabricated arrays of silver nanoscale pillars ⁴	Selective reflection	Dependent on the size and spacing of pillars in a given array; cylinder diameter ranges from 300 to 500 nm and centre-to-centre separation from 320 to 540 nm. At the top of this range arrays appear red because they reflect light of 630 nm wavelength, while at the bottom of the range arrays appear blue, reflecting light of 490 nm.	Possible application as optical filters in digital cameras and in large-area colour displays.
Optically thick metal films perforated with periodic subwavelength hole arrays, either square-lattice or triangular lattice ⁵	Selective transmission	For square lattice arrays, $\lambda_{\max}$ of transmitted light is proportional to the lattice constant; when the lattice constant for a 300 nm-thick silver film increases from 300 to 550 nm, $\lambda_{\max}$ increases from 436 to 627 nm.	Spectral filtering, imaging and high-resolution colour display.

¹Vukusic *et al.* (2000)

²Luiggi (2013)

³To exploit surface plasmons in metallic nanostructures

⁴R&D Mag (2013)

⁵Xu *et al.* (2011)

2.2.2. Colour perception: the observer

The process of colour perception begins with light entering the eye, which is absorbed by detectors which are densely packed (Berns, 2000) on the retina, the membrane lining the inside of the back of the eyeball (MacDougall, 2002a). The retina carries two types of light detector,

which differ in their shape, number, light sensitivity and relative location. The *rods*, numbering 120 million (Hutchings, 2002) have the higher sensitivity to incident light, while the *cones*, numbering seven million (Hutchings, 2002), are much less sensitive (Berns, 2000). Cones are concentrated in the centre of the eye, the fovea, which allows for the perception of fine details (Berns, 2000), and are more widely spread outside the fovea (Berns, 2000; MacDougall, 2002a).

It is only the rods that function under very low-light conditions, under which only shades of grey will be seen, due to there being only one type of pigment (Berns, 2000). The perception of colour is due to the cones, which begin to function as the amount of light increases until they become the only detector type active under daylight or well-lit conditions. There are three cone sub-types which differ in their spectral sensitivities: the blue (β), green (γ) and red (ρ) receptors, which respectively span the short, medium and long wavelength regions of the visible spectrum, peaking in the blue, green and yellow-green regions. The overlap of these regions ensures coverage of the entire spectrum, rather than the perception of three distinct hues (Berns, 2000). The β , γ and ρ receptors are said to be present in the ratio 40:20:1 (Hutchings, 2002) or 6:3:1 (Berns, 2000).

Signals from the rods and cones are transported from the retina to the visual cortex of the brain via the optic nerve. It is the relative magnitude of the signals from the three cone types (McClements, 2005) and their cognitive processing (Berns, 2000) that result in the perception of colour; objects producing different cone signals will have different colours (Berns, 2000). The signals that reach the brain take the form of brightness (achromatic) information, and colour information (Hutchings, 2002). Connections between rods or cones and the brain are not made individually, but through receptive fields, or areas of interconnected receptors (Berns, 2000). It is assumed that three types of receptive field are formed from the addition and subtraction of the different types of cone signals, which are known as the black-white, red-green and yellow-blue opponent channels (Berns, 2000). While literature sources agree on which cones are added and subtracted to form the chromatic opponent channels, they differ in the description of the black-white channel; the achromatic signal is contributed either by all three cone types, weighted for

the relative proportion of each type in the retina, as well as by the rods (Hutchings, 2002), or by the addition of the γ and ρ cones only (Berns, 2000).

Physiological differences among people, and physiological changes over time, mean that colour vision varies widely among those with *normal colour vision*. *Deficiencies in colour vision* on the other hand are caused by the absence of one or both of the γ and ρ cone receptors or by a shift in the spectral sensitivity of one of these receptors; it is unusual for the β cones to be affected (Hutchings, 2002). These defects have a genetic basis, and they are more common in males (8% of the population) than in females (0.5%) (Berns, 2000). Obviously there are consequences for the matching of colours by observers. Observers can be screened for (simply the) presence of a colour vision deficiency using the Ishihara charts. More specific tests for colour vision include the Farnsworth-Munsell 100 hue test.

2.3. Describing colour and the basis of colour measurement

2.3.1. Colour coordinates and colour coordinate systems (colour spaces)

Colours can be described by three orthogonal properties: hue, lightness and chroma. A systematic ordering of colours in a three-dimensional space is therefore possible by using hue, lightness and chroma as the three coordinates. Formal and informal definitions of the coordinates, and their relative axial positions in colour space, are given below.

2.3.1.1. Hue

Hue is the ‘*attribute of a visual perception according to which an area appears to be similar to one of the colors, red, yellow, green and blue, or to a combination of adjacent pairs of these colours considered in a closed ring*’ ([CIE] International Commission on Illumination, 1987). Hue forms a circle around the central axis in colour space. In its meaning, *hue* is akin to the ‘everyday’ descriptions of *colour*. The mixing of hues forms a continuum of hues commonly known as a colour wheel (Minolta Camera Co. Ltd., 1993) (Figure 2.4).



Figure 2.4 A representation of the colour wheel displaying a continuum of hues which have the same level of lightness and the same chroma range (Minolta Camera Co. Ltd., 1993).

2.3.1.2. Lightness

Lightness is defined as the ‘attribute by which a perceived color is judged to be equivalent to one of a series of grays ranging from black to white’ (ASTM International, 2013). Lightness forms the central, vertical axis in colour space. Lightness can be evaluated independently of hue; different hues therefore can have the same lightness. The convention is to represent the continuum of colours in colour space in order of decreasing lightness from top to bottom (Figure 2.5). In ‘everyday’ language ‘bright’ and ‘dark’ are terms commonly used to describe degrees of lightness (Minolta Camera Co. Ltd., 1993).

2.3.1.3. Chroma

Chroma is the ‘attribute of color used to indicate the degree of departure of the colour from a gray of the same lightness’ (ASTM International, 2013). In colour space chroma is represented by the radial axis. Colours increase in chroma, or become more chromatic, with increasing distance from the lightness axis; this increase can be otherwise described as moving from *weak* or *dull* colours to *strong* or *vivid* colours (Figure 2.5). Chroma is independent of both hue and lightness (Minolta Camera Co. Ltd., 1993; Berns, 2000).

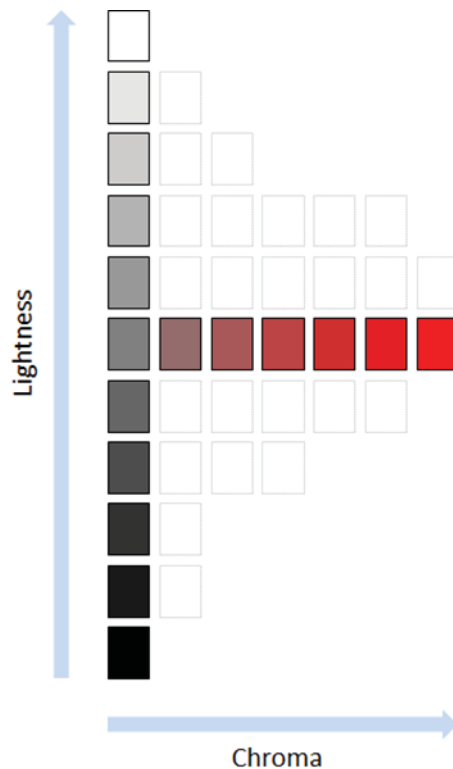


Figure 2.5 A representation of the lightness and chroma dimensions of colour space, shown in a plane of constant hue; increasing chroma is displayed for a single level of lightness only. Adapted from Berns (2000).

2.3.1.4. Attributes for a more complete specification of colour appearance:

Brightness, Colourfulness and Saturation

Two further dimensions, *brightness* and *colourfulness*, are actually required in addition to hue, lightness and chroma for a full specification of colour appearance (Fairchild, 2005):

Brightness is '*the attribute of a visual sensation according to which an area appears to emit more or less light*' (Fairchild, 2005);

Colourfulness is '*the attribute of a visual sensation according to which the perceived colour of an area appears to be more or less chromatic*' (Fairchild, 2005).

Brightness and colourfulness each describe a perception in the absolute sense, whereas lightness and chroma refer to brightness and colourfulness (respectively), relative to a similarly illuminated white, represented as follows (Fairchild, 2005):

$$Lightness = \frac{Brightness}{Brightness(White)}$$

Equation 2.1

$$Chroma = \frac{Colourfulness}{Brightness(White)}$$

Equation 2.2

Therefore, while brightness increases with the level of illumination, lightness is not affected because it is normalised according to the level of brightness under a given set of illumination and viewing conditions (MacDougall, 2002a; Fairchild, 2005). Also, brightness and colourfulness are assessed in isolation from other colours whereas lightness and chroma are assessed in relation to other colours.

Yet another attribute, *saturation*, can be determined from the combinations of colourfulness-brightness or chroma-lightness (the latter being an alternative used in some appearance models):

$$Saturation = \frac{Colourfulness}{Brightness} \quad \text{or} \quad Saturation = \frac{Chroma}{Lightness}$$

Equations 2.3

Although similar to chroma in that it is also a relative colourfulness, saturation is relative to its own brightness, and unlike chroma, is assessed in isolation from other colours. Saturation remains constant as a gradually deepening shadow is cast over a single colour to form a shadow series (Berns, 2000; Fairchild, 2005).

In many situations however, it is only hue, lightness and chroma that are needed to specify colours because these situations involve the judgment of colours in relation to other colours (Fairchild, 2005). Colour spaces defined by hue, lightness and chroma are the subject of the following sections. Further mention will be made of brightness and colourfulness in a later section, with regard to colour appearance spaces for gamut mapping (Section 2.5.3.1).

2.3.1.5. Advantages

Colour coordinate systems enable the assignment of numerical values to colours, thereby providing the basis for precise, standardised colour description and communication which would not be possible if relying solely on descriptions by human observers. Observer descriptions will be more subjective and varied, even for the same object, due to differences in the perception (Section 2.2.2), experiences, vocabulary and descriptive ability between individual observers (Minolta Camera Co. Ltd., 1993; McClements, 2005). These, together with the vast number of possible colours that would need describing (McClements, 2005), mean that observers would have enormous difficulty in quantifying colours.

Each colour space is specific to a single set of viewing and illuminating conditions. Colour spaces also differ in the sampling of the space, and in their application (Berns, 2000). The following sections describe a selection of colour systems that are used in visual and in instrumental colour measurement.

2.3.2. Visual colour description – The Munsell and NCS Colour Systems

2.3.2.1. The Munsell System

In its original form, the *Atlas of the Munsell Colors*, the Munsell colour system was developed to provide a physically realisable, numerical system in which the visual (perceptual) spacing between colours is equal (Berns, 2000). Colours are defined by their Munsell hue (H), Munsell value (lightness, V) and Munsell chroma (C). Ten hues divide the hue circle into equally spaced intervals: the five principal hues purple, blue, green, yellow and red, along with five intermediate hues (Fairchild, 2005). The principal hues were originally selected by Munsell on the basis that they would be perceived as a neutral when spun together (Berns, 2000). Each of the ten hues is divided into ten sub-hues giving a total of 100 steps. Value is divided into 10 steps, from black (zero) to white (ten). Colours seen as intermediate between two hue or value steps are assigned decimal values (Fairchild, 2005). Maximum chroma for a coloured stimulus depends on its hue and value, being limited by the physical properties of the stimulus, the

colorants that are used, and whether it is within range of the human visual response. For example, only low chroma can be achieved for the combinations of yellow hue/low value, and for purple hue/high value (Fairchild, 2005). The Munsell solid therefore is neither cylindrical nor spherical.

Colour communication products based on the Munsell system are among the most commonly used (Fairchild, 2005). Products currently available include the complete Munsell Books of Color, in glossy ('the master atlas') and matte editions, and applications-specific charts for soil, rock and plant tissue colours (X-Rite Incorporated, 2014). These products are used for visual comparisons with samples (Minolta Camera Co. Ltd., 1993) and are organised by one hue (step) per page or chart. Munsell notation for each colour is H V/C; for the colour with H=5.0R (sub-hue 5.0 of hue Red), V=4.0 and C=14.0, for example, the Munsell notation would be: 5.0R 4.0/14.0.

2.3.2.2. Natural Colour System®©

The Swedish Natural Colour System®© (NCS), standard in Sweden and in some European countries, is based on the opponent theory of colour perception (Section 2.2.2) (Fairchild, 2005). In this system colours are described by their hue and '*nuance*', a collective term for *blackness* and *chromaticness*. Each hue is expressed in terms of its similarity to the four principal hues – red, yellow, green and blue – which divide the hue circle into four quadrants. Each quadrant is further divided into 100 equal steps. Nuance is represented by a vertical triangle at each hue. The two corners of the triangle which also define the vertical axis of the NCS space are at the points of maximum whiteness, w, and blackness, s (black = 'swarthy'), with values of zero and 100 respectively, while the remaining, outermost corner is at the maximum chromaticness, c, of 100. Although similar in concept, Munsell chroma and NCS chromaticness are unrelated, as are Munsell value and NCS blackness (Fairchild, 2005).

NCS notation specifies blackness, followed by chromaticness and then hue. It is not necessary to specify whiteness as the sum of blackness, chromaticness and whiteness must be 100. The

notation for a given hue indicates the relative perceptual contributions of the neighbouring principal hues on either side; hue order follows the clockwise positions in the hue circle and numerical values are given for the second hue only. Therefore S 1070-Y10R for example, denotes a colour which has 10% perceived blackness, 70% perceived chromaticness, 20% perceived whiteness, 90% perceived yellow and 10% perceived red (NCS Colour AB, 2014).

2.3.3. Instrumental colour measurement - the CIE systems

The systems of the CIE (Commission internationale de l'éclairage, or International Commission on Illumination) provide a means of standardised colour measurement. The key to the development of these systems was the derivation of the colour matching functions for an average observer, or 'standard observer', which addressed the issue of variability of visual perception among individual observers. The colour matching functions are the amounts of each of three primaries - three monochromatic lights covering short, medium and long wavelengths between them, in line with cone spectral sensitivities - required to match a test light stimulus at each wavelength of the visible spectrum. Because the actual colour matching functions $\bar{r}_\lambda$, $\bar{g}_\lambda$ and $\bar{b}_\lambda$ included negative values (indicating that a primary needed to be added to the test stimulus to enable matching), they were transformed into the positive functions $\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{z}_\lambda$.

Colour matching functions have been defined for two standard observers: the 1931 standard observer or 2° observer, based on the average results of 17 colour-normal observers, for whom the functions are denoted $\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{z}_\lambda$, and the 1964 standard observer or 10° observer, based on a total of 76 subjects, and for whom the functions are $\bar{x}_{10\lambda}$, $\bar{y}_{10\lambda}$ and $\bar{z}_{10\lambda}$. 2° and 10° denote the sizes of the (bipartite) field of view that was used in the experiments; these are equivalent to object diameters of 15 mm and 75 mm respectively when viewed at 45 cm (Minolta Camera Co. Ltd., 1993; MacDougall, 2002a).

The availability of the colour matching functions allows the colour of any stimulus to be described in terms of primaries, by following the steps below:

- At each wavelength of the visible spectrum, the relative power of (or the amount of light from) a standard illuminant (Table 2.3) is multiplied by the *reflectance factor*, R_λ , of the object, which is the ratio of the light reflected from the object to the light reflected from a perfect reflecting diffuser (an ideal surface that neither absorbs nor transmits light) under the same measurement conditions;
- The spectral product is then multiplied, in turn, by each of the three colour matching functions resulting in a further three spectral curves;
- The products at each wavelength in these three curves are added together and then normalised to give the CIE tristimulus values X , Y and Z .

The procedure is illustrated in Figure 2.6. It is common practice for the normalised spectral products of the illuminant and colour matching functions at each wavelength to be pre-calculated as a first step, to give the normalised tristimulus weighting factors, W_x , W_y and W_z (ASTM International, 2008). Tristimulus values X , Y and Z are then computed using W and R .

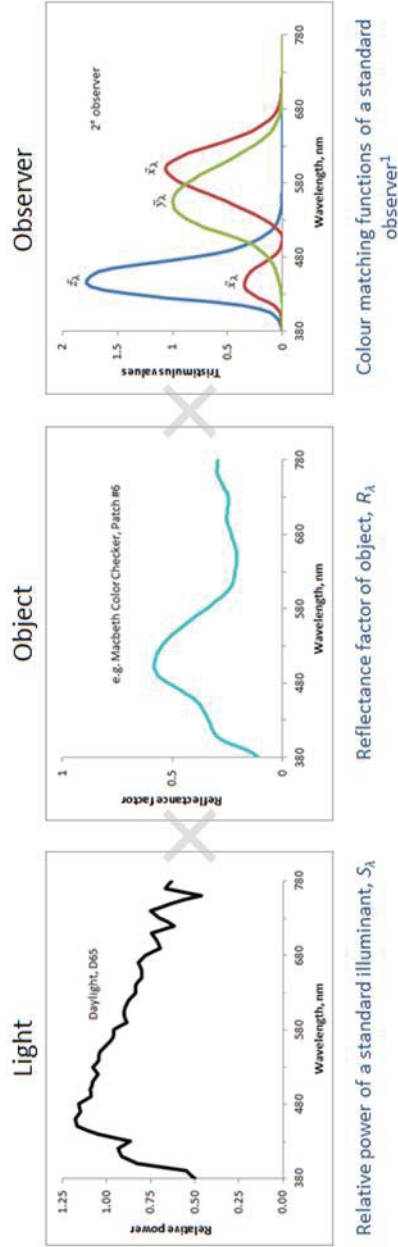
Tables 5 and 6 in ASTM Standard E308-06 (ASTM International, 2008) lists values of W_x , W_y and W_z from 360 nm to 780 nm, for various combinations of standard illuminant and standard observer, and for both the 10 nm and 20 nm measurement intervals. This wavelength range extends beyond the limits of most spectrophotometers (which measure reflectance from 400 nm to 700 nm) but is in keeping with the range for the colour matching functions (360 nm to 830 nm). In order to calculate X , Y and Z , measured spectral reflectance needs to be extrapolated to 360 nm and to 780 nm. The measurement intervals for the weighting factors recognise that spectrophotometers measure in increments of 10 nm or 20 nm, rather than in the single nm intervals for which the colour matching functions are defined. In Figure 2.6, the wavelength range illustrated begins at 380 nm (as in Berns (2000)); “between 360 and 379 nm, values of colour matching functions are so small that their inclusion or omission in the calculations would not lead to significant differences in the resulting tristimulus values” (ASTM International, 2008).

Because the positive colour matching functions $\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{z}_\lambda$ are used in place of the actual $\bar{r}_\lambda$, $\bar{g}_\lambda$ and $\bar{b}_\lambda$ functions, the X , Y and Z tristimulus values are regarded as ‘computational’ or ‘imaginary’ primaries, rather than ‘real’ or visual primaries.

Table 2.3 CIE standard illuminants (relative spectral power distributions¹) for use in describing colour (compiled using information from Berns (2000)).

Illuminant	Light represented	Application/comments
A	Incandescent	
D65	Daylight	Paints, plastics, textiles
D50	Daylight	Graphic arts and computer industries
C	Forerunner to D series	Not recommended as representation of natural daylight
F series	Fluorescent	

¹Spectral power normalised at each wavelength, relative to power at 560nm



$$\begin{aligned}
 X &= k \int_{380}^{780} S_\lambda R_\lambda \bar{x}_\lambda d\lambda \\
 Y &= k \int_{380}^{780} S_\lambda R_\lambda \bar{y}_\lambda d\lambda \\
 Z &= k \int_{380}^{780} S_\lambda R_\lambda \bar{z}_\lambda d\lambda
 \end{aligned}$$

Tristimulus values X, Y, Z ^{1,2}

1 Tristimulus values and colour spaces also defined for the 10° observer (denoted $\bar{x}_{10\lambda}, \bar{y}_{10\lambda}, \bar{z}_{10\lambda}$ and X_{10}, Y_{10}, Z_{10}).

2 Definition of constants:

$$k = \frac{100}{\int_{\lambda} S_\lambda \bar{y}_\lambda d\lambda}$$

is the normalisation constant, assigns $Y=100$ to the ideal white; $d\lambda$ is the measurement wavelength interval (usually 10 or 20 nm).

1931 CIE colour space (coordinates X, Y, Z)

1958 Hunter Lab space (L, a, b)

1976 CIELAB space (L^*, a^*, b^*)

Figure 2.6 Procedure for computing the standard CIE tristimulus values X, Y and Z , or the computational or 'imaginary' colour primaries (ASTM International, 2008). Spectra for light, object and observer were drawn using data files available for download from the Munsell Color Science Laboratory webpage (RIT Munsell Color Science Laboratory, 2010).

The original colour system that was derived using X, Y and Z tristimulus values is the 1931 CIE colour space defined by the lightness coordinate Y, and the chromaticity coordinates x and y (computed from X, Y and Z). In visual terms, colours are not equally spaced in the Yxy system, due in part to the use of computational primaries rather than real primaries which would represent the visual response (Berns, 2000). The original space has undergone a number of (linear and non-linear) transformations in order to develop more uniform colour systems for the purposes of describing colours as perceived visually, and the perceived differences between colours.

Two of the commonly used colour systems of industrial importance are described briefly below. These are based on the concept of an opponent, *rectangular* (Cartesian) coordinate system and a central axis representing the neutral or achromatic colours (Figure 2.7). These colour spaces were developed using the Munsell system (Berns, 2000), to provide an approximation of the visual spacing of the Munsell colours (MacDougall, 2002a):

The 1958 *Hunter Lab* system, where:

L is the lightness coordinate, and

a, b are the red-green and yellow-blue opponent coordinates respectively;

The CIE 1976 L^* , a^* , b^* space, with the official abbreviation CIELAB, where:

L^* is the lightness coordinate, and

a^* , b^* are the red-green and yellow-blue opponent coordinates respectively.

Of the two, CIELAB is now the more commonly used in industrial applications; for this reason, it will be the colour system used in this thesis and detailed formulae will be given here for CIELAB only. However, HunterLab does see continued use in the food industry (MacDougall, 2002a).

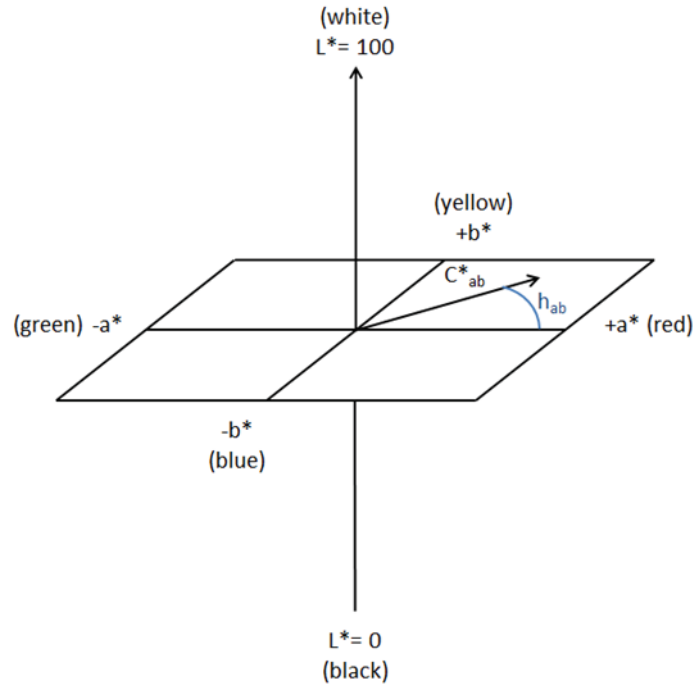


Figure 2.7 CIELAB colour space diagram showing the red/green (+a/-a) and yellow/blue (+b/-b) opponent (rectangular) colour coordinates relative to the lightness, L^* axis, and to the cylindrical polar coordinates chroma, C^* and hue angle, h^* (after MacDougall (2002a)).

CIELAB (and Hunter Lab) can be used for any combination of illuminant and observer, despite the Munsell system being defined for the 1931 standard observer and C illuminant only (Berns, 2000). In colour measurement usually the combination of the D65 illuminant and 10° observer is used, except for very small objects (MacDougall, 2002a) or those occupying a field of view of less than four degrees (Berns, 2000). When the 10° observer is used, corresponding tristimulus and colour coordinate values need to be labelled with the subscript '10'; values otherwise indicate the 2° observer has been used, or are used to illustrate the general form of the equations.

CIELAB formulae are as follows (ASTM International, 2008):

$$L^* = 116f\left(\frac{Y}{Y_n}\right) - 16$$

$$a^* = 500 \left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right) \right]$$

$$b^* = 200 \left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right) \right]$$

Equations 2.4

Where $f(\omega) = (\omega)^{\frac{1}{3}}$ and $f(\omega) = \left(\frac{841}{108}\right)\omega + \frac{4}{29}$

for $\omega > \left(\frac{6}{29}\right)^3$ and $\omega \leq \left(\frac{6}{29}\right)^3$ respectively.

Values of $\left(\frac{X}{X_n}\right)$, $\left(\frac{Y}{Y_n}\right)$ and $\left(\frac{Z}{Z_n}\right) < 0.01$ are not usually associated with coloured materials, but can be a property of some imaging systems (Fairchild, 2005).

X_n , Y_n and Z_n are the tristimulus values for the nominally white object colour stimulus, which is represented by the spectral radiant power of the illuminant reflected to the observer by the perfect reflecting diffuser; illuminant, observer and (spectral) measurement interval (nm) for X_n , Y_n and Z_n are the same as those used for the colours to which X_n , Y_n and Z_n will be applied.

Values of L^* usually range from zero (black) to 100 (diffuse white), though L^* can exceed 100 for some stimuli including those which are highly fluorescent; in fluorescent materials absorbed light or radiation (including ultraviolet radiation) is re-emitted at a longer wavelengths, rather than being lost as heat (Berns, 2000). Given the use of the Munsell system in the development of CIELAB and the limitations on Munsell chroma (Section 2.3.2.1), it follows that the range of values for both a^* and b^* depend on the properties of the stimulus. Values of a^* and b^* are zero for achromatic stimuli, represented by the intersection of their axes with the lightness axis.

The following *cylindrical* polar coordinates, chroma, C^*_{ab} , and hue (angle), h_{ab} , are also defined for CIELAB (Berns, 2000) (Figure 2.7); these terms are derived from a^* and b^* and correspond more to the visual perception of colours (MacDougall, 2002a):

$$C^*_{ab} = \sqrt{a^{*2} + b^{*2}}$$

Equation 2.5

$$h_{ab} = \tan^{-1}\left(\frac{b^*}{a^*}\right)$$

Equation 2.6

Hue angle is expressed in (positive) degrees counter-clockwise from the +a* (red) axis. Appropriate conversions therefore need to be made from the result returned by the above formula, which will be the arctangent, or inverse tangent, of the a* and b* coordinates, in units of *radians*. Also, the arctangent spans up to 180 degrees in either the counter-clockwise or clockwise directions, returning positive and negative values respectively.

2.3.4. Colour differences: formulae

The colours of objects need to be described and quantified for the purposes of describing the difference in colour between them. Using a colour space such as CIELAB allows this difference to be expressed in the form of a numerical index. This index should be able to predict, and represent, the visually perceived difference between colours. In a visually uniform colour space the difference between two colours (1 and 2) should, in theory, equate to the distance between their positions within the space, which is referred to as the Euclidean distance. For CIELAB the formula for this difference, denoted ΔE^*_{ab} - with E standing for *Empfindung*, the German for ‘sensation’ (Berns, 2000) -, is:

$$\Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

Equation 2.7

As well as the total colour differences indicated by ΔE^*_{ab} , the colour differences can be expressed in terms of a difference in the lightness or chromatic attributes:

$$\Delta L^* = L^*_1 - L^*_2$$

Equation 2.8

$$\Delta C^*_{ab} = \left(\sqrt{a^{*2}_1 + b^{*2}_1} \right) - \left(\sqrt{a^{*2}_2 + b^{*2}_2} \right)$$

Equation 2.9

$$\Delta H^*_{ab} = \sqrt{(\Delta E^*_{ab})^2 - (\Delta L^*)^2 - (\Delta C^*_{ab})^2}$$

Equation 2.10

ΔH^*_{ab} is the Euclidean rather than the angular difference in hue. Therefore ΔH^*_{ab} will increase with increasing ΔC^*_{ab} while h_{ab} remains the same (Berns, 2000).

Alternative formulae, for calculating ΔH^*_{ab} directly, are given in Berns (2000), and MacDougall (2002a).

In practice, the correlation between visually perceived and Euclidean colour differences is poor. In the assessment of visual differences a standard colour is paired with a selection of ‘test’ samples of near colours, and the degree of the visual difference between the standard and sample in each pair is made relative to the difference between the samples in an ‘anchor pair’, representing a defined instrumental colour difference. A test sample is ‘passed’ or ‘accepted’ if the difference between it and the standard is the same, or smaller, than the difference displayed by the anchor pair. This process can be repeated for other (standard) colours. When the measured colours of the accepted, test samples are plotted in colour space about each relevant standard, not only does the size of the distributions differ between the standard colour ‘centres’, but the distributions are ellipsoidal rather than spherical. Referring to the comparisons of the anchor pair with the standard/sample pair, this indicates that pairs with the same visual difference do not necessarily have the same measured difference. Further, the differences between colour centres indicate that the disparity between visual and measured colours is a function of the colour centre, while the ellipsoids point to lightness, chroma and hue differences being affected in different ways. These effects are the result of colour spaces not being truly

visually uniform; in reality, this is very difficult to achieve given wide observer variability, factors affecting perception, and that colour spaces very likely to need be described by more than three dimensions (Berns, 2000).

Several weighted colour difference equations derived from CIELAB have since been developed taking into account the above effects, and have been used in a variety of applications, with some preferred by specific industries. Weighted equations for total colour difference include:

The CMC(*l:c*) Colour-Difference Equation (Colour Measurement Committee, Society of Dyers and Colourists) for difference designated $\Delta E_{CMC(l:c)}$, standard for textiles:

$$\Delta E_{CMC(l:c)} = \sqrt{\left(\frac{\Delta L^*}{lS_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{cS_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{S_H}\right)^2}$$

Equation 2.11

The CIE94 equation, for difference designated ΔE^*_{94} , used preferentially by industries such as the textile industry for accurate colour difference measurements related to perception and acceptability (MacDougall, 2002a):

$$\Delta E^*_{94} = \sqrt{\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{k_C S_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{k_H S_H}\right)^2}$$

Equation 2.12

The CIEDE2000 Colour-Difference Formula, difference ΔE_{00} , a further improvement on earlier formulae (Luo *et al.*, 2001a), now a new CIE/ISO standard (Melgosa, 2013); CIEDE2000 applies to colour-uniform samples with colour differences below five CIELAB units ([CIE] International Commission on Illumination, 2001):

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right) \left(\frac{\Delta H'}{k_H S_H}\right)}$$

Equation 2.13

Corresponding formulae for lightness, hue and chroma differences are also available for ΔE_{00} .

2.3.4.1. Experimental conditions and the effects of texture

In the weighted colour-difference equations, the l , c , k_L , k_C and k_H coefficients are adjusting constants which represent the effects of experimental conditions (parametric effects), and the resulting relative influence of lightness, chroma and hue, on perceived total colour difference. The S coefficients are positional functions which account for the lack of visual uniformity in CIELAB. The convention is to align the parametric constants for lightness and chroma (l , c , k_L and k_C) relative to that of hue (denoted k_H in CIE94 and CIEDE2000 but undesignated in CMC($l:c$)) which is set to unity. An l or a k_L of 2 for example would indicate that experimental conditions were such that hue had twice the influence of lightness on the perceived difference (Berns, 2000). The values of k_L and k_C that are used depend on how much experimental conditions deviate from a set of reference conditions, in which a pair of colour-uniform samples are placed in edge contact against a background of $L^*=50$, and viewed by observers with normal colour vision under illuminant D65 at a viewing angle of at least four degrees; under these conditions $k_L=k_C=k_H=1$. Details of the individual formulae for S_L , S_C and S_H will not be given here, but can be found in Berns (2000) and in Luo *et al.* (2001a).

In the textile industry it is common practice to use $k_L=2$ for CIEDE2000 colour differences. Despite this, the correlation between objectively-measured CIEDE2000 (2:1:1) differences displayed by knitted polyester yarn samples of different textures (coarseness) and the corresponding visual differences was found by Gorji Kandi *et al.* (2008) to be poor, with an r value of 0.56 across all the textures. Visual differences were much better correlated ($r=0.94$) with a measure of texture structure known as the Gabor texture difference (GTD), said to be more closely related to the processing by the primary visual cortex of the brain, though r values did vary among the individual colours, being as low as -0.10 for Yellow and 0.15 for Blue (Gorji Kandi *et al.*, 2008). By controlling viewing geometry and illumination conditions to maximise the perceptions of differences in colour, and in the visual texture attributes coarseness

and glint, and together with an instrument capable of coarseness, glint, as well as reflectance measurements, Huang *et al.* (2010) developed two formulae that could predict the total visual difference, ΔT , of pairs of metallic coating samples from their measured colour and texture. Two formulae were proposed: one for diffuse illumination conditions, which includes terms for differences in measured colour (CIEDE2000) and coarseness, and the other for directional illumination, based on total colour and glint differences.

2.3.4.2. Tolerance levels

Limits have been set on the sizes of calculated (total) colour differences beyond which a colour match between samples is deemed unsatisfactory. These limits are referred to as instrumental colour tolerances and in various industry applications usually indicate when the colour difference is predicted to become a *perceptible* difference. Perceptible differences include those which are just-perceptible or just-noticeable ('threshold') and those just above perceptible ('supra-threshold'); for surface colours, perceptibility judgements are made relative to the difference between the samples in a standard pair. Examples of colour tolerances used in various industries, or reported in different studies, based on either CIELAB or HunterLab, are given in Table 2.4. Tolerance levels are seen to vary according to the application and some are above threshold. Perceptibility tolerances can be increased by a commercial factor if colour differences encountered exceed those that are just perceptible (Berns, 2000; MacDougall, 2002a). Tolerances of 2.4 and 0.7 CMC_{2:1} units were used by two different textiles companies producing exactly the same product in similar colours, and both companies were meeting their customer needs, indicating that in these cases tolerances were related largely to commercial requirements (Gay and Hirschler, 2002).

Table 2.4 A selection of colour tolerance limits applied in different industries, or that have been used in various studies.

Industry/application	Difference formula	Tolerance level, and comments
Threshold	CMC(1:1) CIELAB	0.3 – 1.4 units 0.4 – 1.8 units (Melgosa <i>et al.</i> , 1992) ¹
Automotive	CIELAB	< 1 unit
Paint, plastics, textiles	Unspecified Lab space	= 1 unit for approximate commercial match (noticeable difference at $\Delta E=2$ units, unacceptable at $\Delta E=3$ units) (Francis and Clydesdale, 1975)
Textiles	CMC(1:1) CIELAB	0.7 – 2.3 units 1.0 – 2.8 units (Gay and Hirschler, 2002) ²
Food and beverage		
Red wine	CIELAB	= 3 units (Martínez <i>et al.</i> , 2001)
Muffins	CIELAB	= 3 units (Baixauli <i>et al.</i> (2008), referencing Francis and Clydesdale (1975))
Carrot puree with added green food colouring	ΔE , HunterLab	0.1 to 0.15 units (allowed ranking of samples) (Huang <i>et al.</i> , 1970b)
Squash puree	ΔE , HunterLab	~ 0.2 units (allowed ranking of samples) (Huang <i>et al.</i> , 1970a)
Pale beers	CIELAB	1.5 units (Hutchings, 1999)

¹Across surface colours, and experimental threshold results using visual colorimeters (coloured lights)

²Across seven different textiles companies; individual values dependent on product range and marketing situation of companies

Tolerance levels, and the difference formulae used in their calculation, vary also according to how well they correlate with visual assessments. Of several formulae tested (including CIELAB and CIE94) tolerance levels calculated using CMC (2:1) were in best agreement with visual evaluations of textiles (Gay and Hirschler, 2002), while CMC(1:1) was the best performing formula with respect to visual threshold differences (Melgosa *et al.*, 1992). For the purpose of comparing tolerances within and across studies only CMC(1:1) and CIELAB results are shown in Table 2.4; CMC(2:1) was not used in the study by Melgosa *et al.* (1992) while in the study by Gay and Hirschler (2002) the range of tolerance levels was the same for both CMC(2:1) and CMC(1:1), though the individual levels within each range were different. For colour differences larger than threshold, such as those displayed between Munsell colours, CIELAB gave the better results (Melgosa *et al.*, 1992). Tolerances can also change with different surface textures and colours (Gay and Hirschler, 2002), consistent with the variable effects of surface texture, colour and their interaction on measured and perceived colours, described earlier. Colour tolerances (for example, lightness tolerances in the textile industry), increase with sample surface texture.

2.4. Producing colour: colour blending and colour reproduction

Colours are produced by the blending of primary colours which includes varying the total amount and the relative proportions of the primaries within each blend. Primary colours are a small set of base colours which themselves cannot be produced by the blending of other colours. Colour mixing systems differ in their primaries (number and type), but are broadly categorised as being either additive or subtractive.

2.4.1. Additive mixing systems: colours based on the RGB primaries

Additive blending refers to the mixing of coloured lights, for example, in cathode ray tube (CRT) displays; because each colour in an additive blend adds light, the blend is lighter than the individual colours, and becomes lighter as more colours are added, or the intensity of a given colour is increased. In additive blending the primaries are red (R), green (G) and blue (B). RGB colours are described in terms of their hue, lightness and saturation (HLS) in computer graphics applications, but these are not equivalent to perceived saturation and lightness (Berns, 2000).

2.4.2. Subtractive mixing systems: colours based on dyes and pigments

Subtractive blending refers to the mixing of colorants (dyes and pigments) for printing, paint, fabrics and plastics applications; colour is produced in these blends by the selective absorption (subtraction) of light by each colorant. As a result, a subtractive blend is darker than its constituent colours. The colour produced by a subtractive blend depends on the wavelengths absorbed by the colorants; the colour perceived is due to the remaining light that is not absorbed (Section 2.2.1.6.1, see also Figure 2.2).

In subtractive mixing the minimum number of primaries used is three; when three primaries are used these will be typically cyan (C), magenta (M) and yellow (Y), or red, yellow and blue. In theory, mixing based on the C, M and Y primaries will produce the widest range of colours possible, because the resulting blends will reflect light having colours that the visual system responds to: C and Y will subtract red and blue lights respectively, leaving green (G); C and M

will subtract red and green to produce blue (B), and M and Y will subtract green and blue to produce red (R). In reality, this is possible only from theoretical CMY primaries, each of which absorbs light only in their respectively spectral regions, without any overlap with the regions absorbed by the other two primaries; real primaries display some overlap and therefore strategies such as half-toning (explained below) or increasing the number of primaries are needed to maximise the number of possible colours.

2.4.2.1. Mixing based on CMYK primaries

In conventional (two-dimensional) colour printing which uses C, M and Y primary inks, each ink is applied ‘as is’ to the printing substrate, that is, separately and at a single concentration. At first it would appear that only eight, continuous-tone colours are possible: the three primaries; their corresponding secondary colours R, G and B from the overprinting (superimposing) of the two-primary combinations; black, from the overprinting of all three primaries; and white, the background provided by the substrate. Black is usually applied as a separate, fourth ink - denoted ‘K’ (for key) - for a number of reasons: for printing text that accompanies printed images; to extend the colour gamut; to improve image quality (Berns, 2000); and to save on the amount of the coloured primaries that need to be used. The addition of black ink to CMY doubles the number of possible colours to sixteen.

The range of colours that can be achieved using CMYK inks is extended by the use of ‘half-toning’, whereby the inks are printed as small dots which are too small to be perceived individually by the naked eye. By printing dots varying in size, shape and positioning, half-toning simulates the effects of varying ink concentration and therefore the properties of continuous-tone colours. With halftoning, CMYK printing becomes a mix of subtractive blending (from dot overprinting) and additive blending (when light reflected from the dots is ‘mixed’ by the eye). CMYK printing is known to as ‘process printing’, referring to the blending of the primaries after they have been dispensed on to the substrate.

2.4.2.2. The Pantone Matching System (PMS)

Another means of extending the range of colours is to have more than three or four primaries available for blending. The Pantone Matching System (PMS), used mainly in printing but also in paint, fabric and plastics, is based on 13 base pigments, plus black and white. Each of the 1,114 colours – known as spot colours in contrast to process colours - is prescribed by a proprietary ink formula, denoting the quantities of ink to be pre-mixed before they are applied to the printing substrate. CMYK is able to reproduce only a subset of the Pantone colours, due partly to limitations in the reproduction of light, saturated colours in which the halftoning pattern could be exposed.

2.4.3. Mathematical models for colour blending

Mathematical models are used to predict the colours that result from different blends of colours. Colour output depends on the spectral properties and the relative proportions of each colorant in the blend. As suggested by the description of CMYK printing given above, colour output is not due simply to the colorants themselves; the contribution of the substrate is also accounted for in these models.

The models described here are those that involve subtractive primaries and/or subtractive blending, which are applicable to the research objectives of this thesis.

2.4.3.1. The Neugebauer model for CMY printing (additive blending using subtractive primaries)

Although the CMY primaries are subtractive primaries, the use of halftoning renders their blending as largely additive rather than subtractive. Each primary is printed using a unique halftone pattern (the angle at which the grids of dots are printed), and when all three are printed, there are eight possible colours, which are the same as those described earlier. These eight colours are known as the Neugebauer primaries. By using a unique halftone pattern for each CMY primary, each Neugebauer primary can be treated as a random variable, and their probabilities of occurrence, P , calculated “for a given combination of C, M and Y ink areas”

(Berns, 2000). These probabilities are used to weight the contribution of each primary (that is, its spectral reflectance, R_λ) in the Neugebauer model, which predicts the colour (reflectance) of the area in which CMY are printed:

$$R_\lambda = P_c R_{\lambda,c} + P_m R_{\lambda,m} + P_y R_{\lambda,y} + P_r R_{\lambda,r} + P_g R_{\lambda,g} + P_b R_{\lambda,b} + P_k R_{\lambda,k} + P_w R_{\lambda,w}$$

Equation 2.14

The model can be expanded to include more than three primary inks. The modelling for colour printing becomes increasingly complex considering there are actually up to 64 instead of eight unique colours from the printing of three primaries (Berns, 2000), and that any subtractive ink mixing that occurs on the printing surface needs to be accounted for (Berns, 2000).

2.4.3.2. Models based on Kubelka-Munk Theory (for ‘true’ subtractive blending)

In subtractive mixing systems, stepwise increases in colorant concentration do not produce stepwise changes in the level of reflectance or transmittance spectra, that is, the relationship between colorant input and colour output is not linear. When reflectance is expressed in terms of absorption and scatter, and transmittance in terms of absorption, colour prediction becomes more straightforward; after first accounting for non-wavelength-dependent surface reflections the relationships between absorption or scatter, and colorant concentration can often be linear.

Because of the physical nature of the coloration systems (colorant-substrate combinations) that will be used in this thesis, this review is concerned with colour outputs for reflecting materials, specifically opaque materials. To achieve linearity for these materials, spectral reflectance measurements are transformed to spectra of absorption, K_λ , and scatter, S_λ , using functions based on Kubelka-Munk (K-M) Theory. These functions are simplifications which were developed using a translucent colorant layer (on an opaque background) within which light is assumed to be completely diffuse and within which absorption and scattering both occur. K-M Theory is used for three types of material: translucent materials, transparent films on an opaque backing, and opaque materials. Another reason for using absorption and scatter in place of reflectance is that values for the latter can be very low for dark colours (Butts, 2010).

For opaque materials, the function is:

$$\left(\frac{K}{S}\right)_\lambda = \frac{(1 - R_{\lambda,i})^2}{2R_{\lambda,i}}$$

Equation 2.15

This function converts the internal reflectance of the material, $R_{\lambda,i}$, rather than its measured reflectance, $R_{\lambda,m}$. Whereas measured reflectance ‘captures’ the combined effects of surface reflections, scattering and absorption, and losses through repeated cycles of internally reflected light, K-M Theory assumes that light travels only up and down within a colorant layer (perpendicular to its plane) without any light being ‘lost’ at the front or internal surfaces. Internal reflectance is measured reflectance corrected for these external and internal losses of light. Surface reflections are also not wavelength dependent. The *Saunderson correction* can be used to calculate internal reflectance (Berns, 2000). Further details are given in the first experimental chapter (Chapter Four) of this thesis.

Before the K-M function can be applied in models of subtractive blending, linear relationships between the absorption-scatter spectra and concentrations of individual colorants need to be verified. Once verified for the constituent colorants of a blend, the spectra from each of the colorants (weighted by the concentration of the colorant in the blend) can be added together to compute, or predict, the spectrum for the blend. The blending model is validated if the computed spectrum of the blend is the same as the measured spectrum of a prepared sample containing the same blend of colorants.

The form of the K-M blending model that is used to compute the spectrum for a colorant blend depends on the properties of the colorants. The simplest model is the *single-constant* form of the *K-M blending equation*, so called because the contribution of each colorant and of the substrate in the blend is expressed as a single constant, the ratio of its absorption to scatter, $\left(\frac{K}{S}\right)_\lambda$. More specifically for each colorant, this constant is the *unit absorption coefficient*, or the absorption coefficient for unit concentration of dye at wavelength λ , denoted

$\left(\frac{k}{s}\right)_\lambda$ (the slope of the line if the relationship between $\left(\frac{K}{S}\right)_\lambda$ and concentration, c , for the colorant is linear):

$$\left(\frac{K}{S}\right)_{\lambda,blend} = \left(\frac{K}{S}\right)_{\lambda,substrate} + c_{dye1} \left(\frac{k}{s}\right)_{\lambda,dye1} + c_{dye2} \left(\frac{k}{s}\right)_{\lambda,dye2} + c_{dye3} \left(\frac{k}{s}\right)_{\lambda,dye3} + \dots$$

Equation 2.16

The above equation applies to textile and paper dyes, which become dissolved in the substrate, and therefore contribute negligible scatter relative to that contributed by the substrate itself. For textiles, dye concentration is the concentration of dye in the fabric, as distinct from the concentration of dye in the dyebath; uptake of dye by the fabric approaches a maximum as dyebath concentration increases, an effect that needs to be taken into account when developing an overall blending model.

A second form of the blending equation is used for the blending of pigments, which colour paints and plastics. The *two-constant K-M blending equation* is so called because pigments are particulate colorants which scatter as well as absorb light; separate absorption and scatter coefficients therefore, are required for each pigment:

$$\left(\frac{K}{S}\right)_{\lambda,blend} = \frac{K_{\lambda,blend}}{S_{\lambda,blend}} = \frac{K_{\lambda,substrate} + c_1 k_{\lambda,1} + c_2 k_{\lambda,2} + c_3 k_{\lambda,3} + \dots}{S_{\lambda,substrate} + c_1 s_{\lambda,1} + c_2 s_{\lambda,2} + c_3 s_{\lambda,3} + \dots}$$

Equation 2.17

At higher pigment concentrations the two-constant model might not hold. K_λ is proportional to pigment volume fractions or concentrations, even when these are high. But while scatter is related linearly to pigment concentration at low concentration, at higher concentrations pigment particles interact due to the decrease in distance between them and this hinders scattering (Schabbach *et al.*, 2009).

The derivation of separate absorption and scatter coefficients is more complex than deriving the single constants, and is summarised in Berns (2000). Further details will not be given here, as dyes will be the focus of this thesis.

2.4.4. Instrumental colour matching based on the K-M blending equations

When the relationship between colorant input (including the substrate) and colour output is known (that is, the relationship has been modelled and validated) it becomes possible to reproduce or match any colour by combining the substrate with the colorants in the appropriate quantities. When a match is possible between the colour output from the colorant-substrate system and the target colour output, it will be either non-metameric, that is, the two colour outputs will match under all viewing and illumination conditions, or it will be metameric, with the outputs matching under only one set of viewing and illumination conditions. The methods described below form the basis for computer-based colour matching (*'colour recipe prediction'*) used in such industries as the paint, plastics, ceramics and textiles industries.

2.4.4.1. Non-metameric matching using spectral and colorimetric methods

Non-metameric matches are possible only when the substrate and colorants that will be used for matching are the same as those used to produce the target colour, and when the target and match are produced under the same conditions. In a non-metameric match, the spectral outputs of the target and matching systems will be identical, at all wavelengths. For dyes, spectral matching using the single-constant blending equation can be used to compute the quantities needed to match a target. Either:

- a) The equation is written for the wavelength of maximum absorption, $\lambda_{\max}$, for each dye (meaning the number of equations is the same as the number of unknown dye quantities) and the equations solved simultaneously, or
- b) If the number of wavelengths sampled exceeds the number of unknowns, the method of least squares can be used to solve for the unknown dye quantities. This is the preferred method because $\lambda_{\max}$ can change with concentration.

Dye quantities for non-metameric matches can also be computed by the colorimetric method, which aims to match the pseudo- X, Y and Z tri-stimulus values, X^P , Y^P and Z^P , of the target.

These are similar to X , Y and Z proper (Section 2.3.3 and Figure 2.6), but have the reflectance term replaced by $\left(\frac{K}{S}\right)_\lambda$ for the substrate and target colours, or $\left(\frac{k}{s}\right)_\lambda$ for the dyes. The general form of the colorimetric matching equations is given below. Full details can be found in Berns (2000).

$$\begin{aligned} X_{10}^P \text{ target} - X_{10}^P \text{ substrate} &= c_1 X_{10}^P \text{ dye1} + c_2 X_{10}^P \text{ dye2} + c_3 X_{10}^P \text{ dye3} \\ Y_{10}^P \text{ target} - Y_{10}^P \text{ substrate} &= c_1 Y_{10}^P \text{ dye1} + c_2 Y_{10}^P \text{ dye2} + c_3 Y_{10}^P \text{ dye3} \\ Z_{10}^P \text{ target} - Z_{10}^P \text{ substrate} &= c_1 Z_{10}^P \text{ dye1} + c_2 Z_{10}^P \text{ dye2} + c_3 Z_{10}^P \text{ dye3} \end{aligned}$$

Equations 2.18

2.4.4.2. Metameric matching using the colorimetric method

More commonly, it is possible to produce only a metameric match, because target and matching systems often differ in their substrates, dyes and dyeing conditions. Under these conditions it is not possible to produce a spectral match, and attempts at spectral matching will very likely produce a poor visual match. Colorimetric matching is useful in that different spectra can still produce the same tristimulus values, and therefore a visual match, under a single set of viewing and illuminating conditions. Such a match is conditional, specific to the selected observer and illuminant conditions.

For metameric matching using the colorimetric method, the inclusion of a partial derivative weighting function d_λ , in the calculation of X^P , Y^P and Z^P , is needed to aid matching (Allen, 1966). If the colour difference between the target and predicted match is still large, a correction matrix is applied to calculate the changes that are needed in the dye recipe to reduce this difference. Typically, colorimetric matching will be an iterative process (Figure 2.8) in which the colour difference between the target and predicted match is gradually minimised; the process is stopped when the difference falls within a predetermined limit, for example, if the differences in X , Y and Z tristimulus values (not the pseudo-tristimulus values) between the target and match fall within 0.01 (McDonald, 1987). X , Y and Z tristimulus values are computed for the predicted match from the recipe generated at each iteration step. According to

the Allen algorithm (Allen, 1966), the inclusion of the weighting function d_λ , generates a more effective starting recipe, which can reduce the number of iterations required.

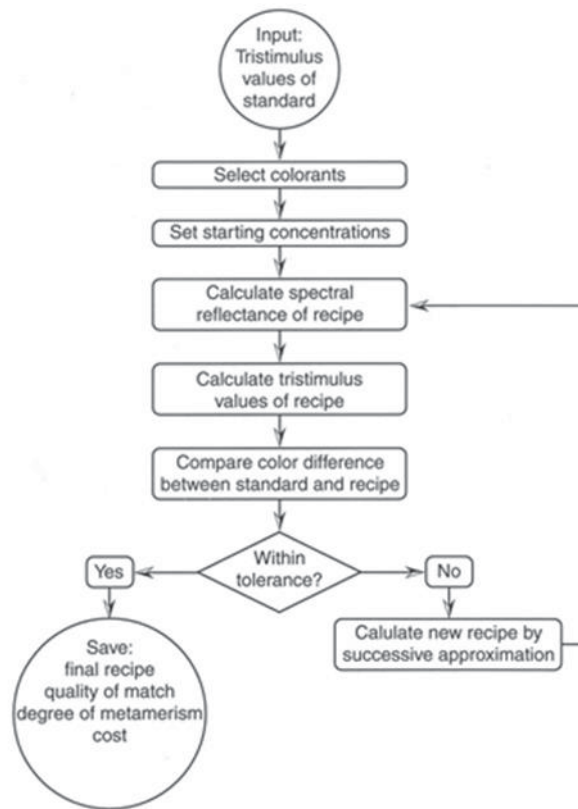


Figure 2.8 The iterative process of producing a match to a target colour using the colorimetric method (Berns, 2000).

2.5. Colour management

2.5.1. Overview and definitions

Colour printing is one version of colour reproduction in which the colours displayed by one medium or device are reproduced in another. The set of colours displayed by the first medium are referred to as the *original* colours while the set displayed by the second medium is the *reproduction*. Typically in colour printing, the original colours are seen in the form of a screen image (such as those displayed by monitors or digital cameras), and their reproduction displayed in hard copy form, such as on a paper surface. Before proceeding it is important to establish some definitions:

- An **image** is a two-dimensional visual stimulus, and has associated **digital image data** (Morovic, 2003);
- A **medium** captures or displays colour information (e.g. a CRT monitor, digital camera or scanner); in printing, the colour reproduction medium is not the printer but the combination of printer, colorants and substrate (e.g. paper) (Morovic, 2008).
- While a printer by itself is not a medium, it is a **device**. Media such as monitors, cameras and scanners double as devices (Morovic, 2003). A device links digital data and colour stimuli (Morovic, 2008); **input devices** (such as digital cameras and scanners) have colour sensors and produce data, whereas **output devices** (e.g. monitors, projectors, printers) receive data and produce colour stimuli. Therefore the terms *input* and *output* do not necessarily refer to *original* and *reproduction* respectively; for example, original and reproduction data could each be monitor RGB data.

The terms device and medium (media) will be used interchangeably in this review.

The systems by which colours are encoded and the ranges of colours that can be displayed are *device-specific* or *device-dependent*. In colour reproduction these incompatibilities are managed by *device characterisation* and *gamut mapping*, allowing the colours to be ‘handled’ within a common, *device-independent* space. An overview of the *colour management* process is given in Figure 2.9.

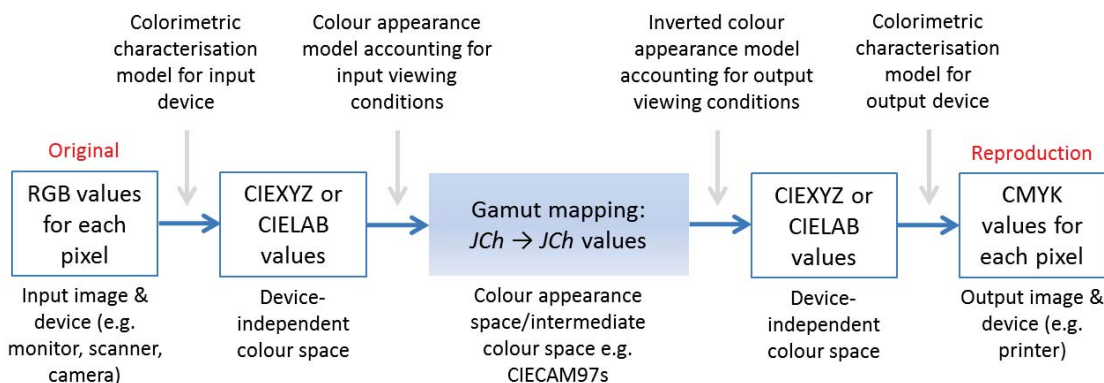


Figure 2.9 Flowchart illustrating the general process of cross-media colour reproduction, using the example of device-independent colour imaging from screen to print. Adapted from Fairchild (2005) and Morovic (2003).

2.5.2. Device characterisation (profiling)

Data used by devices such as monitors, scanners, and digital cameras encode RGB values for each picture element (pixel) in the displayed image, while printers typically use data encoding CMYK values. The device-dependent nature of these data however, actually refers to differences between devices that use the same type of data. For example, the same CMYK values used by different printers can produce slightly different colours and different scanners and digital cameras can produce different RGB values for the same colour (Sharma, 2003). In digital cameras, this is due to the sensitivities of the spectral sensors differing among cameras (Hutchings *et al.*, 2002). In CRT displays, it is the performance (‘colour’) of the phosphors (image dots) which glow and emit light that can vary between monitors (Sharma, 2007). Media or devices displaying the original and reproduction might also use the same type of data, such as when images originally displayed by a camera are viewed on a monitor.

The relationship between device-dependent values and their corresponding values in a device-independent colour space need to be determined. As well as acting as the common colour space in colour reproduction, the device-independent space is one which is based on the visual perception and matching of colours (such as the CIELAB space) rather than the mixing of colours (the RGB and CMYK spaces) (Sharma, 2003; Kang, 2006). Furthermore, sensors in devices such as cameras do not share the same spectral sensitivities as the CIE standard observer (Hutchings *et al.*, 2002). CIELAB (and CIEXYZ) values are device-independent in that colour stimuli with the same values will appear the same when viewed under the same conditions (Hutchings *et al.*, 2002), whereas stimuli having the same device-dependent values, such as RGB, can be different.

The relationship between device-dependent and device-independent values takes the form of a *device profile* or *device colorimetric characterisation model*. Profiles are computer files which follow a format set by the International Color Consortium (ICC), and are most often custom generated (Sharma, 2003). Prior to characterisation devices should be *calibrated* to establish the settings for repeatable performance (Sharma, 2007). The general procedure that is followed

for device *characterisation* is to have the device display or reproduce a series of colour patches, measure the CIE values of the displayed colours and then to derive the mathematical relationship between the CIE colours and the device values (RGB or CMYK) of each patch (Hutchings *et al.*, 2002; Sharma, 2003). Monitor characterisation is based on patches displayed by the monitor that are produced from increasing the digital counts of the three RGB primaries, up to and including each primary at full strength (a maximum count of 255) (Sharma, 2007). Scanner characterisation uses device RGB values obtained by scanning the colour patches in a test chart (such as those in the IT8 series) and the Lab values obtained by measuring the patches using a spectrophotometer. Printer characterisation uses the known RGB or CMYK values for each patch in the digital test chart that is to be printed, and the measured colour values of the printed output (Sharma, 2007). Data from device characterisation are stored in single and multi-dimensional look-up tables (Sharma, 2007) and can be used in either *forward* or *inverse* transform modes, for original and reproduction data respectively.

2.5.3. Colour gamut mapping

The range of colours that can be produced by a given medium is also specific to that medium, a feature that remains after device characterisation. This range, or *colour gamut*, is device- or medium- dependent owing to differences in the imaging process and colorants used by different media, or to differences in their physical properties. Gamuts will differ in size between different media and devices. Referring to the definitions given earlier, a gamut can be the set of colours contained in an image, or the colours that are reproducible by a given device or medium. A colour gamut is also specific to a given set of viewing conditions, and these conditions must be specified (Morovic, 2003).

Gamut differences present a problem for colour reproduction in that some of the original colours might not be able to be displayed or produced by the reproduction unless suitable modifications are made to these original colours. The process of altering colours in the original image, and replacing them with ‘ones that a given medium is capable of reproducing’ (Morovic, 2003) is called ***colour gamut mapping***. Colour gamut mapping is a necessary part of transcribing

display images to hard-copy print, because RGB gamuts are larger than CMYK gamuts (Grey, 2004; Nate, 2004) . RGB colours outside of the CMYK gamut are said to be *out-of gamut*.

In colour gamut mapping, for practical reasons, gamuts are treated as continuous volumes in colour space, rather than as a set of discrete colours (Morovic, 2008). Two properties of these volumes require definition before mapping can take place; these are the CIE colour space for mapping and the colour gamut boundary, which are discussed below.

2.5.3.1. Colour appearance spaces: CIELAB and CIECAM97s

Gamut mapping needs to take place in a device-independent space which also needs to take into account the conditions under which the original, and reproduction, are viewed. This intermediate colour space should therefore be a *colour appearance space* that is based on a *colour appearance model*. As defined by CIE Technical Committee 1-34, a colour appearance model is

“Any model that includes predictors of at least the relative color appearance attributes of lightness, chroma and hue. For a model to include reasonable predictors of these attributes, it must include at least some form of a chromatic adaptation transform. Models must be more complex to include predictors of brightness and colorfulness or to model other luminance-dependent effects such as the Stevens effect or the Hunt effect”
(Fairchild, 2005).

Chromatic adaptation refers to the ability of the human visual system to adjust to changing conditions of illumination, resulting in the colours of objects appearing more or less the same under, for example, daylight and incandescent illumination (Fairchild, 2005).

While CIELAB is unable to predict luminance-dependency (such as the increase in *colourfulness* and *contrast* with luminance), or the effects of background and surround (Fairchild, 2005), it is considered a colour appearance model on the basis of its lightness, hue and chroma predictors and incorporated chromatic adaptation transforms. Strictly speaking however, CIELAB was originally designed as a uniform colour space for the specification of

colour differences between colours of identical size, shape and viewing conditions. Also, CIELAB can lack accuracy in its chromatic adaptation transforms and in its ability to predict hue in different parts of the colour space. The latter feature however, is shared by other colour appearance models (Morovic, 2003).

Another example of a colour appearance space is the one based on the CIE colour appearance model (1997), CIECAM97s, which has correlates for the appearance attributes brightness, colourfulness and saturation, as well as for lightness (denoted J), chroma (C) and hue (h). The space also uses the coordinates J,a,b (Fairchild, 2005). The choice of which appearance attributes to use for gamut mapping depends on the specified contribution of the light source under which the original is viewed, and on the properties that are desired in the reproduction, as specified by a rendering intent (Morovic, 2003). Rendering intents are discussed in Section 2.5.3.3 below.

2.5.3.2. Gamut boundary computation and gamut sampling

The formal CIE definition of a colour gamut boundary is ‘*a surface determined by a colour gamut’s extremes*’ (Morovic, 2008). Being able to describe this boundary, in the form of a computed *gamut boundary descriptor*, or *GBD*, allows gamut mapping lines (as well as their direction, centre of gravity, and their intersections with the boundary) and mapping distances to be established. In the case of colour printing, GBDs are needed for the original image and reproduction medium gamuts. GBDs can be either generic, or medium-specific. Generic GBDs are comprised of the points that form a convex hull or alpha shape around the gamut, or the points which are the maxima of evenly divided spherical segments of the colour space. This type of GBD is suitable for image gamuts or palettes of spot colours (Morovic, 2008). In this respect, the image gamut refers to the gamut of all the image *pixels*; this will differ to the *perceived* gamut of the image because not all pixels will be perceptible, or pixels will occur infrequently in an image. Perceived image gamuts require a different approach which is yet to be firmly established (Morovic, 2003). Medium-specific GBDs can be computed from a characterisation model, as the “the gamut of the device is implicitly quantified” during device

characterisation (Sharma, 2007). One method for computing medium-specific GBDs is based on the Kubelka-Munk equations (Morovic, 2003).

Rather than to base the computation of GBDs on entire sets of colours, which can number into the tens of thousands (for the colours in an image) or hundreds of thousands (for media gamuts), it is more practical to use a smaller sample. Samples can be taken from the entire gamut volume, or from the gamut surface only (Morovic, 2003). Indications are that a subset of around 1,000 colours is needed for volume sampling of image colours, referring to an example given in Morovic (2003). Sampling is not required for smaller sets of colours, such as the 1,114 colours of the Pantone Formula Guide® (Morovic, 2008). In certain situations, a denser sampling is required (see below) which, for imaging media, means that the size of the sample is in the order of the size of the population gamut (Morovic, 2008).

The GBD represents the combined effects of the size of the sample and whether the GBD algorithm results in a ‘tight’ or ‘loose’ gamut boundary. Morovic (2008) gives a detailed discussion on the contributions of these effects, and on the implications for the relationship between sample-derived gamut boundaries and those of the colour population from which the samples are drawn. Briefly, sample-derived gamut boundaries could either under- or over-estimate the population gamut, which itself can be small or large (Morovic, 2008), with consequences such as population colours remaining out-of-gamut even after mapping, colours being mapped unnecessarily, or regions of gamuts not being used. The best estimation of a population gamut boundary will come from a combination of dense sampling and a ‘tight’ boundary.

2.5.3.3. Gamut mapping algorithms and rendering intents

In the process of altering colours in the original image, and replacing them with ‘ones that a given medium is capable of reproducing’ (Morovic, 2003) it is not only the difference between the gamuts of the original and reproduction (the *source* and *destination* gamuts respectively) that need to be taken into account. Within these constraints, the properties that are desired in

the reproduction, relative to the original, also need to be specified. Broadly speaking, either an *accurate* or a *pleasant* reproduction will be aimed for, and within each there are various sub-types (Morovic, 2003). These objectives are referred to as *rendering intents*. An accurate reproduction specifies that the reproduction be as close as possible to the original, whether it is pleasant or unpleasant (Morovic, 2003), and both are compared side-by-side as in a copying environment (Braun *et al.*, 1999). A pleasant reproduction aims to be pleasant, irrespective of the pleasantness of the original (Morovic, 2003), and is not compared to the original, as in a printing environment (Braun *et al.*, 1999). The rendering intent decides the set of appearance attributes that are the focus of mapping. The combination of lightness and chroma are used if the appearance of an original is taken to be its appearance relative to a reference white, while brightness and colourfulness are used in situations such as art reproduction where the conditions of the original surroundings are more important (Morovic, 2003).

Typically it is accurate reproduction that is aimed for, because these are the better understood, and the more straightforward to achieve (Morovic, 2003). There are two main types of mapping algorithm that are used to achieve an *accurate* reproduction: clipping algorithms and compression algorithms. Clipping algorithms are applied to out-of-gamut original colours only, which are replaced by those on the surface of the destination gamut boundary, with the aim of maintaining overall accuracy. Compression algorithms transform all colours, whether within or out-of-gamut, and are replaced by colours inside the destination gamut, thereby preserving relativity. Clipping and compression algorithms are usually hue-preserving, that is, they take place within a plane of constant hue angle; colours are clipped or compressed along pre-defined lines (for example, towards a ‘centre of gravity’ on the lightness axis, Figure 2.10), or clipped along the line with the shortest distance (*minimum ΔE clipping*), toward the reproduction gamut boundary. Alternatively, there are minimum ΔE clipping algorithms which do not preserve hue (Morovic, 2008).

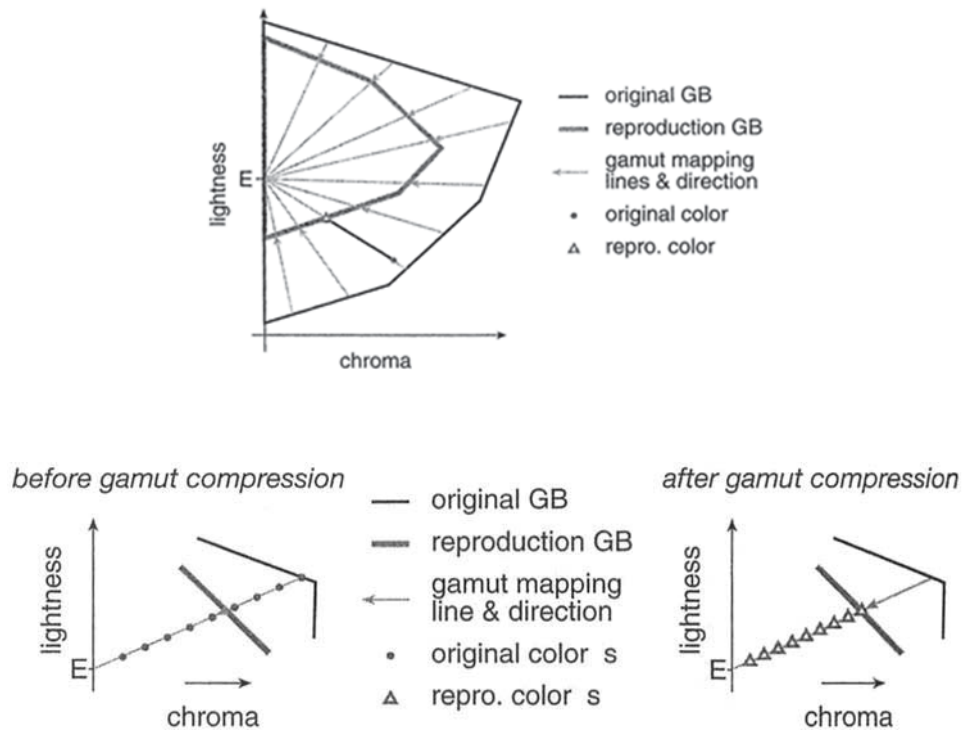


Figure 2.10 An illustration of colour gamut clipping (top) and colour gamut compression (bottom) towards a centre of gravity, E, on the lightness axis (Morovic, 2003).

2.5.3.4. Quality (evaluation) of reproduction: print

The evaluation of the reproduction is made against the rendering intent, and will apply only to the image and media that are involved (Braun *et al.*, 1999; Morovic, 2003). However no established model exists for quantifying the appearance of complex images or for quantifying the difference between original and reproduction (Kang, 2006). Braun *et al.* (1999) used panels of individuals (with various levels of experience) to judge reproductions of colour images that were made using various gamut mapping algorithms. Clipping algorithms were overall the better performing when the reproduction was compared to the original. Contrast-boosting algorithms newly developed by the authors did better than clipping algorithms when images were ranked in order of preference in the absence of the original. The latter result highlights the influence of lightness or darkness in source image content (Morovic, 2003); the contrast-boosting algorithms may have lightened images that were dark to begin with (Braun *et al.*, 1999).

2.6. Colour in food

2.6.1. The role of colour in food: Colour is a part of total appearance

In the context of this review, the role of colour in food refers to the role that colour plays in the selection and consumption of food, as distinct from the physiological role of pigments within the foods in which they naturally occur.

Colour is an appearance characteristic which contributes to the visual assessment of food quality. Judgements of the safety, sensory characteristics (taste, texture, and flavour) and acceptability of a given food, prior to its selection and/or consumption, are made relative to the range of acceptable colours for that food (Clydesdale, 1993; Francis, 1999). Learned associations of colours with different qualities create expectations of how foods might taste and of their flavour. As a result, basic tastes in solution are detected at lower concentrations when solutions are coloured and flavoured appropriately for a given taste (Maga, 1974; Johnson and Clydesdale, 1982). Fruit-flavoured beverages need to be appropriately coloured in order for the flavour to be correctly identified (DuBose *et al.*, 1980), and perceived flavour intensity increases with increasing colour intensity. Increasing levels of added red or orange colour increased the overall acceptability of cherry- and orange- flavoured beverage samples respectively, up to a point, before levelling off or decreasing, at most levels of added flavour. A more interactive effect was seen between the levels of added yellow colorant and added flavour in cakes, with overall acceptability of cakes peaking at different concentrations of yellow colorant for each of the levels of added flavour (DuBose *et al.*, 1980).

While colour itself does provide a ‘very useful and intuitive indicator’ (Joshi and Brimelow, 2002) of visual food quality, the role of colour in influencing judgements and expectations of quality depends on its importance relative to other appearance characteristics. Colour is of major importance in the selection of paints and clothes (Hutchings, 2002), and the same could be presumed for transparent coloured beverages, such as the ones discussed above. The psychophysical properties of foods (and beverages), such as translucency, gloss, surface texture

and shape, can have more influence in their colour appearance than the colorants contained within (Joshi and Brimelow, 2002). For example, small changes in scatter could be more effective than changes in pigment concentration in changing colour appearance (MacDougall, 2002a). As well, individual appearance characteristics of foods can change over the lifetime of a product, or with different processing conditions (Hutchings, 2010).

In turn, expectations of food quality are formed from their *total appearance* (Hutchings, 2002). Contributors to total appearance are the characteristics of the product, or scene, itself (including material and optical properties, and lighting) as well as those of the viewer (including such factors as vision, inherent and learned responses and need). Images are derived in the brain of the viewer from total appearance. These images are comprised of basic, and derived, perceptions. *Basic perceptions* of food appearance are formed from the colour, translucency, gloss, size (including shape) and visual texture of each element of visual structure. A slice of bacon is an example of a food having a multi-element visual structure. Basic perceptions lead to *derived perceptions*, or *expectations* of taste, flavour and in-mouth texture (which together help to identify the food), safety, and satisfaction (Hutchings, 2003). Expectations can be either positive or negative, based on previous experience. Expectations are also created of similar foods. Acceptability depends on the extent to which these expectations are met.

An understanding of the contribution of colour to food quality, and of its effects on other sensory characteristics will be needed given the increased role that colour is expected to have in the design of new foods to meet dietary recommendations, which match the appeal of their traditional counterparts (Clydesdale, 1993). For the traditional products themselves, colour and appearance can be optimised using methods to quantify acceptability tolerances and the expected levels of a range of sensory characteristics, based on the visual assessment of a large number of digitally-rendered colours, as has been done for orange juice (Wei *et al.*, 2012). The use of virtual colours in CIELAB space allows more detailed product profiles or maps to be developed for quality control and marketing purposes. Control of food colour and appearance is important because acceptable or preferred colours for the same product can differ between

different international markets and even within a country as is the case for tomato soup colour in the UK (Hutchings, 2002). At the same time, customers expect a high degree of product uniformity (Hutchings, 1999).

2.6.2. Describing and measuring food colour

2.6.2.1. Visual measurement

In the food industry, colour is usually assessed using visual methods, rather than by the instrumental methods used for non-food materials that have been discussed earlier. In non-food surfaces “colour can be isolated as a single visual and instrumental property” (Hutchings, 1999), and as previously described small tolerances are applied to the matching of surface colours, requiring accurate measurement. In contrast, food colour and appearance is more complex in nature, and differences among food colours that exceed threshold or supra-threshold are less of a concern. Visual assessments are typically performed under controlled viewing and illumination conditions by expert sensory panels that have been specially selected, screened and trained for the task (Hutchings, 2002). Basic and derived perceptions of food colour and appearance are described using sensory descriptors and scales that are based on either memory, or comparison to physical standards representing foods (Hutchings, 1999). Examples of the latter are colour atlases such as the Munsell system, and product-specific colour charts, photographs or standards such as the Roche Yolk Colour Fan, plastic tube standards for processed orange juice, and the Lovibond glass standards for beer, butter, milk and oils.

2.6.2.2. Instrumental measurement

On the other hand, sensory evaluation can be time- and labour- intensive (Joshi and Brimelow, 2002), and a number of factors could affect panel performance such as fatigue, poor memory and an inadequately controlled environment (Hutchings, 1999). In its place instrumental methods offer speed, standardisation and convenience. As with non-food materials, instruments that are used to measure colours are proxies for human perception. To this end reflectance should be measured using an illuminant close to the lighting conditions under which the food is

normally viewed (Joshi and Brimelow, 2002). CIELAB values of meat measured under the D65 and 10° standard conditions might differ from the colour perceived under retail or domestic conditions, particularly with respect to hue (brown or red) (MacDougall, 2002a). The specular component-excluded viewing geometry (SCE) eliminates front surface reflections and is applicable to most situations covering opaque, translucent and transparent samples (Joshi and Brimelow, 2002). For glossy samples the SCE condition is the instrumental equivalent of an observer having to move the sample to view the colour independently of the mirror reflection (Berns, 2000).

Importantly, as most instruments (colorimeters and spectrophotometers) have been designed to measure homogeneously coloured, flat and opaque surfaces such as paint and paper, consideration needs to be given to sample presentation, when catering to the much broader range of colour and appearance properties displayed by foods. Flat surfaces can be created when needed by grinding, milling, cutting or pressing. For non-colour-uniform surfaces, a number of measurements can be taken from different areas in order to obtain an average result. Translucent samples can be measured at a thickness at which it is optically opaque (i.e. the thickness beyond which there is no change in measured reflectance) or at a lower, standardised thickness against a white backing, using a large measurement aperture to ensure the light that is diffused within the sample is captured when it re-emerges.

2.6.2.3. Describing colours, including the use of the Kubelka-Munk function

Measured food colours can be expressed in a number of ways, depending on the application: as full reflectance curves or reflectance at a specified wavelength, or as CIELAB or HunterLab values. $L^*a^*b^*$ is ideal for colour monitoring during production runs, while $L^*C^*H^*$ might be better correlated with visual sensory data (Joshi and Brimelow, 2002).

The Kubelka-Munk approach to describing colour in terms of colorant content, which forms the basis of computer colour matching for non-food materials, has been attempted for foods, but for a different reason: to identify pigments and determine their concentrations in foods without

having to do chemical analysis (Hutchings, 1999). A linear relationship was demonstrated between the log K/S values at around 510-520nm and concentration of added pigment in a model system for salmon (Hutchings, 1999), and the K-M function has been used to determine pigment content in fresh meat, also based on reflectance measurements at selected wavelengths (Dean and Ball, 1960). Caution should be exercised when using this approach because of the contribution of effects other than pigment content to measured colour, such as those of sample structure. Still, the K-M approach can be used to characterise a translucent sample in terms of scattering effects as well; the relative contributions of absorption and scatter can be determined by measuring thin sample layers against black and white backgrounds. K/S ratios for tomato pericarp increased with storage time for cut fruits, relative to stored, intact fruits, in line with development of visual translucency. The decrease in scatter might have been due to a decrease in refractive index differences as liquid replaced gas in the intracellular space (Lana *et al.*, 2006).

2.6.2.4. Colour differences and colour tolerances

Colour difference equations and tolerance levels, described earlier in Section 2.3.4 for non-food applications are used also in food applications. These are used to correlate instrumentally-measured colour data with sensory colour data for which CIELAB and CIE94 have seen increasing use (Joshi and Brimelow, 2002), or to describe the distance from a standard (Hutchings, 1999) where differences based on CIELAB and HunterLab have been used (Table 2.4). Colour matching in the food industry does not require the same high levels of accuracy as seen in non-food industries (Francis, 1999; Joshi and Brimelow, 2002), and therefore advanced colour equations (from CIE94 upwards) might be either too precise for needs (Joshi and Brimelow, 2002), or in the case of CIEDE2000, the need for this level of precision is not yet known (MacDougall, 2002a).

As with non-food applications, the relative contributions and importance of lightness, hue and chroma to overall colour differences might differ according to the specific food application. For example hue has more importance than the degree of lightness in tomato juice, while in roasted

ground coffee and canned tuna, lightness is more important (Francis and Clydesdale, 1975). Francis and Clydesdale (1975) suggested that for quality control purposes tolerance levels be based on all three (lightness and chromatic) dimensions, giving more weight to those dimensions having more importance, while something simpler could suffice for the evaluation of consumer acceptability. Adding a red pigment to squash puree both reddens and darkens the colour, but acceptability may be based only on the change in redness (Francis and Clydesdale, 1975).

2.6.2.5. Challenges in correlating instrumental measurements with visual assessments

Problems still arise because instrumental measurement conditions are ‘fixed’ or stipulated, whereas perceptions of colour and appearance can change according to the angles of viewing and illumination, the type of illumination, and orientation of the sample (Hutchings, 1999). In a dilution series of orange juice concentrate the most dilute sample, when measured, is found to be the darkest (at infinite thickness) due to the lower concentration of scattering particles, consistent with a decrease in scatter coefficients from thin layer measurements against black and white backgrounds. Visually however, the most dilute sample is perceived to be the lightest, due to multi-directional illumination creating ‘glow’ in translucent samples (MacDougall, 2002a). Similarly the measured lightness of semi-skimmed milk and tomato juice is around 10 L* units (CIELAB, D65) lower than that of the NCS atlas colours which are the closest visual matches to these beverages (MacDougall, 2002b). In the same study, measured L* values for cereals and baked goods were found to be up to 21 units lower than those of their NCS matches. In the case of the bread and cake, instrumental measurement includes the bubbles resulting in darker colours whereas visual assessments of colour are made separately from the bubbles (MacDougall, 2002b). The flash illumination used in colour measuring instruments has a high power to compensate for the short illumination time, but this also means that the light is able to pass through most materials, and that therefore samples will be recorded as being darker than they are actually (Negueruela, 2010).

2.6.2.6. Calibrated digital image analysis systems

The instrumental measurement of food colour and appearance is better served by calibrated digital image analysis systems. These systems offer a controlled, non-contact, non-destructive means of measuring colour and appearance characteristics, including surface textures and uneven colours, meaning samples are measured as they would be viewed by the consumer. As a digital format, so long as images are taken with consistency, calibrated imaging facilitates direct product comparisons across different locations. Changes in food colour and appearance that occur over time and/or with changes in processing conditions can be monitored more effectively. In contrast colorimeters and spectrophotometers are capable only of measuring average colour, and often the sample being measured will not be (or cannot be presented) in its original form.

Table 2.5 lists the features of two different calibrated image analysis systems – DigiEye (Luo *et al.*, 2001b) and the machine vision (MV) system by Luzuriaga *et al.* (1997) - designed specifically for food applications. These systems are similar in their basic features, being made up of a digital camera, an enclosed cabinet or light box simulating the diffuse, D65 condition (additionally angled illumination for DigiEye), a monitor, and image analysis software. DigiEye also comes with a printer. DigiEye is a fully calibrated system in which the camera, monitor and printer undergo characterisation. Less detail is given about MV system calibration, only that it was calibrated using the Gretag Color Checker colour standards, and that a red reference object was placed next to the sample tray to calibrate fruit images (Balaban *et al.*, 2008). The software in both systems measures the colours of individual pixels in the captured images and then groups the pixels according to a number of representative colours, thereby forming a useful basis for the analysis of all food colours, particularly the non-homogeneous colours in many natural and multi-component foods (Table 2.5). DigiEye software also does simulations and runs the camera and monitor characterisation.

Table 2.5 Features comparison of the DigiEye and Machine Vision calibrated colour image analysis systems for food applications.

	DigiEye (Luo et al., 2001)	Machine Vision System (Luzuriaga et al., 1997)
Camera	Characterised SLR camera	CCD colour video camera (Luzuriaga et al., 1997) or progressive scan digital camera (Balaban et al., 2008) used for capturing still images
Light box: illumination and background	Two sets of lamps simulating D65 standards, each at 45° to the sample, from above; diffuse illumination (from both sides) used for measuring colours <i>per se</i> , and removes specular reflections from wet or glossy foods, angled illumination (single side only) produces higher contrast suitable for textured surfaces and fine detail; light box interior provides a neutral grey background.	Originally developed with light box interior housing the sample being lit from above and below using two bulbs at each position; diffuse illumination provided by white interior walls and translucent acrylic sheets placed between bulbs and light box interior (Luzuriaga et al., 1997). Two fluorescent light bulbs simulating D65 used in the study by Balaban et al. (2008), therefore samples presumed to have been lit from above; also in this study, samples were placed against neutral grey paper on a tray.
Software for image capture and image analysis	DigiEye Colour Clustering software: pixels in captured images grouped according to colour, each colour calculated as a percentage of the total number of pixels within the image. The software can also be used to digitally alter images to simulate the effect of adding different colours to different textures or to new and existing products, and to simulate the effects of other standard light sources.	LensEye software (Balaban, 2008); analyses include those of: • average colour - from L*,a*,b* values of every pixel (Balaban et al., 2008); • indicators of non-homogeneity (Balaban, 2008), including: ○ colour blocks - division of RGB colours into 64 (4³), 512 (8³) or 4096 (16³) blocks each represented by the colour at the block centre; pixels falling within each block counted and percentage area of each colour (centre) calculated based on total number of pixels; ○ colour primitives – continuous areas of the image within which the intensity of each pixels falls within a given threshold value, relative to an anchor or reference pixel; primitives share the same threshold constraint but differ in their reference pixel
Examples of food applications	Effect of baking time on bread crust colour and its surface distribution; separate <i>in situ</i> measurements of sauce and bean colours to compare different brands of baked beans (Leedham and Boulter, 2007); DigiEye images used by others as the basis for analysing the distribution of fruit pieces in a cake product as a function of viscosity when different cooking methods and times were used (Leedham and Boulter, 2007)	Colour changes in shrimp during refrigerated storage (Luzuriaga et al., 1997); non-homogeneity of colours in fresh fruit and meat, and in ripening banana (Balaban, 2008; Balaban et al., 2008)
Features/use supporting the colour sensory analysis of foods	Characterised printer allows hard copy images to be produced which can be used as accurate and reliable reference or master product standards for visual assessments; assessments by panellists could also be made via characterised monitors.	Colours representing colour blocks occupying more than 1% of the sample area from the image analysis of fruit samples were selected as reference colours (n=15) for visual evaluation of the same fruits (on trays or on screen) by untrained panellists; average colour of samples based on visual evaluations compared to average colours from image analysis of samples (Balaban et al., 2008).

2.6.2.6.1. As a tool supporting the colour sensory analysis of foods

The performance of (untrained) panellists was found not to differ significantly between evaluations made of real samples and their images (Balaban *et al.*, 2008). Because it provides a visual record of a food at the time of imaging, calibrated image analysis is ideally placed to support the colour sensory analysis of foods in a number of ways. These include the production of reference colour standards which are related directly to processing and pigment effects, and the visual evaluation of products by distance or at a time beyond the shelf life of perishable foods (Balaban *et al.*, 2008; Harkness *et al.*, 2010).

The benefits of using a system such as DigiEye which is capable of simulations is that panellists can view virtual instead of real products thereby saving time on sample preparation; calibrated digital displays were used for the visual assessment of rendered orange juice colours in the study by Wei *et al.* (2012) in building an acceptability and expectations profile for this product.

Another application of digital colour analysis in colour sensory evaluation is the use of machine vision to quantify sensory panel assessments of non-homogeneous food colours, the rationale being that consumers and industry still rely on visual inspections to make choices or in grading assessments (Balaban *et al.*, 2008). Fifteen colours from image analysis (see Table 2.5) were selected as reference colours for the visual evaluation (on trays or on screen) of fruit samples (displaying uniform and non-uniform colours) by untrained panellists. Based on the selection of three reference colours and the estimated percentage area occupied by each, average $L^*a^*b^*$ colours were calculated for each sample, and compared with the average colours for the same samples from image analysis. The ΔE difference between the average colours from panel evaluations and image analysis (or the 'error of a panellist in quantifying the colour of a sample') increased the more non-uniform the sample colour. It was however, acknowledged that the size of the error might have been a function of the number of colours that the panellists were asked to select in their evaluations, and also of the number of reference colours provided.

No mention was made of the possible use of appropriate weighted colour difference equations (refer Section 2.3.4) which might have had an impact on the size of the error.

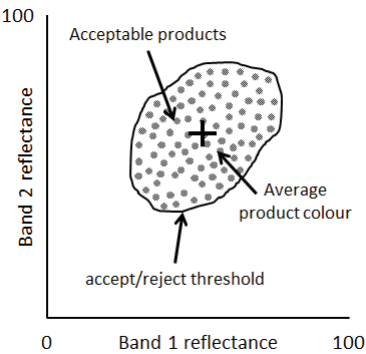
2.6.2.7. Colour sorting of bulk foods using image analysis

Image processing also forms the basis of large throughput sorters used in the food industry for the bulk sorting of products based on colour. These machines offer an automated, more consistent and more cost-effective alternative to hand sorting. The purpose of sorting is to maintain product quality, for example, by the removal of contaminants and/or blemishes, though for various reasons, colour sorters can never remove defects with 100% efficiency (Bee and Honeywood, 2002). The types of products that are sorted include seeds, rice, coffee, nuts, fresh fruit, and fresh and frozen vegetables. After products are fed into the sorting machine, the optical system measures the reflectance of each particle or object in the product stream; the image processing algorithm decides whether to ‘accept’ or ‘reject’ particles on the basis of information collected by the optical system, with the rejected particles removed by the ejection system. Acceptability limits will have been determined beforehand in the laboratory to finalise the settings appropriate for the bulk sort.

2.6.2.7.1. Reflectance measurement

Rather than being based on colour *per se*, bulk sorting is based on the measured reflectance at selected single or multiple wavelengths, as described in Table 2.6. At these wavelengths there is a difference between the spectra of accepted and rejected particles. The wavelengths are set with the aid of band-pass optical filters.

Table 2.6 Descriptions of image-based methods for the bulk sorting of foods according to the wavelengths of light used.

Sorting basis	Description	Application/examples
Monochromatic ¹	Measured reflectance at single band of wavelengths	Removal of dark items from peanuts, dried peas and white rice
Dual monochromatic	Separate reflectance measurements at two different bands	Rejection of two types of defects/foreign material, each having different spectra
Bichromatic ¹	Simultaneous reflectance measurements at two different bands, expressed as ratio of the two measurements 	Green Arabica coffee beans to sort discoloured from acceptable beans
Trichromatic	Typically, measured reflectance at bands in the green and red visible wavelength regions and a third band in the infra-red region	Detection of foreign bodies e.g. glass, stones, insects; size/shape sorting
Fluorescence	Measured reflectance after irradiation with ultra-violet light	Detection of non-visible defects e.g. bacteria
Laser	Narrow laser beam of single wavelength (within or beyond visible spectrum) used to illuminate product, which is then scattered and/or internally diffused	Sorting based on structural properties (texture and sub-surface), in addition to colour; detection of foreign objects

¹Simultaneous monochromatic and bichromatic measurements can be made by some sorters

2.6.2.7.2. Illumination and background

With the exception of laser-based optical sorting, uniform lighting for sorting is provided by fluorescent tubes, incandescent filament bulbs (Bee and Honeywood, 2002) and increasingly, by Light Emitting Diodes (LED) (Woodside Electronics Corporation, 2013; Cimbria, 2014; Satake Europe Ltd, 2014). Fluorescent lamps, which emit in selected wavelength regions within the UV-visible range, can meet most needs and are preferred for their diffuse light and cool operation; incandescent lamps with broad emission ranging from the visible blue to the near IR wavelengths, are used for bichromatic sorting or when IR is needed. LED lighting is long lasting (for 100,000+ hours (Cimbria, 2014) or a minimum lifespan of three years (Satake Europe Ltd, 2014)), reliable and efficient, and has low heat dissipation (Cimbria, 2014).

For sorting based on the rejection of dark defects, particles are viewed against an illuminated background with brightness the same as the average brightness of the product, with and without the defect. Dark particles will decrease the signal amplitude while light particles will increase it. This type of sorting is made independently of the particle size. For the sorting of shapes, the brightness of the background should differ from that of the product average, to highlight object boundaries.

2.6.3. The addition of colour to food: reasons colorants are added

The importance of the role colour has in food is indicated by the need to add colorants to preserve, restore or change the appearance of foods and beverages. As previously discussed the addition of colour influences flavour identification and intensity perception, and judgements of food quality are made relative to an acceptable range; “we are comfortable if the food we are eating is the appropriate colour” (Hutchings, 1999). Because consumers have learned to expect a high degree of product uniformity (Hutchings, 1999) the addition of colour is particularly useful where products vary naturally in colour, or where colour and appearance characteristics have been lost or damaged through processing. Furthermore, by adding colour, colourless foods can be given an attractive appearance, and the intensity of colours can be increased in foods where it is naturally low. On the flipside, the benefits of colour addition also mean that colorants have been used for adulteration purposes, including to mask deterioration, aging, poor quality and low nutritional values, and to dilute more expensive food materials, as with the replacement of cherry with grape and beetroot mixtures. Bright, high contrast, ‘non-natural’ colours, whether added to the foods themselves, or used on packaging, are being used to attract people of all ages to consume foods and beverages that are frequently high in fat, sugar and salt (Hutchings, 2010).

2.6.4. Synthetic food colorants

In this part of the review, coverage of food colorants is limited to the synthetic or manufactured (‘artificial’) non-nature-identical colorant additives. In this thesis, synthetic colorants will be

used to test the suitability of predictive colour matching algorithms being developed for the 3D colour food printer. Synthetic colorants are being preferred over their natural counterparts which in general have produced dull shades, have poor stability and fade rapidly, and have been more difficult to handle (Roefeldt Nielsen and Holst, 2002). Synthetic colorants also come in a number of different formats which should provide a range of colouring options for a potentially diverse range of food printing substrates. However it should be noted that use of natural colorants in foods and beverages has been growing at a more rapid rate than that of synthetic colours, owing to improved functionality through, for example, microencapsulation and emulsion technologies (Roefeldt Nielsen and Holst, 2002), and to increased consumer demand for ingredients from natural sources for their associated quality, safety and nutritional benefits. The latter feature will be compatible with the customised nutritional outputs offered by the 3D colour food printer.

It is not the goal here to give detailed information on the manufacture, chemistry (structure, stability and solubility) and toxicological aspects of synthetic food colorants. Such information can be found elsewhere (Francis, 1999; Beatriz and Gloria, 2005), and in Section 2.6.6 with reference to stability in different food systems. Here, and in the following sections, the focus is on the applications of synthetic food colorants, including the selection of suitable colorants and the factors that may affect their performance in foods, and on the legislative restrictions on their use. Because of the focus on synthetic colorants, detail is also reserved for addressing the concerns surrounding the link between synthetic colorant consumption and hyperactive behaviours in children.

2.6.4.1. Available colorants and restrictions on use

Table 2.7 is a list of synthetic colorants that are available for use in foods and beverages across a range of countries including New Zealand and Australia, the USA and the UK. As well as their common names the labels by which they are otherwise known are also given. The ‘FD&C’ labels refer to colorants that are certifiable for use in foods, drugs and cosmetics, and which belong to one of the three categories of coal-tar colorants created by the US Federal Food, Drug

and Cosmetic Act of 1938 (Francis, 1999). An 'E' number is given to an additive that has passed safety tests and has been approved for use in the UK and in the rest of the European Union (Food Standards Agency UK, 2014). Table 2.8 is more specific in listing the synthetic colorants allowed by various countries.

Table 2.7 Colour guide to the common synthetic food colorants. Compiled using Francis (1999), Sensient Colors Inc. (2005) and Food Standards Agency UK (2014).

FDA name	E number	Common name	λ_{max} (nm)	Approximate hue
FD&C Blue No.1	133	Brilliant Blue	630	Greenish blue (turquoise blue)
FD&C Blue No.2	132	Indigotine/Indigo Carmine	610	Deep blue (royal blue)
FD&C Green No.3	143	Fast Green FCF	625	Bluish green (sea green)
FD&C Red No.3	127	Erythrosine	526	Bluish pink (Watermelon red)
FD&C Red No.40	129	Allura Red	504	Yellowish red (Orange red)
FD&C Yellow No.5	102	Tartrazine	426	Lemon yellow
FD&C Yellow No.6	110	Sunset Yellow FCF	485	Reddish yellow (Orange)
	123	Amaranth	520	Magenta red
	122	Azorubine/Carmoisine	516	Magenta red
	124	Ponceau 4R	505	Strawberry red
	104	Quinoline Yellow	411	Lemon yellow
	142	Green S	632	Greenish blue
	155	Brown HT	460	Chocolate brown
	151	Brilliant Black BN	570	Purple

Table 2.8 Synthetic food colorants listed according to the countries in which their use is permitted. Adapted from Beatriz and Gloria (2005).

Colorant	Aus/NZ ¹	Brazil ²	Canada ²	Japan ²	UK/EU ³	USA ⁴
Brilliant Blue	+	+	+	+	+	+
Indigotine/Indigo Carmine	+	+	+	+	+	+
Fast Green FCF	+	+	+	+	-	+
Erythrosine	+	+	+	+	+	+
Allura Red	+	+	+	-	+	+
Tartrazine	+	+	+	+	+	+
Sunset Yellow FCF	+	+	+	+	+	+
Amaranth	+	+	-	-	+	-
Azorubine/Carmoisine	+	+	+	-	+	-
Ponceau 4R	+	+	-	-	+	-
Quinoline Yellow	+	-	-	-	+	-
Green S	+				+	-
Brown HT	+	-	-	-	+	-
Brilliant Black BN	+	-	-	-	+	-

¹ Australia New Zealand Food Standards Code, Standard 1.3.1 (Food Additives), Schedule 4 (Australia New Zealand Food Authority, 2000)

² Beatriz and Gloria (2005)

³ UK Food Standards Agency (2014)

⁴ US Food and Drug Administration (2011)

Restrictions apply also to the amounts of synthetic colorants that can be added to foods, and to the types of foods to which they can be added. In Australia and New Zealand these colorants

are permitted in a range of beverages and foods to a maximum level of 70mg/L and 290mg/kg respectively. Exceptions are erythrosine which is restricted to preserved cherry products (such as maraschino, cocktail or glace cherries) to a maximum level of 290 mg/kg (Australia New Zealand Food Authority., 2000), due to the erythrosine molecule containing iodine, which has been linked to thyrotoxicosis (Leatherhead Food International, 2008), and amaranth which is permitted only in confectionery, in fish roe and in formulated supplementary sports foods to a maximum of 300 mg/kg, in fruit and vegetable spreads (including jams, chutneys and related products) to 290 mg/kg, and in selected beverages to 30 mg/kg, including fruit and vegetable juice products, water-based flavoured drinks, wine-based drinks and reduced-alcohol wines, and spirits and liqueurs. Equivalent information for the EU can be found in the food additives database on the European Commission website (<http://ec.europa.eu/food/food/fAEF/additives>). Restrictions must be taken into account when importing or exporting food products containing colouring additives.

2.6.4.2. Synthetic colorants and hyperactivity in children: interpretations of findings

A study commissioned by the UK Food Standards Agency (FSA), and conducted by the University of Southampton (McCann *et al.*, 2007), investigated whether a link could be found between the intake of synthetic food colorants and adverse behavioural changes in children who were drawn from the general population and represented the full range of hyperactivity levels. Children in two groups – those aged three years, and those aged eight and nine years (with 137 and 130 subjects respectively completing the study) – were given fruit juices containing sodium benzoate and one of two colorant mixes (A or B), or a placebo mix, according to a randomised, double-blinded, crossover study design. The colorants used were those commonly found in food for children, while sodium benzoate is used as a preservative in soft drinks. Mix A contained Sunset Yellow, Tartrazine, Carmoisine and Ponceau 4R to a combined total of 20mg or 25mg, plus 45mg sodium benzoate, and Mix B Quinoline Yellow, Sunset Yellow, Carmoisine, Allura Red to a combined total of 30mg or 62mg, plus 45mg sodium benzoate. The higher totals were the dosages for the older group. The dosages in the study were

equivalent to those contained in two to four 56g bags of sweets per day. The study reported significant adverse effects (increases in the mean level of hyperactivity) of Mix A on the behaviour of the three year old children, and of Mix A or Mix B on behaviour of the older children, relative to the placebo. Further, Mix A had a greater effect on the younger group than it did on the older.

The findings from the study were said to strongly support the argument “that food additives exacerbate hyperactive behaviours (inattention, impulsivity, and overactivity) in children at least up to middle childhood” (McCann *et al.*, 2007). The advice to concerned parents from the FSA following the study was to reduce or exclude the six colorants from their children's diets. A European Parliamentary committee voted to ban all synthetic colorants from foods consumed by babies and small children (Institute of Food Technologists, 2011b). At present any food or drink in the European Union (except for drinks containing more than 1.2% alcohol) containing any of the six colorants that were the subject of the study must include a mandatory warning of the possible effects of colorant consumption on children (Food Standards Agency UK, 2014). At the same time, the FSA is encouraging manufacturers to use alternatives.

The position of the US FDA was that there was “no information (in the Southampton study) to suggest that the behavioural changes noted were adverse, detrimental, or maladaptive” (Institute of Food Technologists, 2011b), a position it maintained after the vote of an expert panel it convened, and further, that there was no need for special warning labels on foods containing artificial colorants (Institute of Food Technologists, 2011a). One of the notable shortcomings of the study pointed out by the FDA and by others, including the study authors themselves, was that the adverse effects could not be attributed to any of the individual additives, given that mixtures of colorants were used, and in combination with the preservative (McCann *et al.*, 2007; European Food Safety Authority, 2008; Institute of Food Technologists, 2011b). Significance of findings was based on means levels of hyperactivity; however large variation in the responses of individual children to the additive mixtures relative to the placebo meant that Mix B did not have any significant effects for the three-year-old children (Food Standards

Agency UK, 2007; McCann *et al.*, 2007). Factors other than dietary additives, such as genetics, are also associated with hyperactivity (Food Standards Agency UK, 2014). Perhaps the larger concern is that the colorants can encourage the consumption of high-fat, high-sugar and high-salt foods when added to these foods (Hutchings, 2010).

Estimates of average exposure to synthetic colorants for children and adolescents, based on mean levels in foods likely to contain a high amount (such as brightly coloured soft drinks) together with data collected in a 24 hour recall of 3000 children and adolescents in the 2002 National Children's Nutrition Survey, were less than 5% of the relevant acceptable daily intake (ADI), and at most were 15%. In animal toxicology studies, there were no adverse effects observed for most colours, even when fed at 5% of the total diet; typical human consumption would be less than 0.01% of the diet (New Zealand Food Safety Authority (NZFSA), 2008). Use of synthetic colorants is self-limiting due to their high colouring strength and to good manufacturing practice; this means that the amount of colorant needed is small anyway (Beatriz and Gloria, 2005).

2.6.4.3. Synthetic colorant formats

Synthetic colorants come in a number of forms each of which is suited to a different application, and there are advantages and disadvantages to using each form. Synthetic colorants are available in soluble and insoluble forms which can be added either dry, or pre-dissolved or pre-dispersed in a suitable solvent or carrier before use. Table 2.9 compares the different properties of soluble and insoluble colorants, and Table 2.10 lists examples of the types of food applications to which the different formats are suited. The examples in Table 2.10 are limited to those having some relevance to the 3D food printing substrate under development (refer Literature Review, Part 2) in that they share ingredients (e.g. sugar, starch, cake mixes) or physical properties (e.g. the consistency of edible inkjet inks and icings) in common.

2.6.4.3.1. Soluble formats: Dyes

Soluble dye powders are used in applications in which water is added at the time of manufacture, or is added later by the consumer. This includes the manufacture of coloured, dry mixes and ingredients, such as coloured sugar, which are sprayed with a liquid dye, before being dried. When dissolved in water, dyes offer a convenient and efficient means of colour addition, though blends of primary-coloured powders may ‘flash’ momentarily when a dry mix is reconstituted with water, revealing spots of the individual colours until the mixture is stirred. For low moisture or non-aqueous applications, the dyes can instead be pre-dissolved in propylene glycol, or glycerine. The higher solubility of dyes in glycerine allows for concentrated dye solutions to be prepared, which helps to keep the amount of added liquid to a minimum, and in doing so offsets the higher cost of glycerine (Sensient Colors Inc., 2005). The potential for speckling and uneven colouring in high-fat applications can be mitigated by the addition of lecithin. Specialist products such as gels and food-grade printing inks also require the highly concentrated colours that are made possible by using synthetic dyes.

2.6.4.3.2. Insoluble formats: Lakes

Lakes are an insoluble form of synthetic dyes which are produced by reacting the dye with an insoluble base. Although they have a lower colorant content than their dye counterparts, they offer a number of advantages over dyes. Dry mixes can be coloured more efficiently using lakes: lakes are easily incorporated into dry media, and there is no need for the mix to be sprayed with a liquid (dye) and subsequently dried. By using lakes, the potential for uneven colour and speckling (as seen with dye use) in reconstituted dry mixes, high-fat fillings and coatings, and from residual moisture in the pan-coating of candies, can be avoided. For applications other than dry, lakes are added in the form of a suspension or dispersion; suitable carriers include vegetable oils, propylene glycol, and glycerine. However there is still a place for using dispersed *dyes* in coating applications, rather than lakes, if needed (Table 2.10).

Table 2.9 Properties of soluble and insoluble food colorants. Adapted from Francis (1999), to include additional information from Sensient Colors LLC (2014a).

Property	Lakes	Pure colorants (dyes)
Solubility	Insoluble in most solvents (lakes are prepared by precipitating soluble colorants onto an insoluble base – only alumina permitted as the base for food colorants)	Soluble in water, alcohol, propylene glycol (1,2-propanediol) and glycerol/glycerine; glycerine preferred for higher solubility, offsets costs by keeping addition of liquid to a minimum
Method of colouring	Dispersion (pre-dispersed in carrier or added directly as powder)	Solution or as dispersion
Pure colorant content	10-40%	90-93%
Rate of use (usage level?)	0.1-0.3%	0.01-0.03%
Particle size	Approx 5microns	74-1,200 microns
Stability Light Heat	Better Better	Good Good
Colouring strength	Not proportional to pure colorant content; higher opacity	Directly proportional to pure colorant content
Hue	Varies with pure colorant content; colouring properties depend on manufacturing conditions, affecting particle size, crystal structure, colorant content and water content	Less variation with pure colorant content
Cost	More expensive, however: more finely ground forms are available, giving more surface area for light reflection/coloration, therefore money can be saved by using less	Less expensive
Suitable applications related to colorant properties (rather than to the properties of carrier)	- where light stability and non migration properties are desired e.g confectionery and pharmaceutical coatings, icings/fondants and sandwich fillings - hydrophobic food - food packaging. - may bleed out if food outside pH 4.5 – 8.0; may settle out of low viscosity foods	Any applications where colorant is dissolved as part of processing (see Table below)

Table 2.10 Examples of coloured foods and colorant formats suitable for each.

Applications		Colorant format				
		Dry		+ Solvent or carrier		
		Dyes (soluble)	Lakes (insoluble)	Liquid dyes (or dispersions where stated)	Lake dispersions	Gels
Dry mixes	Cake mixes	Use fine grinds for rapid dissolution, to avoid streaking and speckling on reconstitution, or add pre-coloured sugar	Preferred for this application	Use for more attractive-looking mixes; if dry dye used, mix will remain uncoloured		
	Coloured sugar	Add dry colour to sugar, before blending with other ingredients in dessert mixes		Alternative method for colouring cakes mixes, which contain added sugar		
	Gelatin desserts	Add fine grinds directly to the mix, or add pre-coloured sugar				
Baked goods	Cake batters			Yes		
	Fillings and coatings			Use propylene glycol and/or glycerine as solvent; + lecithin if fat content is high	Gives the best results, especially in high-fat applications	Highly concentrated and viscous preparations used to colour icings; gel ingredients include dyes, water, corn syrups, glycerine, sugar, modified food starch, and gums (Wilton Industries, 2014b)
Confections/candies	Starch jellies			Recommended		
	Cream centres			Yes		
	Pan-coated candies			If opacity is not desired; use dye dispersions containing titanium dioxide (TiO ₂) for opaque coatings	Produce uniform colour with fewer coats, can also contain TiO ₂	
Inkjet edible printing				High viscosity preparations of dyes in glycols, and optionally water and glycerine, for printing of coloured surface designs; high dye solubility in glycerine can help prevent dye solidification and clogging of printer nozzles (Baydo <i>et al.</i> , 2008)		

2.6.5. Formulation of dye blends for food applications

2.6.5.1. General considerations

In most cases, the best results are achieved for minimal amounts of added colorant; these give delicate, bright and clear colours, which are suggestive of food flavours. Attempts to intensify colours by adding more colorant will only result in darker and duller shades with an unappealing and artificial appearance. The physical and chemical properties and manufacturing conditions of the food being coloured need to be considered in working out how much dye to add. This is highlighted later in Section 2.6.6 by descriptions of possible mechanisms affecting coloration in different food systems. The following describe some of the more general considerations. For the same dye concentration, thicker materials having some degree of transparency will appear more intensely coloured than thinner pieces of the same material. The colours of candy starch jellies containing added dyes are darkened and dulled by prolonged cooking (meaning dyes should be added towards the end of cooking), and lightened by the finishing process of sugar sanding. For a given food substrate, the strategy of adding a dye concentrate at different volumes to change the added dye concentration and therefore the intensity of the colour may also cause the colour (hue) itself to change. The challenge in using lakes, rather than dyes, to achieve a specified hue and intensity of colour is that the colouring properties of lakes are highly dependent on their conditions of manufacture.

2.6.5.2. Available resources

While instrument-based methods are used to produce dye recipes in non-food applications, in the food industry blends are developed by technical experts, who will make suitability judgments on a visual basis (Francis, 1999). Because foods are very diverse in their formulations and processing conditions, added dyes are exposed to a much broader range of physical and chemical environments than those presented by the non-food substrates. The potentially variable impact on the added colorants, and on the colours that result, makes the prediction of the final colour difficult, and the application of more ‘universal’ computer colour matching tools, which rely on knowing the relationship between colorant concentration and

colour, impractical. Experts are needed to produce custom blends specific to a given food application, and blends should always be tested in the intended application. Furthermore, food coloration does not require the same level of accuracy as do the non-food applications, making it difficult to justify the time and cost that would be needed to develop a spectral database of colorants derived using different foods, for the purposes of computer colour matching (Francis, 1999).

As a first step, industry clients can visit on-line colour selector tools such as the Automated Color Expert™ by Sensient Technologies, and the Hawkins Watts NZ Colour Selector (Figure 2.11). Both provide charts of colours from the Pantone Matching System to assist in shade selection. The Sensient tool gives an assessment of compatibility between desired shade and application in response to information entered by the client and is used to generate a 'recommended product' sample request; in deciding the final colouring system the performance of the sample is then to be evaluated by the client and subsequently discussed with a technical specialist. Alternatively, details of the desired shade, food product and process are sent directly to the specialist, as directed by the Hawkins Watts resource.

Start
Color Options
Mfg. Criteria
Compatibility
Review
Profile
Sample Request
Finish

Step 1: Select a color and application
AUTOMATED Color Expert

Please select your color from the family below

Black/Grey
Blue
Brown
Green
Orange
Purple
Red/Pink
White
Yellow/Cream

Application: Bakery
Subcategory 1: Cakes
Subcategory 2:
Finished Product Clarity: Clear
PH:
Processing Conditions: Retort
Color Type: Fusion Precise Natural Colors™
Intended Product Market: Asia

Info Request
Matches: 11
Next

Start
Color Options
Mfg. Criteria
Compatibility
Review
Profile
Sample Request
Finish

Step 2: Initial Shade Choices
AUTOMATED Color Expert

Choose a product from the selection below. Maximum of 10 color choices are available
Reset

Shade choices by pantone number
361C
348C
370C
360C
362C
349C
351C
374C
363C
325C
352C
375C
353C
326C
7486C
376C
354C
327C
7487C
7479C

Info Request

Choice 1
Choice 2
Choice 3
Choice 4
Choice 5
Choice 6
Choice 7
Choice 8
Choice 9
Choice 10

361C
370C
7479C

Colors shown are interpretations of pantone colors and are not exact matches for specified pantone colors. For an accurate, visual representation of a specific pantone color, please refer to a printed pantone color guide book.
Previous
Next

HawkinsWatts
COLOUR SELECTOR

Which colour is required?
Purple
Artificial

Options:
AMARANTH

Notes:
Temperature stability: HIGH
Light stability (light-fastness): HIGH
pH stability: HIGH
SO₂ stability: MEDIUM
AMARANTH is WATER-SOLUBLE.
For Oil-based products, please request the Lake Dispersion variant of the colour you require - Lake Dispersions are OIL-DISPERSIBLE.

PLEASE NOTE this is only a generic recommendation. Hawkins Watts carries a full range of Natural and Synthetic colours manufactured by FMC BioPolymer, DD Williamson, Felix Koch Offenbach (FKO), and Cathay Industries. We also have the capability to blend two or more colours together to achieve almost any hue.
To help us assist you in selecting the correct hue, grade and usage level for your application, please:
Select the PMS number closest to the desired shade from this chart: click here.
List specific details of your product and process.
Enter these into an email to our colour technical specialist: click here.

Figure 2.11 Screenshots of on-line tools available to assist customers with the selection of suitable colorants for food and beverage applications. Left: Steps 1 and 2 only of the Automated Color Expert by Sensient Food Colors (Sensient Colors LLC, 2014b). Right: Sample recommendation from the Colour Selector by Hawkins Watts (Hawkins Watts Limited, 2014).

Although done mainly on a visual basis, the assessment of colour blends for foods by experts can also make use of measured colours. The relative positions of the colours of single colorants and their blends on a chromatic (i.e. a^*b^*) plot can be used to determine which colorants, and how much of each, are needed to produce a given blend (Francis, 1999). Experts can also be guided by the generic recipes that are available for producing specific colours.

2.6.6. Factors affecting coloration in food materials: examples

2.6.6.1. Stability of colorants to cooking conditions

The reactivity of the double bonds in a conjugated system of a colorant molecule will have a bearing on food colour. Food systems are a potential source of reducing agents (donors of electrons which become oxidised as a result) which can cleave double bonds and lead to loss of colour, but the extent to which this occurs can depend on the colorant (Scotter and Castle, 2004). Hydrogen is a reducing agent which can be produced from the reaction of tartaric and citric acids with the metal of cans. High temperatures (110°C to 170°C and above) are reached in confectionery manufacture which can degrade sugars to highly reactive (reducing) agents. In simulated candy manufacture Amaranth was degraded to naphthionic acid and amino R-salt, while Tartrazine and Sunset Yellow were not affected. However low levels of these degradation intermediates (<1%) can already be present in dyes from dye manufacture. Synthetic dyes contained in soft drinks can potentially be reduced by ascorbic acid (AA) which is added as a dietary antioxidant and vitamin supplement, unless AA can be protected from oxidation within the drink by, for example, chelation of metal ion catalysts by sugars. Dissolved oxygen, or tungsten light at pH 5.5 can enhance AA oxidation. The stability of most food dyes to reduction by sulfites which are used as food preservatives, ranges from fair to excellent, with the exception of Indigo carmine, which has poor stability (Scotter and Castle, 2004).

Natural pigments have been the subject of studies investigating the effects of shorter-time cooking processes – microwave cooking and extrusion cooking - on food colorants. The effect of microwave cooking on the level of natural pigments appears to depend on the type of food. Microwave heating reduced total carotenoid content in papaya puree by up to 57%, and in kiwifruit puree loss of chlorophylls a and b was significant (de Ancos *et al.*, 1999). Anthocyanin content of strawberries was unchanged, but this may have been due to more efficient extraction provided by heat-induced cellular disruption. The stability of pigments to microwave cooking relative to other forms of heating could be due to its shorter duration. For

some green vegetables, levels of pheophytins a and b (the degradation products of chlorophylls a and b) were lower after microwaving and steaming, compared with after boiling (Turkmen *et al.*, 2006). Loss of bixin, the major lipid-soluble carotenoid in annatto, was negligible or nil in biscuits containing added annatto that were cooked by microwave heating for 60 seconds. Losses were higher for conventionally baked cakes and deep fried flour based snacks where heating times were longer (Prabhakara Rao *et al.*, 2005). These latter findings should be viewed with some caution, as each cooking regime used a different recipe; the recipes had different concentrations of added annatto (82 to 340 mg/kg for the biscuits, 113 to 465 mg/kg for cakes and 125 to 513 mg/kg for the deep fried snacks), and for conventional baking and deep frying, bixin losses increased with increasing concentration.

Some natural pigments show good stability to the thermal and physical stresses of extrusion cooking, where the maximum temperatures reached can be higher than those in microwave cooking. 94% of the norbixin (the water-soluble pigment from annatto) added to rice flour and water was retained after extrusion at 155°C, as determined by thin layer chromatography. Retention levels of bixin decreased from 74% in annatto before extrusion to 72% and 69% after extrusion at 125°C and 155°C respectively. Degradation products from oil-soluble turmeric accounted for 27% and 38% of the colorant at the two temperatures. Under the same conditions beet was the least stable, with only 29% of the original colorant remaining at 155°C (Maga and Kim, 1990).

2.6.6.2. Colorant content and other contributors to colour appearance

In some cases the level of colorant present in a food is seen in the final appearance of the food. Rice flour and water mixtures containing beet that were extruded at 125°C retained 63% of the original colorant and visually had a characteristic red colour. On increasing the extrusion temperature to 155°C measured lightness (L^*) increased from 64.6 to 76.2 units, yellowness (b^*) from 3.8 to 8.6 units, and redness (a^*) decreased from 19.0 to 10.3 units, in line with a visually observed change in colour to a very faded pink (Maga and Kim, 1990). The significant decreases found in the levels of chlorophylls a and b in kiwifruit puree after microwave cooking

were accompanied by a significant change in instrumentally measured colour (as indicated by ΔE^*) relative to the untreated puree. High correlations (r^2 0.89 to 0.96) were found between chlorophyll levels and measured chroma (de Ancos *et al.*, 1999).

At other times colorant level is not necessarily a good indicator of final colour, due to the colour contributed by other processes. Significant changes in the lightness of strawberry puree were found for some microwave cooking conditions, but these were not strongly related to anthocyanin content. It is likely that the colour change was the result of browning, given that polyphenol oxidase and peroxidase (responsible for enzymic browning in fruit) in strawberry showed resistance to inactivation under the same conditions (de Ancos *et al.*, 1999). The change in the greenness of vegetables after cooking could be due to changes in light scattering as water replaces intracellular air (Hutchings, 1999), rather than to a change in the level of chlorophylls. Despite a difference in the amount of pigment degradation products in rice flour and water extruded with oil-soluble turmeric at 125°C and 155°C (27% and 38% respectively), yellow values were unchanged between the two temperatures (at 30.3 and 30.5 units respectively) suggesting that degradation products from oil-soluble turmeric were themselves coloured (Maga and Kim, 1990).

2.6.6.3. Colorant-ingredient interactions

The distribution of colour within a food is an indication of binding or interaction with food components, such as polysaccharides, starches and proteins. These interactions depend on the structure and physical characteristics of the components, which determine the potential for electrostatic interactions, or for hydrogen and van der Waals bonding. For proteins, these interactions can be enhanced by heating. Heating at 60°C helped to preserve bands in SDS-PAGE electrophoresis when proteins were stained with Sunset Yellow and Allura Red, and made otherwise very light stains produced at low and high pH conditions more visible (Badaruddin *et al.*, 2007; Umer Abdullah *et al.*, 2008). For Sunset Yellow, heating may have enhanced electrostatic binding of the dye with protein via SO_3^{2-} groups on the dye, with heat-induced denaturation and unfolding of protein molecules exposing more binding sites. The

coloration of reticulated waxy corn starch by the natural red colorants Cochineal Carmine and Beet Red could be explained by electrostatic interactions between the positively-charged pigment compounds and negatively-charged phosphoric groups in the starch (Berset *et al.*, 1995). Anionic (negatively-charged) polysaccharides (carrageenans, pectins, alginic acid) were found to be ineffective removers of dyes from solutions mimicking dyehouse effluent, owing to electrostatic repulsion between the polysaccharides and the anionic dye molecules. Although non-ionic, the galactomannans locust bean gum, guar gum and cassia gum performed very well as effluent dye removers. Strong chain interactions between galactomannan molecules are prevented by their branched galactose residues, meaning galactomannans are available for hydrogen bonding with dyes (Blackburn, 2004). The non-ionic starch, by comparison, was an ineffective effluent dye remover, as temperatures much higher than the one used (20°C) would have been needed to break the inter- and intra- molecular hydrogen bonding between amylose and amylopectin chains in starch for these to have become available for bonding with dye molecules.

The binding of dyes to components can be enhanced by the addition of other agents. In textile dyeing, mordants are used to increase the affinity of dyes for the substrate. Metal salt-based mordants form complexes with dyes, and tannins increase adsorptivity via hydrogen bonding and van der Waals forces (Bechtold *et al.*, 2007). The addition of positively-charged electrolytes may overcome the electrostatic repulsion between negatively-charged dye and polysaccharide molecules in dye effluent, but this will depend on the strength of these charges (Blackburn, 2004).

For starches, another property that could influence dye binding is the size of the starch grains. Native corn, native wheat and reticulated waxy corn starches retained higher levels of Cochineal Carmine and Beet Red (as determined from the absorbance of the supernatant), than did potato starch, yet potato starch was as strongly coloured as the other starches. This was possibly due to the saturation of colorant binding sites on the potato starch grains, given the larger size of these

grains and their lower specific area (total surface area per unit mass, or per unit volume (Berset *et al.*, 1995).

2.7. The effects of changes in substrate on the modelling and prediction of colour and appearance

In this thesis, an understanding of how changes in the colour appearance of materials are related to changes in the processing or physical characteristics of the material is of prime interest. In order for the 3D colour food printer to be able to customise outputs it needs to be able to account for changes in the substrate. The focus in this section therefore, is on effects other than those of added colorants which have been covered earlier in this review.

The degree of light scattering from a material can be altered by changes in the physical properties of the material which, in turn, can affect the perceived intensity of its colour. Such changes are brought about by processing or by deliberate manipulations, or they represent the (usual) variations within a product range. The decrease in scatter causing visual translucency to develop in tomato pericarp in cut fruits with storage time was noted earlier (Section 2.6.2.3). The effects of light scattering from other materials have been quantified and it has been found, for example, that lightness of oil-in-water emulsions increases with increasing droplet concentration and with decreasing droplet size, and decreases the intensity of the colour from the added dye (Chantrapornchai *et al.*, 1998); increasing the surface roughness of chocolate samples (by casting onto sandpaper of decreasing grit size) decreases gloss significantly and exponentially, while values for lightness and for whiteness index (as determined from image analysis) decreased significantly and linearly (Briones *et al.*, 2006). Fabrics made of finer fibres are lighter when dyed with the same amount of dye as fabrics made from coarser fibres (Li *et al.*, 2009). The relative contributions of bulk and surface reflectance, with increasing dye concentration, to measured reflectance differ between fibres of different denier. Coarser fibres have larger diameter providing a longer distance for light to travel meaning more light is absorbed, but as dye concentration increases these fibres display decreasing colour efficiency as

the contribution of surface reflectance increases; the lower surface curvature of larger diameter fibres results in smoother surfaces compared with finer fibres (Li *et al.*, 2009). The K/S ratio calculated from the reflectance at selected wavelengths of injected-moulded pigmented plastics for automotive parts which differed in their measured gloss, decreased with decreasing gloss; the scattering coefficient increased as the roughness increased (Ariño *et al.*, 2005). In these studies, the only changes made to the samples were to characteristics affecting scattering, such as surface roughness and droplet size and concentration; no other changes, including changes to dye concentration, composition and processing, were made.

A number of studies have gone further than to simply characterise the relationship between changes in light scattering and perceived or measured colour, and have developed mathematical models that show the potential to predict colour from physical measures of surface texture and droplet characteristics. Such models might enable the appearance of food emulsions to be optimised (McClements *et al.*, 1998), increase the performance and efficiency of dye formulations for textile dyeing (Li *et al.*, 2009), and predict the impact of substrate and printer parameters on gloss in xerographic printing (Dalal and Natale-Hoffman, 1999). Some of these models are based on adaptations to the Kubelka-Munk (K-M) equation. In the prediction of food emulsion colour, K-M absorption and scattering coefficients (K and S respectively) were expressed in terms of the absorption and scattering cross-sections of the droplets, and their asymmetry factor, which were calculated by applying diffuse scattering theory (McClements *et al.*, 1998). Predicted and measured reflectance of emulsions that were based on the same concentrations of red food dye, mean droplet size, and droplet concentrations were in good agreement between 380 nm to 600 nm, however predictions overestimated reflectance at higher wavelengths. In the prediction of fabric depth of shade, the ‘colour efficiency’ (equivalent to the dye coefficient relating dye concentration to absorption and scatter) was expressed collectively in terms of fibre diameter, geometric roughness of the fabric, and a dye parameter (Li *et al.*, 2009). In both cases, surface effects were accounted for – in the emulsions case, measured reflectance was corrected for the effects of the cuvette wall (McClements *et al.*,

1998), while in the fabric study surface reflectance constants for each fibre diameter x dye combination were incorporated into the predictions together with predictions of bulk reflectance using K-M Theory (Li *et al.*, 2009).

The distinction between surface and sub-surface effects is also a feature of the model of gloss effects in xerographic printing developed by Dalal and Natale–Hoffman (1999). In this model, measured reflectance is the sum of the portion of total front surface reflectance captured by the detector (with the amount captured in turn depending on both gloss, and on the measurement geometry), and sub-surface ‘intrinsic reflection’. Intrinsic reflection appears to be constant for a given colour, and while not directly measurable, can be derived as the difference between specular included measurements (capturing all light from the sample) and the portion of total front surface reflectance in this measurement mode, which is calculated from the Fresnel equations using normal angle of incidence and refractive index. The portion of total front surface reflectance captured by the detector for use in the predictive model of measured reflectance, for each measurement geometry, was derived using a set of black samples printed on different coated and uncoated papers, and expressed for each geometry as a function of gloss. This model allows measured colour of papers of different colour and gloss to be predicted from the gloss and intrinsic reflection values. The approach used by Dalal and Natale–Hoffman (1999) was used and adapted by Ariño *et al.* (2005) to model the effect of both gloss and different surface textures on the colour of injection-molded plastics for the automotive industry. Included in this latter study were physical measures of topography (as well as gloss) of injection-molded plaques produced with smooth (glossy), fine and coarse surface textures, and the calculation of absorption/scatter (K-M) ratios based on measured reflectance predicted from the model.

2.7.1. Alternative model for print, based on Principal Components

Analysis (PCA)

Having the capability to predict the effect of printing substrate (paper) properties on colour outputs means that time and effort can be saved in not having to profile a printer every time the substrate is changed. As stated earlier (Section 2.5.2), profiles are most often custom generated (Sharma, 2003). For printers, a custom profile will be specific to the printer, paper and ink that were used to build the profile; changes to any of these require the profile to be reconstructed. Shaw *et al.* (2003) investigated and compared several methods, including one based on K-M Theory, for their ability to predict colour on a test substrate, based on the profile for a reference substrate, and a small amount of information about the test substrate. Of these, an empirical method based on Principal Components Analysis (PCA) gave the lowest colour error - the difference between actual and predicted colour - compared to no recalibration. In PCA multivariate data are 'collapsed' into orthogonal vectors (or dimensions) which each progressively account for more of the variability in the original data. The reflectance data for a large number of colour patches on the reference substrate were able to be 'expressed' in terms of 10 basis vectors. Based on the measured reflectance of the same set of patches on both the reference and test substrates, weights for each spectrum were determined corresponding to the 10 basis vectors. A linear transformation matrix was used to map the reference substrate PCA weights to the test substrate PCA weights. The test substrate PCA weights were then converted back to reflectance spectra.

Chapter Three: Literature Review, Part 2 – Customising foods using 3D colour printing

Part 1 of this Review dealt with the theory and application of coloration techniques used in both food and non-food industries, and which are relevant to the goal of developing a predictive coloration algorithm for a novel 3D colour food printer. Attention now turns, in Part 2, to the specific context of this research, namely the areas of customisation, 3D printing and 3D coloration. As with Part 1, contributions are drawn from various industries, including food.

Part 2 ends with conclusions from the entire Review, leading to the aims and objectives of the thesis.

3.1. The concept of customisation

Mass production of goods has been the traditional way of meeting demand in *mass* consumer markets, and has its origin in the early 1900s in the Ford car production lines. Mass production lines produce units which are the same. Originally devised to meet skilled labour shortages (Day, 2011), mass production is an efficient and therefore cost-effective means of production (Boland, 2006).

Customisation refers to being able to meet the needs of an *individual* customer. Customisation recognises the increasing importance of meeting the preferences and needs of the individual, and in affording the individual the power to make their own choices; the ‘final customer’ is involved ‘in the design of a product prior to manufacture’ (Boland, 2006). On a larger scale, a system of *mass customisation* can meet the individual needs of many customers. Paradoxically, mass customisation can also be an efficient and cost-effective means of production. For large numbers of customers, the individual needs of each are able to be met by assembling a relatively small range of component parts in a seemingly endless number of combinations (Boland, 2006), rather than by a range of mass-produced finished units that would require storage. Mass production still features in mass customisation, in the prefabrication of component parts for later assembly.

3.2. 3D printing technologies

3D printing is a digitally controlled process of building objects layer-by-layer. Objects are built from typically one only of a variety of possible materials. The successive layers of material correspond to successive cross-sections from a digital image file representing the object.

Traditionally, 3D printing has been used for the purpose of rapid prototyping, but has been developing as a manufacturing technology in its own right; in this context ‘3D printing’ is also referred to as ‘additive manufacturing’ (AM) or ‘additive layer manufacturing’ (ALM), which distinguishes it from subtractive methods whereby objects are shaped by the removal of material from a starting block, using traditional machining techniques such as cutting or grinding.

Available 3D printing technologies differ in their layering process, and in the materials to which they are applied. Examples include:

3.2.1. Fused deposition modelling, or extrusion deposition

A coil of plastic filament or metal wire is progressively unwound and fed into an extrusion nozzle, which heats and extrudes the material and controls the flow (Wikipedia, 2014a). The nozzle can moved horizontally across a platen so that layers of material can be formed. The platen can be moved vertically to allow successive layers to be built. The material hardens immediately after extrusion, creating a self-supporting structure.

3.2.2. Granular materials binding

Objects are built from layers of powder or granules. Within each layer, regions corresponding to the relevant cross-section of the object are selectively fused using laser sintering (for plastic, metal, ceramic and glass powders) (Wikipedia, 2014b), inkjet binding (for plaster or resins) or heated air (for granulated sugar) (The CandyFab Project, 2014). Melting, using lasers or electron beams, can be used in place of fusing to create denser and stronger materials from metal powders (Wikipedia, 2011). As each layer is finished, the printing platform is lowered

before the next layer is deposited. Unfused powder acts as a support for the growing structure, and is later removed.

3.2.3. Laminated object manufacturing

Sheets of paper (Mcor Technologies Ltd., 2013), plastic or metal (Wikipedia, 2011) are selectively cut to shape (following the outlines of each cross-section) and glued together. Knives or lasers are used for cutting (Wikipedia, 2011). Support during the build is provided by the un-glued material.

3.2.4. Advantages and applications

As a manufacturing process, 3D printing offers a number of distinct advantages. Objects can be produced without the use of a pre-cast mould, because the printing process by itself is able to (re)produce accurately any shape and to handle complex geometries. Changes in object design are managed much more easily with 3D printing, and without the need to machine new moulds. 3D printing brings together the design and manufacturing processes, but at the same time, the storage and portability of design files means that objects can be produced as and when needed. In a home use setting with a desktop 3D printing unit, these features mean that printing can be a single person, one-stop operation. Alternatively, services are available which will 3D print objects to order from files sent by customers. Both situations could allow for mass customisation of a single product type to occur. For mobile phone cases, companies provide either web-based customisation software as well as a printing service (Vance, 2012), or the design files for the customer to do the printing themselves (BBC News, 2013). In industry, parts can be printed locally when needed, rather than being manufactured offshore. 3D printing can be scaled up to such an extent as to produce buildings from concrete (Day, 2011).

3D printing has been applied to a range of novel materials to create new versions of existing products which are intended to be better performing, and less time- and labour- intensive to produce than the conventional items. Examples include: bicycles built from high-strength nylon powder, which are lightweight, all-in-one structures, custom built for the rider and therefore

requiring no adjustment (Airbus Group Inc., 2011); custom 3D-printed horseshoes offering a lightweight alternative to traditional shoes and therefore the opportunity to improve racing times (CSIRO Australia, 2013); facial prostheses printed from starch powder which are filled with silicone post printing (Wainwright, 2013). Another potential application of the technology is the printing of tissue from living cells, for the purposes of transplantation or repair. Potentially the earliest success will be with the printing of cartilage due to it lacking internal structure and vascularisation (blood supply) (Palmer and Danzico, 2011).

3.3. Customisation of food

(Mass) customisation to some extent, already occurs in the food industry, as seen in the assembly of fast food items (such as pizzas and sandwiches) to individual orders, and in the hot beverage vending machines which house a range of drink components which are selectively blended and dispensed to order (Boland *et al.*, 2010). Fully customised food outputs are possible if specifications for individual health needs can also be met, along with those for sensory outcomes. Not only do consumers show a growing interest in, and awareness of, the link between the different foods they consume and their health, the fulfilment of health needs can be more important than meeting sensory needs (Boland, 2006). Nutrigenomics is an area of research that aims to identify what these health needs are on a genetic and epigenetic level; certain foods or food components might have to be avoided or consumed in abundance by individuals of certain genotypes because of the effects of these components on their unique gene expression, and because of the (in)ability of their unique metabolism to accommodate these components.

US Patent 7,762,181 B2 (Boland *et al.*, 2010) describes a system, named POSIFoods™ (Point Of Sale Individualised Foods), by which such fully customised food outputs could be realised. The system takes the form of a vending machine which can formulate and dispense, on-the-spot, a customised food or beverage product. Like conventional vending machines, the POSIFoods™ system serves food of a particular type, for example smoothies, ice creams, nutritional bars, or

pizza. Unlike conventional machines however the system will be able to provide fully customised outputs on the basis of stored customer profile data (nutritional and health needs and sensory preferences), recipes and expert nutritional guidelines, and stored ingredients allowing the food items to be made from scratch. The system uses algorithms to ensure that outputs are compatible with customer needs, including the need for safe foods by either keeping certain ingredients within safe limits, or excluding them altogether. Based on the above information menu choices are presented to the customer after they have entered a personal identification number, from which they make their selection. Once a choice has been made, select ingredients are dispensed, mixed and processed (i.e. cooked and formed, as necessary) before the serving is dispensed from the machine. There is flexibility and scope for the customer to refine the formulation, within limits, depending on their specific needs at the time of consumption.

3.4. 3D food printing

As with ‘traditional’ 3D printing, 3D food printing is a digitally controlled process, beginning with a data file containing a CAD design or drawing or image of the object, and is designed to provide customised outputs, on demand, with most technologies on offer available as counter-top models and using variations on layer-by-layer extrusion deposition. As with non-food 3D printers, designs and recipes are in digital file format, and 3D printing templates can be saved, re-used and shared as open source hardware and software through online communities, forums and social networks, or as mobile ‘phone apps.

Where food printers differ from each other, are in their main purpose of printing, their build material, their target consumers, whether they are capable of cooking the food during printing, and also in their stage of development (Table 3.1). Some print conventional food items (such as chocolate and pizza), or conventional ingredients (e.g. sugar) into new shapes and forms, though sugar is used primarily as a safe and inexpensive material for model building rather than as an edible ingredient in CandyFab open source 3D printing (Cohen *et al.*, 2009). Other printers allow for the creation of new recipes and formulations from a set of base ingredients, and for the

control of (any or all of) shape, flavour, texture and nutritional value of the food through the control of the mixing, layering and cooking processes. With ingredients stored in separate canisters and combined only when needed, 3D printing is particularly suited to long-distance space travel; NASA is funding the development of a 3D printer to supply the needs of astronauts during such missions with cartridges of powdered ingredients being designed to last 30 years. These printers need to be able to work in zero-gravity; results are pending for a Zero-G 3D (non-food) printing demonstration by NASA in September 2014 (NASA, 2014). The printing of artificial raw meat from ‘bio-ink’ containing live stem cells is being developed as an alternative to slaughter. Although a prototype meat has been produced, it is not yet ready for consumption, and in the longer term 3D meat printing will face issues with production scale-up and consumer acceptability (Moskvitch, 2013).

Between them available 3D food printers can meet several needs. Printers designed for the main purpose of printing conventional foods in new shapes fulfil mainly an aesthetic need, bypassing the more fundamental need for health and well-being, or ‘safety’ in Maslow’s hierarchy. Due to the digital nature of object design enabling the sharing of ideas, it can be argued that printers (both food and non-food) meet the need for belonging and esteem (again on Maslow’s hierarchy) which lie above the need for safety. 3D food printers capable of producing outputs that are fully customised for nutritional needs and sensory preferences are the only devices that will fulfil all needs, from safety upwards.

3.4.1. 3D food printing: inputs and outputs

As with non-food 3D printing, suitable build materials for 3D food printing include those that can be fused to form 3D structures, such as sugar (for granular materials binding), or that can be extruded from a nozzle (for freeform fabrication), and which can also be supported during the build to maintain the printed shape. In freeform fabrication this support is provided by the solidifying of each layer before the next is deposited, or by the food composition itself having sufficient rigidity post extrusion to be self-supporting (Yang *et al.*, 2001). 3D printed foods that undergo subsequent cooking need to retain their shape, and to have satisfactory texture and

flavour. Foods such as chocolate, frosting, and processed cheese can be extruded ‘as is’ or after heating, and solidify upon cooling (Lipton *et al.*, 2010). In other cases, food compositions should include a liquid ingredient for flowability (with an optional heating element situated at nozzle to control fluidity) (Yang *et al.*, 2001), and ingredients which enhance body and viscosity, for example starches, sugars (Yang *et al.*, 2001) and edible natural polymer gels (Yang *et al.*, 2001; Cohen *et al.*, 2009) so that the food can be self-supporting during printing. ‘Conventional foods’ (e.g. cookie dough) require changes to ingredient ratios, or processing to a paste (turkey and seafood purees) and the inclusion of additives to retain rheological properties, so that they can be both extruded, and retain their printed form when cooked by conventional methods (baking, deep-frying and sous-vide). The printed foods cooked by the latter two methods (scallop and turkey respectively) largely retained their shape and were judged have acceptable flavour and texture by chefs (Lipton *et al.*, 2010).

The storage and on-demand combining of ingredients make 3D printers devices of convenience and creativity. In reality, the potential for new and unlimited ingredient combinations or for the recreation of natural food matrices and structures, in the form of a ‘universal’ 3D food printer, is constrained by the impractical and uneconomical housing of every possible ingredient that would be needed. Instead, a more focused and practical approach to printing is needed, in either its input or output. An example of a more focused output is to create novel foods for personalised nutrition, such as the printing of nutrient-enriched soft foods for dysphagia sufferers (Hadhazy, 2013), or the printing of only one type or class of food; notably 3D printers at the prototype or retail unit stages of development are designed to print one type (chocolate, sugar), or class of related foods (wheat-based bakery and pasta products), while those designed for creativity have remained (largely) as concepts. Alternatively, a limited number of input base materials could be used to produce a (wider) range of outputs, such as having three proteins, three carbohydrates, etc. This approach requires an understanding of how to combine inputs to produce the outputs. These principles have been applied by Cohen *et al.* (2009) in a proof of concept where a range of food textures could be simulated using mixtures of only xanthan gum

and gelatin in different relative proportions (Table 3.1) and printed using the syringe-based deposition tool in the open source Fab@Home printer. And, owing to the neutral flavour of the two hydrocolloids, there is scope also for adding a range of flavours.

Table 3.1 Forms and descriptions of 3D food printers: concepts, prototypes and retail units.

Printer name/type and/or designer/manufacturer	Development stage or availability	Output	Ingredients and printing technology	Cooking facility within printer	Target market	Other/special features
'Moleculaire' designed by Nico Klaber for Electrolux	Concept	Complex food structures, shapes and patterns; desserts	3D layer-by-layer printer from blister pack inserted into reservoir at top of unit, or from own ingredients + software; straight-to-plate printing, as unit can be placed on top of a plate			Minutes-long process
'Food Creation' by Philips Design	Concept	Inspired by molecular gastronomy: deconstruction of foods and reassembly in new and different ways	Ingredients combined and printed into desired shapes and consistencies, in the style of stereolithography			Nutritional value of printed foods monitored and adjustable
Digital Chocolatier	Prototype	Design and assembly of customised, multi-component chocolate candies	Layer-by-layer, carousel of ingredients canisters (each containing a single ingredient), rotated according to selections made through GUI; ingredients extruded from select canisters into cup which rapidly cools and hardens the chocolate			
Digital Fabricator: a personal 3D printer for food	Concept	Creation of new and elaborate ingredient combinations; design flexibility As above	Food canisters atop the unit store favourite ingredients, precision mixing, extrusion deposition and layering Three layer rotating carousel: ingredients canisters form the top layer, mixing containers the middle layer and extrusion tray the third layer upon which the final mixture is deposited	Yes, heating or cooling during deposition Yes, heating and cooling of food on extrusion tray		Offers control of flavour, texture and nutritional content In its complexity it lies between the Digital Chocolatier and the Digital Fabricator; has carousel set-up of the Chocolatier, but like the Fabricator, allows for more experimentation with

Printer name/type and/or designer/manufacturer	Development stage or availability	Output	Ingredients and printing technology	Cooking facility within printer	Target market	Other/special features
CandyFab 4000 model, The CandyFab Project (CandyFab.org)	Open source	Primarily for non-food applications (models, prototyping, sculpture); sugar used as inexpensive, non-toxic building material for larger scale printing	Granular materials binding/inkjet printing; sintering of sugar using heated air	Heated air		ingredient combinations Other low melt, low cost, low toxicity materials could be used as printing medium; low to medium print resolution to produce relatively large pieces
Solid Freeform Fabrication of food using Fab@Home printer, Cornell University	Open source	Outputs based on conventional foods and ingredients, printed into desired shapes and cooked by conventional methods	Cookie dough with modified ingredient ratios, baked after printing; pureed turkey and scallop meats with added transglutaminase to retain rheological properties and cooked sous-vide (turkey) or deep fried (scallop)	No		Overall (printed) shapes mostly preserved; printed and cooked meats passed assessment by expert chefs for taste and texture
		Hydrocolloid mixtures simulating a range of food textures	Mixtures of only xanthan gum and gelatin (in water) in different relative proportions, ranging from 0.5% to 4% w/w gelatin and from 2% to 16% w/w xanthan	No		Scope to add/achieve a range of flavours due to neutral flavour of hydrocolloids
3D chocolate printer, ChocEdge, UK (chocedge.com), company founded to commercialise printer developed by Hao et al, University of Exeter	Retail product	Chocolate in a variety of desired shapes	Chocolate melted, tempered and deposited by extrusion into layers of 2D cross sections; material solidifies after extrusion and is self-supporting	Not applicable, substrate resets on cooling	Restaurant and food preparation industry	

Printer name/type and/or designer/manufacturer	Development stage or availability	Output	Ingredients and printing technology	Cooking facility within printer	Target market	Other/special features
'Foodini' by Natural Machines, Barcelona	Prototype, retail product available from mid-2014	Conventional food items (e.g. pizza, pasta, cakes) in a variety of shapes	Layer-by-layer formation; capsules of fresh ingredients sold separately	No, but able to keep food warm	Domestic and restaurant	
Chef Jet and Chef Jet Pro 3D printers by 3D Systems	Prototype, retail product available from late-2014	3D edible candies and decorative cake toppers in a vast array of complex geometries	Granular materials binding/inkjet printing using fine layers of sugar as substrate and water as binding material, allowing the sugar to recrystallise and harden	No	Professional bakers	Printing available in colour, and printing materials also come flavoured
TNO, Netherlands	Funding granted for research and development, as at March 2013	3D-printable, nutrient-enriched soft replacement foods	Not given	Yes, laser-based technique available for fast, localised cooking within the substrate	Nursing home residents suffering from dysphagia (i.e. trouble with chewing and swallowing food) and in danger from suffering from appetite and nutrient loss from avoiding conventional, unpalatable soft food options	
3D food printer, NASA	Funding granted as at May 2013 to build prototype using open-source hardware (based on RepRap printer) and software	Prototype can build chocolate, attempts now to print pizza (with 'non-descript' protein layer as topping)	Basic food components in replaceable powder cartridges with lifespan of 30 years, and combined when needed to produce foods (e.g. tomato powder mixed with water and oil to make pizza sauce)	Yes, e.g. dough layer in pizza to be cooked as it is being printed	Astronauts during long-distance space travel	Non-food 3D printer developed for NASA demonstrated to work in zero gravity conditions

Printer name/type and/or designer/manufacturer	Development stage or availability	Output	Ingredients and printing technology	Cooking facility within printer	Target market	Other/special features
Rapid prototyping and fabrication method for 3D food objects, Yang et al, 2001	US Patented system, describes apparatus, operation and suitable food compositions for printing, features seen in 3D food printers subsequently	Prototype foods for evaluation before scale-up/mass production; unique, custom-designed food items of complex geometries e.g. birthday cakes	Layer-by-layer extrusion deposition, food composition should include a liquid ingredient for flowability and ingredients to enhance body and viscosity (e.g. starches, sugars and edible natural polymer gels), so that the structure is sufficiently rigid and self-supporting during the build	No		Coloration option, either by multiple channels feeling colorants into nozzle just prior to the point of extrusion, or by extruding different pre-coloured food compositions using multiple dispensing heads
Modern Meadow (US start-up)	Prototype food	Bioprinting of artificial raw meat	'Bioink' containing live stem cells, cells printed into moulds made from agarose gel, cells fuse to form tissue after several days, mould removed and tissue placed into bioreactor to mature muscle fibres, before being 'killed'	No	Alternative to slaughter	Scale-up and consumer acceptability likely to be difficult

3.5. Baked goods as model substrates for the development of printable food pastes

The question is then raised of the type of substrate or class of substrates that would be suitable for the 3D colour food printer, taking into account developments in printable foods to date, and the outputs the printer aims to provide. Work on printable foods discussed in the previous section has focused largely on producing a range of satisfactory textures (for both real foods and in model systems) for minimal (ingredient) input *or* on meeting (personalised) nutritional needs, whereas the 3D colour food printer is being designed to do both, and simultaneously where needed. Flour-based bakery products, another category of foods that are printable by current prototype printers or retail units, could be tailored to meet both nutritional and sensory needs. For a given product in this category (for example bread, cakes or cookies) not only can a range of textures be produced for different combinations of the same basic ingredients, the nature of these ingredients mean they are often the target of substitutions designed to improve the nutritional profile of the product. This, together with the availability and convenience of rapid baking technologies, points to baked goods being suitable candidate substrates for the 3D colour food printer - which aims to produce customisable food outputs, and rapidly - or at the very least, being the type of food on which the substrate can be modelled.

The following sections discuss in some detail the features of a selected baked product and its preparation that are relevant to 3D food printing. The discussion focuses on cooked cake batters more than it does on bread and biscuit or cookie dough, as dough in its raw form might be less easy for current, early generation syringe-based printers to handle. Issues concerning the storage or limiting the number of base ingredients will not be addressed here; rather it is the relationships between ingredients, processing and product characteristics that is being explored. The level of detail that will be presented is justified in that there is a need to understand the substrate environment into which dyes will be mixed and against which the final colours will be perceived.

3.5.1. Description of cake characteristics and the role of ingredients and processing

A cake is a baked batter in which the basic ingredients are commonly wheat flour, sugar, eggs, shortening, leavening agents, salt, non-fat dry milk, flavours and water, in varying proportions across different ‘standard’ or ‘conventional’ formulations. The terms ‘standard’ or ‘conventional’ have been adopted here to distinguish usual cake formulations from their equivalent counterparts in which major ingredients have been replaced with alternatives, as discussed in later sections. Before baking the batter is a complex emulsion of dispersed air bubbles and fat particles or oil droplets (the discontinuous phase) in a continuous aqueous sugar phase (Sahi, 2008). Also dispersed or suspended within the emulsion are flour particles, starch granules and cell wall fragments. In low-fat or fat-free formulations (such as Angel food cake) the emulsion takes the form of a conventional liquid foam in which air bubbles are surrounded directly by the aqueous phase. In high-fat batters (such as pound cake) much of the air has become trapped within the emulsified fat particles through mechanical aeration (Sahi, 2008). After baking the batter becomes a semi-solid, porous, soft structure (Sahin, 2008), described as a sponge (Figoni, 2008), in which gas cell walls have fractured and set giving an open-celled elastomeric solid foam termed a crumb structure containing interconnected cells.

High quality cakes are tender due to a high volume and a fine and uniform crumb, and have good tolerance to staling, giving cakes a long shelf life, as well as having good colour and flavour. The keys to achieving desirable volume and texture are: the incorporation of fine, stabilised and uniformly distributed air and gas bubbles at the batter mixing stage together with sufficient viscosity in the batter to prevent the bubbles from coalescing and to slow their rise to the surface which would allow air to escape (Gomez, 2008; Sahin, 2008), and the timing of the leavening and structure formation processes that occur during baking. For example, low volumes may result if structure development occurs either too early, ahead of leavening, or too late, when the structure is not yet able to support the leavening that has taken place, and collapses (Francis, 1999). Another example of striking the right balance in baking is the

inclusion of tenderising ingredients to offset the development of toughness from structure formation (Figoni, 2008).

3.5.1.1. From batter to cake: The effects of processing (mixing and heating)

The processing of cake batter begins with mixing. Mechanical mixing of the batter serves several purposes: it incorporates air; as it proceeds it breaks down the initially large bubbles of air and CO₂ (from leavening agents activated in the presence of water), into finer and more evenly distributed bubbles; it helps to dissolve or hydrate ingredients so that they can thicken the batter so that it can better retain the bubbles. Although more gas is generated during baking it is the bubbles existing already in the batter that will be inflated and expanded by these gases.

The changes to the batter that occur during baking are the result simultaneous heat transfer and mass transfer (the movement of water) brought about by the high temperatures used. In a conventional baking oven the heat reaching the baking pan and product surface is supplied by a combination of radiant heat from oven walls, and the movement of hot air from inside the oven by natural or fan-assisted convection. Driven by temperature gradients, heat is transferred to, and within the product by mainly conductive heat transfer (molecular transfer without material movement) and also by convection (though movement of water) (Zhou and Therdthai, 2008). Pressure gradients created by the heating of the outer batter layers and the resulting increase in partial water vapour pressure inside pores within the batter, drives vapour towards the centre, where it condenses due to the cooler temperatures at the centre. In turn, a liquid gradient is created driving water through the pores back to the batter surface, and evaporates to the air surrounding the surface by mass convection owing to concentration gradients between the surface and air (Zhou and Therdthai, 2008). Because the movement of water towards the batter surface is slower than that towards the centre, the crumb can become wetter than batter at the centre (Zhou and Therdthai, 2008). Mass transfer is enhanced by the increasing porosity of the product as it sets to a sponge-type structure.

The combination of heat and mass transfer brings about the reactions leading to structure development, such as the melting or further dissolution of ingredients, the generation and/or expansion of leavening gases (air, steam and carbon dioxide), the subsequent gelatinisation of starches and coagulation of proteins which set the expanded structure, and crust formation and browning.

In the early stages of baking, the skin that forms on the batter surface is not strong enough to retard volume expansion allowing expansion and structure setting to progress. Surface drying after moisture has evaporated, together with heat from the oven, causes a hard, dry crust to form in its place. Once evaporative cooling slows down and the surface temperature rises, the initially pale crust starts to develop colour and flavour due to caramelisation and Maillard browning. More detail on caramelisation and Maillard browning is given in Section 3.5.5.2.2 below.

3.5.1.2. Role of ingredients

The contributions of different ingredients to the development of structure, colour and flavour across different types of ‘conventional’ cake formulations are detailed in Table 3.2. ‘Conventional’ cake formulations differ in the relative proportions of their ingredients, and the ways in which they are processed, which will in turn produce different variations on cake structure.

Table 3.2 The functions of different ingredients in the development of structure, colour and flavour in cake formulations. No single cake formulation is represented here; functions described are across different formulations.

Ingredient	Function of ingredient in batter	Function of ingredient during baking	Structure formation	Colour and flavour
Wheat flour	Aeration and stabilisation	Leavening	✓ Pasting and gelatinisation of starches from flour; limited development of gluten proteins (cakes are relatively low-gluten formulations)	✓ Contributes protein, small amounts of sugar, and starches for Maillard browning; degree of browning depends on protein content of flour
Sugar	✓ Stabilises egg foams (whipped whites, whole eggs or yolks); stabilises whipped egg white foams (see below) by slowing egg protein denaturation which protects against over whipping and by forming slow-draining viscous syrup protecting bubbles from collapse; adds air which is contained between sugar crystals during creaming of fat (see below); undissolved sugar crystals help to thicken high sugar or low moisture batters		✓ Once dissolved, tenderises by disrupting and delaying structure formation: sugar strongly attracts the water that is needed for protein coagulation, gluten development, and starch gelatinisation (increasing gelatinisation temperatures); structure formation therefore also better timed with leavening; increases batter boiling point, affecting the amount of steam generated at a given temperature	✓ Imparts sweetness; sugars undergo caramelisation, and Maillard browning in presence of protein; some sweeteners directly contribute colour and flavour
Eggs	✓ Beating/whipping of egg whites in low-fat formulations, otherwise whipping of whole eggs or egg yolk in other formulations, to incorporate air before other ingredients added; egg proteins denatured by beating form films around air bubbles; eggs contribute water for thickening batter; emulsifiers in egg yolk help to keep air or fat dispersed in batter	✓ Water from eggs contributes to steam vapour	✓ Coagulation of proteins from egg white and egg yolk; eggs supply water for structure-forming reactions; yolks contain tenderising fats and emulsifiers	✓ Egg yolk colour carried through in batter; egg yolk also contributes flavour because of its fat content
Fat	✓ Beating/creaming of solid fats in high-fat formulations to incorporate air before other ingredients added; also, fat ingredients such as butter and margarine (80% fat) already a source of air and water, even without creaming; emulsifiers (where added) in shortening help proteins to trap and hold air in batter (shortening is 100% fat)	✓ Melting of solid fat releases air and water contained in the fat; steam formed, expansion of air and steam	✓ Melted fats, and oils, tenderise by coating gluten, egg proteins, and starches, which interferes with structure formation; fats also increase the temperature of starch gelatinisation	✓ Fats, especially butter and lard, contribute flavour and can directly contribute colour; butter and some margarines contain milk solids that undergo Maillard browning; fats increase the rate of heating and therefore the rate of browning; colour also from added beta-carotene in margarine
Leavening agents	✓ Production of CO₂ from baking powder (acid + alkali) in the presence of water, or from baking soda	✓ In the presence of water and heat, dissolution and		✓ Baking soda often added to increase the rate of browning, by

Ingredient	Function of ingredient in batter	Function of ingredient during baking		
	(alkali) reacting with acidic ingredients in the presence of water; as well as creating new gas bubbles, CO ₂ also makes batters less dense and easier to mix	activation of (slow acting) baking powders, and activation of baking soda (alone, without acid) to produce CO ₂ ; CO ₂ moves to, and expands existing air and gas bubbles		increasing pH; on its own baking soda is less efficient than when mixed with acid, and the high amounts needed will produce an objectionable chemical taste and cause yellow-green crumb discoloration
Salt				✓ Lowers batter caramelisation temperature; adjusts sweetness and flavour
Non-fat dry milk	✓ Milk proteins form stable foams; proteins aid air incorporation and stabilisation in creamed shortenings		✓ Contributes proteins which undergo coagulation; milk proteins and calcium salts strengthen coagulated egg structure	✓ Source of protein and lactose for Maillard browning; and adds flavour
Water	✓ Dissolves or hydrates dry ingredients to increase batter viscosity, and to activate ingredients and processes	✓ Produces steam; pressure created by expanding water vapour inside batter; steam moves to, and expands existing air and gas bubbles	✓ Required for structure-forming reactions	
All	✓ Beating of entire cake batters in high-fat formulations contain high-ratio liquid shortening (which contains added emulsifiers)			

3.5.2. The effect of formulation and processing changes

Given the important roles of the different ingredients described above in the formation of structure, colour and flavour in cakes, it follows that changing their relative proportions and the manner in which they are processed will produce different product outcomes. This is already evident in the variety of textures that result from different ‘conventional’ cake recipes, which for example may or may not contain fat, or differ in their degree of mechanical aeration at the batter stage. Changes to recipes can also take the form of full or partial substitution of ingredients in a standard formulation with alternatives in order to modify the nutritional profile of the product (the challenge here being to make the substitution for as little change in volume or texture as is possible), or the inclusion of functional additives in small amounts to improve textures, where needed. Furthermore, as the behaviour of the ingredients during baking have so far been described for conventional baking oven conditions, it would be expected that other baking technologies, such as rapid baking, with different modes of heating will have their own effects on product quality.

The facility to make rapid, called-for changes to a given product formulation to achieve desired textural and/or nutritional profiles will be one of the essential features of the 3D colour food printer, where the characteristics of the printing substrate itself will be able to be customised, in addition to the customisation of its appearance through the 3D rendering of colour images. Continuing this discussion using cake as a model system for the 3D colour food printing substrate proves useful here because, not only are the effects of conventional formulations and processing conditions well understood, cakes and related products have been the subject of numerous studies investigating the effects of alternative ingredients and baking environments. This has been for reasons of enhancing nutritional value and convenience, in line with what the printer aims to provide.

3.5.2.1. To alter, improve, or correct volume and texture

Although this discussion so far has focused on aeration of cake batters to achieve light textures and a fine and uniform crumb, it might also be desirable to have cakes that are deliberately

denser in texture. Dense textures are achieved for (non-cake like) muffin formulations which are not beaten, but rather blended lightly, just until the dry ingredients are moistened by the liquid ingredients, including liquid fat (Figoni, 2008). Fudge-type brownies, denser and moister than their cake-type counterparts, have relatively high sugar to flour content in batter. The sugar competes with starch for available water, interfering with, and limiting the extent of starch gelatinisation; the structure is therefore unable to support the leavening that has taken place, and collapses after baking. Likewise, *unintentional* low cake volumes can be corrected by adjusting sugar and water levels (Thomas and Atwell, 1999). The replacement of solid fat ingredients (such as shortening and butter) with liquid oil is another way to achieving a dense and coarse crumb, though it will be moist and tender (Figoni, 2008). Oils do not contribute to leavening, because it lacks air and water, but is able to coat structure-forming ingredients as early as during the batter mixing stage, without first having to melt.

Textures can be adjusted or improved by the use of additives in small amounts. Examples are pre-gelatinised (cold-water swelling) starches, and hydrocolloids or gums (which are high molecular weight, water soluble polysaccharides), that bind water and increase batter viscosity and bubble stabilisation. The binding of moisture also improves product tenderness and shelf life. Hydrocolloids also increase the water absorption capacity of flour (Sahin, 2008) and modify the pasting properties of starch, delaying the ‘setting’ of starch granules. Emulsifiers, such as mono- and di- glycerides and lecithin, make their contribution by keeping fat and oil droplets dispersed in batter, and by strengthening the protein films around expanding air and gas bubbles. Emulsifiers can be added as a separate ingredient, but it is more typical to use ingredients that contain natural (butter, egg yolk) or added emulsifiers (margarine and solid and liquid shortenings) (Figoni, 2008). The use of liquid shortenings containing emulsifiers allows cake ingredients to be beaten together in a single step process.

3.5.2.2. To alter nutritional profiles of formulations

Changes to cake formulations to improve their nutritional profile, or to meet specific dietary needs or restrictions, will invariably alter final cake characteristics because the targets of these

changes are the very ingredients that are involved in leavening, structure formation and in colour and flavour development. Examples of such changes included the partial or full replacement of fat and/or sugar to reduce energy content, the substitution of wheat flour with gluten-free alternatives, and the use of dairy- and egg- free ingredients. It is clear therefore that a technological challenge is presented by modifying formulations to give more nutritionally beneficial product profiles that are also acceptable to the consumer. By way of example, discussion here focuses on the replacement of fat and sugar.

3.5.2.2.1. Replacement of fat and sugar

High fat and sugar intakes, which increase dietary energy consumption, are implicated as causes of obesity, and also displace more beneficial protein- and carbohydrate- rich foods such as cereals and legumes from the diet. High intakes of fat and sugar are due to a combination of high energy density (in the case of fat), the presence of fat and sugar in relatively high proportions in foods such as cakes, and the appealing tastes, flavours and textures that fat and sugar contribute to foods. Other reasons to target fat and sugar for replacement in baked goods include the increased risk of cardiovascular disease from high fat intakes *per se*, or from high intakes of saturated fats that are part of high total intakes, and the reduced ability of individuals with diabetes for the cellular uptake of blood glucose. Sugars can also promote the development of tooth decay (Gomez, 2008).

Strategies to lower the energy contributions from fat and sugar in foods, and yet retain favourable textural characteristics, include: the replacement of sugars by alternative bulking agents which are either absorbed slowly and incompletely (such as polyols) or are metabolised to a limited extent (such as oligosaccharides), and replacing fat ingredients with those having a high capacity to absorb water (such as maltodextrin, fibres, gums and cellulose), thereby diluting energy content and imparting useful gel-like properties for structural purposes. The oligosaccharides polydextrose and inulin double as fat replacers because of their ability also to absorb large amounts of water, though inulin is used mainly as a fat replacer (Gomez, 2008). Compared with sucrose, polyols and oligosaccharides do not promote tooth decay and are better

tolerated by diabetics but are lower in sweetness (thus requiring the addition of intense sweeteners such as saccharin and aspartame), and their excessive consumption can have a laxative effect.

Fats can also be replaced by the use of small, spherical, protein-based insoluble micro-particles mimicking their mouthfeel because the particles are perceived collectively as smooth and creamy (Gomez, 2008). The effects of fat on health could also be mitigated by the use of oils containing poly- or mono- unsaturated fatty acids in place of saturated fats, which comes with the added benefit of producing moister and tender cakes, though the grain tends to be coarser (Gomez, 2008).

Details of some studies investigating the effects of fat and/or sugar replacement on final cake characteristics is given in Table 3.3. Not all bulking agents have been found to have the same effect in sugar replacement. Polyols (which are hydrogenated sugars) have been found to differ in their effect on the specific volume of sugar-free sponge cakes (Ronda *et al.*, 2005). Findings on the effects of polydextrose vary with respect to crumb structure in high-ratio cakes, with the population of small, sphere-like cells in the crumb either increasing (Hicsasmaz *et al.*, 2003) or decreasing (Kocer *et al.*, 2007) with increasing sugar substitution level, despite relative cake height and porosity being decreased, and bulk density increased in both studies. Polydextrose raises starch gelatinisation temperatures, but not protein denaturation temperatures (Hicsasmaz *et al.*, 2003). On the one hand, the formation of the protein matrix at the crust lowers the rate of heat transfer, and therefore reduces the build-up of vapour pressure required to expand the bubbles (Hicsasmaz *et al.*, 2003); on the other hand, bubbles in the crumb are able to be expanded by the moisture and vapour pressure that is prevented from escaping by the developing crust (Kocer *et al.*, 2007). Replacement of fat in reduced-fat cakes by maltodextrin, a starch derivative, was more effective when substitution was partial rather than full, or in the presence of an emulsifier (Lakshminarayan *et al.*, 2006). Sponge cakes in which up to 70% of the oil in the control formulation was replaced by inulin (a collection of fructose polymers which in this study had an average chain length of between eight and 12) did not differ

significantly to the control cakes in selected sensory attributes, despite changes in crumb structure related to inadequate bubble expansion in batter (similar to the findings of (Hicsasmaz *et al.*, 2003)) and in cake texture due in part to the lack of the lubricating effect of oil (Rodríguez-García *et al.*, 2012). Full replacement of fat by inulin resulted in significantly less acceptable cakes relative to the control, in line with the results from texture measurements.

The replacement of sugar or fat with carbohydrate-based alternatives such as the ones described above would be expected also to have an effect on the colours of the cakes themselves. As well as their contributions to structure and texture development, carbohydrates are involved in two types of non-enzymatic browning reactions: Maillard browning, which is the reaction of reducing carbohydrates and amino acids, and caramelisation, which is the breakdown of sugars in the presence of high heat. For 3D colour food printing, the background colour of the printing substrate needs to be taken into account when computing dye quantities needed to render colours in 3D, and these same colours might be needed across substrates that differ in their 'native' colour. For 3D coloration, any changes in *crumb* colour that occur with carbohydrate substitutions are of the most interest. Browning of the *crust* might either be a desirable feature to retain in the printed food (and could introduce an element of surprise in that rendered 3D colours are 'hidden' before eating), or a lighter crust colour may be preferred so that rendered colours can also be seen on the surface.

While sucrose ('sugar') is itself not a reducing sugar, it does undergo caramelisation, during which it breaks down into glucose and fructose. Glucose and fructose themselves undergo caramelisation, and along with starch (a glucose polymer), are also reducing sugars, though the Maillard reaction occurs more slowly with fructose than it does with glucose (Damodaran *et al.*, 2008). Carbohydrate-based fat- and sugar- replacers that are a source of reducing sugars include: starch derivatives such as maltodextrin and dextrin, and the fructose polymers inulin and its shorter chain length counterpart oligofructose which is derived from inulin degradation. Polydextrose, a manufactured complex carbohydrate made from glucose, sorbitol and citric acid also reacts with amino acids to produce Maillard browning (Mitchell, 1996). Polyols, from the

catalytic hydrogenation of different sugars, do not undergo Maillard browning or caramelisation.

Accordingly, polyols were found not to affect the measured lightness of crumb in sugar-free sponge cakes, and increased crust lightness relative to the control cake containing sucrose (Ronda *et al.*, 2005). Polydextrose was found to decrease the measured lightness and increase the measured redness of cake crumb (Hicsasmaz *et al.*, 2003; Ronda *et al.*, 2005), as well as to decrease crumb yellowness (Hicsasmaz *et al.*, 2003; Kocer *et al.*, 2007). The pH of the cake batters in the study by Hicsasmaz *et al.* (2003) favoured the Maillard reaction over caramelisation. Oligofructose was also found to increase the redness of cake crumb (Ronda *et al.*, 2005). On the other hand, increasing the inulin content increased the measured lightness of cake crumb and did not change the values for the chromatic parameters (Rodríguez-García *et al.*, 2012). No explanation is offered as to why this might have been the case, however in this study inulin was used to replace the fat in the formulation, while sugar content remained unchanged; in the other studies polydextrose and oligofructose were used in the partial or full replacement of the sugar. The increase in measured lightness of the crumb with increasing inulin content could have been due to the significant decrease that was seen in total (air) cell area; the inclusion of such ‘bubbles’ in instrumental colour measurement can lead to the finding of colours that are darker than when observed visually (MacDougall, 2002b). Both oligofructose (in its role as a sugar replacer) and inulin (as a fat replacer) have been found to decrease the measured lightness and to increase the redness of cake crust (Ronda *et al.*, 2005; Rodríguez-García *et al.*, 2012), with inulin also shown to decrease measured yellowness (Rodríguez-García *et al.*, 2012). It should be noted that the colour measurement illuminant and observer conditions differed between the studies, meaning their findings should be compared in relative, rather than in direct terms.

Table 3.3 Descriptions of studies investigating the effects of fat and/or sugar replacement in cake formulations.

Formulation changes under investigation, and degree of substitution	Effects on measured volume and texture parameters	Effects on measured colour and/or appearance* attributes	Sensory evaluation or comments
Sugar replacement Increasing substitution of polydextrose for sugar in high ratio cakes, replacing 0%, 25%, 50%, 75% and 100% of the sugar in a conventional formulation (Hicasmaz et al., 2003); results are relative to the conventional formulation	Significant decrease in relative cake height from 25% substitution upwards; mean bulk density significantly decreased at 25% and 50% substitution but increased at 75% and at full substitution; significantly lower mean porosity at 75% and full substitution; cell structure characterised by increasing population of small, sphere-like cells in the crumb with increasing polydextrose substitution indicating decrease in expansion	Decreases in mean measured lightness (L*) and yellowness (b*) of crumb ; increase in crumb redness (a*) ¹	A product similar to the conventional cake was achieved when 25% of the sugar replaced, equating to a 18.75% calorie reduction
Replacement of sugar by polydextrose in high-ratio cake formulation, replacing 20%, 40%, 60%, 80% and 100% of the sugar in a conventional formulation (Kocer et al., 2007); results are relative to the conventional formulation, the same as that used by Hicasmaz et al. (2003)	Significant decrease in relative cake height from 20% substitution upwards, significant increase in bulk density and decrease in porosity from 40% substitution; increasing sugar replacement levels decreased the population of sphere-like pores in the crumb	Significant decrease in measured lightness of crumb from 20% substitution, significant decrease in measured yellowness from 40% substitution ¹	
Effects of polyols and oligosaccharides (oligofructose and polydextrose) on characteristics of sugar-free sponge cakes (Ronda et al., 2005); full substitution of each bulking agent for sucrose in the control sponge cake formulation; results are relative to the control cake	Specific volume (volume to weight ratio) of sugar-free cakes lower than control cakes, though results for sorbitol, oligofructose and xylitol cakes close to control cake; mannitol cake had lowest specific volume and higher crumb firmness	Crust : relative to control cake, increase in measured lightness, with exception of a decrease with oligofructose; notable changes in hue with use of oligofructose (towards red) and with isomaltose (towards yellow); Crumb : lightness largely unaffected with exception of a decrease with polydextrose; notable changes with polydextrose and oligofructose towards red ²	No significant differences between sugar-free cakes in <i>preference</i> ratings for flavour and texture, despite differences in perceived flavour <i>intensity</i> and in firmness, with exception of mannitol cake texture being the least preferred; besides mannitol cakes, polydextrose and oligofructose cakes had the lowest overall acceptability scores compared to the control cake due to their being the least sweet and least preferred for aftertaste.
Fat replacement Replacement of fat in a pound cake formulation with maltodextrin (MD) ± emulsifiers: fat reduced by 60%, 70% and 80% in formulation and MD added at 5%, 10% and 15%; emulsifiers	Effects of MD : significant decrease in measured compression force as indicator of texture; some increases seen in specific volume, but not significant;		Hedonic ratings indicated improvement in crumb grain and texture at higher levels of MD- only addition in cakes reduced in fat by 60% and 70%, as well as in crust and crumb colours and

Formulation changes under investigation, and degree of substitution	Effects on measured volume and texture parameters	Effects on measured colour and/or appearance* attributes	Sensory evaluation or comments
GMS ³ and SSL ³ added at 0.5% to formulation with 80% reduction in fat and containing 10% MD (Lakshminarayan et al., 2006); results given here are comparisons to reduced-fat cakes without additives, not to full-fat cakes	Effects of emulsifiers: GMS and SSL increased and decreased cake volume respectively, despite both decreasing batter viscosity; GMS also improved texture		taste of 80% reduced fat cakes; GMS further increased ratings of crust colour, crumb grain and mouthfeel; ratings of crumb colour decreased by both emulsifiers
Increasing substitution of inulin for oil in sponge cake formulation (Rodriguez-Garcia et al., 2012); inulin used to replace 0%, 35%, 50%, 70% and 100% of oil on a weight basis; results presented are relative to the control (full-fat) formulation	Decreases in total cell area (significant), cake height (significant) and cell density (number of cells per crumb area) and cells smaller and significantly more circular , with increasing inulin content; full replacement resulted in significantly harder crumb and significantly decreased springiness, while adhesiveness was significantly increased due to presence of fructan molecules, and the lack of oil as lubricant	Crumb: Significant increase in measured L* values of crumb with increasing inulin content; while b*, C _{ab} * and h _{ab} remained largely similar, with perceptible difference predicted between the control cakes and the cakes in which 35% and 70% of the fat was replaced by inulin; Crust: L* and b* values significantly decreased and a* values significantly increased; all cakes predicted appear obviously different in colour to the control ⁴	Cakes with fat replacement up to 70% did not differ significantly from the control in mean sensory acceptance scores for appearance, colour, texture, taste and overall acceptability by an untrained panel of consumers, but 100% replacement significantly lowered scores for all attributes relative to the control, with the low score for taste likely due to sweetness from the inulin
Replacement of fat by polydextrose in high-ratio cake formulation, replacing 20%, 40% and 60% of the fat in a conventional formulation (Kocer et al., 2007); results are relative to the conventional formulation, the same as that used by Hicasmaz et al. (2003)	At 20% substitution, no significant differences to conventional recipe in bulk density and porosity, otherwise bulk density significantly increased, and significant decrease in relative cake height at all replacement levels	At 20% substitution, no significant difference to conventional recipe in measured crumb yellowness, significant decreases in measured crumb lightness at all replacement levels ¹	

Formulation changes under investigation, and degree of substitution	Effects on measured volume and texture parameters	Effects on measured colour and/or appearance* attributes	Sensory evaluation or comments
Sugar and fat replacement			
Simultaneous sugar- and fat- replacement, with the aim of further reducing energy content relative to reductions with sugar-only or fat-only replacement (Kocer et al., 2007); replacement levels determined by response surface experimental design	Simultaneous sugar- and fat- replacement of up to 25% of fat and 22% of sugar resulted in a 22% calorie reduction compared to 6.5% and 10% reductions due to sugar-only and fat-only replacement respectively; this was achieved for a 4% decrease in cake height.....	and a 6.5% decrease in the yellowness of the crumb ¹	
¹ Hunter Lab values (Hicasmaz et al., 2003; Kocer et al., 2007) ² Measured CIE L*a*b* values, for the D65 illuminant & 2° standard observer (Ronda et al., 2005) ³ Glycerol monostearate (GMS) and sodium steryl lactylate (SSL) (Lakshminarayan et al., 2006) ⁴ Measured CIE L*a*b* values, for the C illuminant & 2° standard observer (Rodriguez-Garcia et al., 2012)			

3.5.3. Alternative (rapid) baking technologies: Jet impingement oven technology and microwave cooking

Other than customisation, a key feature of the 3D colour food printer under development is convenience; in this context, *convenience* refers specifically to the provision of outputs on-demand and in short-time, and the integration of the printing and cooking steps into a single unit process. The contribution that the cooking step could make to this rapid and integrated process is the subject of this section. Currently the facility to heat printed foods as they are being extruded, or when they are on the printing tray exists only as a concept in the ‘Digital Fabricator’ and ‘Virtuoso Mixer’ (see Table 3.1), or is under development, as in the cooking of pizza dough layers in the NASA 3D food printer. Modified cookie dough developed as a printable food for the Fab@Home printer, is baked after printing by conventional means away from the printer, and the dough is refrigerated for a time between printing and baking.

If bakery- and cake- type formulations are being considered as model printing substrates, alternative cooking methods to conventional baking should be sought, as conventional baking by natural convection is a slow and inefficient process (Kocer *et al.*, 2008). Rapid baking technologies such as jet impingement oven and microwave oven technologies provide lower energy and shorter time alternatives to conventional oven baking. Their higher efficiency is due to the faster rates of heat and mass transfer that can be achieved in the food product. In jet impingement technology high-speed (10 to 50 m/s) jets of hot air (100°C to 250°C) impinge vertically on the food, from above and below. Unlike conventional baking, heat is distributed more evenly and the surrounding cold boundary layer which normally acts as an insulating barrier to heat transfer is removed, leading to higher rates of heat and mass transfer at the surface. In microwave cooking, electromagnetic energy is absorbed by charged particles and polar molecules such as water and salt, which directly and rapidly heats the product interior; in this case increased rates of heat and mass transfer are caused by the pressure and concentration gradients created by the internal heating. Heating from the inside is a more efficient way of

cooking aerated doughs (such as bread) in which the insulating effect of the entrapped air would otherwise slow heat transfer from the outside into the product.

Rapid baking technologies differ one to the other, and to conventional baking, in their effects on product quality. Products baked by jet impingement have improved texture and structure, and a more uniformly baked surface, when compared with their conventionally-baked counterparts. Although the rate of moisture loss is higher with jet impingement technology, rapid crust formation, aided by the removal of surface moisture under hot air, and the shorter baking times result in higher moisture retention. At the same time, an increased rate of heat transfer leads to faster cooking of the crumb. However, lower temperatures should be applied in the earlier stages of baking to avoid premature formation of a crust which would act as insulation against further heat transfer. Moisture can also be added to prevent crust formation, by spraying the product with water as it enters the oven, and then by steam or water injectors during the first half of baking (Loh *et al.*, 1998). Due to the dependence of browning reactions on high temperatures ($>100^{\circ}\text{C}$) and the faster increases in surface temperatures seen with jet impingement, the rate of surface colour development is also faster than when using conventional baking.

In contrast, microwave-baking is associated with numerous quality defects in the final product. These include dryness, low volumes, and dense and tough textures, as well as a soggy surface lacking crust and colour. As with jet impingement baking, rates of moisture loss from microwave baking are high compared with conventional baking, however the high internal pressures created by microwave heating pushes more water to the product surface. Formation of a crust that would curb moisture loss cannot occur, due to the cool, ambient temperature surrounding the product inside the oven causing condensation and cooling at the product surface. Under these conditions browning reactions also cannot take place. Low volumes and textural defects are due to structure-forming processes such as starch gelatinisation and expansion being limited by the short cooking time. Microwave-induced gluten changes might also contribute to problems with structure. Strategies to improve quality in microwave-baked

cakes include the addition of hydrocolloids, instant starches and pre-gelatinised starches to aid moisture retention; use of pre-gelatinised starches doubles as a solution for incomplete starch gelatinisation (Sumnu, 2001). In optimising formulations for microwave-baked cakes, it has been found that volume is affected by the type of starch used (higher with wheat starch) and the gluten level in flour (higher with lower gluten); volume and texture are affected by microwave power level, and by monocalcium phosphate monohydrate in baking powder, with specific volume decreasing and crumb firmness increasing with increasing concentration (Kocer *et al.*, 2008).

Due to their modes of heating being internal and external respectively, microwave- and jet-impingement baking complement one another and are used in combination ovens. As well as further decreasing the cooking time relative to the individual technologies, hot air is available from jet impingement to surround the product and to dry and heat the surface which allows for crust formation and browning. This means that more moisture is retained in the product (preventing excessive drying), than when using microwave heating alone. Due to the short cooking time, baking using combined technologies may require the use of creaming or a rapid-acting chemical leavening agent to ensure sufficient leavening in the product before its structure sets. Microwave-infrared ovens are another type of combination oven, in which halogen lamps emitting near-infrared radiation provide surface heating. Results comparable with conventional baking can be obtained for comparatively less baking time, given the right combination of time and power level. These include high-quality gluten-free cakes containing added gums and emulsifier (Kocer *et al.*, 2008).

3.5.4. A 'case study': low-fat cake doughnuts

A process for making low-fat cake do(ugh)nuts, invented by Loh *et al.* (1998), provides a very good example on which the printing substrate for 3D colour food printing could be modelled. Whereas conventional cake-type donut batters are not self-supporting and are deep-fried, a conventional formulation was modified by the inventors to be formable, and intended for rapid baking in an air-impingement oven, thereby reducing the fat content. The batter was made

formable by the inclusion of thermally-reversible gel, which made up 20% to 30% of the batter by weight, allowing the resulting dough to be shaped (by sheeting, stamping or extrusion) and to retain its shape during the early stages of baking; in the latter stages of baking, by which time heating has melted the gel, the dough itself has developed into a leavened, self-supporting structure. The gel is comprised of 85% to 90% (preferably) of water, 8% to 12% of an insoluble, water-binding fibre (such as powdered cellulose), and 0.4 to 1% of a thermally-reversible hydrocolloid gelling agent (such as agar). This type of formulation and its processing combines a number of properties that are suited to a 3D food printing substrate, which individually have been described in the preceding sections: that is, it can be extruded due to the addition of a gel ingredient, it is a cake-type formulation that can be baked rapidly, and it is the result of modifying a conventional formulation to improve nutritional value.

3.5.5. Predictive studies: modeling the development of structure and colour in food systems of relevance to baking, and to 3D colour food printing

Better control and optimisation of baking outcomes is possible using mathematical models that can predict the effects of formulation and processing changes on the physical and chemical characteristics of the product. Not only is predictive capability useful for product development *per se*, but necessary for the 3D colour food printer which is being designed as an on-demand, customised food production system. From a coloration point of view, the formulation and therefore the physical characteristics of the printing substrate – ‘the blank canvas’ - will vary according to user-defined specifications for sensory and nutritional properties. If substrate characteristics likely to affect colour rendition, such as the degree of browning and light scattering (texture) can be predicted, then the dye recipes needed to reproduce desired colours in the substrate can accordingly be computed and adjusted.

This section focusses on examples of studies in which the development of browning and structure under various conditions has been modelled, in different food systems, and is

organised by the different modelling methodologies used. These studies have been selected for inclusion here because of their direct relevance to baking (De Cindio and Correra, 1995; Kocer *et al.*, 2007; Mundt and Wedzicha, 2007), or because they cover ingredients or processes that feature in baking, such as browning (Han and Floros, 1998) and carbohydrates and caramelisation (Sleeuwen *et al.*, 2013). Browning has been modelled for reasons of it being a desirable quality in some food systems, but not in others.

3.5.5.1. Using response surface methodology

Response surface methodology (RSM) is used to measure then model the simultaneous effects of multiple independent variables, or factors, on the output(s) of a given system or process, usually with the goal of determining the combination(s) of factors that are needed give optimal outputs (Bezerra *et al.*, 2008). In developing the model, data are collected according to an experimental design that defines the levels of the different factors, and tests different combinations across multiple experimental runs. Polynomial functions are fitted to the experimental data; a good fit is indicated by low residual values, or small differences between computed and experimental data. The term ‘response surface’ refers to the graphical representation of the modelled data. The predictive ability of RSM models is limited to the range of factor levels that are used in their development.

Of direct relevance to baking, Kocer *et al.* (2007) modelled the interactive effects of simultaneous sugar- and fat- replacement by polydextrose in a high-ratio cake formulation, on batter and cake properties (including relative cake height, average bubble size, and Hunter L and b values) using response surfaces. This was done to determine whether further reduction in energy content (relative to sugar-only and fat-only replacement) was possible for ‘tolerable’ changes in expansion characteristics and crumb colour (see also Table 3.3).

Response surfaces were used by Han and Floros (1998) to model the change in colour of potassium sorbate powder as a function of heating time and temperature, to investigate the possible use of the powder as an indicator for high temperature processes such as baking. As

indicated by the respective decrease and increase in measured HunterLab L and b values, heating caused the powder to turn a dark yellow, which was likely due to oxidative degradation. The implication for the addition of potassium sorbate as a preservative to foods is that the foods could discolour during heating, reducing their quality, by either oxidation of the preservative in the presence of other food components, or the involvement of its carboxyl group in Maillard browning.

3.5.5.2. Using kinetic models

Whereas RSM relies on producing replicate outputs from known factor and factor level combinations and using statistical techniques to fit an appropriate empirical function (Berns, 2000, Bezerra et al., 2008), other models aim to describe a more direct relationship between outputs and changes in raw materials or processing variables (de Cindio and Correra, 1995), by investigating the rates at which these processes occur, and the factors influencing the rates of reaction. Factors affecting reaction rates include the type, physical state and concentration of the reactants, temperature and pressure, and the presence of catalysts.

3.5.5.2.1. Texture

The kinetics of the various processes contributing to baking were combined to develop a comprehensive model for the baking process as a whole (De Cindio and Correra, 1995), with the model intended for use in the optimisation of textural characteristics. The model takes into account the processes occurring at the level of bubble and the paste directly surrounding and interacting with the bubble (incorporating leavening kinetics, bubble expansion, paste rheology and diffusion of CO₂ and water), and at the dough level (heat transfer and mass transfer of CO₂ and water). Parameter values for the model were determined experimentally or taken from literature data (De Cindio and Correra, 1995). In a simulation of the three main phases of baking – mixing, leavening and heating - using a yeast-leavened formulation, the model was able to predict changes in total mean specific volume (representing softness), moisture content (firmness) and pH, with time.

3.5.5.2.2. Browning

The Maillard reaction is a non-enzymatic reaction between reducing carbohydrates and amino acids or proteins that contributes much of the desirable roasted flavours and brown colour on the surface of baked goods (Figoni, 2008). It can also cause undesirable browning in processes such as during the preparation of condensed milk (Hofmann, 2001), and during the storage of milk powders because that the reaction can also occur at room temperature given enough time. Nutrients such as the amino acid lysine are lost through their involvement in the reaction (Koksel and Gokmen, 2008). Usually temperatures of at least 50°C are needed for the Maillard reaction to occur (Zhou and Therdthai, 2008). Caramelisation, which is the degradation of sugars in the presence of temperatures of at least 160°C to 170°C, also contributes browning, and gives cooked sugar flavours.

Other than temperature and heating duration, the Maillard and caramelisation reactions are affected by such factors as pH, moisture content (as indicated by the level of water activity, a_w , or available water), and the types of amino acid and sugar that are involved. In both reactions, the rate of browning is increased by increasing the pH or in the presence of reducing monosaccharides, while lowering the pH slows browning (Figoni, 2008). The presence of salt lowers batter caramelisation temperatures (Sahin, 2008). For the Maillard reaction, colour development increases at intermediate moisture levels (a_w 0.3 to 0.7), with the implication that the reaction will be slow in high moisture foods, and when temperatures are low, or in dry systems. Aroma (flavour) development also depends on the total amount and relative proportions of amino acid and sugar on the product surface; unique aromas are produced with each different combination of temperature and time conditions (Sahin, 2008).

Kinetic models that have been developed to predict the extent of browning in baked goods, and in other food systems, with time and under different experimental conditions, are used to predict changes in either CIELAB values (Zanoni *et al.*, 1995; Broyart *et al.*, 1998), or in reflectance or absorption spectra (Mundt and Wedzicha, 2007; Smeuwen *et al.*, 2013). Although following a kinetic process, the direct fitting of a model to CIELAB values as a function of time is an

empirical approach (Mundt and Wedzicha, 2007). Modelling of spectral changes with time effectively describes chemical kinetics, following the formation of reaction intermediates and products (Mundt and Wedzicha, 2007), since the concentration of a coloured species in solution has direct relationship to the measured absorption of the solution. Where available, predicted changes in full absorption/transmission spectra as a function of time and temperature (rather than changes at a single wavelength or a few wavelengths) can then be expressed as a perceived change under specified illuminant and observer conditions, by subsequent derivation of CIELAB, followed by ΔE^*_{ab} or Browning Index, values (Sleeuwen *et al.*, 2013).

Mundt and Wedzicha (2007) developed their kinetic model to predict the change in measured reflectance (RGB values) with time during the browning of biscuit dough under controlled temperature and water activity conditions, with reflectance in the model expressed in terms of the Kubelka-Munk function. The model fitted well to experimental RGB data collected for ‘standard’ dough samples at three levels each of temperature and water activity, a_w (and thereby revealing that a_w had no effect on the rate of browning across the range observed). The model also fitted well to data obtained from test doughs containing three levels of added sugar, where again a_w was found not to have an effect on the browning kinetics. The focus of the kinetic model developed by Sleeuwen *et al.* (2013) was the control of browning in a carbohydrate system in which excessive browning during heating might cause colour and flavour to deviate from specification. Glassy carbohydrate microcapsules which are used for the encapsulation of food flavours, and which should be either un-coloured, or contain added colorants for providing visual appeal to foods, are exposed to elevated temperatures during their production. The model was based on wavelength-dependent reaction rate constants and Arrhenius parameters (indicating respectively the kinetics and temperature dependence of colour formation) obtained from measured absorption/transmission spectra of maltodextrin (MD) and maltodextrin/sucrose (MD/S) melts which were used as model systems. For both types of melt, when subjected to a simulated industrial thermal process, there was found to be little difference between the spectra predicted by the model and the experimental spectra.

In neither of the studies discussed (Mundt and Wedzicha, 2007; Sleenuwen *et al.*, 2013) was the concentration of the browning intermediates and products themselves actually measured; the Maillard reaction for example leads to the formation of a multitude of low and high molecular weight compounds (Hofmann, 2001), through a complex series of reactions (Koksel and Gokmen, 2008). However in future, there might be scope to relate the kinetics of browning, and perceived changes in browning directly to the formation of key Maillard browning reaction products. Hofmann (2001) characterised the key chromophores in a Maillard reaction mixture of D-xylose and L-alanine by a process of HPLC analysis, screening by Color Dilution Analysis for the most intensely coloured HPLC fractions, and then, following identification of the compounds their relative colour impact was defined by a novel Color Activity Value (CAV), which is the ratio of concentration to visual detection threshold. Furthermore, the percent contribution of each compound to the colour of the mixture was determined from the ratio of the CAV of the compound to the Color Dilution factor for the mixture.

The spectral approach to the kinetic modelling of browning is compatible with the spectrally-based Kubelka-Munk predictive colour blending models discussed earlier in Part 1 of this review. This raises the possibility of combining principles from the two methods to model the effects of the 'native' colour of the 3D colour printing substrate on the dye quantities that are needed to render colours in the substrate. In addition to investigating colour changes in melts that were initially un-coloured Sleenuwen *et al.* (2013) modelled the effect of browning reactions on a hypothetical MD/S melt initially light blue in colour (as referenced by a solution of Brilliant Blue FCF), which was predicted to change to green.

Of course, the type of browning that 3D colour food printing is concerned with is internal (crumb) coloration rather than external crust browning, before any dye is added. Kinetic studies of surface browning (such as the ones described above) do however provide useful modelling principles that could be applied to the printer. Examples of variables whose effects might need to be modelled include the colours of egg yolk and of various and alternative fat, sugar and flour ingredients that get carried through from the batter stage to the final product. The effects of

these ingredients would be set against a background of a structure developing over time, which in the end, depending on its density and moistness should make its own contribution to perceived (un-dyed) crumb colour.

3.6. Controlled 3D coloration in food and non-food matrices

Conventionally, 3D coloration in baked goods and confectionery is achieved by hand. To make checkerboard-, zebra- and Battenberg-style cakes (Figure 3.1) the batters are coloured and then arranged manually into patterns either before or after baking. Recipes have been posted on recipe community and blogging sites (Handmade Charlotte and Denneler, 2013; Hungry Happenings and Klosterboer, 2014) for so-called ‘Tie-Dye (Surprise) Cakes’ in which each slice of the baked, rectangular-shaped cakes reveals the same multi-coloured shape embedded within (Table 3.4). This effect is achieved by following a time- and labour- intensive process in which two cakes need to be prepared; in short, shapes are cut from the first, coloured, cake and embedded in the second, uncoloured cake batter. Also made by hand are the stick-shaped, boiled sugar confections known as ‘rock’ (Brighton Rock or Blackpool Rock in the UK), produced for both the consumer and corporate markets, in which wording (a town or company name) or a pattern (such as a company logo) is embedded along the entire length of the stick, and therefore seen in every bite or slice (Figure 3.2; Table 3.4). Production of rock confectionery is a multi-step process during which a skilled person is needed to build the letters and shapes, and at many times their final size to allow for a decrease in diameter of the bulk mixture when it is later stretched and pulled (Attractions Blackpool, 2014).



A collection of approximately 15 custom-decorated cookies, likely for a special occasion. The cookies are round and feature various designs, including text, symbols, and patterns. Some of the visible text includes "SKAGEN HAVN 100 ÅR", "P200", "Vision Pipeline", "den 11. time", "VI SKAL LØKKEN BRØD", "SKAGEN HAVN 100 ÅR", "P200", "Vision Pipeline", "den 11. time", "VI SKAL LØKKEN BRØD", "SKAGEN HAVN 100 ÅR", "P200", "Vision Pipeline", "den 11. time", "VI SKAL LØKKEN BRØD". The cookies are decorated with various colors and patterns, including stripes, polka dots, and solid colors. Some have small symbols like a paw print or a heart. The cookies are arranged on a light-colored surface.

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An alternative, more efficient means of 3D food coloration is offered by some versions of 3D food printers. The capability to colour in 3D is a feature of an existing food printer (Inspix, 2014) and printer concept (Yang *et al.*, 2001) (see also Table 3.4); by delivering colorants ‘in-line’, coloration can be fully integrated into the food production process. Printers such as these could be used to produce 3D-coloured cakes and confections in less time and for less effort than their handmade counterparts. For the 3D colour food printer currently under development, this application of the technology is an attractive prospect given that cake formulations themselves are ideal targets for the customisation of food outputs.

With 3D colour food printing there is the potential also for colours to be embedded within the substrate with greater control and in finer detail than is possible when using batters coloured by hand. In turn, this sets up the potential for complex colour images or designs to be rendered in 3D within the printed food matrix. A precedent for fine colour resolution as a desirable feature in edible form exists in the printing of colour images directly onto cake frosting sheets using combinations of primary inks, and conventional 2D printing techniques. In 3D, a patented food cooker extruder (Weinstein and Tolson, 1997) can add line colour detail at widths ranging from 0.1 mm after extrusion (and without subsequent puffing) to 0.5 mm or more after expansion, using colorants, and coloured doughs or pastes added in-line. The ProJet® 660 Pro (3D Systems, 2014) and the Objet500 Connex3 (Stratasys Ltd., 2014) are examples of non-food 3D printers that can print models and prototypes in full colour as well as with fine build resolution; ProJet® 660 Pro capabilities include detailed text labelling and colour topographical maps in 3D (Figure 3.3). It is conceivable that a similar level of detail could be achieved using a 3D colour *food* printer; like the ProJet® 660 Pro, the Chef Jet printers use inkjet technology and can print in full colour, but use sugar instead of high performance composite as the printing substrate (Figure 3.3). Fine colour detail might be more difficult to achieve if extrusion deposition technology were to be used for printing, due to the moving food stream and the potential for diffusion between each volume element (voxel) of colour if the rheological properties of the colorant and (raw) food substrate are not properly matched.



Figure 3.3 Outputs from various printers which can print objects in full 3D colour. Left: Chef Jet printers using sugar as the printing substrate. Middle: Objet500 Connex3. Right: ProJet 660 Pro.

Specifications for the cooker extruder and for existing 3D food printers which are capable of in-line 3D food coloration do not include any descriptions of methods for producing individual colours, including the number and types of primaries to use and methods for computing the quantities of primaries needed for each blend. No indication is given also of the likely effects of food properties on target colour outputs. It is presumed that the Chef Jet 3D food printers might use a set of primaries, with the sugar substrate providing the white background needed for obtaining the most chromatic colours possible when the primaries are blended. Coloration methods are specified for 2D colour printing for food, and for non-food 3D printing in colour. Edible surface printing uses C, M, Y and K primary inks (All American Manufacturing and Supply Co., 2010); the ProJet® 660 Pro non-food printer uses five print heads (C, M, Y, K and Clear) from which up to 390,000 colours can be produced, while ten different colour palettes are available with the Objet500 Connex3, with each palette the result of combining sets of three colours from the group C, M, Y, K, Clear and White (Figure 3.4). White printing backgrounds are provided by the frosting sheets used in edible surface colour printing, by the high performance composite used in the ProJet® 660 Pro, and by various materials in the Objet500 Connex3. The availability of translucent and transparent substrates for the Objet500 Connex3 widens further the range of possible colours.

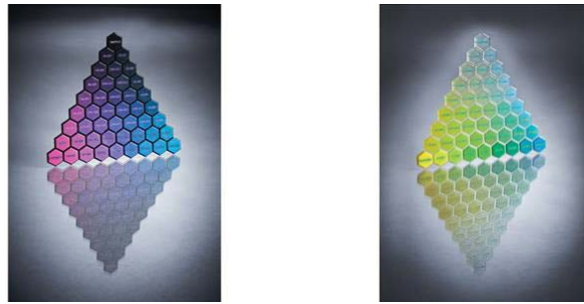


Figure 3.4 Two of the ten colour palettes used in the 3D colour printing of objects by the Objet500 Connex3 printer, which has multi-material capability. Shown are the palettes from combining Cyan, Magenta and Black for opaque materials (left) and from combining Cyan, Yellow and Clear, for transparent and translucent material (right).

3.6.1. Summary and conclusions

Aspects of existing coloration technologies, both 2D and 3D, and both food and non-food, have something to contribute to the development of 3D food printing in full, complex 3D colour. Conceptually, 3D food colour printing lies between the printing of colour images onto edible surfaces, and the bulk coloration of cake batters in baking recipes and their arrangement in controlled patterns before or after baking. In terms of available technologies, on the one hand it is possible to obtain the widest possible range of colours from a set of primaries, and in fine detail, using inkjet based methods and a white printing substrate, but, in reality, foods as (3D) printing substrates will not necessarily provide a white background.

The 3D printing of food substrates modelled on baked goods, which undergo expansion upon cooking, is at present better suited to a freeform style of fabrication rather than to inkjet technologies in which the binding of powders sets the structure immediately. This would appear to limit the preferred delivery method of colorants in 3D colour food printing to an in-line method such as the one described by Yang *et al.* (2001), rather than the potentially more precise jetting methods. A 3D colour food printing technology that could be considered in future is one based on the Objet500 Connex3 which is capable of combining several materials (including composites formed on-demand) in a single model, and in full colour; materials are jetted in layers and cured instantly by UV light. The technology could provide another all-in-

one 3D colour food printer, should suitably performing food formulations, and structure forming and setting methods be developed.

Whereas the purpose of adding colour in non-food 3D printing is to create realistic and life-like models and prototypes, that of 3D colour food printing, in this thesis, is to customise the visual appearance and visual appeal of 3D printed foods in a novel and unusual way, by the rendering of any chosen complex image or design in 3D within the food matrix. Coloration capability can be integrated into the 3D food printing process, and fits well with, and adds a further element of customisation to the printed food, beyond customising nutritional content and sensory characteristics. The impact of 3D colour should be greater from a printed food than from a 3D printed non-food prototype because the internal colours of a food will be seen as it is being consumed, while prototype structures might remain largely unbroken, meaning their colours will essentially be viewed in 2D. Although colour is normally strongly associated with flavour, the use and presence of novel and unusual colours in food (such as those from colour images) can be made acceptable by strategically ‘celebrating the very incongruity of a novel food colour’ (Garber Jr *et al.*, 2001). Given the unusual colours already used in baking recipes (i.e. cakes), such a strategy has already been successful; perhaps the only expectation of flavour from these colours is that of sweetness. ‘Celebrating’ the use of novel and detailed colour in 3D colour food printing could be considered a major feature and point of difference of the technology.

Table 3.4 Examples of methods available currently for the printing of two-dimensional images or designs for food, and for rendering colours in 3D printing of food and non-food materials

Type or manufacturer	Setting	Description	Ingredients and technology
2D food colour:			
Kopykake Enterprises (www.kopykake.com), and PhotoFrost (www.photofrost.com)	Domestic or commercial	Printing of edible colour images and designs for placement on to cake surfaces	Edible inks (CMYK) and thin, blank, white, frosting sheets and wrap-arounds that can be used with existing computer, scanner and printer, or with all-in-one units (scanner, printer, copier) without a computer; sheets absorb into cake frosting for seamless result
All American Manufacturing and Supply Company (http://neoflexprinter.com/edible-ink-printing)	Commercial	Printing of colour designs directly onto the surface of cookies, cakes, pies, confectionery, tablets and capsules, in a version of their Neoflex direct-to-garment textile printing and solvent printing technologies	Edible inks available in CMYK and in solvent and aqueous variations; inks said to have good finish as well as excellent water, scratch and smear resistance
3D food colour:			
Rock candy ('Brighton Rock' or 'Blackpool Rock')	Commercial	Hard, stick-shaped, coloured and flavoured confections usually between 1 and 2.5 cm in diameter, and 20 to 25 cm in length; wording (up to 24 letters (Bolcheriet, 2014)) or a design is embedded along the entire length inside a white central core, and therefore seen in every bite or slice; embedded designs and outer casing available in different colours;	Made from a boiled, then cooled, sugar-glucose mixture (toffee); central core and filler material prepared by aerating the toffee for characteristic texture and density (which turns white in the process) and by adding flavour; letters and/or designs are formed skillfully by the hand-layering of long strips of coloured (non-aerated) and white (filler) toffee; strips of coloured and filler toffee used to form a sheet for the outer casing; lettering and core wrapped together first, then wrapped in outer casing; finally the bulk mixture is rolled, pulled and then cut.
Baking recipes	Domestic or commercial	Cakes coloured internally, in controlled patterns	Controlled placement of batters of different colours prior to baking (e.g. checkerboard cakes and zebra cakes), or cutting and rearrangement of cakes of different colours after baking (e.g. Battenberg cake).
	Domestic	Tie-Dye (Surprise) Cakes: Rectangular-shaped cakes based on a pound cake recipe in which a multi-coloured shaped is embedded along the length of the cake, inside uncoloured cake crumb, therefore the same cross-section of the shape is revealed by each slice of the cake. One recipe also has the cake finished with a multi-coloured fondant icing (Handmade Charlotte and Denneker, 2013; Hungry Happenings and Klosterboer, 2014).	Effect achieved by following a time- and labour-intensive process in which two cakes need to be prepared. The batter for the first cake is divided and coloured five ways, before the colours are piped alternately and freehand into the baking tin. For the final (second) cake, the shape to be embedded is cut from slices of the baked, first cake, and packed closely together in slice formation along the length of tin, down the centre; the tin is then filled in with plain (un-

Type or manufacturer	Setting	Description	Ingredients and technology
Patented food cooker extruder, Weinstein et al, 1997	Commercial	Cooked cereal dough with complex shapes and coloured patterns; surface and internal coloration; extrudates can be cooked by microwave cooking causing expansion or puffing; finer levels of line colour detail can be achieved than with using other methods, ranging from 0.1mm after extrusion, to 0.5mm ⁺ after puffing/expansion	coloured) batter, and baked. Pattern forming die insert divides the dough as it passes through, creating interstitial gaps into which food colours, coloured dough, or fruit pastes can be injected, before progressing to the outlet at shallow convergence angle, reducing the cross-sectional area by 50x to 100x; different die inserts can be substituted to create different patterns (swirls, spirals, lines, planes).
Rapid prototyping and fabrication method for 3D food objects, (Yang <i>et al.</i> , 2001)	Domestic/commercial?	Prototype foods for evaluation before scale-up/mass production; unique, custom-designed food items of complex geometries e.g. birthday cakes	Layer-by-layer extrusion deposition; in-line coloration either by multiple colorant channels feeding into nozzle just prior to the point of extrusion, or by extruding different pre-coloured food compositions using multiple dispensing heads; number and types of colorants or primaries not given
Chef Jet Pro by 3D Systems	Professional/commercial	3D edible candies and decorative cake toppers in a vast array of complex geometries, and in full 3D colour if desired	Granular materials binding/inkjet printing using fine layers of sugar as substrate and water as binding material; number and types of colorants or primaries not given
3D non-food colour			
ProJet® 660 Pro 3D printer from 3D Systems (3D Systems, 2014)	Professional	Life-sized, realistic parts and prototypes in full, high resolution 3D colour with detailed text labelling as needed; 600 x 540 dpi resolution and layer thickness 0.089 to 0.102 mm	Layer-by-layer inkjet binding (with liquid binder) of powder material; model is able to produce 390,000 colours from 5 print heads (Cyan, Magenta, Yellow, Black and Clear); powder material is High Performance Composite

Type or manufacturer	Setting	Description	Ingredients and technology
Objet500 Connex3, Stratasys Ltd. (Stratasys Ltd., 2014)	Professional	Full 3D colour prototypes as for ZPrinter®650 3D printer, but also able to combine different materials, and different on-demand composites in a single model giving a much more life-like mix of properties such as rigidity, flexibility, durability, transparency and translucency; build resolution is 600 x 600 x 1600 dpi (corresponding to layer thickness of 16 microns); examples of prototype objects include helmets, glasses, shoes, headphones, shavers and bicycle seats	Jetting of layers of liquid photopolymer which are cured instantly by UV light; different materials can be combined in a single model by jetting simultaneously with selective positioning, or materials combined on demand to form jetted composites; materials include white and clear; materials or composites can be combined with colours from any one of 10 palettes covering opaque to translucent colours, with each palette of 45 colours based on combinations of three colours from the following group: C, M, Y, K clear and white; a single prototype or model can have up to 46 colours

3.7. Conclusions from this Review

From this survey of the literature it can be concluded that the concept of a 3D colour food printer which produces rapidly fully customisable food outputs, including the 3D rendering of complex colour images within the food matrix, is as yet unexplored. Advancing the concept however, can draw on the features it shares with a number of existing methods and technologies that have been covered in this review:

- customised foods i.e. POSIFoods™, or the tailoring of recipes (such as baking recipes) to achieve specific nutritional or sensory properties;
- 3D printing technologies to produce customised outputs using a variety of food, non-food and biological build materials;
- rapid cooking (baking) technologies;
- conventional (2D) colour printing on a variety of surfaces, including food;
- conventional food coloration, tailoring dye recipes to the substrate, also the manual creation of 3D colour patterns (in home baking);
- computer colour matching algorithms that draw on a database of colorant and substrate spectra, used in non-food industries;
- mechanisms to deliver colorants in-line during food extrusion;
- 3D printing or prototyping in full colour, including the use of *simple* food substrates i.e. sugar.

In bringing together these features in the form of a 3D colour food printer, the major challenge that will be faced will be in trying to achieve ***simultaneous*** rapid customisation of complex food formulations ***and*** of complex 3D colour outputs. This thesis is concerned largely with the latter. On the one hand customised, rapid, automated, accurate, and complex coloration in both 2D and

3D is possible using available printing and computer colour matching techniques, but involve a limited range of substrates. On the other, customisation of complex food outputs has not yet reached the same level of rapidity and neither has coloration of such outputs. Although dye recipes can be tailored to food substrates, this requires the intervention of an expert due to the much broader range of substrates that foods present.

3.7.1. Required experimental approach

Predictive colour matching capability for the 3D colour food printer should be based ideally on techniques such as computer colour matching and colour printing, for the speed and complexity of their outputs, but have the means of adapting to more complex and diverse *food* outputs.

3.7.1.1. Application of Kubelka-Munk (K-M) Theory

K-M Theory could form the basis for developing a predictive colour matching algorithm for the 3D colour food printer, as supported by the following:

- The blending of dyes to produce colours can be modelled using functions based on K-M Theory, and in turn the quantities of an unknown blend can be computed to match a given colour, as done routinely in a number of non-food industries; the food industry already makes use of the same relationships between colorant concentration and colour output, but more for the purposes of pigment identification and quantification, and for the modelling of food appearance, rather than for computing dye recipes;
- For both food and non-food applications, the contributions of the physical properties of the substrate, especially in terms of the degree of light scattering produced, to the measured or perceived colour of the substrate has been modelled using K-M or spectral principles; an understanding of these effects is needed in order to optimise the product by either adjusting the quantities of added colorant or the conditions bringing about the changes in physical properties.

Therefore, a K-M based model for the 3D colour food printer has the potential to not only compute dye quantities to match colours, but to take into account the physical properties of the substrate being coloured when computing these quantities. This is compatible with the provision of food outputs customised for both formulation and colour appearance.

3.7.1.2. Colour gamut mapping

The range of colours (including their strength) that can be achieved from the addition of colorants to foods depends on many factors. Broadly speaking these include the absorption characteristics of the colorants and their physical format (whether soluble or insoluble), the physical and chemical properties and processing conditions of the substrate (including temperature and heating time, and ingredients that bind dyes), and legal restrictions on the final concentrations of colorants in the foods. Therefore the range of colours that can be produced will be specific to a given combination of colorants and substrate, and also to the viewing conditions under which the coloured product is viewed.

Therefore, as well as to determine the impact of colorants and substrate on food coloration *per se*, the limit of the achievable colour range for a coloured food needs to be formally computed so that image colours can be transcribed by the 3D colour food printer to fit within the colour range of the food, using colour gamut mapping. This is because the range of colours in an image will far exceed that which can be produced by the combination of the 3D food printing device, the food substrate and colorants. Further, the printer will need to have the capability to compute rapidly colour gamuts for different blank food substrates containing dye blends in line with its capability to customise food outputs (i.e. their formulations). Again, this is where models based on K-M Theory should prove useful; such models can be used for the characterisation (profiling) of the 3D colour food printer, linking dye quantities with CIELAB values, as well as providing the basis for computing gamuts quickly.

3.7.1.3. Experimental samples and evaluation of coloration algorithms

Baked goods, especially cakes, are a class of food that satisfies many of the requirements for the 3D colour food printer substrate: these types of formulations are often targeted for modifications designed to achieve specific nutritional and/or sensory outcomes. They can also be rendered extrudable and are able to be cooked rapidly. Properties of the finished substrate affecting final colour rendition such as background colour, surface texture and volume can therefore be expected to vary according to changes in substrate formulation. To have the printer compute on-demand dye recipes for changing formulations, something that would normally be done manually, represents a formidable challenge, and demands a novel approach. This approach might involve investigating either the effects of each property on colour rendition in isolation from the rest, or the effects of several properties combined using representative ‘whole’ formulations. The job of the predictive coloration algorithm within the 3D colour food printer software would then be to combine this information according to the substrate and image specifications ‘keyed-in’ by the user. This algorithm would work in tandem with predictors of the substrate properties themselves; relevant predictive models developed by others for various applications should prove informative here.

Although the 3D colour printed foods are being designed to contain voxels of many colours, it will be far more practical in this thesis research to apply a single colour per experimental sample. In the wider printer research project, the mechanisms to deliver colorants for multiple voxels are yet to be settled. As an automated process, the 3D coloration of food by the printer will need to rely on computed colour differences rather than the visually assessed differences between the original image colours and the food-rendered equivalents. While models have not yet been established to evaluate the quality of colour (print) reproductions, the matching of single colours can be evaluated using colour difference formulae and associated tolerance indices, with consideration given to using formulae appropriate for the physical characteristics of the samples being compared.

To colour the printed foods, it should be safe to use synthetic colorants provided they:

- i. remain relatively stable to the formulation and processing conditions of the substrate;
- ii. are added to levels which ensure their final concentrations in the finished substrate do not exceed legal limits (and adhering to this limit for each voxel must ensure that the entire food remains compliant);
- iii. are permitted for use in the country in which the food will actually be printed; it is entirely possible that digital colour printing files could be sent from one country in which certain colorants are permitted, to a country in which they are not.

3.7.2. Consumer aspects

While the proposed 3D colour food printer can be seen as filling a technological gap, it needs also to be justifiable from a consumer point of view. The coloration of food by the printer is less about the role of colour as an indicator of food quality and more about dissociating this colour-quality link in order to customise food appearance in an unusual, creative and appealing way. The printing of colour images in 2D as cake toppers and the colouring of cake batters have paved the way for the acceptance of a technology that is able to print complex colour images in 3D *within* foods. Another appealing aspect of the technology is that it could allow food production to become a social activity through the sharing of digital files containing design ideas or ready-to-print designs for printing off-site, which taps into the surge in the use of social media in recent years.

3.8. Research aims and objectives of thesis

The aim of this thesis is to develop a predictive coloration model for use by the new 3D colour food printer, one which can transform RGB image data into dye recipe data, taking into account the variable effects of food properties. This research was separate to the other aspects of printer development.

In support of this aim, the non-food methods of colorimetric matching and colour gamut mapping were to be applied to the problem of matching a set of standard colours with model

food substrates containing blends from a set of three primary dyes. The objectives therefore, were:

- To develop model food substrates appropriate to 3D colour food printing, and to the application of the coloration methods being tested;
- To determine the absorption behaviour of each primary dye in each substrate, leading to the development and validation of models of dye blending for each substrate;
- To use colorimetric matching to compute dye recipes for each target colour;
- To use colour gamut mapping to find the best equivalent of each target colour and its corresponding dye recipe in each model substrate, including those which differ only in their level of a single food characteristics to measure the impact of this characteristic on the solutions possible;
- To make appropriate assessments of the closeness of matching between target colours and the solutions provided by colorimetric matching and by colour gamut mapping;
- To compare colorimetric matching and colour gamut mapping for the closeness of their solutions to the target colours, and in the dye quantities computed.

Chapter Four: Food coloration using computer colour matching

4.1. Introduction

Three-dimensional (3D) printing is an additive manufacturing technology whereby objects are built layer by layer, from a 3D image file held in a computer, using base materials as diverse as metal powders (Wikipedia, 2011), molten plastics (Wikipedia, 2014a), concrete (Day, 2011) and paper (Mcor Technologies Ltd., 2013). 3D printing offers an economical and convenient alternative to traditional forms of manufacturing: it does not require the use of a mould, and it is designed to produce objects on-demand. 3D printing is also a developing technology for food manufacture, providing an ideal means for personalising food production to meet customer specifications for selected product characteristics. Currently, 3D food printers exist as concepts (Seth, 2009; Coelho, 2010) or as prototypes (Moskvitch, 2011), or are available in the form of open-source hardware and software (fab@home Project, 2011) or retail units. Open-source and retail units are designed to print conventional food items - such as chocolate (Hao *et al.*, 2010), cookie dough (Lipton *et al.*, 2010) and cakes (Natural Machines, 2014) - or ingredients (e.g. sugar) into new shapes and forms (Inspix, 2014; The CandyFab Project, 2014), while concept printers allow for new ingredient combinations to be created, leading to more fully customised outputs. The technology being developed in the wider 3D food printing research project, of which this thesis forms one part, is a realisation of the latter type. The provision of outputs which meet individual customer specifications for such product characteristics as shape, texture, flavour, appearance and nutritional value, will be underpinned by a thorough understanding of how these characteristics develop as a function of formulation. Therefore it should be possible each time for the printer to not only select the appropriate ingredients, but to combine the ingredients and deposit the mixtures accurately in raw form, before the food is cooked rapidly to develop and set the structure.

A less explored aspect of personalised foods is the concept of being able to customise the visual appearance of any prepared food. The focus of this thesis is on customising the visual

appearance and visual appeal of 3D printed foods in a novel way: by the rendering of any chosen complex colour image or design in 3D *within* the food matrix. During the printing process, dye blends will be delivered in small volumes to predetermined positions within the colour-neutral raw food, so that a multitude of colour voxels (volume elements) are produced in the finished food to match the original design. Each blend, corresponding to a single voxel, will be produced from the same three or four primary dyes, but blends will differ in the relative proportions of these dyes.

The formation, coloration and cooking of 3D colour printed foods is being designed as a rapid, bench-scale, one-stop, on-demand process, for home or industrial use. The specifications for printing present a number of challenges to developing suitable colour matching capability. The printed foods have the potential to be hugely diverse in their physical and chemical attributes (varying according to the formulation selected), all of which will affect final colour rendition. This, together with the need for colour matching capability to be fast, and built-in, rules out methods currently used by the food industry, such as custom blending by expert formulators, which are applied on a case-by-case basis and are based usually on visual assessment. While conventional colour printing does use primaries (CMYK inks), it relies also on the size and positioning of fine ink dots on a two-dimensional, white printing surface to produce colours whereas the printed foods will require coloration in 3D, and not necessarily against a white background. Potentially more suitable is the Pantone Matching System (PMS) which is used for a range of materials including dyed textiles and pigmented plastics, as well as for colour printing. Pantone systems however, are based on a larger number of primaries (10 to 14) and take the form of extensive colour palettes with a proprietary ink recipe for each colour, which are used to communicate colour between designers and printers. In contrast, the 3D colour food printer will need to compute (unknown) dye quantities on demand from a smaller number of available primaries. And while non-food 3D colour printers are available which are capable of producing up to 390,000 colours with high resolution, using up to five print heads, printing again uses a white substrate (or alternatively, a clear substrate), in the form of a powder (3D

Systems, 2014). In addition, the processes of structure formation and coloration in these printers differ to those being proposed for the 3D colour food printer.

Predictive computer colour matching techniques used in the paint, textiles, plastics and ceramics industries might be more suitable for use by the 3D colour food printer. These techniques are based on linear, additive models in which the relative contributions of colorants and substrates to measured colour are expressed in terms of their light absorption-scatter spectra (McDonald, 1987; Berns, 2000). Drawing on a spectral database, either spectral or colorimetric matching algorithms are used to select quickly and accurately the colorants, and the quantities of each, that are needed to match target colours. Colorimetric matching, which is the conditional matching of tristimulus values under specified illuminant and observer conditions in spite of spectral differences, is more commonly used because in most situations the coloration systems of the target and match are not identical (McDonald, 1987). Although measurements of absorption and scatter have been used in the analysis of various aspects of food appearance, such as the relationship between visual translucency and storage time of tomatoes (Lana *et al.*, 2006), the determination of pigment composition (Hutchings, 1999) and the prediction of food emulsion colour (McClements *et al.*, 1998), predictive computer colour matching has not found wider application in the food industry. Compared to the other industries, the food industry does not normally need the same level of precision for matching colours; the much broader range of substrates presented by foods has made it difficult to justify development of a spectral database for food colorants and substrates (Francis, 1999).

The aim of the research which is the subject of this chapter was to develop a predictive color matching model based on colorimetric matching, which can compute the quantities of primary-coloured food dyes that need to be added to a model food, in order for the food to match a range of target colours. This work forms the first step in the development of colour matching capability for the 3D colour food printer. Because it serves as an in-principle demonstration of the application of computer colour matching to food, the research used only a single food as the model substrate: a microwave-baked cake. Microwave cooking suits the rapidity of 3D

printing, while baked goods are an ideal model on which to base 3D printed foods, providing potentially a range of desired characteristics in both raw and cooked states, which can be made to vary with changes in formulation.

The specific objectives of this research were:

- To derive the light absorption spectrum for the model substrate and the unit absorption spectra for each of three primary-coloured dyes when these are added separately to the substrate;
- To validate the unit absorption spectra by investigating the colour outputs when the dyes are blended within the substrate;
- To match a set of standard colours using the dye-substrate system and a modified colorimetric matching technique; and
- To evaluate the degree of matching using colour difference formulae.

4.2. Materials and General Methods

4.2.1. Dyes

Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) dye powders were obtained as complimentary samples (Hawkins Watts Limited, Auckland, New Zealand). These are permitted in processed foods in New Zealand to a maximum of 290 mg per kg (Australia New Zealand Food Authority., 2000) Liquid concentrates were prepared from powders using reverse osmosis water.

4.2.2. Microwave cake substrate

The recipe for the microwave-baked cake was adapted from Sakiyan *et al.* (2007). The recipe and its ingredients are described in Table 4.1. All ingredients, except for water, were purchased from a local supermarket.

Table 4.1 Details of formulation and ingredients for the microwave-baked cake used as the coloration substrate.

Ingredient	Brand and manufacturer	Description	Amount (g) per quantity of batter (yielding six individual cake samples)*
White wheat flour	'Champion' brand, Goodman Fielder New Zealand Limited	11% protein by weight, manufacturer's analysis	140
White cane sugar (granulated)	Chelsea®, New Zealand Sugar Company Limited		140
Margarine	Meadow Lea®, Goodman Fielder New Zealand Limited	65% vegetable oil, also containing beta-carotene colour	35
Skim milk powder	Anchor®, Fonterra Brands (New Zealand) Ltd	0.1 g fat, and 3.8 g protein, per 100 ml when reconstituted	16.8
Egg white (from fresh cage eggs)	Farmer Brown® eggs, Waikouaiti, New Zealand		12.6
Baking powder	Edmonds®, Goodman Fielder New Zealand Limited	Containing diphosphates, sodium carbonates, sodium aluminum phosphate and potassium biatrate	7
Iodised table salt	Cerebos®, Cerebos-Skellerup Limited, NZ	Containing salt, anti-caking agent, potassium iodate	4.2
Water			126
Total			481.6

*This amount is in excess of what was needed for six individual samples, to allow for additional samples in the event of any losses.

To prepare the batter, sugar and egg white were first mixed together for 30 seconds using a 320 Watt hand mixer (Sunbeam™ Beatermix Pro, model JM5900, Sunbeam Corporation Limited) set to speed 1 within the high-speed ('HI') range. Melted margarine was added and mixed for another 30 seconds. The remaining pre-mixed dry ingredients and water were then added and the batter mixed for 60 seconds at 'HI' speed 1, 60 seconds at 'HI' speed 2, and then 30 seconds at 'HI' speed 1. Three equal-sized portions (mean portion weight 120.2 grams, SD 0.1) were weighed from each quantity of prepared batter. Different dyes or dye blends (as described below) were added to each portion. Each portion yielded two replicate cake samples. For each sample, batter (50.2 grams, SD 0.1) was cooked in a lightly-greased 200 ml glass beaker, and two beakers cooked at a time in a 900 W microwave oven (model MW786, Kenwood Limited) at 50% power for 2 minutes, with a half turn of the beakers after the first and second 45 seconds. Cakes were left to cool to room temperature for two hours. Beakers were weighed before cooking and after cooling to determine weight loss (6.0%, SD 0.7). Mean measures are

‘indicative measures’ based on the samples used in development and validation of the dye blending model (Section 4.3 below). Weight data were recorded for 83 of the 102 batter portions prepared, and recorded for all samples before and after cooking ($n = 204$).

4.2.3. Colour targets

Targets for colour matching were 12 glazed ceramic tile colour standards (Series 2, CERAM, Staffordshire, UK), each measuring 10 cm x 10 cm. There were three neutral standards (Deep Grey, Mid Grey, Pale Grey), seven chromatic standards (Cyan, Deep Blue, Deep Pink, Green, Orange, Red, Yellow), and two colour difference standards (Difference Green, Difference Grey). The standards are normally used to check the performance of colour measuring instruments.

4.2.4. Colour measurement

The colours of the cake samples and tiles were measured using a Minolta CM-2600d reflectance spectrophotometer (Minolta Co., Ltd., Osaka, Japan) with d:8 integrating sphere geometry, using standard illuminant D65, the 10 degree standard observer, and an eight mm diameter measuring area. Measured data was captured using SpectraMagic NX software (Konica Minolta Sensing, Inc.). Measurements were made with either the specular component included, SCI (for the tiles), or the specular component excluded, SCE (for tiles and cakes). Reflectance, R_λ , was measured between 360 nm and 740 nm (at 10 nm intervals) relative to the white calibration plate supplied with the instrument, and CIELAB colour coordinates also measured, where L^*_{10} = position on the lightness axis, a^*_{10} = position on the green to red axis, and b^*_{10} = position on the blue to yellow axis. Measurements were made directly on the tile and cake surfaces.

Twelve measurements were made of each tile, on two separate days. The data were also used in a separate study of spectrophotometer performance (results not shown). The spectrum of mean reflectance values, and the mean L^*_{10} , a^*_{10} and b^*_{10} values for each tile were calculated from all measurements ($n = 24$). Cooked cakes were cut in half vertically, and three measurements each

made of the two cut surfaces. Mean reflectance, and mean L^*_{10} , a^*_{10} and b^*_{10} , for cake samples were calculated as described below in Sections 4.3.2 and 4.3.3.

4.2.5. Calculation of colour coordinates from measured reflectance

Mean reflectance spectra (R_λ) were converted to X_{10} , Y_{10} and Z_{10} tristimulus values following CIE standard procedure (ASTM International, 2008), using the visual response curves of the standard observer, $\bar{x}_{10\lambda}$, $\bar{y}_{10\lambda}$ and $\bar{z}_{10\lambda}$, and the energy distribution of the standard illuminant, S_λ :

$$X_{10} = k \int_{\lambda} S_{\lambda} R_{\lambda} \bar{x}_{10\lambda} d\lambda$$

$$Y_{10} = k \int_{\lambda} S_{\lambda} R_{\lambda} \bar{y}_{10\lambda} d\lambda$$

$$Z_{10} = k \int_{\lambda} S_{\lambda} R_{\lambda} \bar{z}_{10\lambda} d\lambda$$

$$k = \frac{100}{\int_{\lambda} S_{\lambda} \bar{y}_{10\lambda} d\lambda}$$

Equations 4.1

Where:

k is the normalisation constant which assigns the value $Y=100$ to the perfect reflecting diffuser (an ideal white reflecting 100% at all wavelengths), and

$d\lambda$ is the measurement wavelength interval (here 10 nm).

L^*_{10} , a^*_{10} and b^*_{10} values for the CIE 1976 $L^*a^*b^*$ (CIELAB) colour space were calculated from X_{10} , Y_{10} and Z_{10} using formulae also detailed in the standard (ASTM International, 2008):

$$L_{10}^* = 116 \left(\frac{Y_{10}}{Y_n} \right)^{1/3} - 16$$

$$a_{10}^* = 500 \left[\left(\frac{X_{10}}{X_n} \right)^{1/3} - \left(\frac{Y_{10}}{Y_n} \right)^{1/3} \right]$$

$$b_{10}^* = 200 \left[\left(\frac{Y_{10}}{Y_n} \right)^{1/3} - \left(\frac{Z_{10}}{Z_n} \right)^{1/3} \right]$$

Equations 4.2

Where:

X_n , Y_n and Z_n are the tristimulus values for the nominally white object colour stimulus i.e. the spectral radiant power of the illuminant reflected to the observer by the perfect reflecting diffuser;

$\left(\frac{X_{10}}{X_n} \right)$, $\left(\frac{Y_{10}}{Y_n} \right)$ and $\left(\frac{Z_{10}}{Z_n} \right)$ are > 0.01 (as usually associated with coloured materials, see Literature Review, Section 2.3.3); and

the illuminant, observer and (spectral) measurement interval (nm) for X_n , Y_n and Z_n are the same as those used for the colours to which X_n , Y_n and Z_n will be applied.

4.2.6. Calculation of colour differences

Colour differences were used to assess the degree of matching between computed and measured cake colours in the modeling of dye blending, and between tile targets and cake matches (computed or measured) in colorimetric matching. Colour differences were calculated using the following formulae, which are based on the 1976 CIELAB colour space.

ΔE^*_{ab} is an index of total colour difference, and is the Euclidean distance between two points (each defined by their individual $L^*a^*b^*$ coordinates) in the CIELAB colour space (Berns, 2000):

$$\Delta E^*_{ab,10} = \sqrt{(\Delta L^*_{10})^2 + (\Delta a^*_{10})^2 + (\Delta b^*_{10})^2}$$

Equation 4.3

In non-food applications, a ΔE^*_{ab} difference of three or more units is considered a visually unacceptable match (Francis and Clydesdale, 1975). This tolerance limit has been applied to differences between muffin samples (Baixauli *et al.*, 2008), and is a suggested limit for red wines (Martínez *et al.*, 2001). The same criterion was used in this study to determine whether or not a match would be visually acceptable. Values of ΔE^*_{ab} indicating a commercial match ($\Delta E^*_{ab} = 1$), or perceptibly different samples ($\Delta E^*_{ab} = 2$) (Francis and Clydesdale, 1975) were not used in this study, due to the likely influence of physical differences between tile and cake on perceived differences.

$\Delta E^*_{ab,10}$ was also divided into lightness, chroma and hue differences, ΔL^*_{10} , $\Delta C^*_{ab,10}$ and $\Delta H^*_{ab,10}$ respectively (Berns, 2000). Chroma is equivalent to the perceived purity of colour, and hue the equivalent to a colour description:

$$\Delta L^*_{10} = L^*_{10(1)} - L^*_{10(2)}$$

Equation 4.4

$$\Delta C^*_{ab,10} = \left(\sqrt{a^*_{10(1)}^2 + b^*_{10(1)}^2} \right) - \left(\sqrt{a^*_{10(2)}^2 + b^*_{10(2)}^2} \right)$$

Equation 4.5

$$\Delta H^*_{ab,10} = \sqrt{(\Delta E^*_{ab,10})^2 - (\Delta L^*_{10})^2 - (\Delta C^*_{ab,10})^2}$$

Equation 4.6

CIEDE2000 or ΔE_{00} ([CIE] International Commission on Illumination, 2001) is the latest in a series of improvements to ΔE^*_{ab} , designed to give better predictions of visually-perceived colour differences. It applies to data obtained under a set of reference experimental conditions (including uniform, non-patterned sample colours, with ΔE^*_{ab} differences below five units):

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right) \left(\frac{\Delta H'}{k_H S_H}\right)}$$

Equation 4.7

The dependence of lightness, chroma and hue differences on lightness, chroma and hue position (arising from the lack of visual uniformity in the CIELAB space) are accounted for by positional functions S_L , S_C and S_H . k_L , k_C and k_H are parametric factors denoting experimental conditions; under reference conditions $k_L = k_C = k_H = 1$. The R_T term is used to improve performance in the blue region. Equations for each term, and worked examples of ΔE_{00} , are given by the [CIE] International Commission on Illumination (2001), and by (Luo *et al.*, 2001a).

4.3. Development and validation of the dye blending model

4.3.1. Background

Colour blending models should be based on a linear relationship between colorant input and colour output, specifically spectral output; that is, one where the relationship between input and output is scalable, and where the spectral output for mixtures is the sum of the spectra from the individual components. For subtractive blending, spectral data need to be transformed to achieve linearity. For materials that both absorb and scatter light, *reflectance* measurements are transformed using functions based on Kubelka-Munk (K-M) Theory. For opaque materials, the function is:

$$\left(\frac{K}{S}\right)_\lambda = \frac{(1 - R_{\lambda,i})^2}{2R_{\lambda,i}}$$

Equation 4.8

Where:

$\left(\frac{K}{S}\right)_\lambda$ is the ratio of absorption to scatter at wavelength λ ;

$R_{\lambda,i}$ is the ‘internal’ or corrected reflectance: K-M Theory assumes that light travels only up or down, within a translucent absorbing and scattering layer, perpendicular to its plane, and that there is no change in refractive index at the boundaries which would otherwise change the direction of travel. K-M Theory therefore does not account for front surface reflections, nor does it account for light reflected back into the sample from inside surfaces. $R_{\lambda,i}$ is measured reflectance corrected for these losses, and is calculated using the Saunderson correction (Hutchings, 1999):

$$R_{\lambda,i} = \frac{R_{\lambda,m} - k_e}{(1 - k_e)(1 - k_i) + k_i R_{\lambda,m} - k_e k_i}$$

Equation 4.9

Where:

$R_{\lambda,m}$ is reflectance measured with the specular component included (SCI), capturing all surface reflections, or without the specular component (SCE), $0 < R_{\lambda,m} < 1$;

k_e is the fraction of incident light reflected externally, usually ~ 0.04 for most coatings and plastics (Berns, 2000), which is the maximum value (Hutchings, 1999); k_e is removed from the numerator for specular excluded (SCE) reflectance measurements (Berns, 2000);

k_i is the fraction lost internally through repeated cycles of reflection from the inside surfaces, usually between 0.4 and 0.6.

For opaque and coloured materials, there are two forms of the colour blending model based on the K-M function, according to whether dyes or pigments are used. Pigments, which are used to colour paints and plastics, are particulate colorants which selectively scatter as well as absorb light. Separate absorption and scatter coefficients are therefore needed for each colorant, giving rise to the two-constant form of the equation (Berns, 2000). Dyes, which are used to colour

textiles and paper, become dissolved in the substrate and therefore contribute negligible scatter relative to the substrate. Only a single constant, the (unit) ratio of absorption to scatter, is needed for each dye, which can be referred to simply as the absorption coefficient. The single-constant form of the K-M colour blending equation is used here in this chapter, and throughout this thesis. The equation is as follows (Berns, 2000):

$$\left(\frac{K}{S}\right)_{\lambda,blend} = \left(\frac{K}{S}\right)_{\lambda,substrate} + c_1 \left(\frac{k}{s}\right)_{\lambda,1} + c_2 \left(\frac{k}{s}\right)_{\lambda,2} + c_3 \left(\frac{k}{s}\right)_{\lambda,3} + \dots$$

Equation 4.10

Where:

$\left(\frac{K}{S}\right)_{\lambda}$ is the ratio of absorption to scatter at wavelength λ ;

c is dye concentration;

subscripts 1, 2, and 3 denote the different dyes;

$\left(\frac{k}{s}\right)_{\lambda}$ is the absorption coefficient for unit concentration of dye, at wavelength λ ; these are derived for each dye when added separately to the substrate in a concentration series, and validated using dye blends to confirm additivity, as described in the next sections.

4.3.2. Derivation of unit absorption coefficients for dyes in the cake substrate

4.3.2.1. Method

Brilliant Blue, Ponceau 4R (red), and Tartrazine (yellow) dyes were added separately to raw cake batter at 0, and at 1.7, 3.5, 6.9, 13.8 and 27.4 mg/100 g batter (denoted levels ‘1’, ‘2’, ‘3’, ‘4’ and ‘5’ respectively) (Figure 4.1), representing a doubling concentration series. Six samples were independently prepared for each dye-level combination. All samples were designed so

that final dye levels in the cake fell within the legal limit (290 mg/kg), allowing for weight loss (see 4.2.2) after cooking. However, at the highest level of dye addition, the final level in the cake will have exceeded this limit slightly.



Figure 4.1 Samples of a microwave-baked cake containing Ponceau 4R (red), 'P', Tartrazine (yellow), 'T', or Brilliant Blue, 'B', food dyes. Each dye was added to raw cake batter at 1.7, 3.5, 6.9, 13.8 and 27.4 mg/100 g batter (denoted by labels 1, 2, 3, 4 and 5 respectively). Samples 'P0', 'T0' and 'B0' were prepared from the same standard microwave cake recipe but do not contain added dye.

Individual reflectance measurements (SCE only) from all cakes were pooled to calculate a spectrum of mean reflectance values for each dye-level combination ($n = 36$). Mean reflectance spectra (SCE) for each dye-level combination were converted to spectra of $\left(\frac{K}{S}\right)_\lambda$ values, using an adapted form of the K-M function, Equation 4.8:

$$\left(\frac{K}{S}\right)_\lambda = \frac{(1 - R_{\lambda,m(SCE)})^2}{2R_{\lambda,m(SCE)}}$$

Equation 4.11

For cakes, the reflectance measured with the specular component excluded (SCE), was used in place of internal reflectance to approximate $\left(\frac{K}{S}\right)_\lambda$ spectra, given the observed lack of reflection from the cut surfaces of the cakes, and also of an appropriate k_i term.

By way of example, Figure 4.2 shows the mean reflectance spectra, and corresponding $\left(\frac{K}{S}\right)_\lambda$ spectra, for Brilliant Blue.

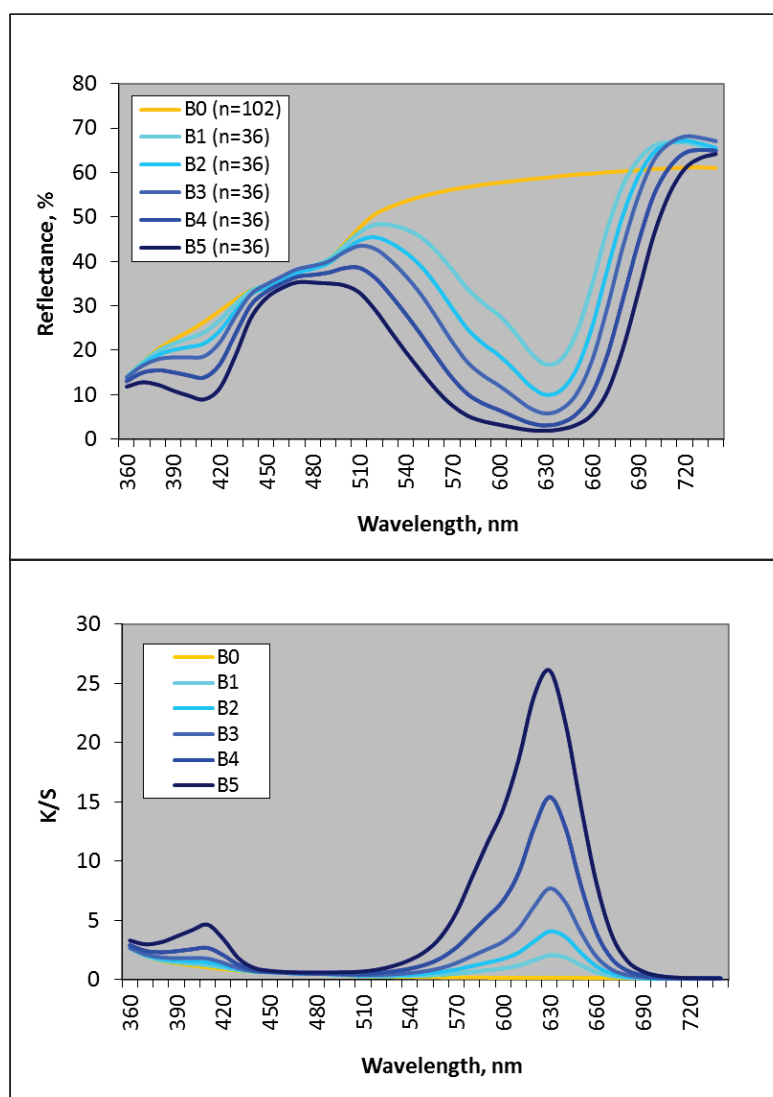


Figure 4.2 Spectra of percentage light reflectance (top), and corresponding light absorption spectra (bottom), for samples of a microwave-baked cake containing Brilliant Blue ('B') food dye which was added to raw cake batter at 1.7, 3.5, 6.9, 13.8 and 27.4 mg/100 g batter (denoted by labels 1, 2, 3, 4 and 5 respectively). The cake sample which does not contain added dye is labelled 'B0'.

The results for each dye were inspected at selected wavelengths for a linear relationship between $\left(\frac{K}{S}\right)_\lambda$ and dye concentration. A linear relationship was not immediately apparent from plots such as the one in Figure 4.2 due to the use of a doubling concentration series; it was displayed more clearly when the $\left(\frac{K}{S}\right)_\lambda$ values for the five dyed samples and the un-dyed cake at a given wavelength were plotted against dye concentration. This is shown for Brilliant Blue in Figure 4.3.

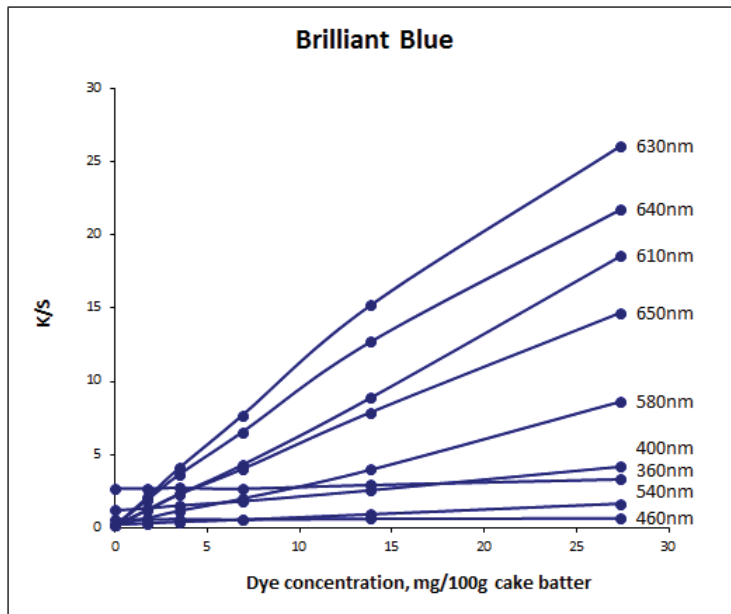


Figure 4.3 Absorption against dye concentration for the Brilliant Blue dye in the microwave-baked cake, at selected wavelengths including the wavelength of maximum absorbance, $\lambda_{\max}$, for the dye (630 nm).

Unit absorption coefficients, $\left(\frac{k}{s}\right)_\lambda$, denoting the increase in absorption, $\left(\frac{K}{S}\right)_\lambda$, for every milligram of dye in 100 grams of cake batter, were determined as the slopes of the lines at each measurement wavelength by a rearrangement of a shortened form of Equation 4.10 (McDonald, 1987):

$$\left(\frac{K}{S}\right)_{\lambda, \text{sample}} = \left(\frac{K}{S}\right)_{\lambda, \text{substrate}} + c_1 \left(\frac{k}{s}\right)_{\lambda, 1}$$

Equation 4.12

At wavelengths where $\left(\frac{k}{s}\right)_\lambda$ was more than 50% of the value at $\lambda_{\max}$ for each dye, the value of the squared Pearson correlation coefficient, R^2 , for the fitted model was either 0.99 or 1.00, confirming the relationship between $\left(\frac{K}{s}\right)_\lambda$ and dye concentration as being linear. At other wavelengths (e.g. at 460 nm in Figure 4.3) the $\left(\frac{K}{s}\right)_\lambda$ of the sample appears not to change with increase in dye concentration; this indicates that $\left(\frac{K}{s}\right)_\lambda$ – the value at the intercept – is due entirely or almost entirely to the un-dyed substrate.

In reality, values of $\left(\frac{k}{s}\right)_\lambda$ might approximate the relationship between $\left(\frac{K}{s}\right)_\lambda$ and dye concentration at wavelengths where the relationship appears to deviate from linearity. This deviation is seen at around $\lambda_{\max}$ (630 nm and 640 nm) for Brilliant Blue (Figure 4.3) and is likely due to slight shifts in $\lambda_{\max}$ that can occur with changes in dye concentration.

4.3.2.2. Results

The unit absorption, $\left(\frac{k}{s}\right)_\lambda$, spectra for Brilliant Blue, Ponceau 4R and Tartrazine, and the absorption, $\left(\frac{K}{s}\right)_\lambda$, spectrum of the cake substrate, are shown in Figure 4.4. Although these spectra were derived using means for pooled cake reflectance data (Section 4.3.2.1), measures of uncertainty were not available for the absorption spectra themselves because absorption spectral data were not mean data (Equation 4.11).

Further analysis provided the standard errors that are displayed superimposed on the dye spectra in Figure 4.4. Pooled cake reflectance data for each dye-level combination ($n = 36$) were regrouped as three replicates (each $n = 12$, corresponding to the measurements from each pair of samples prepared from a quantity of batter, see Section 4.2.2), and unit absorption spectra for the three dyes derived for each replicate. Standards errors were for the mean of the three replicate spectra for each dye.

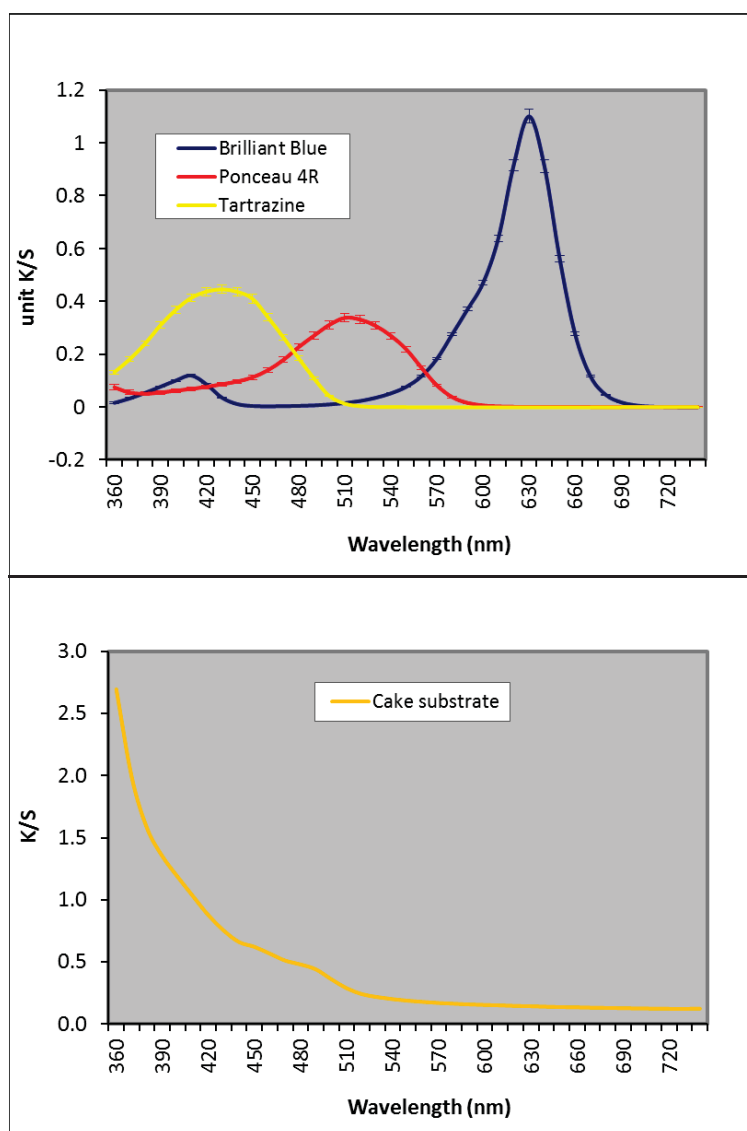


Figure 4.4 The unit absorption spectra for Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) dyes in the microwave-baked cake (top) and the absorption spectrum for the cake without added dye (bottom). Standards errors displayed for the unit absorption spectra are for mean spectra based on a regrouping of the original reflectance data (see main text).

4.3.3. Validation of unit absorption coefficients by investigation of dye blends

4.3.3.1. Methods

To validate the spectra of unit absorption coefficients for the dyes, spectra were used to compute (predict) the colours of cakes containing selected dye blends, and predictions then compared with the measured colours of cakes prepared using the same dye blends. Two-dye blends

contained dyes (X and Y) in the following combinations: X1Y1, X1Y4, X2Y3, X4Y1 and X4Y4. Selected three-dye blends contained dyes in 1:1:1 and 1:1:4 combinations. Again, blends were designed so that the dye levels in the cakes were within the legal limit, post cooking.

To compute colours, the dye concentrations for the blends, together with the unit absorption spectrum of each dye, and the $\left(\frac{K}{S}\right)_\lambda$ spectrum of the cake substrate, were substituted into Equation 4.10 to give the computed $\left(\frac{K}{S}\right)_\lambda$ spectrum for the blend. This was converted to computed reflectance, by the inverse of Equation 4.11, and then to computed X_{10} , Y_{10} and Z_{10} and $L^*_{10}a^*_{10}b^*_{10}$ values for the blend (Equations 4.1 and Equations 4.2).

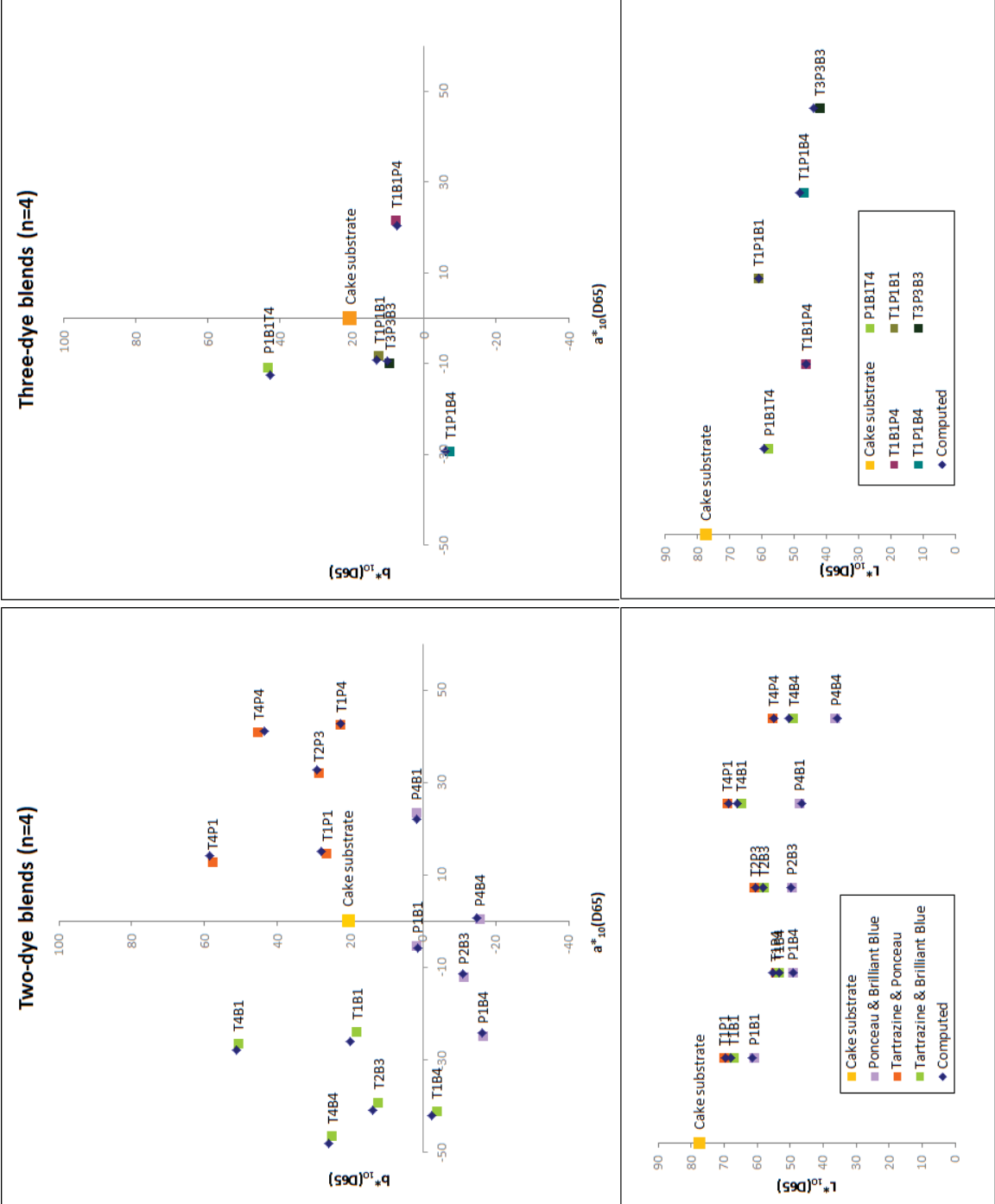
Four cakes were prepared for each two-dye and three-dye blend described above. L^*_{10} , a^*_{10} and b^*_{10} were measured with the specular component excluded. Mean measured L^*_{10} , a^*_{10} and b^*_{10} was calculated for each blend, using individual replicate cakes (n = 4).

Computed $L^*_{10}a^*_{10}b^*_{10}$ values were compared with the mean measured $L^*_{10}a^*_{10}b^*_{10}$ (SCE) of the samples by the colour difference indices $\Delta E^*_{ab,10}$ and ΔE_{00} , to test the strength of the predictions, and therefore the validity of both the dye unit absorption spectra and the blending model.

4.3.3.2. Results

Figure 4.5 shows the positions of the $L^*_{10}a^*_{10}b^*_{10}$ cake colours computed using the K-M blending model (Equation 4.10) as the first step, and the corresponding mean measured cake colours in $L^*a^*b^*$ space. All individual computed and measured $L^*_{10}a^*_{10}b^*_{10}$ values are given in Appendix Table 4.5. Also shown in Figure 4.5 is the position of the un-dyed cake substrate. Visually, the cake without added dye was pale yellow in colour (Figure 4.1), with mean measured L^*_{10} , a^*_{10} and b^*_{10} values of 77.4 (SD 3.3), 0.1 (SD 0.3) and 20.7 (SD 1.6) units respectively (n=17).

Figure 4.5 Positions in the three-dimensional $L^*a^*b^*$ colour space of cake colours computed using the Kubelka-Munk blending model from selected dye blends, and the measured colours of cakes prepared using the same dye blends. Values are L^*_{10} , a^*_{10} , b^*_{10} .



The $\Delta E^*_{ab,10}$ and ΔE_{00} differences between computed and measured cake colours are shown in Table 4.2. Total differences between computed and measured $L^*_{10}a^*_{10}b^*_{10}$ colours ranged from 0.6 to 2.9 for $\Delta E^*_{ab,10}$, and from 0.4 to 1.9 for ΔE_{00} . All except one of the $\Delta E^*_{ab,10}$ differences were less than three units, indicating a visually acceptable match. These results indicate that the spectrum of unit absorption coefficients derived for each of the dyes separately can be used to predict the colours of blends of any two or three of the dyes, in the combinations tested. The size of the difference, and therefore the strength of the prediction, appears to depend on the dye blend. For two-dye blends, Tartrazine and Brilliant Blue blends resulted in the largest $\Delta E^*_{ab,10}$ and ΔE_{00} differences, including a $\Delta E^*_{ab,10}$ of three units for one of the blends. Differences between computed and measured colours could be due to dye-dye interactions that cannot be predicted from the dyes individually (Butts, 2010), or to the use of linear unit absorption coefficients for dyes having non-linear relationships between $\left(\frac{K}{S}\right)_\lambda$ and dye concentration at some wavelengths.

Separation of $\Delta E^*_{ab,10}$ differences into differences between computed and measured L^*_{10} , a^*_{10} or b^*_{10} reveal that for all but two of the blends, at least one of the constituent differences is *statistically significant*, despite $\Delta E^*_{ab,10}$ being *visually significant* for only one of the blends (Appendix Table 4.5). This suggests that the differences themselves were not large enough in magnitude to increase the $\Delta E^*_{ab,10}$ difference towards visual significance. Differences between computed and measured L^*_{10} , a^*_{10} or b^*_{10} that are statistically significant could still prove useful in refining the dye blending model. For the Tartrazine and Brilliant Blue blends, computed values were found to consistently, and significantly (except in one case), underestimate measured a^*_{10} and to overestimate measured b^*_{10} (Figure 4.5 and Appendix Table 4.5). When the trends appear consistent for given blends, and cause a discrepancy between computed and measured colours, deviations can be quantified and corrections built into colour matching software (Butts, 2010).

Table 4.2 $\Delta E^*_{ab,10}$ and ΔE_{00} differences between cake colours computed using the Kubelka-Munk blending model from selected dye blends, and the measured colours of cakes prepared using the same dye blends. Dye blends are described in the main text.

Two dye blends (n=4)						Three dye blends (n=4)					
Ponceau 4R, red (P) and Brilliant Blue (B)			Tartrazine, yellow (T) and Ponceau 4R			Tartrazine and Brilliant Blue					
$\Delta E^*_{ab,10}$	ΔE_{00}		$\Delta E^*_{ab,10}$	ΔE_{00}		$\Delta E^*_{ab,10}$	ΔE_{00}		$\Delta E^*_{ab,10}$	ΔE_{00}	
P1B1	0.6	0.6	T1P1	1.7	0.8	T1B1	2.9	1.3	P1B1T4	2.4	1.9
P1B4	0.9	0.4	T1P4	0.8	0.7	T1B4	1.7	1.0	T1B1P4	1.1	0.6
P2B3	1.0	0.8	T2P3	1.0	0.5	T2B3	2.4	1.0	T1P1B1	1.2	0.8
P4B1	1.4	1.0	T4P1	1.7	0.9	T4B1	1.9	1.2	T1P1B4	1.6	1.3
P4B4	1.1	0.9	T4P4	1.6	0.8	T4B4	2.4	1.5	T3P3B3	2.0	1.8

4.4. Matching cake colours to tile colours using the colorimetric method

4.4.1. Background

The method used to match tile colours with cakes containing dye blends, was colorimetric, rather than spectral, matching. Colorimetric matching is used when the target and matching systems, and therefore their spectral properties, are different to one another (see Literature Review, Section 2.4.4.2). Target and match can still be made to match conditionally in their tristimulus values under a single set of viewing and illumination conditions.

The tristimulus values being matched are the pseudo- X , Y and Z tri-stimulus values X^P , Y^P and Z^P of the target, rather than X , Y and Z proper (Equations 4.1). X^P , Y^P and Z^P differ from X , Y and Z in that they have the reflectance term replaced by $\left(\frac{K}{S}\right)_\lambda$ or $\left(\frac{k}{s}\right)_\lambda$ spectra. A partial derivative weighting function, d_λ , is included in the calculation of X^P , Y^P and Z^P to improve matching (Allen, 1966):

$$X_{10}^P = k \int_{\lambda} S_{\lambda} d_{\lambda} \left(\frac{k}{s}\right)_{\lambda} \bar{x}_{10\lambda} d\lambda$$

$$Y_{10}^P = k \int_{\lambda} S_{\lambda} d_{\lambda} \left(\frac{k}{s}\right)_{\lambda} \bar{y}_{10\lambda} d\lambda$$

$$Z_{10}^P = k \int_{\lambda} S_{\lambda} d_{\lambda} \left(\frac{k}{s}\right)_{\lambda} \bar{z}_{10\lambda} d\lambda$$

$$k = \frac{100}{\int_{\lambda} S_{\lambda} \bar{y}_{10\lambda} d\lambda}$$

Equations 4.13

In colorimetric matching Equations 4.14 are solved for the unknown dye concentrations:

$$X_{10}^P{}_{target} - X_{10}^P{}_{substrate} = c_1 X_{10}^P{}_{dye1} + c_2 X_{10}^P{}_{dye2} + c_3 X_{10}^P{}_{dye3}$$

$$Y_{10}^P{}_{target} - Y_{10}^P{}_{substrate} = c_1 Y_{10}^P{}_{dye1} + c_2 Y_{10}^P{}_{dye2} + c_3 Y_{10}^P{}_{dye3}$$

$$Z_{10}^P{}_{target} - Z_{10}^P{}_{substrate} = c_1 Z_{10}^P{}_{dye1} + c_2 Z_{10}^P{}_{dye2} + c_3 Z_{10}^P{}_{dye3}$$

Equations 4.14

More typically, colorimetric matching is an iterative process in which larger differences between the target and prediction are gradually minimised (McDonald, 1987). According to the Allen algorithm (Allen, 1966), the inclusion of the weighting function, d_{λ} , generates a more effective starting recipe, which can reduce the number of iterations required. At each iteration step a correction matrix is applied until the colour difference between target and match falls within a predetermined limit. This will be explained in more detail in Chapter Six, Section 6.8.1.

4.4.2. Methods

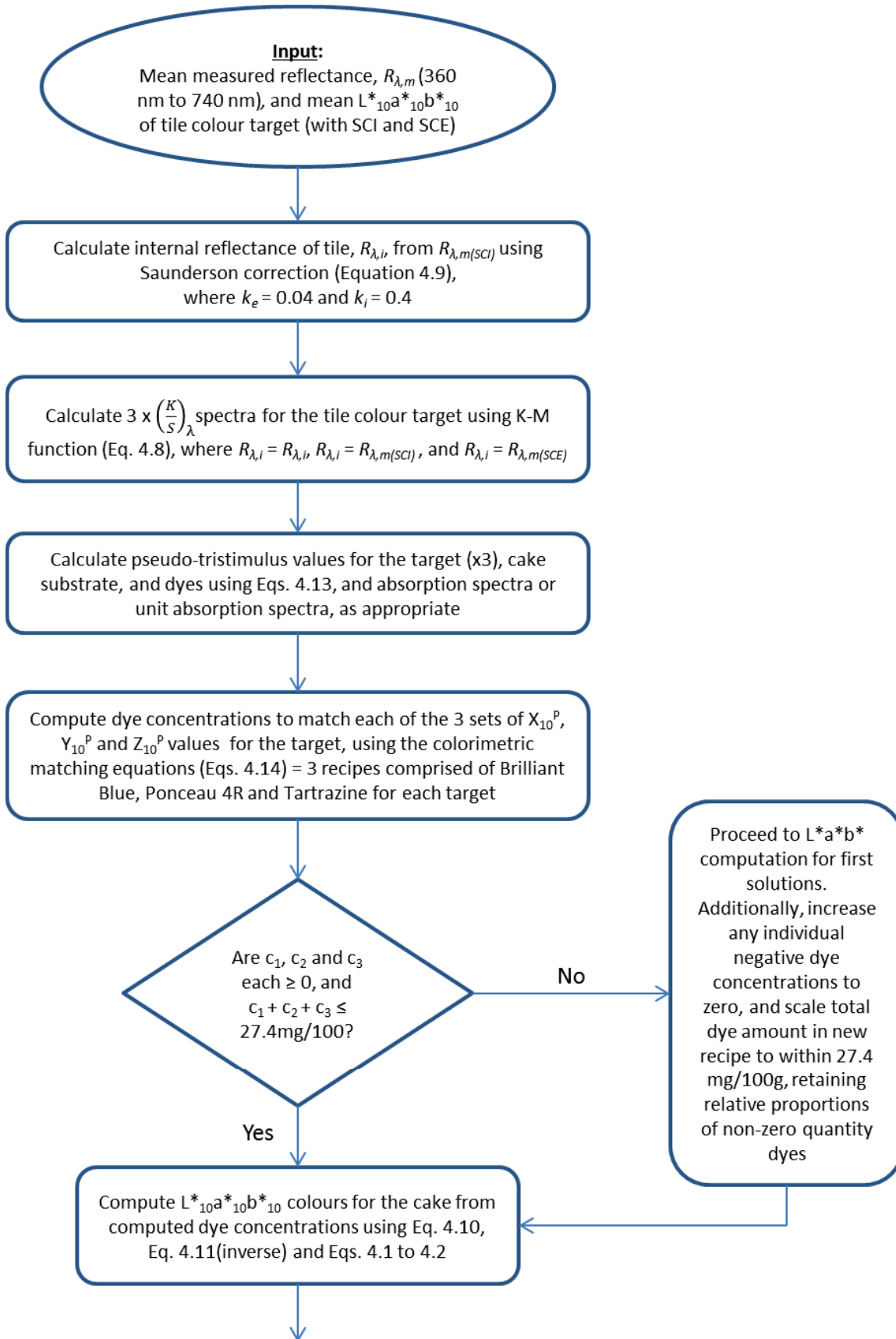
In this study only the Allen algorithm was used to generate recipes for each target, without any subsequent iterations. Because the range of achievable cake colours was unlikely to match the range of the tile colours, it was expected that negative dye concentrations would be computed; negative concentrations can stop the iteration process (McDonald, 1987). Accepting the starting recipe as the solution was also designed to reduce computational load. Furthermore, three sets of X^p , Y^p and Z^p values were computed for each tile colour target, based on $\left(\frac{K}{S}\right)_{\lambda}$ derived from

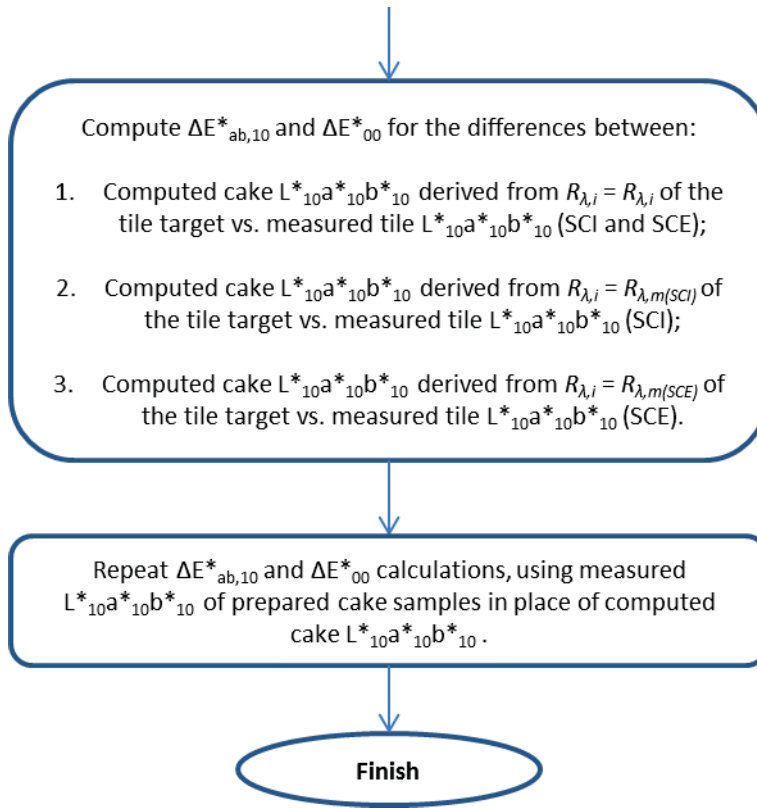
$R_{\lambda,i}$ (Equation 4.8 and Equation 4.9; Figure 4.6), and directly from $R_{\lambda}(\text{SCI})$ and from $R_{\lambda}(\text{SCE})$ without using the Saunderson correction. The latter approaches were used given the obvious physical differences between the tiles and cakes, which were unlikely to have similar contributions of surface reflectance and internal losses to their measured reflectance. This meant that three separate recipes were computed for each tile colour target. Any necessary adjustment of recipe concentrations to within usable range meant up to six possible L*a*b* match predictions were generated for each target colour.

4.4.2.1. Steps used to match each target colour

Figure 4.6 shows a flow diagram of the steps used to compute cake matches for the tile colours.

Figure 4.6 Flow chart outlining the steps used to compute dye concentrations for cake colours to match tile colours, based on the colorimetric approach.





4.4.2.2. Sample photography

Photographs were taken of the tile colour standards (matching targets) and the microwave-baked cake samples prepared to match the tiles. Cake samples were those prepared using dye concentrations computed on the basis of measured reflectance of the tiles. Photographs were taken indoors in non-standardised, combined fluorescent/daylight conditions with an Olympus EP-1 camera. A neutral gray card with 18% reflectance (Jessops, Leicester, England) was used to set the white balance. Images (4032 x 3024 pixels) were taken with the following settings: ASA 100, lens aperture f8, shutter speed 1/6 sec, without flash, and saved in the memory card as RAW files. Images were downloaded using a USB digital reader and compensation applied in the purple-green region using Adobe Photoshop Lightroom 3, to correct for a slight colour cast affecting the white balance. Files were saved in JPEG format.

4.4.3. Results and Discussion

4.4.3.1. First match predictions based on computed concentrations

Table 4.3 shows the computed $\Delta E_{ab,10}^*$ and ΔE_{00} differences between tile colours and the cake colours computed to match the tiles. These cake colours were the first solutions computed from colorimetric matching before any adjustments were made for negative or out-of-range dye concentrations. Cake $L_{10}^*a_{10}^*b_{10}^*$ computed using X_{10}^P , Y_{10}^P and Z_{10}^P values of the tile target derived from measured reflectance - $R_{\lambda,m}(SCI)$ and $R_{\lambda,m}(SCE)$ – in place of internal reflectance, $R_{\lambda,i}$, gave closer matches to tiles than computed $L_{10}^*a_{10}^*b_{10}^*$ derived from $R_{\lambda,i}$ *per se*, for 11 of the 12 tiles ($R_{\lambda}(SCE)$) and for all 12 tiles ($R_{\lambda}(SCI)$). Eight of the 12 matches ($R_{\lambda}(SCE)$) and seven of the 12 matches ($R_{\lambda}(SCI)$) had $\Delta E_{ab,10}^*$ of less than three units, indicating the colour matching algorithm gave good first solutions. For nine of the 12 tiles, the match for $R_{\lambda}(SCI)$ was better than for $R_{\lambda}(SCE)$.

All computed concentrations had been used to compute *SCE* cake colours: concentrations were substituted into the colour blending equation (Equation 4.10) and the resulting $\left(\frac{K}{S}\right)_{\lambda,blend}$ substituted into the inverse of Equation 4.11 to give $R_{\lambda,m}(SCE)$. As explained in the methods, Equation 4.11 for the cake defined a relationship between $\left(\frac{K}{S}\right)_{\lambda}$ and measured (SCE) reflectance, rather than between $\left(\frac{K}{S}\right)_{\lambda}$ and corrected reflectance (Equation 4.8) as normally. Had the matching system been a tile rather than a cake, concentrations computed based on *target* tile corrected reflectance would have sufficed, and computed $\left(\frac{K}{S}\right)_{\lambda}$ for the *matching* tile would have been converted to internal (corrected) reflectance before conversion to computed measured reflectance (using the inverse of Equation 4.9). It was thought not appropriate to use Equation 4.8 when computing cake reflectance using dye concentrations based on the corrected reflectance of the tiles, as the cakes were regarded as not having any significant specular reflectance to ‘add back’. This approach however, resulted in the poorest computed matches; in

hindsight both the specular and internal reflectance of the tiles may have been needed when computing the cake colours.

The alternative approach of replacing the internal reflectance of the tiles with their measured reflectance (SCI or SCE) in the K-M equation was an attempt to ‘capture’ the overall visual colour appearance of the tiles (and the associated dye concentrations) in the cakes, and indeed resulted in closer computed matches between the two. Because these findings support the use of $R_{\lambda}(\text{SCI})$ and $R_{\lambda}(\text{SCE})$ of the (tile) target, in place of $R_{\lambda,i}$, in the matching of cake colours to tile colours, subsequent discussion is based on target $R_{\lambda}(\text{SCI})$ and $R_{\lambda}(\text{SCE})$ only.

Table 4.3 $\Delta E_{ab,10}^*$ and ΔE_{00} differences between measured $L^*_{10}a^*_{10}b^*_{10}$ tile colours (SCI and SCE) and the cake colours (SCE) computed to match the tiles, before any adjustments were made for negative or out-of-range dye concentrations. Matching was targeted at either the corrected (internal) reflectance, $R_{\lambda,i}$ or measured reflectance - $R_{\lambda,m}(\text{SCI})$ and $R_{\lambda,m}(\text{SCE})$ – of the tiles.

Form of tile target reflectance used to compute first solutions for cake $L^*_{10}a^*_{10}b^*_{10}$ (SCE) matches:		$R_{\lambda,i} = R_{\lambda,i}$		$R_{\lambda,i} = R_{\lambda,m}(\text{SCI})$	$R_{\lambda,i} = R_{\lambda,m}(\text{SCE})$
Form of measured tile $L^*_{10}a^*_{10}b^*_{10}$ against which computed cake $L^*_{10}a^*_{10}b^*_{10}$ (SCE) compared:		SCI	SCE	SCI	SCE
Cyan	$\Delta E_{ab,10}^*$	7.4	11.0	2.1	2.5
	ΔE_{00}	5.8	10.0	1.5	1.7
Deep Blue	$\Delta E_{ab,10}^*$	35.7	16.7	3.3	26.5
	ΔE_{00}	13.5	7.6	2.8	7.8
Deep Grey	$\Delta E_{ab,10}^*$	3.9	10.5	3.3	3.7
	ΔE_{00}	4.3	8.7	3.9	4.4
Deep Pink	$\Delta E_{ab,10}^*$	9.8	11.8	4.3	4.7
	ΔE_{00}	6.2	10.7	2.9	3.0
Difference Green	$\Delta E_{ab,10}^*$	8.3	11.1	2.3	2.5
	ΔE_{00}	6.0	10.1	1.4	1.5
Difference Grey	$\Delta E_{ab,10}^*$	6.8	10.9	1.7	2.0
	ΔE_{00}	5.8	9.5	2.0	2.4
Green	$\Delta E_{ab,10}^*$	8.1	11.0	2.3	2.5
	ΔE_{00}	6.0	10.2	1.5	1.5
Mid Grey	$\Delta E_{ab,10}^*$	6.8	11.0	1.6	2.0
	ΔE_{00}	5.9	9.6	2.1	2.6
Orange	$\Delta E_{ab,10}^*$	17.2	23.7	3.9	4.9
	ΔE_{00}	10.4	10.6	2.5	3.2
Pale Grey	$\Delta E_{ab,10}^*$	8.4	10.3	1.8	1.2
	ΔE_{00}	7.4	8.5	1.9	1.2
Red	$\Delta E_{ab,10}^*$	17.7	19.5	7.9	2.8
	ΔE_{00}	7.5	14.0	4.7	1.7
Yellow	$\Delta E_{ab,10}^*$	15.6	15.2	2.7	1.7
	ΔE_{00}	7.7	8.4	1.6	0.6

4.4.3.2. Second match predictions based on adjustments to computed concentrations

For some colours, first recipes prescribed negative dye concentrations, and for others, the sum total of concentrations exceeded the legal maximum for processed foods. Negative concentrations can result when trying to adjust a starting recipe which is far away from the target in colour space (McDonald, 1987). Figure 4.7 shows the positions in the three-dimensional $L^*a^*b^*$ space of the tile colours relative to the gamut of cake colours that can be achieved by the addition of dye blends. The colours of cakes containing a single dye or two-dye blend at a range of concentrations up to the allowable maximum, were used to construct the view of the lightness range; this boundary is comprised of the colours with the minimum and

maximum a^*_{10} value at each value of L^*_{10} . This is a more detailed view of the lightness range than the one given in Kim *et al.* (2012) in which the range was defined only by the lightest and darkest cake samples. The chromatic limit of the boundary is defined by the colours of cakes containing a single dye or two-dye blend at the maximum allowable concentration only. Those tile colours which lie outside the gamut of cake colours are those for which out-of-range dye concentrations were computed.

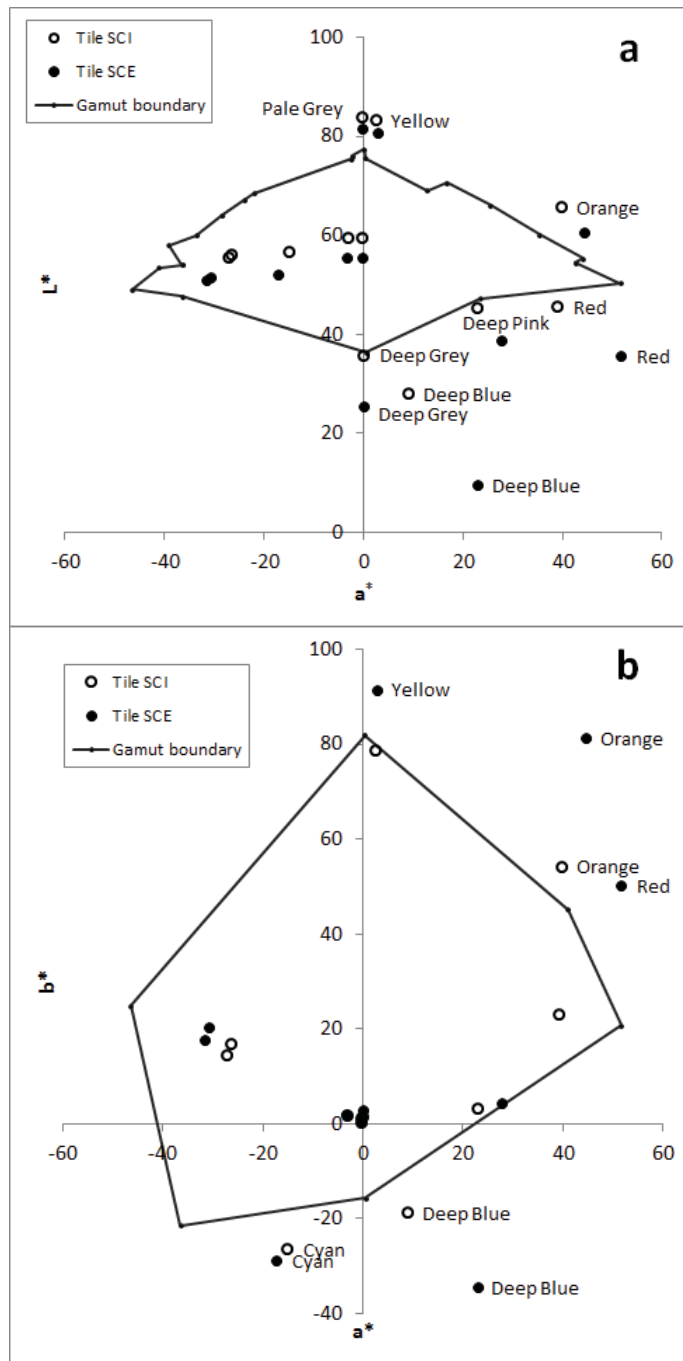


Figure 4.7 Positions in the three-dimensional $L^*a^*b^*$ colour space of the measured target tile colours relative to the gamut of computed colours achievable in the cake-dye matching system. Values are $L^*_{10}a^*_{10}b^*_{10}$. (a) Frontal a^*L^* view of the lightness range; (b) Chromatic a^*b^* view.

Adjustments involved increasing individual negative dye concentrations to zero, and scaling the new dye totals which were in excess of the legal maximum of 27.4 mg/100 raw cake batter, back to this level, whilst retaining the relative proportions of the non-zero quantity dyes. At this

point Pale Grey was excluded as a matching target; the first recipe computed for this colour called for negative quantities for all three dyes which were then adjusted to zero. As expected, for the other out-of-gamut targets (Cyan, Deep Blue, Deep Grey, Deep Pink – SCE only, Mid-Grey – SCI only, Orange, Red and Yellow), the effect of adjusting concentrations was to increase the $\Delta E^*_{ab,10}$ and ΔE_{00} differences between tile colour and computed cake colour. Discussion is focused here on the $\Delta E^*_{ab,10}$ differences which are presented in Table 4.4, with ΔE_{00} differences given in Appendix Table 4.7. The resulting increase in $\Delta E^*_{ab,10}$ ranged from 0.5 and 0.8 units respectively for Mid Grey SCI and Deep Pink SCE (suggesting these targets were not very far out-of-gamut), to 30 units for Orange SCE. For Orange, as well as for Deep Blue and Deep Grey, the increase in $\Delta E^*_{ab,10}$ for the SCE colour was larger than that for the SCI colour. Darker, high-gloss tile colours are not only lower in their SCE-measured reflectance and SCE-measured lightness relative to their lighter-coloured counterparts, they are subject to much larger increases in these measures when the specular component is included as uniform white light (MacDougall, 2002a). Because $\left(\frac{K}{S}\right)_\lambda$ is inversely related to reflectance, X_{10}^P , Y_{10}^P and Z_{10}^P values of the tile targets would have been higher for R_λ (SCE)-based predictions, demanding higher concentrations for matching (Equation 4.8, Equations 4.13 and Equations 4.14). Much larger changes were therefore needed to bring these concentrations to within usable range.

4.4.3.3. Comparison of computed (predicted) differences between tile and cake colours with measured (actual) differences

$\Delta E^*_{ab,10}$ differences between measured tile and *measured* cake colours ('measured $\Delta E^*_{ab,10}$ '), excluding Pale Grey, are also given in Table 4.4 and again alongside ΔE_{00} differences in Appendix Table 4.7. Measured cake $L^*_{10}a^*_{10}b^*_{10}$ values are given in Appendix Table 4.6. In many cases, measured cake L^* , a^* or b^* values were found to differ significantly to their computed values. Despite this, measured $\Delta E^*_{ab,10}$ values were in good agreement with $\Delta E^*_{ab,10}$ differences between measured tile and *computed* cake colours ('computed $\Delta E^*_{ab,10}$ '); for 19 out

of the 22 colours (SCI and SCE), the difference between computed $\Delta E^*_{ab,10}$ and measured $\Delta E^*_{ab,10}$ was less than three units. Among the remaining colours, the difference was as high as nine units for Orange SCE, though computed $\Delta E^*_{ab,10}$ and measured $\Delta E^*_{ab,10}$ were of a similar order of magnitude, at 35 and 26 units respectively. This suggests that computations for some colours need refinement, or that a criterion other than a $\Delta E^*_{ab,10}$ difference of three units is needed to evaluate computed differences as predictors of measured differences.

Table 4.4 $\Delta E^*_{ab,10}$ differences between tile colours (SCI and SCE) and computed or measured cake colours (SCE). Cake colours were computed on the basis of matching to measured tile reflectance (SCI or SCE as appropriate). Also shown are the ΔL^*_{10} , $\Delta C^*_{ab,10}$ and $\Delta H^*_{ab,10}$ differences between tile colours and measured cake colours.

Tile colour	$\Delta E^*_{ab,10}$ difference between first computed solution for cake $L^*_{10}a^*_{10}b^*_{10}$ and tile $L^*_{10}a^*_{10}b^*_{10}$ (also seen in Table 2.2).	$\Delta E^*_{ab,10}$ difference after scaling computed dye concentrations to between zero and legal maximum, as necessary	$\Delta E^*_{ab,10}$ difference between measured cake $L^*_{10}a^*_{10}b^*_{10}$ and tile $L^*_{10}a^*_{10}b^*_{10}$	$\Delta E^*_{ab,10}$ difference between computed $\Delta E^*_{ab,10}$ and measured $\Delta E^*_{ab,10}$ (i.e. the difference between (1) & (3), or between (2) & (3), as appropriate)	ΔL^*_{10} , measured	$\Delta C^*_{ab,10}$, measured	$\Delta H^*_{ab,10}$, measured
Cyan	SCI SCE	2.1 2.5	20.1 17.2	19.3 21.3	-0.8 4.1	0.9 9.4	6.3 19.1
Deep Blue	SCI SCE	3.3 26.5	11.1 38.7	9.0 37.1	-2.1 -1.6	4.9 24.3	7.0 27.4
Deep Grey	SCI SCE	3.3 3.7	3.8 13.8	3.4 12.6	-0.4 -1.2	0.7 12.2	2.6 3.0
Deep Pink	SCI SCE	4.3 4.7	5.5 5.5	4.5 5.2	0.2 -0.3	1.2 0.4	3.3 3.8
Difference Green	SCI SCE	2.3 2.5	3.4 3.9	3.4 3.9	1.1 1.4	1.8 1.3	2.7 3.7
Difference Grey	SCI SCE	1.7 2.0	2.1 2.5	1.4 2.5	-0.3 0.5	0.4 1.8	0.2 0.6
Green	SCI SCE	2.3 2.5	3.8 6.1	3.8 6.1	1.5 3.6	2.4 4.2	2.9 4.4
Mid Grey	SCI SCE	1.6 2.0	2.1 2.5	5.0 2.4	2.9 0.4	4.4 1.2	1.9 1.5
Orange	SCI SCE	3.9 4.9	17.2 34.5	18.4 25.5	1.2 -9.0	4.5 2.5	13.8 25.2
Red	SCI SCE	7.9 2.8	7.8 24.2	7.3 23.2	-0.5 -1.0	1.9 18.3	5.8 13.1
Yellow	SCI SCE	2.7 1.7	15.9 15.0	18.6 17.3	2.7 2.3	11.1 9.4	14.5 14.3
							2.2

4.4.3.4. Comparison of tile colours with measured colours of prepared cake matches

For tile colour targets that were originally within the gamut of the cake-dye system, differences between tile colours and measured colours of cakes that were prepared to match the tiles ranged from 1.4 to 7.3 units for $\Delta E_{ab,10}^*$ and from 1.6 to 4.8 units for ΔE_{00} , across SCI and SCE colours. For targets that were originally out-of-gamut, differences between cake and tile colours ranged from 3.4 to 37.1 units for $\Delta E_{ab,10}^*$ and from 3.7 to 20.7 units for ΔE_{00} . ΔE_{00} values are given in Appendix Table 4.7.

A sample photograph of the tile colour standards and microwave-baked cake samples prepared to match the tiles is shown in Figure 4.8. The cake samples shown in Figure 4.8 were those prepared using dye concentrations computed on the basis of the measured reflectance of the tiles, with the specular component included (SCI). Overall these cake samples were closer matches to the tiles, as indicated by the $\Delta E_{ab,10}^*$ differences between measured tile $L^*_{10}a^*_{10}b^*_{10}$ (SCI) and measured cake $L^*_{10}a^*_{10}b^*_{10}$ (SCE) (Table 4.4).



Figure 4.8 Tile colour standards and microwave-baked cake samples prepared to match the tiles, on the basis of measured reflectance (SCI) of the tiles. Values are $\Delta E_{ab,10}^*$ differences between tile and cake colours.

4.5. General Discussion: Visual implications

4.5.1. Interpretation of total colour differences between tile and cake colours

Ultimately, the goal of computer colour matching is to achieve a good *visual* match. The convenience and speed of computer colour matching is balanced against the need for a colour difference index applied to the computed match which represents the degree of the visual match between the colours of two samples. This discussion is focused largely on the $\Delta E^*_{ab,10}$ differences between tile and cake colours, rather than on both the $\Delta E^*_{ab,10}$ and ΔE_{00} differences, because tolerance limits are available for $\Delta E^*_{ab,10}$ albeit mostly from non-food industries. Put simply, tolerance limits indicate the limit of an acceptable colour match. These limits can vary according to the application: while a $\Delta E^*_{ab,10}$ of three units or more is considered a visually unacceptable match in non-food applications (Francis and Clydesdale, 1975), the tolerance limit can be as low as less than one $\Delta E^*_{ab,10}$ unit in the automotive industry (for a commercial match). In the middle of this range, a $\Delta E^*_{ab,10}$ of two units can indicate a perceptible difference (Francis and Clydesdale, 1975).

The physical differences between target and matching systems (tile and cake respectively) were very likely to influence how the differences in colour between them would be perceived, despite best matching efforts. Differences in the range of colours (i.e. the colour gamut) that can be achieved in each system also need to be taken into account. In 3D colour food printing also, target and match might not necessarily be viewed side-by-side, and the perception of each colour voxel might be influenced by the colours of the surrounding voxels. Therefore, applying a tolerance limit in this study which is higher than that for a visually perceptible difference was reasonable. Without the benefit of having established an appropriate tolerance limit for use in this study with a panel of observers, this study was instead guided by values from the literature. The tolerance limit chosen was a $\Delta E^*_{ab,10}$ difference of three units, which was also used by Baixauli *et al.* (2008) for a bakery type product (muffins) and by Martínez *et al.* (2001) for red

wines. It should be noted however that while this limit was established for red wines on the basis of both observer and instrumental data, for the muffin work the reference for the three-unit limit on $\Delta E^*_{ab,10}$ was also Francis and Clydesdale (1975) with no explanation given as to whether this tolerance limit is actually suitable for muffins.

Eight of the original 24 tile target $L^*_{10}a^*_{10}b^*_{10}$ colours (across SCI and SCE) were within the cake colour gamut. Of these eight colours, seven had a $\Delta E^*_{ab,10}$ difference between tile colour and measured cake colour of more than three units. For SCI and SCE tile colours that were originally out-of-gamut, the $\Delta E^*_{ab,10}$ differences between tile colour and measured cake colour ranged from 3.4 to 37.1. As expected, these latter differences were comparatively large as a result of having to adjust concentration outputs from colorimetric matching. Visual inspection of the matches between tile and cake, for the SCI colours at least (Figure 4.8) suggests that these matches are closer than are indicated by their $\Delta E^*_{ab,10}$ differences, and that new, more appropriate tolerance limits, or alternatively another colour difference index, are needed. The tolerance level of three ΔE^*_{ab} units has typically been used to compare samples of the same type, and might be too strict to compare samples such as the tiles and cakes, which differ physically. A new tolerance limit could take into account that in baked goods, measured colours are found to be darker than visually perceived colour; instrumentally-measured colour averages the effect of surface crumb texture by including the bubbles, yet visual colour is seen as separate from the bubbles (MacDougall, 2002b). Formulae for the total difference between samples that differ in colour and surface texture have been proposed (Huang *et al.*, 2010), which are based on physical measurements of the samples, and which could be used to predict visual differences.

4.5.1.1. The use of ΔE_{00} vs. $\Delta E^*_{ab,10}$

The need for a more precise colour difference index, such as ΔE_{00} , in food applications warrants further consideration (MacDougall, 2002a). Measures of ΔE_{00} were included in this study because ΔE_{00} is the most recent colour difference formula, providing an improvement on previous colour difference formulae. As was the case here, the size of the ΔE_{00} difference is

usually smaller than the $\Delta E^*_{ab,10}$ difference for a given comparison between two samples, but the units for the two indices are on different scales. Strictly speaking, ΔE_{00} applies to uniform surface colours with $\Delta E^*_{ab,10}$ differences below five units. With the exception of a small subset of the $\Delta E^*_{ab,10}$ differences between tile colours and measured cake colours being less than five units, the experimental conditions in this study differ to the reference conditions to which ΔE_{00} applies. This will affect the performance of ΔE_{00} as an indicator of visually-perceived colour differences ([CIE] International Commission on Illumination, 2001).

4.5.2. Differences in lightness, hue and chroma

The $\Delta E^*_{ab,10}$ and ΔE_{00} formulae give an index of total colour difference, incorporating lightness, hue and chroma differences, but do not indicate the relative contributions of each. Table 4.4 also shows the $\Delta E^*_{ab,10}$ differences between tile colours and measured cake colours expressed in terms of lightness, chroma and hue differences. For Cyan and Orange, $\Delta E^*_{ab,10}$ stemmed predominantly from hue and chroma differences. Lightness difference was the largest contributor for Deep Grey SCE, whereas lightness and chroma largely influenced the difference for Deep Blue and Red SCE. Yellow colour difference was most influenced by lightness and chroma differences, to a similar extent for the SCI and SCE colours; the SCI and SCE colours also displayed similar $\Delta E^*_{ab,10}$ differences between tile and cake $L^*_{10}a^*_{10}b^*_{10}$. For future reference, ΔE_{00} , like $\Delta E^*_{ab,10}$, can also be expressed as separate lightness, hue and chroma differences.

Tiles and cakes could differ also in the relative *importance* of lightness, chroma and hue in the visual perception of their colours, with implications for interpreting the degree of overall colour matching between tiles and cakes. Even within foods, hue is much more important visually for some foods (such as tomato juice), and lightness more so for others (for example, roasted ground coffee and canned tuna) (Francis and Clydesdale, 1975). Furthermore, humans are able to better detect changes in hue and lightness, but less so changes in chroma. With the parametric factors in the formula for ΔE_{00} kept as $k_L = k_C = k_H = 1$ (as in reference experimental conditions), lightness, chroma and hue were assumed to be of equal importance for both tile

colours and cake colours in this study. Further work is needed to determine parametric factors more appropriate to comparing food colours to standards.

4.5.3. The appropriateness of using tile colours as matching targets

For glossy materials such as the tiles, their colours measured with the SCE may have been the more appropriate as matching targets; the exclusion of specular reflections is equivalent to an observer being able to see mirror reflections and having to move the sample at different angles to observe the colour (Berns, 2000). The conditions in which the visual equivalent of SCI measurements can occur are rare in reality (Berns, 2000).

The tiles may appear to have been an unusual choice of target for colour matching; compared to cake colours, tile colours were uniform and glossy, with more than half being out-of-gamut. The tiles were not specially procured for this project; a set was available within the Institute and therefore a set of useful colour standards was already accessible. Out-of-gamut colours as matching targets were not to be avoided as the problem of out-of-gamut colours will be encountered in the transcribing of screen or image colours to food colours by the 3D colour food printer.

4.6. Conclusion

The (computed) $\Delta E^*_{ab,10}$ colour differences based on the first outputs from colorimetric matching indicate that good visual matches to tiles could be achieved using the cake-dye matching system. This implies that colours can be reproduced in this food system to an acceptable degree. The findings validate the use of the derived unit absorption spectra of the dyes, and the use of the colorimetric matching technique. However an extra step may be required in that colorimetric matching should be aimed at the measured reflectance of the tile target (with the SCI or SCE) rather than its corrected reflectance, due to physical differences between the target and matching systems. Adjustment of computed concentration outputs can result in large $\Delta E^*_{ab,10}$ and ΔE_{00} colour differences for out-of-gamut colours, but the true visual impact remains to be assessed. Visual inspection of colour matches between tiles and prepared

cake samples suggests that the matches might be closer than are indicated by their measured $\Delta E^*_{ab,10}$ differences (across within-gamut and out-of-gamut tile colours), and that the tolerance limit of three $\Delta E^*_{ab,10}$ units needs to be revised for this type of matching scenario.

In 3D colour food printing a voxel must be coloured to match a target contained in an image file rather than a glossy target, and images might also contain out-of-gamut colours. On balance it appears that the colorimetric algorithm overlaid by adjustment of computed dye quantities to remain within legal limits, or to zero where a negative concentration is called for, will indeed provide a rapid and accurate calculation tool. Ensuring no voxel contains an unsafe dye amount will ensure the entire printed food item remains compliant.

In the following chapters *colour gamut mapping* is investigated as a technique for handling target colours (labelled ‘original’ colours in a mapping context), especially out-of-gamut colours, before dye recipes are computed for these colours. Colour gamut mapping, used in the cross-media colour reproduction of images, aims to replace each out-of-gamut colour with the best equivalent of that colour within the range achievable by the reproduction system. Selection of the method to find the ‘best equivalent’ is made according to the attributes of the original colours (and of the relationships between them) that are to be retained, or preserved, in the reproduction.

To address some of the issues raised by using samples with surface texture (cakes) to match colour-uniform targets (tiles), work on colour gamut mapping initially uses a simpler food system without surface texture, a gel, to replace the cake as the reproduction system (previously referred to as the ‘matching system’). In keeping with the purpose of 3D colour food printing, where colour outputs need to be produced for any specified combination of food characteristics, the gel system will allow the impact of changing the level of a single characteristic on possible colour outputs to be seen. Later, to consolidate findings, work returns to the cakes to compare the solutions from colour gamut mapping with those from colorimetric matching.

4.7. Appendix

Table 4.5 Computed and measured $L^*_{10}a^*_{10}b^*_{10}$ values for the microwave-baked cake containing selected blends of Brilliant Blue ('B'), Ponceau 4R (red, 'P') and Tartrazine yellow ('T') dyes, and the $\Delta E^*_{ab,10}$ and ΔE_{00} differences between computed and measured $L^*_{10}a^*_{10}b^*_{10}$ cake colours. Cake colours were computed using the Kubelka-Munk blending model. Numbers in labels denote dye concentrations in raw batter, mg dye/100 g batter: 1 = 1.7, 2 = 3.5, 3 = 6.9, 4 = 13.8.

Two-dye blends (n = 4)

Blend				Blend				Blend									
		Computed	Measured (SD)	$\Delta E^*_{ab,10}$	ΔE_{00}			Computed	Measured (SD)	$\Delta E^*_{ab,10}$	ΔE_{00}			Computed	Measured (SD)	$\Delta E^*_{ab,10}$	ΔE_{00}
P1B1	L* ₁₀	61.4	60.9 (3.3)	0.6	0.6	T1P1	L* ₁₀	69.5	70.0 (2.1)	1.7	0.8	T1B1	L* ₁₀	67.8	67.2 (2.4)	2.9	1.3
	a* ₁₀	-5.7	-5.4 (0.1)		a* ₁₀		15.1	14.6 (0.6)		a* ₁₀	-25.9		-23.8 (0.8)				
	b* ₁₀	1.6	1.7 (0.8)		b* ₁₀		28.0	26.4 (0.5)		b* ₁₀	19.9		18.1 (0.4)				
P1B4	L* ₁₀	49.0	49.1 (2.0)	0.9	0.4	T1P4	L* ₁₀	55.1	54.4 (1.3)	0.8	0.7	T1B4	L* ₁₀	53.2	53.4 (2.0)	1.7	1.0
	a* ₁₀	-24.1	-24.9 (0.6)		a* ₁₀		42.7	42.6 (0.5)		a* ₁₀	-42.1		-41.1 (0.4)				
	b* ₁₀	-16.2	-16.4 (0.3)		b* ₁₀		22.6	22.5 (0.4)		b* ₁₀	-2.4		-3.8 (0.5)				
P2B3	L* ₁₀	49.8	49.4 (2.4)	1.0	0.8	T2P3	L* ₁₀	60.4	60.7 (2.1)	1.0	0.5	T2B3	L* ₁₀	58.2	58.0 (1.8)	2.4	1.0
	a* ₁₀	-11.3	-12.1 (0.5)		a* ₁₀		32.8	32.0 (0.3)		a* ₁₀	-40.9		-39.1 (0.4)				
	b* ₁₀	-10.9	-11.1 (0.6)		b* ₁₀		29.3	28.7 (0.3)		b* ₁₀	13.9		12.3 (0.3)				
P4B1	L* ₁₀	46.5	47.2 (1.5)	1.4	1.0	T4P1	L* ₁₀	68.7	69.1 (1.5)	1.7	0.9	T4B1	L* ₁₀	66.0	64.7 (1.5)	1.9	1.2
	a* ₁₀	22.2	23.4 (0.5)		a* ₁₀		14.2	12.8 (0.3)		a* ₁₀	-27.8		-26.4 (0.3)				
	b* ₁₀	1.6	1.8 (0.7)		b* ₁₀		58.6	57.8 (0.7)		b* ₁₀	51.3		50.7 (1.1)				
P4B4	L* ₁₀	35.7	36.3 (1.6)	1.1	0.9	T4P4	L* ₁₀	55.0	55.1 (1.9)	1.6	0.8	T4B4	L* ₁₀	50.5	49.0 (1.3)	2.4	1.5
	a* ₁₀	0.8	0.5 (0.5)		a* ₁₀		41.2	40.9 (0.8)		a* ₁₀	-48.0		-46.4 (0.3)				
	b* ₁₀	-14.7	-15.6 (0.1)		b* ₁₀		43.7	45.2 (0.6)		b* ₁₀	25.9		24.9 (0.2)				

= Difference between computed and measured values is significant at 5% for two-tailed, one-sample t-test (threshold critical value for t of 3.18 for 3 degrees of freedom)

Three-dye blends (n = 4)					
Blend		Computed	Measured (SD)	$\Delta E_{ab,10}^*$	ΔE_{00}
P1B1T4	L* ₁₀	59.4	57.9 (2.1)	2.4	1.9
	a* ₁₀	-12.5	-10.8 (0.3)		
	b* ₁₀	42.8	43.3 (0.4)		
T1B1P4	L* ₁₀	46.3	46.1 (1.8)	1.1	0.6
	a* ₁₀	20.4	21.5 (0.3)		
	b* ₁₀	7.6	7.7 (0.1)		
T1P1B1	L* ₁₀	60.8	61.0 (1.9)	1.2	0.8
	a* ₁₀	-9.1	-8.3 (0.4)		
	b* ₁₀	13.4	12.6 (0.4)		
T1P1B4	L* ₁₀	48.2	47.0 (1.4)	1.6	1.3
	a* ₁₀	-29.2	-29.3 (0.6)		
	b* ₁₀	-5.9	-7.0 (0.2)		
T3P3B3	L* ₁₀	43.8	42.0 (2.0)	2.0	1.8
	a* ₁₀	-9.5	-9.9 (0.5)		
	b* ₁₀	10.3	9.6 (0.2)		

Table 4.6 Primary data set of the measured $L^*_{10}a^*_{10}b^*_{10}$ tile colours (SCI and SCE) and $L^*_{10}a^*_{10}b^*_{10}$ cake colours (SCE) computed, and measured, to match the tiles. Cake colours were computed on the basis of matching to the corrected reflectance, $R_{\lambda,i}$, or measured reflectance - $R_{\lambda,m}(SCI)$ and $R_{\lambda,m}(SCE)$ - of the tiles.

	Cake colour									
	Tile colour ^a					Computed, adjusted				
	Computed			Measured (SD)		Computed			Measured (SD)	
	SCI (n = 24)	SCE (n= 24)	$R_{\lambda,i} = R_{\lambda,i}$	$R_{\lambda,i} = R_{\lambda,i}(SCI)$	$R_{\lambda,i} = R_{\lambda,i}(SCE)$	$R_{\lambda,i} = R_{\lambda,i}(SCI)$	$R_{\lambda,i} = R_{\lambda,i}(SCE)$	$R_{\lambda,i} = R_{\lambda,i}(SCI)$ (n= 6) ^b	$R_{\lambda,i} = R_{\lambda,i}(SCE)$ (n= 4) ^c	
Cyan	 L^*_{10}	52.0	62.9	57.8	53.1	56.6	51.9	57.5 (0.3)	42.6 (2.6)	
	 a^*_{10}	-17.2	-15.8	-13.3	-15.0	-23.2	-24.6	-22.5 (0.3)	-8.0 (0.4)	
	 b^*_{10}	-28.9	-30.1	-26.1	-29.2	-7.6	-13.3	-8.6 (0.2)	-12.1 (0.3)	
Deep Blue	 L^*_{10}	9.5	19.3	29.1	11.8	35.6	35.5	32.9 (1.3)	33.8 (1.3)	
	 a^*_{10}	22.9	31.8	12.0	43.0	7.5	4.4	7.9 (0.4)	4.5 (0.2)	
	 b^*_{10}	-34.4	-44.6	-18.7	-51.6	-10.7	-12.6	-11.2 (0.4)	-13.2 (0.1)	
Deep Grey	 L^*_{10}	25.4	35.5	36.8	26.5	38.0	38.6	35.1 (1.8)	37.7 (0.4)	
	 a^*_{10}	0.1	2.7	2.6	3.0	2.5	2.4	3.1 (0.3)	1.1 (0.1)	
	 b^*_{10}	2.9	4.4	3.3	4.7	3.4	6.2	2.8 (0.3)	5.8 (0.2)	
Deep Pink	 L^*_{10}	38.8	50.1	47.3	41.0		42.2	44.1 (2.5)	39.2 (1.8)	
	 a^*_{10}	27.8	31.0	25.1	30.1		30.1	25.6 (0.4)	30.7 (0.4)	
	 b^*_{10}	4.3	6.2	6.3	7.9		7.9	6.5 (0.4)	8.6 (0.4)	
Difference	 L^*_{10}	51.6	62.6	57.0	52.4			54.4 (2.4)	50.3 (2.3)	
	 a^*_{10}	-30.8	-29.6	-24.6	-28.5			-23.7 (0.3)	-27.4 (0.4)	
	 b^*_{10}	20.3	21.1	18.0	21.0			16.2 (0.3)	18.8 (0.4)	

Cake colour										
Tile colour ^a				Computed			Computed, adjusted			
				Computed			Measured (SD)			
				SCI (n = 24)	SCE (n= 24)	R _{h,i} = R _{h,i}	R _{h,i} = R _h (SCI)	R _{h,i} = R _h (SCE)	R _{h,i} = R _h (SCI) (n= 6) ^b	R _{h,i} = R _h (SCE) (n= 4) ^c
Difference Grey	L* ₁₀	59.5	55.4	66.3	60.1	56.1			59.2 (1.9)	53.6 (2.9)
	a* ₁₀	-3.0	-3.4	-2.4	-1.7	-1.8			-2.0 (0.4)	-1.7 (0.2)
	b* ₁₀	1.8	2.2	2.4	2.6	3.2			2.6 (0.6)	2.9 (0.2)
Green	L* ₁₀	55.5	50.9	61.8	56.4	51.7			53.1 (1.6)	46.6 (3.0)
	a* ₁₀	-27.0	-31.6	-30.5	-25.2	-29.4			-24.3 (0.5)	-27.5 (0.7)
	b* ₁₀	14.6	17.8	18.3	15.7	18.5			13.6 (0.2)	16.1 (0.4)
Mid Grey	L* ₁₀	59.6	55.4	66.4	60.2	56.1	60.1		55.2 (2.9)	54.2 (2.9)
	a* ₁₀	-0.3	-0.4	0.5	0.9	1.2	0.6		0.9 (0.6)	1.4 (0.2)
	b* ₁₀	0.3	0.5	0.8	1.1	1.6	2.1		2.2 (0.4)	1.7 (0.3)
Orange	L* ₁₀	65.8	60.7	71.7	67.5	63.6	63.5	68.0	61.3 (3.8)	58.2 (2.3)
	a* ₁₀	39.8	44.4	29.4	36.7	41.7	23.5	13.1	23.1 (0.6)	34.5 (0.6)
	b* ₁₀	54.3	81.3	66.6	56.0	84.0	49.1	68.7	48.2 (1.3)	57.9 (1.3)
Pale Grey	L* ₁₀	84.0	81.6	90.0	84.2	81.8				
	a* ₁₀	-0.3	-0.3	2.9	0.4	0.0				
	b* ₁₀	1.1	1.2	-3.9	-0.7	0.1				
Red	L* ₁₀	45.6	35.6	49.8	49.4	37.5	49.9	54.9	47.5 (1.4)	53.9 (3.0)
	a* ₁₀	39.1	51.6	48.5	42.2	52.8	41.8	38.5	41.7 (0.5)	38.7 (0.2)
	b* ₁₀	22.9	50.2	37.3	29.1	51.9	28.8	43.8	29.5 (0.7)	44.4 (0.4)
Yellow	L* ₁₀	83.2	80.8	88.4	83.7	81.6	75.1	74.3	72.1 (2.5)	71.5 (3.4)
	a* ₁₀	2.6	2.8	-9.6	0.1	3.3	-2.5	-0.9	-1.0 (0.4)	0.3 (0.6)
	b* ₁₀	78.7	91.5	86.9	79.3	90.0	66.0	78.5	64.2 (0.8)	77.2 (1.3)

^aSD for tiles ranged from 0 to 0.1 for L^*_{10} , from 0 to 0.2 for a^*_{10} and from 0 to 0.2 for b^*_{10} ; ^b $n = 2$ for Cyan and Orange; ^c $n = 3$ for Deep Grey; Shaded L^*_{10} , a^*_{10} , b^*_{10} labels indicate differences between computed and measured values are significant at 5% for two-tailed, one-sample t-test, as follows:  = $t \geq 2.57$ for 5 df for SCI-based comparisons;  = $t \geq 3.18$ for 3 df for SCE-based comparisons;  = significant for both SCI- and SCE- based comparisons. (Note: $t \geq 4.30$ for 2 df for Deep Grey SCE-based comparison.)

Data in columns sharing the same shade were used to compute 'final' $\Delta E^*_{ab,10}$ and ΔE_{00} differences (with corresponding shading in Table 4.7)

Table 4.7 All $\Delta E^*_{ab,10}$ (top row) and ΔE_{00} (bottom row) values for the differences between tile colours (SCI and SCE) and computed or measured cake colours (SCE). Most values have been presented already in Table 4.3 and Table 4.4. Shading corresponds to the shading of the constituent L^*_{10} , a^*_{10} and b^*_{10} values in Table 4.6).

Target tile color used to calculate $\Delta E^*_{ab,10}$ and ΔE_{00}										
$L^*_{10}a^*_{10}b^*_{10}$ (SCI)					$L^*_{10}a^*_{10}b^*_{10}$ (SCE)					
Form of reflectance, R, of target, used to calculate dye concentration										
$R_{t,i} = R_{t,i}$	$R_{t,i} = R_t(SCI)$				$R_{t,i} = R_{t,i}$	$R_{t,i} = R_t(SCE)$				
Computed difference	Computed difference	Computed, adjusted difference	Measured difference	Difference between computed and measured ΔE (shaded values)	Computed difference	Computed difference	Computed, adjusted difference	Measured difference	Difference between computed and measured ΔE (shaded values)	
Cyan	7.4	2.1	20.1	19.3	-0.8	11.0	2.5	17.2	21.3	4.1
	5.8	1.5	12.7	12.1	-0.6	10.0	1.7	10.0	13.1	3.1
Deep Blue	35.7	3.3	11.1	9.0	-2.1	16.7	26.5	38.7	37.1	-1.6
	13.5	2.8	7.9	6.1	-1.8	7.6	7.8	22.1	20.7	-1.4
Deep Grey	3.9	3.3	3.8	3.4	-0.4	10.5	3.7	13.8	12.6	-1.2
	4.3	3.9	4.2	4.3	0.1	8.7	4.4	11.3	10.0	-1.3
Deep Pink	9.8	4.3		4.5	0.2	11.8	4.7	5.5	5.2	-0.3
	6.2	2.9		2.7	-0.2	10.7	3.0	3.9	2.9	-1.0
Difference	8.3	2.3		3.4	1.1	11.1	2.5		3.9	1.4
Green	6.0	1.4		2.2	0.8	10.1	1.5		2.0	0.5
Difference	6.8	1.7		1.4	-0.3	10.9	2.0		2.5	0.5
Grey	5.8	2.0		1.6	-0.4	9.5	2.4		2.8	0.4
Green	8.1	2.3		3.8	1.5	11.0	2.5		6.1	3.6
	6.0	1.5		2.7	1.2	10.2	1.5		4.6	3.1
Mid Grey	6.8	1.6	2.1	5.0	2.9	11.0	2.0		2.4	0.4

Target tile color used to calculate $\Delta E^*_{ab,10}$ and ΔE_{00}										
$L^*_{10}a^*_{10}b^*_{10}$ (SCI)					$L^*_{10}a^*_{10}b^*_{10}$ (SCE)					
Form of reflectance, R, of target, used to calculate dye concentration										
$R_{x,i} = R_{x,i}$	$R_{x,i} = R_i$ (SCI)				$R_{x,i} = R_{x,i}$	$R_{x,i} = R_i$ (SCE)				
Computed difference	Computed difference	Computed, adjusted difference	Measured difference	Difference between computed and measured ΔE (shaded values)	Computed difference	Computed difference	Computed, adjusted difference	Measured difference	Difference between computed and measured ΔE (shaded values)	
Orange	5.9	2.1	2.3	4.8	2.5	9.6	2.6		3.0	0.4
	17.2	3.9	17.2	18.4	1.2	23.7	4.9	34.5	25.5	-9.0
	10.4	2.5	8.2	8.9	0.7	10.6	3.2	16.5	6.1	-10.4
Pale Grey	8.4	1.8			-1.8	10.3	1.2			-1.2
	7.4	1.9			-1.9	8.5	1.2			-1.2
Red	17.7	7.9	7.8	7.3	-0.5	19.5	2.8	24.2	23.2	-1.0
	7.5	4.7	5.1	3.7	-1.4	14.0	1.7	18.9	17.9	-1.0
Yellow	15.6	2.7	15.9	18.6	2.7	15.2	1.7	15.0	17.3	2.3
	7.7	1.6	7.1	8.9	1.8	8.4	0.6	5.7	7.5	1.8

Chapter Five: Colour gamut boundary computation allowing for the effects of browning

5.1. Introduction

The work of the previous chapter demonstrated that by using a food substrate, together with primary food dyes and a computer-based coloration method appropriate to the development of a 3D colour food printer, target colours could be matched satisfactorily by the combination of the substrate and dyes, as long as the targets were within the colour gamut of the substrate-dye system. For out-of-gamut colours, much larger colour differences between target and match resulted from having to adjust computed dye quantities to remain within legal limits.

The cake formulation that was used as the substrate for the previous chapter provided only one example from a class of substrates – baked goods - that are potentially suitable for 3D colour food printing. The printer however is intended to provide fully customised outputs not only in terms of colour, but also in the selection of substrate ingredients, in order to meet specifications for nutrition, taste and flavour, and texture. Changes in formulation might change substrate characteristics and in turn change the colour output, even though it might be desirable to reproduce the same image or design in different substrates. Examples of the physical effects of these types of changes on colour rendition include the decrease in colour intensity with increasing droplet concentration in emulsions (McClements *et al.*, 1998), the higher lightness of dyed fabrics made with finer fibres when compared to fabrics made of coarser fibres (Li *et al.*, 2009), and the dilution of colour intensity when a smooth, glossy, coloured surface is roughened, increasing light scattering. These effects are seen when dye concentration is kept the same between the different sample variants. The printer will need to have the ability to react to changes in the substrate by computing and adjusting the dye quantities that are needed, to produce as close as is possible to the same colour output.

Colour gamuts will also very likely change with changes in substrate characteristics. For example, a darkening of substrate colour, combined with restrictions on the level of dye addition, might be expected to decrease the range of colours that are achievable when dyes are added, when compared with a lighter coloured version of the substrate. Therefore a vital part of printer capability will be the handling of out-of-gamut colours, a step that needs to be taken before dye quantities can be computed for these colours. This chapter, and the following chapters, investigates more closely the subject of colour gamuts, and of *colour gamut mapping*, the process by which out-of-gamut colours are replaced with in-gamut colours (Morovic, 2003), in the context of 3D colour food printing. As in the previous chapter, the approach involves applying techniques from a non-food application, which this time is the cross-media colour reproduction of images. Different media, such as on-screen displays and print, usually differ in their colour gamuts, often making gamut mapping necessary. Various techniques are available for mapping, and for the computation of the gamut boundary (Morovic, 2003).

The intention in this thesis work was to take colour gamut boundary and colour gamut mapping data analysis a step further, and to see whether these could be used to develop simple transformations by which dye quantities are adjusted for a given substrate characteristic. These would form part of an overall colour matching algorithm for the printer, which would be comprised of different transformations for different characteristics. The characteristic which was the subject of this research is *browning*. Browning in baked goods is the combined darkening and reddening of substrate colour caused by Maillard and caramelisation reactions which also contribute to flavour development. Furthermore, changes in formulation designed to improve nutritional quality (as one might want to do with the 3D printed food) target ingredients which are also involved in colour formation. For example measured lightness and yellowness of crumb decreases, and crumb redness increases, with increasing substitution of polydextrose for sugar in high ratio cakes (Hicsasmaz *et al.*, 2003), and with oxidised oat β -glucan supplementation of wheat-flour sponge cakes (Lee *et al.*, 2011). Similar effects are seen with

increasing substitution of chickpea flour for wheat flour in bread (Mohammed *et al.*, 2012) except that crumb yellowness increases.

As a first step in colour gamut research in this thesis, the aim of the work in this chapter was to compute the colour gamut boundary when the same blends of dyes were added to variants of a model substrate which differed in their level of browning. To date, no-one has published a gamut boundary calculation for a coloured food. Appropriate model substrates and methods for colour gamut boundary computation needed to be developed and established. A model substrate was needed that could display the browning attribute in isolation, to different degrees, including a completely un-coloured version against which to compare the effects of browning.

In the previous chapter the colour gamut boundary that was drawn for the cake-dye system was based on only a few points. The computation of a more detailed boundary would allow colour gamut mapping techniques to be applied to provide better, closer solutions for each tile colour, however the number of individual points (colours) required was not known. For non-food media, indications are that around 1,000 colours are needed, whether these form a subset of the gamuts of image colours and of imaging media (Morovic, 2003), or are entire sets of colours, such as the 1,114 colours of the Pantone Formula Guide[®]. For foods coloured with synthetic food dyes, legal limits on dye addition naturally impose a limit on the range of colours that can be achieved; therefore it should be possible to describe the boundary using samples containing up to and including the maximum allowable dye quantity, without the need to sample the entire gamut. In the absence of a published gamut calculation for coloured foods a targeted spacing of three $\Delta E^*_{ab,10}$ units or less between gamut boundary colours could be used potentially as a 'sampling rule' for food colours, with a $\Delta E^*_{ab,10}$ of three units being considered one limit of a visually acceptable match (Francis and Clydesdale, 1975).

For practical reasons, the colour gamut boundaries in this study were comprised of colours that were computed using the Kubelka-Munk (K-M) linear, additive blending model, rather than the measured colours of real samples. Therefore the first objectives were to derive the absorption

spectra for the variants of the model substrate, and to derive and validate the unit absorption spectra for the primary dyes in each variant. The next objectives were to validate the consistency of the unit absorption spectra of each primary dye across all the substrate variants, and then to compute the colour gamut boundaries for all variants when they contain the same blends of the primary dyes.

5.2. Materials and General Methods

5.2.1. Model system

5.2.1.1. General description and preparation

The substrate used in this chapter was not intended to be a model of a rapidly cooked food (as was the cake in Chapter Four), but instead to be a more simple system that could be manipulated to model different substrate characteristics separately from one another. The model substrate chosen was a wheat starch gel. The gel also contained added whitener, with or without added brown dye, and primary dyes or dye blends. Brown dye was added to create variants of the gel which differed only in their degree of browning. Composition of the gels is summarised Table 5.1. The selection of appropriate levels of whitener, browning and primary dyes is discussed in subsequent sections.

Table 5.1 Composition of the model gel system used in this study

Component		Ingredient	Format	Concentration in raw gel mix
‘Brown1’ ‘Brown2’ ‘Brown3’ gel substrates	‘White’ gel substrate	Unmodified wheat starch	Powder	8% w/w (based on dry weight of starch)
		Titanium dioxide pigment (whitener)	Anatase crystal type	0.5% w/w
		Chocolate Brown HT dye (‘Brown HT’)	Liquid concentrate	2.5, 5.0, 10.0 mg/100 g
Primary dyes		Brilliant Blue, Ponceau 4R, Tartrazine	Liquid concentrates	As specified in text for derivation of derivation and validation of unit absorption coefficients
Reverse osmosis (RO) water				To 100 g per batch of raw gel mix (yielding two gel samples)

Gels were prepared in batches of 100 g of raw mix. Ingredients and RO water were weighed into a 200 ml stainless steel beaker and mixed together at moderate speed for 30 seconds (using a magnetic stirrer) before heating, to help disperse the particles. The mix was then covered with aluminium foil and heated in a 93°C water bath with a magnetic stirrer plate (Heidolph MR 3001, Germany) placed underneath, and stirred at 200 rpm, for 15 minutes. Heated gel mix was cast on to a smooth surface (trays from the Baccarat ‘Professional’ non-stick bakeware range, model 1010589) by pouring into plastic rings with an inner diameter of 32 mm and a height of 20 mm. The upper (uncast) surface was levelled using a palette knife. Rings containing the gels were removed from trays after cooling to room temperature for two hours and kept on their sides in lidded plastic containers until colour measurement.

5.2.1.2. Starch

Unmodified wheat starch (Penford Corporation, USA) was selected as the basis for the substrate because of its (visually) white colour, and because it could be prepared reproducibly to form a simple solid with a visually smooth surface. Starch is also fundamental to the formation of structure during the cooking of baked goods (the type of food that the 3D printer might produce), and could be used to increase the viscosity of the raw batter so that it is sufficiently rigid and self-supporting during the build process (Yang *et al.*, 2001).

Moisture content of the unmodified wheat starch (n=3) was determined as 12.37% (SD 0.02) using AACC Method 44-15A (American Association of Cereal Chemists and American Association of Cereal Chemists. Approved Methods Committee, 1995). After initial trials, 8% w/w was selected as the starch concentration in the raw (unheated) gel mixtures, based on the dry weight of the starch. The mean weight of wheat starch (n=109) added to a single 100 gram batch of raw gel mix was 9.14 grams (SD 0.01).

5.2.1.3. Gel whitening

Although visually white, starch gels are also translucent. The model substrate needed to be white and *opaque*, in order to represent a close approximation to a non-coloured, non-textured

surface to which primary dye blends can be added to derive a 'standard' colour gamut. Titanium dioxide pigment (TiO₂), anatase crystal type (No. 03970, Sensient Colors Inc., St. Louis, USA), with at least 99% purity, and 90% of particles less than 1.70 microns in size (manufacturer's analysis), was added to the gel to achieve this effect. It is permitted in processed foods in accordance with Good Manufacturing Practice in New Zealand and Australia (Australia New Zealand Food Authority., 2000), but restricted to 1% by weight of the finished food in the USA (Sensient Colors Inc., 2008).

The selection of a suitable TiO₂ concentration for the gel was based on visual assessment and colour measurement; of gel samples ranging in TiO₂ concentration from 0.1% to 0.5% w/w raw gel, the sample containing 0.5% w/w raw gel was visibly the most white and most opaque, and reflected the most light at all wavelengths, ranging from 89% to 94% reflectance between 400 nm and 740 nm (Figure 5.1). Reflectance of gels was measured as described below, Section 5.2.2. The TiO₂ levels used in the concentration series were within existing restrictions, and within range of those used in studies investigating the use of TiO₂ as a whitener in other food gels (Hsu and Chiang, 2002; Benjakul *et al.*, 2004). In these studies, TiO₂ was shown to be an effective whitener when used in surimi at concentrations up to 0.8% w/w, without affecting gel texture, for a gel moisture content of around 80% (which is within range of the moisture content of the starch gels used in the present study, of close to 90%).

Based on these results, TiO₂ was added to raw gel mix at 0.5% w/w, on a wet basis, with the resulting cooked gel referred to as the 'White' gel, or substrate. The mean weight of TiO₂ (n=103) added to a single 100 gram batch of raw gel mix was 0.50 grams (SD 0.001).

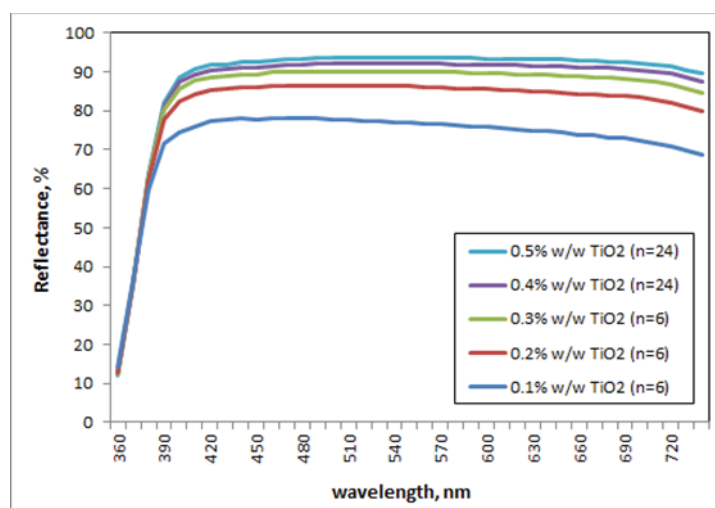


Figure 5.1 Mean measured reflectance of cooked wheat starch gels (8% w/w starch in raw gel mix), containing titanium dioxide, TiO₂, added to raw gel mix at concentrations ranging from 0.1% w/w to 0.5% w/w.

5.2.1.4. Gel browning

Chocolate Brown HT powder ('Brown HT'), minimum pure dye content 70% (Cathay Industries, Sydney, Australia), was used for artificial browning of the starch-TiO₂ gel. Brown HT was prepared as a liquid concentrate (2.5% w/w in RO water) and added at 2.5, 5.0 and 10.0 mg/100 g raw gel mix to three create variants of the gel which differed only in their degree of browning, denoted 'Brown1', 'Brown2' and 'Brown3' respectively.

The selection of brown dye levels was also based on visual assessment of the finished gels; browned gels needed to be visibly different to the white gel and to each other, and to become obviously darker with increasing level of brown dye. The level of browning also needed to be relevant to a (printed) food context. While it was not the aim here to match exactly the colour of the microwave cake using the combination of the whitened gel and brown dye, the cake was found to be similar to the computed Brown3 substrate colour in lightness and chroma (see Appendix Table 5.5).

5.2.1.5. Primary dyes

Brilliant Blue, Ponceau 4R and Tartrazine were again used as the primary colorants. Brilliant Blue (denoted 'B') and Tartrazine (yellow) ('T') granules, minimum pure dye content 85% (Cathay Industries, Sydney, Australia), and Ponceau 4R (red) powder ('P'), minimum pure dye

content 85% (Vidhi Dyestuffs, India), were used to prepare liquid dye concentrates (2.5% w/w) in reverse osmosis (RO) water.

5.2.1.6. Sample weight loss after cooking

For practical reasons weight loss measurements were approximated, based on additional bulk samples ($n=13$, including four samples from the trials to determine the TiO_2 level for the White gel, Section 5.2.1.3), single replicates of which were prepared on different days. These were samples containing starch (9.13 grams, SD 0.009), TiO_2 (0.5 grams, SD 0.001), and water, mixed and heated together for 15 minutes, as for normal gel preparation. After heating, the beaker was removed from the water bath, the foil cover removed, and the sample left to cool completely to room temperature. Weight loss was determined as the difference in the weight of the sample (which included the beaker) before heating, and after cooling.

Mean weight loss of the *bulk* cooked sample ($n=13$) was 5.39% (SD 0.42), giving a mean final sample weight of 94.79 grams (SD 0.47). On this basis, dye levels in the *individual* cooked gel samples should have remained at or within the legal maximum. At the maximum level of dye addition, 27.5 mg of dye to 100g of raw gel mix, the final dye content of the cooked gel should have been at the maximum allowable concentration of 290.1 mg/kg, assuming that the dye had remained stable during cooking.

5.2.2. Colour measurement

The reflectance, R_λ , and $L^*_{10}a^*_{10}b^*_{10}$ of cooked gels were measured as reported in Chapter Four, for the D65 standard illuminant and 10 degree standard observer. Therefore the colour gamut boundaries computed in this, and in the following, chapters are specific to these measurement conditions, but for convenience they will be referred to often as simply as the ‘gamut boundary(ies)’. Measurements were made with the specular component included (SCI) only and made directly on the cast surface of the gels, with the sample still in the mould, which was held against the measurement port when the spectrophotometer was laid on its side.

Keeping the samples in the mould provided additional rigidity to the gels to prevent distortion of the surface while the gels were handheld for measurement.

Gel preparation yielded two samples (of the same dye blend x concentration combination) for every 100 grams of raw mix. Three measurements were made of each sample. The two samples equated to one replicate measurement, which was the mean of the six individual measurements. Typically each replicate (for a given dye blend x concentration combination) was prepared and measured on a different day to the other replicates. The exceptions to this were the TiO₂ samples in the concentration series used to determine the TiO₂ level for the White gel; for each TiO₂ level, individual measurements from all samples from different days were pooled together to calculate mean R_{λ} and $L^*_{10}a^*_{10}b^*_{10}$.

The numbers of replicate samples prepared for each dye blend x concentration combination is given in the following sections.

5.3. Development and validation of dye blending models

5.3.1. Derivation of dye unit absorption coefficients and substrate absorption coefficients

5.3.1.1. Methods

Kubelka-Munk unit absorption coefficients for Brilliant Blue, Ponceau 4R and Tartrazine in the White gel substrate were derived using the method reported previously in Chapter Four, with the following changes:

- a) Each dye was added separately to the White gel at 0, and at 5.0, 12.5, 20.0, and 27.5 mg/100g (denoted 'Blank', and levels '1', '2', '3', and '4' respectively) prior to heating, to provide a more even spacing between concentration levels, in place of the doubling concentration series used for the cakes in Chapter Four;

- b) Each dye was also added separately to the Brown1 and Brown3 substrates in an abridged concentration series of 0, and 12.5 and 27.5 mg/100 g raw gel mix (levels ‘2’ and ‘4’ respectively); Brown1 and Brown3 (and not Brown2) were selected for derivation of $\left(\frac{k}{s}\right)_{\lambda,dye}$, as they represented the ‘extremes’ of browning in this study;
- c) Unit absorption coefficients for the dyes, $\left(\frac{k}{s}\right)_{\lambda,dye}$, and absorption coefficients for the substrates, $\left(\frac{K}{S}\right)_{\lambda,substrate}$, were calculated from internal reflectance, $R_{\lambda,i}$, of the gels, that is, reflectance measured with the specular component included, SCI, corrected for surface losses (see Equation 4.9, from Chapter Four). Previously, in Chapter Four, absorption coefficients were calculated directly from reflectance of the cake samples measured with the specular component excluded (SCE), as an approximation. However, because the gel surface visually had more gloss than the cake surface, it was expected that front surface reflections would have a greater contribution to the measured reflectance of the gels.

Two replicate measurements of reflectance were made of each dye x level combination (for example, of B1, B2, B3 and B4), in each substrate. For each substrate (White or Brown), a separate spectrum of $\left(\frac{k}{s}\right)_{\lambda,dye}$ for each dye (e. g. for Brilliant Blue, ‘B’) was derived for each replicate. The final $\left(\frac{k}{s}\right)_{\lambda,dye}$ spectrum for each dye (in each substrate) was the mean of the replicate spectra.

For the un-dyed White substrate itself (the ‘Blank’), the total number of gels prepared was more than the number of samples for any given dye x concentration combination, with the former having been prepared on each day that the dyed samples were prepared. Blank samples were divided into two groups according to whether the date of preparation corresponded to the dates for the first or second replicates of the dyed samples. The pooled mean reflectance measurements for each group were used to calculate two replicate $\left(\frac{K}{S}\right)_{\lambda,substrate}$ spectra, and in

turn, a grand mean $\left(\frac{K}{S}\right)_{\lambda, \text{substrate}}$ spectrum for the White gel. Two replicate measurements were made of each Brown substrate, and the data handled in the same way as for the dyed samples described above.

5.3.1.2. Results

Figure 5.2 shows the replicate plots of absorption against dye concentration at the wavelength of maximum absorbance, λ_{max} , for the Brilliant Blue, Ponceau 4R and Tartrazine dyes in the White gel substrate. These give a good indication of a linear relationship between absorption and dye concentration for each dye, and are being used to represent the same findings at each wavelength.

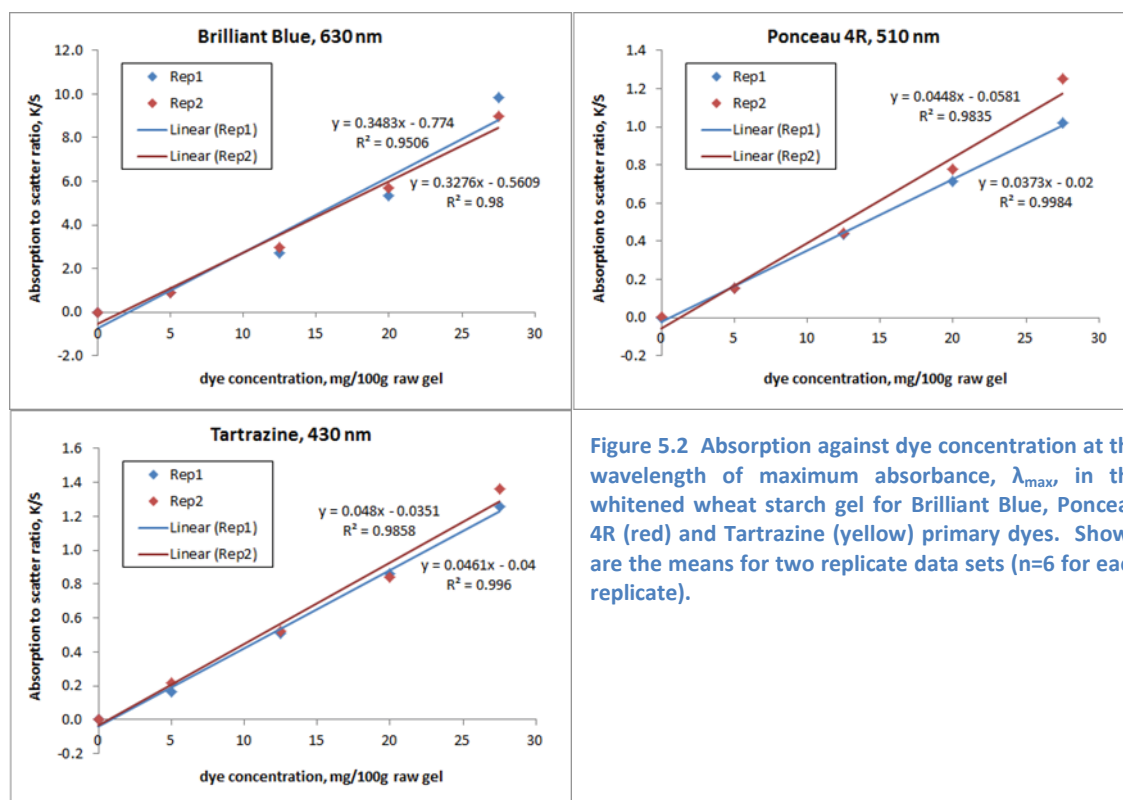


Figure 5.2 Absorption against dye concentration at the wavelength of maximum absorbance, λ_{max} , in the whitened wheat starch gel for Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) primary dyes. Shown are the means for two replicate data sets ($n=6$ for each replicate).

The relationship between absorption and concentration was also found to be linear at λ_{max} for the dyes in the Brown1 and Brown3 substrates (Appendix Figure 5.10 and Figure 5.11). Brown1 and Brown3 were selected for the additional derivation of $\left(\frac{k}{s}\right)_{\lambda, \text{dye}}$, as they represented the ‘extremes’ of browning in this study.

Figure 5.3 shows the full spectra of White gel-derived linear unit absorption coefficients for each of the dyes, and for each dye, overlaid unit absorption spectra derived from the White, Brown1 and Brown3 substrates. The absorption spectra for the un-dyed White, Brown1, and Brown3 gel substrates, as well as the spectrum for the Brown2 substrate are shown in Figure 5.4. Dye absorption is seen to occur at a much smaller scale in the gels than was observed for the cakes (Figure 4.4, Chapter Four), despite the effects of the substrate itself having been subtracted. As well as being due to darker samples, higher absorbance readings can result from more light being lost from samples during colour measurement (Negueruela, 2010). This may have been the case for the cake samples, which were more porous than the gels. Sample presentation itself was also not standardised for the different substrates.

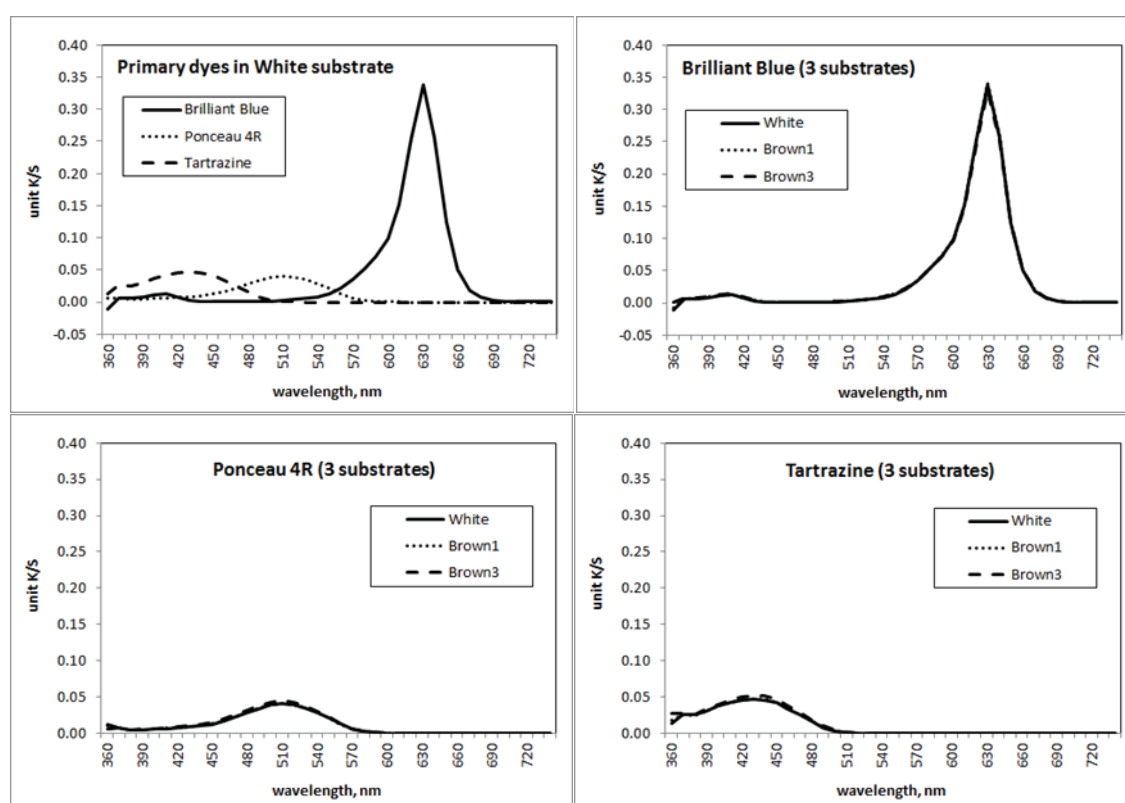


Figure 5.3 The mean unit absorption spectra (of n=2 replicates) for Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) primary dyes in the whitened wheat starch gel ('White' substrate) (top left), and the mean unit absorption spectra for the dyes derived from the White substrate and from its artificially-browned counterparts Brown1 and Brown3, superimposed in a single plot for each dye.

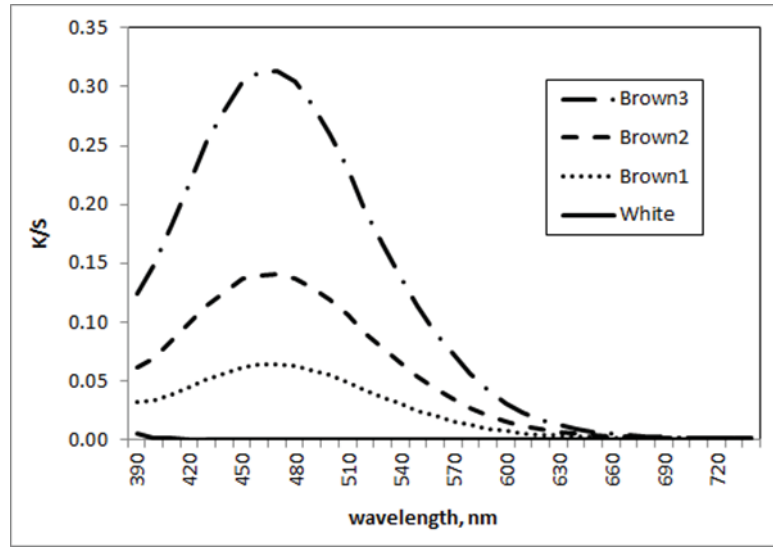


Figure 5.4 Absorption spectra for the 'White', 'Brown1', 'Brown2' and 'Brown3' gel substrates without added primary dyes. Brown1, Brown2 and Brown3 are each the same gel as the White substrate, but contain added Brown HT dye at 2.5, 5.0 and 10.0 mg/100 g raw gel respectively.

5.3.2. Validation of dye unit absorption coefficients (1)

5.3.2.1. Methods

Computed (predicted) $L^*_{10}a^*_{10}b^*_{10}$ colours from selected dye blends were compared with the measured (actual) colours of samples prepared using the same blends, to validate the derived unit absorption coefficients of the dyes. Two-dye blends were a 50:50 blend, and three-dye blends a 1:1:1 blend. Totals for the blends were either 12.5 mg/100 g raw gel (denoted 'low'), or 27.5 mg/100g raw gel (denoted 'high'). The dye blends that were used to validate the Brown gel-derived $\left(\frac{k}{s}\right)_{\lambda, dye}$ were a subset of the ones used to validate the White gel-derived $\left(\frac{k}{s}\right)_{\lambda, dye}$.

To compute $L^*_{10}a^*_{10}b^*_{10}$ values, dye concentrations from the blends were substituted into the Kubelka-Munk blending model together with grand mean $\left(\frac{K}{S}\right)_{\lambda, substrate}$ and derived $\left(\frac{k}{s}\right)_{\lambda, dye}$ from the White, Brown1 and Brown3 substrates as appropriate. Computed $\left(\frac{K}{S}\right)_{\lambda, blend}$ was converted to computed *internal* reflectance, $R_{\lambda, i}$, before being converted to computed *measured* reflectance, $R_{\lambda, m}$, and then to X_{10} , Y_{10} , Z_{10} , rather than being converted directly to $R_{\lambda, m}$ as

previously for the computation of $L^*_{10}a^*_{10}b^*_{10}$ cake colours. Measured $L^*_{10}a^*_{10}b^*_{10}$ of samples were compared with computed $L^*_{10}a^*_{10}b^*_{10}$ by use of $\Delta E^*_{ab,10}$.

For further validation of a linear, additive dye blending model based on $\left(\frac{k}{s}\right)_{\lambda,dye}$, the model can be used to compute the colours of samples containing single dyes at concentrations that were not part of the series for the derivation of $\left(\frac{k}{s}\right)_{\lambda,dye}$ (Butts, 2010). In the present study colours were computed and measured for additional White gel samples containing single dyes at concentrations intermediate to the ones used in the original series. In these samples dyes were added at 8.75 mg/100g raw gel (denoted ‘1.5’) and 23.75 mg/100g raw gel (denoted ‘3.5’).

A full list of the blends used for validation is given in Table 5.2.

5.3.2.2. Results

Table 5.2 shows the $\Delta E^*_{ab,10}$ differences between the computed (predicted) and measured (actual) $L^*_{10}a^*_{10}b^*_{10}$ colours for selected dye blends and for additional single dye concentrations in the White substrate, and also shows the equivalent differences for a subset of these dye blends in the Brown1 and Brown3 substrates. For all blends in all substrates the measured values were compared to the computed values which were based on the mean unit absorption spectrum for each dye, as well as to computed values based on each of the two replicate unit absorption spectra from which each mean spectrum was derived. Unit absorption spectra that were used to compute $L^*_{10}a^*_{10}b^*_{10}$ colours for a given gel substrate were the ones that had been derived in that same substrate.

In the previous chapter a $\Delta E^*_{ab,10}$ of three units or less was used to indicate the validity of the spectral unit absorption coefficients, and of the dye blending model. For the White gel samples containing the additional single dye concentrations, which were intermediate to the ones used in the original series used to derive the unit absorption spectra, *mean* unit absorption coefficients and the blending model were able to predict the measured colours to within three $\Delta E^*_{ab,10}$ units, providing one form of validation (Butts, 2010). For some of the blends in each substrate,

$\Delta E^*_{ab,10}$ exceeded three units, when predictions were based on mean unit absorption values. The values for $\Delta E^*_{ab,10}$ when predictions were based on unit absorption values from individual replicates suggest some effect of variability; for the three-dye blends ('BPT high' and 'BPT low') in the White gel, $\Delta E^*_{ab,10}$ was within three units when using data from replicate #2, but exceeded three units when using data from replicate #1 and mean data. Also, because $\left(\frac{k}{s}\right)_{\lambda,dye}$ is taken as the slope of the line in plots of $\left(\frac{K}{S}\right)_{\lambda,dye}$ against dye concentration, the intercept, at zero dye concentration, might not necessarily correspond to the $\left(\frac{K}{S}\right)_{\lambda,substrate}$ value for the undyed substrate at that wavelength. The effects of this discrepancy would become apparent when the derived unit absorption values for the dyes are used in the predictive colour blending model, but added to the correct $\left(\frac{K}{S}\right)_{\lambda,substrate}$ for that wavelength.

Table 5.2 $\Delta E^*_{ab,10}$ differences between $L^*_{10a^*10b^*10}$ gel colours computed using the Kubelka-Munk blending model from additional single dye levels added to the White gel substrate and from selected dye blends added to the White, Brown1 and Brown3 substrates, and the measured colours of the gels prepared using the same single dyes and dye blends. Colours were computed using mean unit absorption spectra for each dye ('Mean'), or the individual replicate unit absorption spectra ('rep #1' and 'rep #2').

Single dyes				Blends											
White substrate				White substrate				Brown1 substrate				Brown3 substrate			
$\Delta E^*_{ab,10}$				$\Delta E^*_{ab,10}$				$\Delta E^*_{ab,10}$				$\Delta E^*_{ab,10}$			
	Mean	rep #1	rep #2		Mean	rep #1	rep #2		Mean	rep #1	rep #2		Mean	rep #1	rep #2
B 1.5	3.3	3.4	3.2	BP high	1.5	2.5	1.5		1.9	1.9	1.9		2.0	1.8	2.1
B 3.5	0.6	0.6	0.6	BP low	3.2	3.9	2.8								
P 1.5	2.3	1.6	3.2	BT high	3.1	3.0	3.3								
P 3.5	0.7	0.9	1.7	BT low	5.0	4.9	5.1		4.8	4.8	4.8		4.6	4.3	4.9
T 1.5	3.1	2.5	3.8	PT high	1.5	0.6	2.5		0.8	0.7	0.9		0.4	0.4	0.5
T 3.5	1.2	0.5	2.6	PT low	2.4	1.5	3.3								
				BPT high	3.7	4.7	3.1								
				BPT low	3.8	4.6	3.2		4.7	4.7	4.7		4.6	4.3	4.8

Key to labels: 'B' = Brilliant Blue, 'P' = Ponceau 4R, 'T' = Tartrazine, '1.5' = 8.75 mg/100 g raw gel, '3.5' = 23.75 mg/100 g raw gel, 'high' = combined dye total of 27.5 mg/100 g raw gel, 'low' = combined dye total of 12.5 mg/100 g raw gel. Dyes in the blends contributed an equal amount.

Based on the $\Delta E^*_{ab,10}$ values, the linear blending model appears to be less effective in predicting the $L^*_{10}a^*_{10}b^*_{10}$ colours from some dye blends, across the White and Brown substrates. $\Delta E^*_{ab,10}$ exceeded three units (ranging from four to five units), when the blue and yellow dyes, with or without the red dye, were blended in equal amounts to the lower combined total dye level. This is a significant result because this was found for both the White and Brown substrates even though $\left(\frac{k}{s}\right)_{\lambda,dye}$ for each dye was derived separately in each. Interestingly, the blue-yellow combination at the lowest combined total dye level also had the highest $\Delta E^*_{ab,10}$ between the computed and measured colours (though this was still within three units, at 2.9) in Chapter Four where $\left(\frac{k}{s}\right)_{\lambda,dye}$ was derived for the same dyes in the cake substrate.

As discussed previously in Chapter Four, $\Delta E^*_{ab,10}$ is better expressed as separate chroma, lightness and hue differences because $\Delta E^*_{ab,10}$ by itself does not indicate which of these individual differences contributes most to the overall difference. The magnitude of these differences, and their implications for gamut boundary computation, are discussed later in Section 5.5.1.

5.3.3. Validation of dye unit absorption coefficients (2): Comparison of dye unit absorption spectra derived from the different substrates

5.3.3.1. Methods

The second type of validation of $\left(\frac{k}{s}\right)_{\lambda,dye}$ sought to confirm whether or not for each dye, its unit absorption spectrum was (largely) unchanged across White and Brown substrates. If this were shown to be the case, then the impact of browning on colour gamuts could be determined by computing the new colours using only the absorption spectra of the Brown substrates as new information, without having again to derive dye unit absorption spectra in the Brown substrates. (Or in other words, that the unit absorption spectra of the dyes are interchangeable.)

$L^*_{10}a^*_{10}b^*_{10}$ colours of dyed Brown1 and Brown3 gels were computed using the $\left(\frac{K}{S}\right)_{\lambda,substrate}$ of the Brown gels and the $\left(\frac{k}{s}\right)_{\lambda,dye}$ for the primary dyes that were derived from the *White* gels, and compared with those previously computed using the $\left(\frac{K}{S}\right)_{\lambda,substrate}$ of the Brown gels and the $\left(\frac{k}{s}\right)_{\lambda,dye}$ for the dyes that were derived from the *Brown* gels as described in Section 5.3.2 above, for the same dye blends. New predictions were not compared with any measured colours.

5.3.3.2. Results

Ideally, the colour gamut that results from the browning of the *White* gel (containing blends of primary dyes) could be computed quickly using the absorption spectrum for the browned version of the *White* gel (not containing primary dyes) as the only new information. For this to be possible, the spectrum of unit absorption coefficients for each dye will need to be the same whether they are derived from the *White* substrate or from the *Brown* substrates. Therefore computation of the new gamut would require only the substitution of the spectrum of the *Brown* substrate for that of the *White* substrate in the blending model, while retaining the *White* gel-derived unit absorption coefficients for the dyes. Figure 5.3 shows, for each dye, the unit absorption spectra derived in the *White*, *Brown1* and *Brown3* substrates. A very small increase is seen in the $\left(\frac{k}{s}\right)_{\lambda,dye}$ values for Ponceau 4R and Tartrazine in the *Brown3* substrate, relative to the values for the *White* and *Brown1* substrates which appear not to be different from each other. Table 5.3 compares the predictions of gel substrate colour made using $\left(\frac{K}{S}\right)_{\lambda,substrate}$ for the *Brown* gels added to the *Brown* gel-derived $\left(\frac{k}{s}\right)_{\lambda,dye}$, with those made using $\left(\frac{K}{S}\right)_{\lambda,substrate}$ for the *Brown* gels added to the *White* gel-derived $\left(\frac{k}{s}\right)_{\lambda,dye}$, when applied to the same blends. The two groups of computed $L^*_{10}a^*_{10}b^*_{10}$ colours are well within three $\Delta E^*_{ab,10}$ units of each other. These findings imply that in going from the *White* to *Brown* gamuts, the

only step that is required is substitution of the Brown substrate for the White in the blending model.

Table 5.3. ΔE^*_{ab} differences between $L^*_{10}a^*_{10}b^*_{10}$ colours computed using Brown gel substrate absorption spectra and Brown gel-derived unit absorption spectra for the three dyes, and those computed using Brown gel substrate absorption spectra and White gel-derived dye unit absorption spectra.

Blend	Substrate	Gel colour computed using substrate and dye spectra from Brown gels (1)			Gel colour computed using substrate spectra from Brown gels and dye spectra from White gel (2)			$\Delta E^*_{ab,10}$ for the difference between (1) and (2)
		L^*_{10}	a^*_{10}	b^*_{10}	L^*_{10}	a^*_{10}	b^*_{10}	
BP high	Brown1	55	-5	17	55	-5	-17	0.7
	Brown3	53	-5	-8	53	-6	-9	1.1
BT low	Brown1	70	-32	7	70	-32	7	0.8
	Brown3	63	-19	9	64	-20	9	0.8
PT high	Brown1	72	32	32	72	32	31	0.3
	Brown3	68	30	31	68	30	30	1.2
BPT low	Brown1	66	-12	2	67	-12	2	0.3
	Brown3	62	-7	7	63	-7	7	0.9

5.4. Colour gamut boundary computation

5.4.1. Colour gamut boundary for the ‘White’ gel containing primary dye blends

Having validated the unit absorption coefficients for the primary dyes that were derived in the White gel substrate, the Kubelka-Munk blending model (Equation 4.10, from Chapter Four) was used to compute individual $L^*_{10}a^*_{10}b^*_{10}$ gamut boundary colours for the White gel containing added primary dyes and dye blends:

$$\left(\frac{K}{S}\right)_{\lambda,blend} = \left(\frac{K}{S}\right)_{\lambda,substrate} + c_1 \left(\frac{k}{s}\right)_{\lambda,1} + c_2 \left(\frac{k}{s}\right)_{\lambda,2} + c_3 \left(\frac{k}{s}\right)_{\lambda,3}$$

For each blend, the absorption values for the un-dyed White gel substrate, $\left(\frac{K}{S}\right)_{\lambda,substrate}$ and the White gel-derived unit absorption coefficients for each dye, $\left(\frac{k}{s}\right)_{\lambda,n}$, at wavelength λ , together with dye concentrations, c_n , were substituted into the equation to compute a spectrum for the

blend. Colours were computed first from single dyes, then from two-dye blends, and lastly from three-dye blends, as explained in the following sections.

5.4.1.1. Computed $L^*_{10}a^*_{10}b^*_{10}$ colours from single dyes:

For each of Brilliant Blue ('B'), Ponceau 4R ('P'), and Tartrazine ('T'), a series of colours was computed for concentrations ranging from 0 mg/100 g raw gel, to 27.5 mg/100g of raw gel. The concentrations were selected to ensure a $\Delta E^*_{ab,10}$ difference of three units between the colours in the series for each dye. The maximum concentration was chosen to keep the concentration of dye in the finished gels to within the legal limit, allowing for weight losses after cooking.

5.4.1.2. Computed $L^*_{10}a^*_{10}b^*_{10}$ colours from two-dye blends:

The two-dye blends were the combinations of Brilliant Blue and Tartrazine ('BT'), Brilliant Blue and Ponceau 4R ('BP'), and Ponceau 4R and Tartrazine ('PT'). For each blend, multiple series of colours were computed, with the colours in each series computed for total dye concentrations ranging from 0 mg/100 g raw gel, to 27.5 mg/100g of raw gel. The multiple series for each blend differed in the relative proportions of the dyes; within a given series the same relative proportions of the dyes was applied to each total dye concentration. The relative proportions were designed by gradually decreasing the proportion of one dye in the blend from 100%, while gradually increasing the proportion of the second dye towards 100% (with 100% of either dye corresponding to the colours from the single dyes, as explained above). Again, the dye blends (including dye totals and relative dye proportions) were selected to maintain a three-unit $\Delta E^*_{ab,10}$ difference between all colours.

Following the computation of gamut boundary colours from single dyes and from two-dye blends, the boundary was starting to take shape. These colours formed a 'canopy' with the colour of the un-dyed White gel substrate (the lightest and least chromatic) at the apex. The colours from the apex to the 'rim' represent increasing total dye concentration and become

progressively higher in chroma and lower in lightness. A chromatic view of this canopy is shown in Figure 5.5.

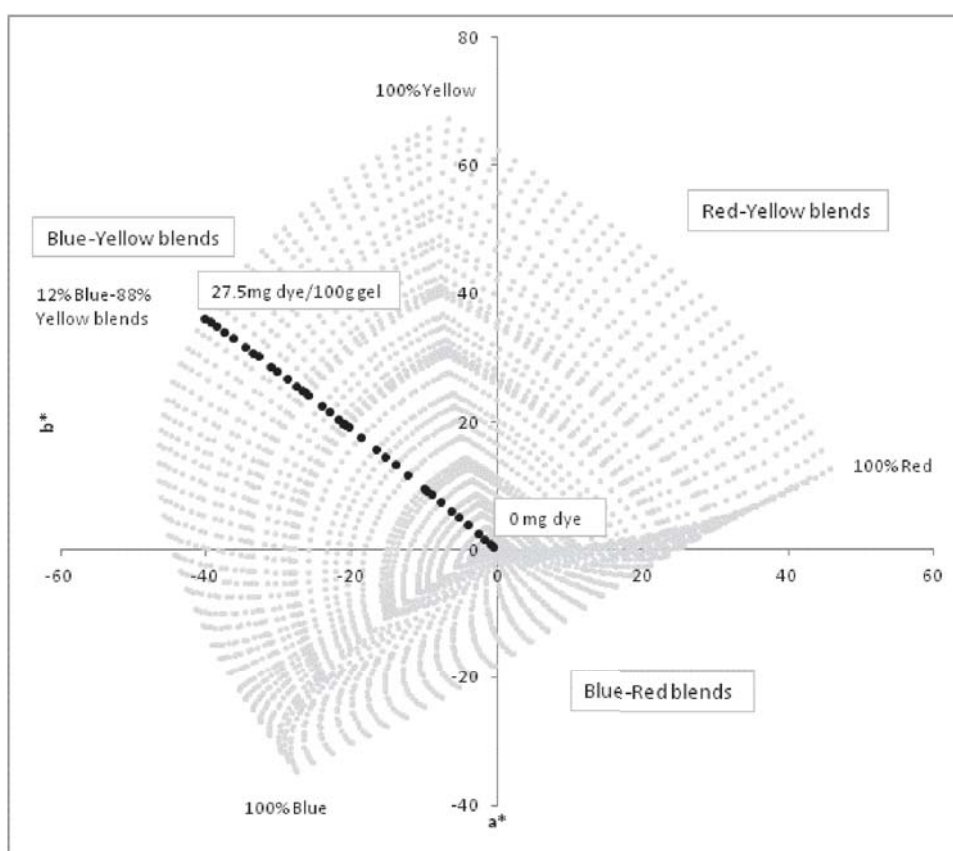


Figure 5.5. Chromatic (a^*b^*) view of individual $L^*_{10}a^*_{10}b^*_{10}$ colours computed for a whitened starch gel containing single primary dyes or two-dye blends at concentrations up to and including the maximum allowable in foods. Blends are described in the main text. As an example the series of colours computed from blending 12% blue and 88% yellow is highlighted in bold.

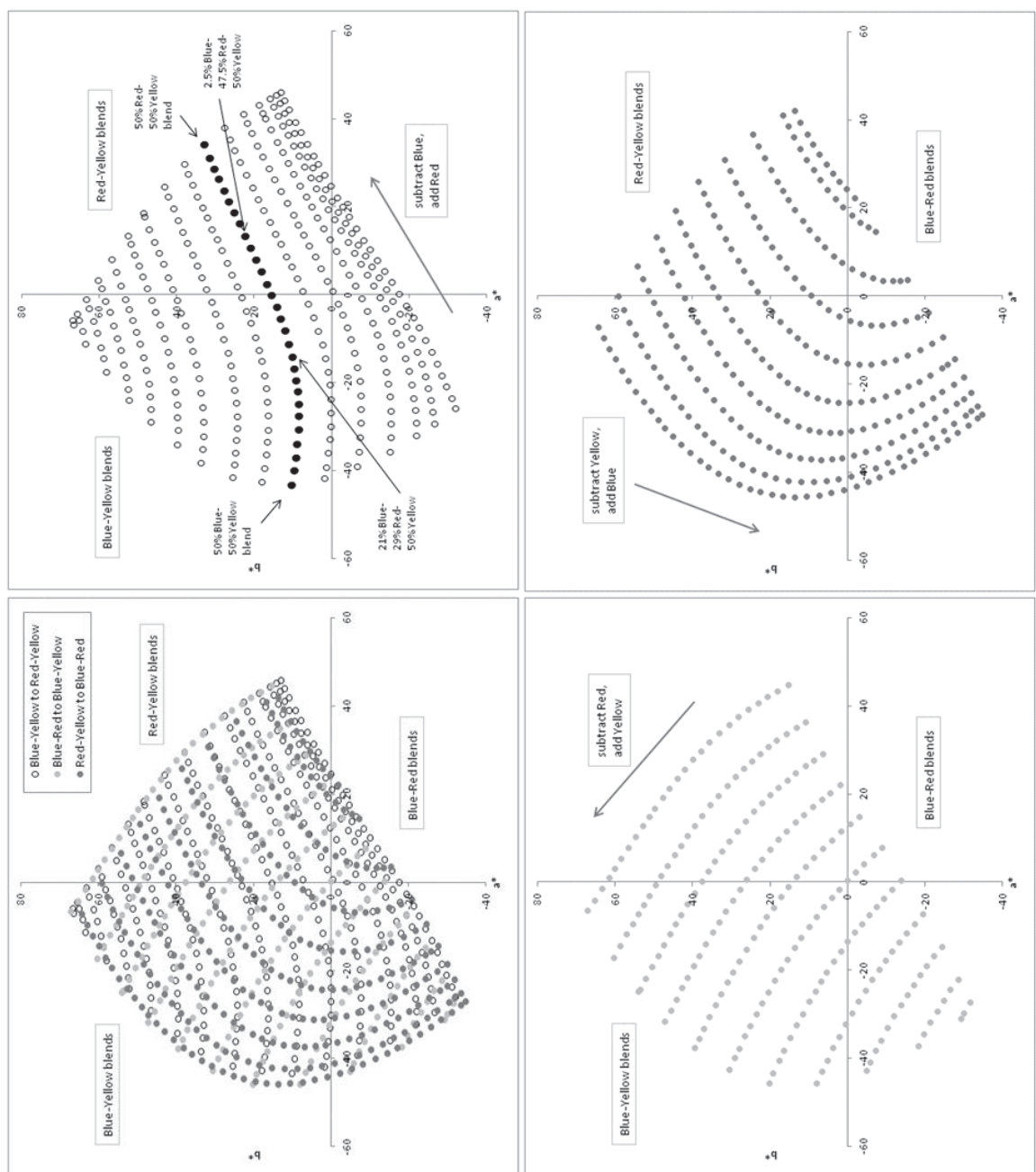
5.4.1.3. Computed $L^*_{10}a^*_{10}b^*_{10}$ colours from three-dye blends:

According to the theory of subtractive mixing, the addition of further dye to an existing blend will result in darker colours. Therefore any colours from three-dye blends that are derived from the two-dye blends should fall inside the canopy, with colours from three-dye blends containing the maximum total dye concentration forming the bottom surface of the shape. Because only boundary colours were required, colours were computed from three dye blends containing only the maximum allowable total dye concentration of 27.5 mg/100g of raw gel.

Each series of colours computed from three-dye blends was generated by starting with a two-dye blend corresponding to the maximum total dye concentration (located on the chromatic rim

of the canopy), fixing the level of one dye and progressively adding the third at the expense of the second, and finishing with a two-dye blend comprising the first and third dyes in the same proportions as the starting blend of the first and second dyes. Not every two-dye blend corresponding to a rim colour was used as a starting point; however the total number of series was divided roughly equally between BT, BP and PT as the starting two-dye combinations, and the series were roughly evenly spaced (starting with approximately every third two-dye blend on the rim). The three-unit $\Delta E^*_{ab,10}$ spacing was applied to the colours within each series, but not to the colours in adjacent series. Figure 5.6 provides an illustration of how each series of colours was generated.

Figure 5.6. Chromatic (a^*b^*) view of individual $L^*_{10}a^*_{10}b^*_{10}$ colours computed for a whitened starch gel containing three-dye primary dye blends at the maximum allowable concentration only. The full set of computed colours is at top left. In the remaining plots colours are separated into series which begin with selected blends from the two-dye combinations. Blends are described in the main text. A sample series is highlighted top right.



The establishment of the $\Delta E^*_{ab,10}$ spacing rule between computed colours, and the consequent selection of dye blends to enter into the model, resulted in the computation of 4,724 individual colours.

5.4.2. Effect of substrate browning

On the basis of ‘cross-validation’ of the spectra of unit absorption coefficients for the primary dyes in the White, Brown1 and Brown3 gel substrates (Section 5.3.3), gamut boundary colours for each of the three Brown substrates (including Brown2), each containing the same blends as the White gel, were computed by the simple substitution the absorption spectrum of the Brown gel for that of the White in the K-M blending model, while keeping dye blends and total dye concentrations the same.

$\Delta E^*_{ab,10}$ differences of three units between computed colours were retained with all levels of browning. Browning decreased the lightness and chroma ranges that were achievable in the White substrate, with the ranges decreasing with increasing level of brown dye addition to the White substrate (Figure 5.7). A type of dose response is observed in the way that the gamut ‘reacts’ to increasing levels of browning; basic shape characteristics are retained, but the magnitude of the shape changes. The largest reduction in the lightness range occurs in the higher lightness region, and is accompanied by a slight shift of the bottom surface in the direction of decreasing lightness. For chroma, the direction of shape reduction appears to follow the changing position of the substrate colour, towards the red-orange a^*b^* quadrant. The dose response-like effect is also seen in the various hue angle views of the four gamut boundaries in the next chapter.

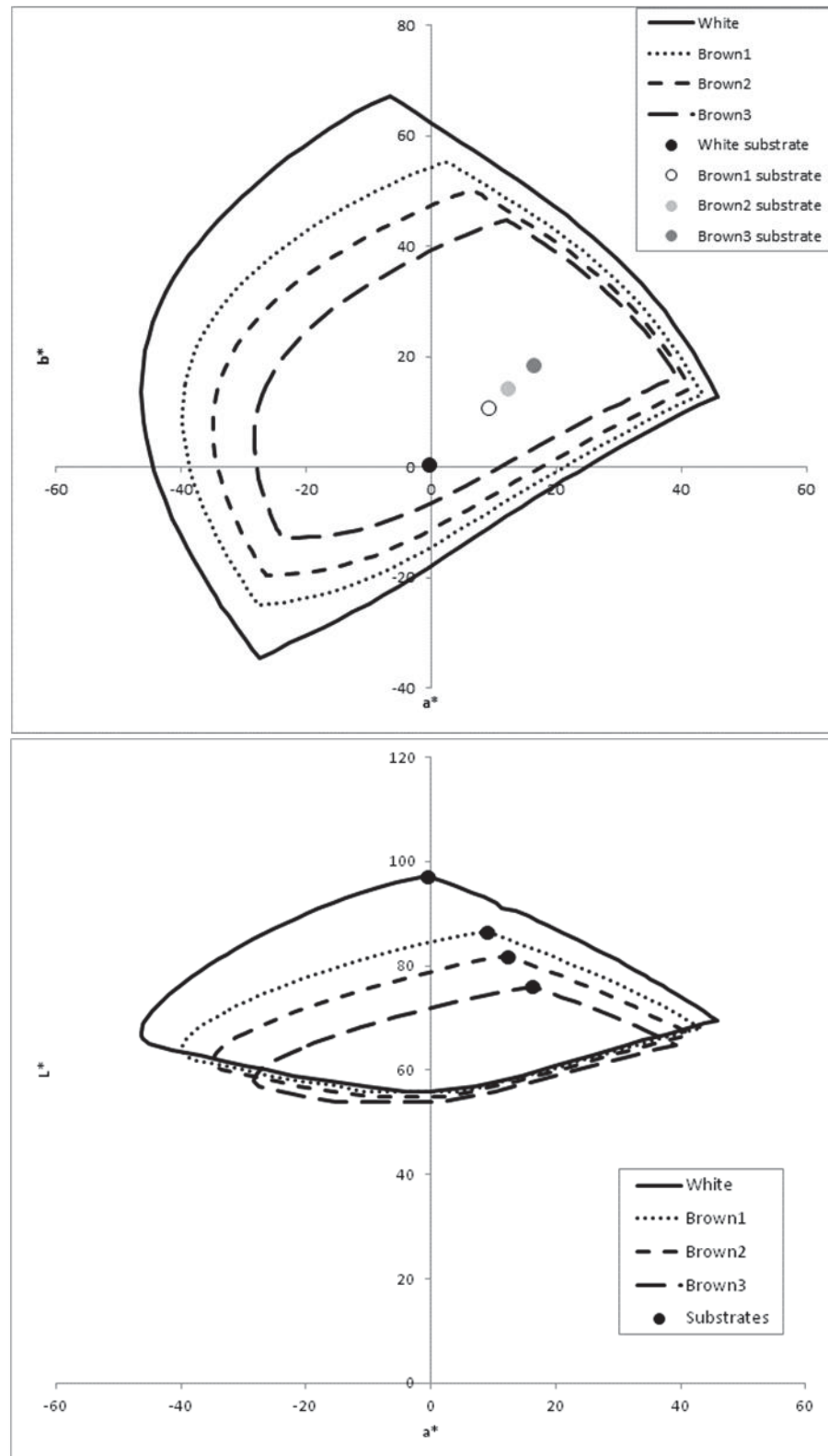


Figure 5.7 Outlines of the colour gamut boundaries computed for the four gel substrates containing the same blends of primary dyes: the whitened wheat starch gel ('White') and the same gel with increasing levels of artificial browning ('Brown1' to 'Brown3'). Also shown are the positions of the un-dyed gels. Constituent gamut boundary colours are $L^*_{10}a^*_{10}b^*_{10}$. Top: chromatic a^*b^* view. Bottom: 'frontal' a^*L^* view.

For colour gamut mapping, the implication of the reduction in gamut size is that out-of-gamut blue-green-purple-type colours will likely require mapping over longer distances than will out-of-gamut red-orange-brown colours, and that for the former colours, there might be a larger difference between the original colour and the nearest, or best possible, equivalent in the reproduction gamut. This will depend of course on the exact characteristics of the original colour, and on the rendering intent of mapping.

5.4.3. Visualisation of the gamut boundaries in colour

To visualise the gamut boundaries in colour, $L^*a^*b^*$ values were transformed to values in the sRGB colour space and plotted using MATLAB[®] software, Release 2011b (The MathWorks, Inc.). The X, Y, Z values of the reference white point (i.e. the ideal white, see Literature Review) were those specified for the D65 standard illuminant. To achieve continuous colour in the plots, marker size was increased to 10 point.

The MATLAB[®] code used to generate the colour gamut boundary plots is given in the Appendix (Section 5.7.3). A description and explanation of the commands used can be found at www.mathworks.com.

Figure 5.8 shows, in colour, the gamut boundary colours computed for the White and Brown3 gels (the lightest and darkest substrates before dye addition). Visually, the colours computed for the Brown3 gel are darker and less chromatic than those computed for the White gel. This is consistent with a reduction in the lightness and chroma ranges of the colour gamut resulting from the addition of artificial browning to the White gel.

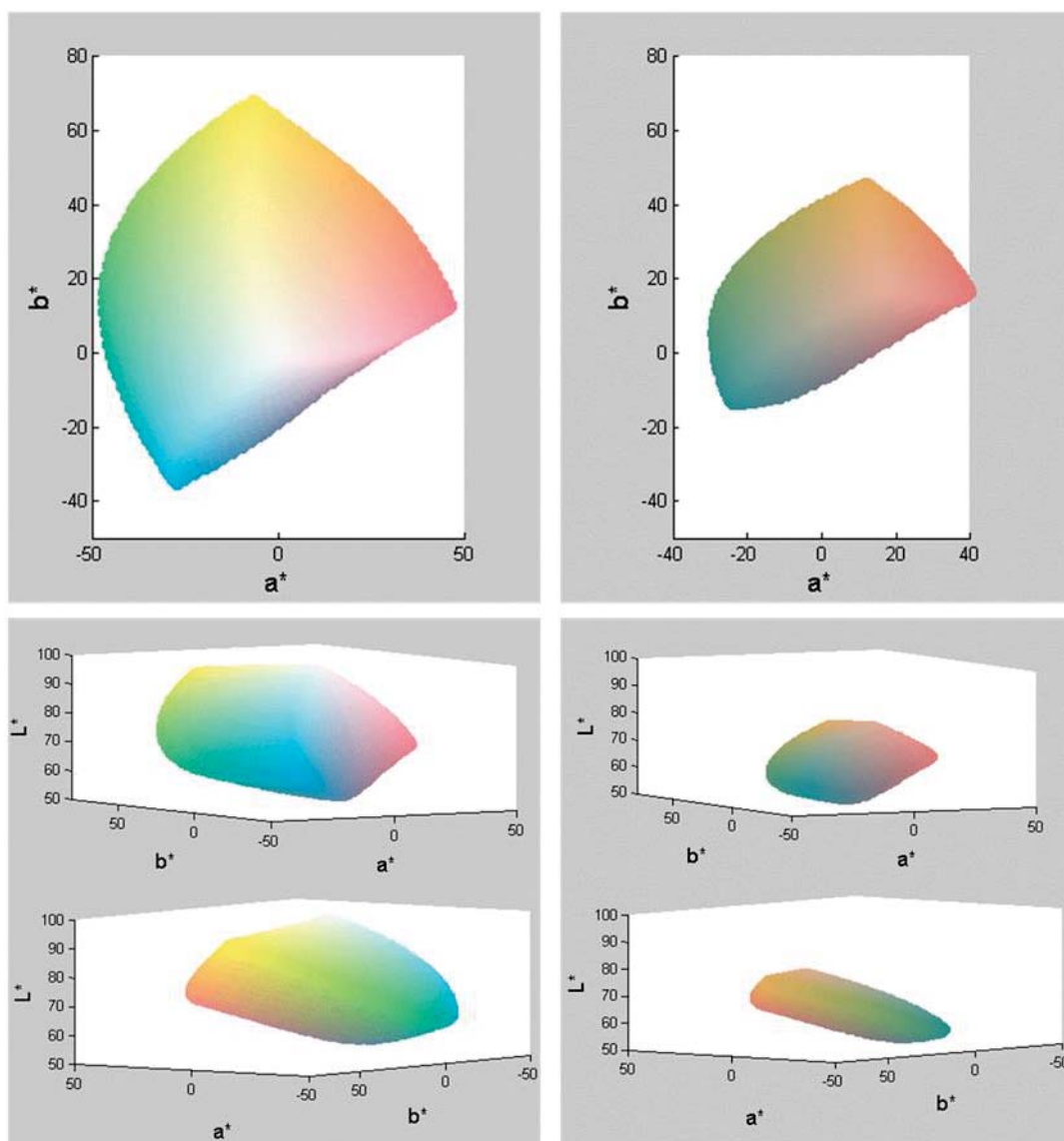


Figure 5.8 Visualisation in colour of the gamut boundary $L^*_{10}a^*_{10}b^*_{10}$ colours for the White (left) and Brown3 (right) gel substrates containing the same blends of primary dyes. Colours were transformed to sRGB values and plotted using MATLAB® R2011b (7.13.0.564). Code is given in the Appendix. Top: chromatic a^*b^* view. Bottom: three-dimensional L^* and a^*b^* view, with rotation around the L^* axis. Gamut boundary colours are specific to the D65 standard illuminant and 10 degree standard observer measurement conditions.

5.5. General Discussion

5.5.1. Strength of colour predictions and implications for gamut shape

For gamut boundary computation, examining chroma, lightness and hue differences individually, rather than collectively as $\Delta E^*_{ab,10}$, between computed (predicted) and measured (actual) colours, takes on even more importance as colour gamut mapping is performed in these dimensions. The hue differences here are the angular differences, Δh_{ab} , rather than the Euclidean distances, $\Delta H^*_{ab,10}$ that were used previously in Chapter Four, because it is hue angle that is used in gamut mapping. Overall, predictions of colour that were based on the derived dye unit absorption coefficients and the linear blending model overestimated measured chroma and underestimated measured lightness (Table 5.4). This means that the actual shape of the gamut is likely to be smaller than the one computed, needing to be ‘pulled in’ slightly in three dimensions towards the apex. The extent to which this may be necessary differs between samples containing different dye blends, which in turn corresponds to different regions of the gamut surface. For example, the largest reduction in chroma is needed for the sample containing blue and yellow dyes at the lowest combined total dye level (i.e. ‘BT low’), which also had the highest $\Delta E^*_{ab,10}$ of five units between computed and measured $L^*_{10}a^*_{10}b^*_{10}$ in all substrates. The sample containing all three primary dyes at the lowest combined total dye level (‘BPT low’), which also had an associated high $\Delta E^*_{ab,10}$, had the largest difference between computed and measured lightness in all substrates. The difference between computed and measured hue angle also varies among the samples. The differences range from zero, for the additional single dye samples in the white substrate, to 25 degrees for the ‘BPT low’ sample in Brown3. This blend also had associated with it the largest Δh_{ab} difference in Brown1, and the second to highest Δh_{ab} difference in the White substrate. The high Δh_{ab} for the ‘BPT’ low sample is a result of the point being close to the origin. In polar coordinates, when close to the origin, any small error will result in a relatively large variation in angle. A large mismatch between computed and measured hue angle is potentially more problematic than the lightness and chroma differences because many gamut mapping algorithms aim to preserve hue. The

effect of a discrepancy between computed and measured gamut boundary colours is illustrated for the White gel colour gamut, by way of example, in Figure 5.9.

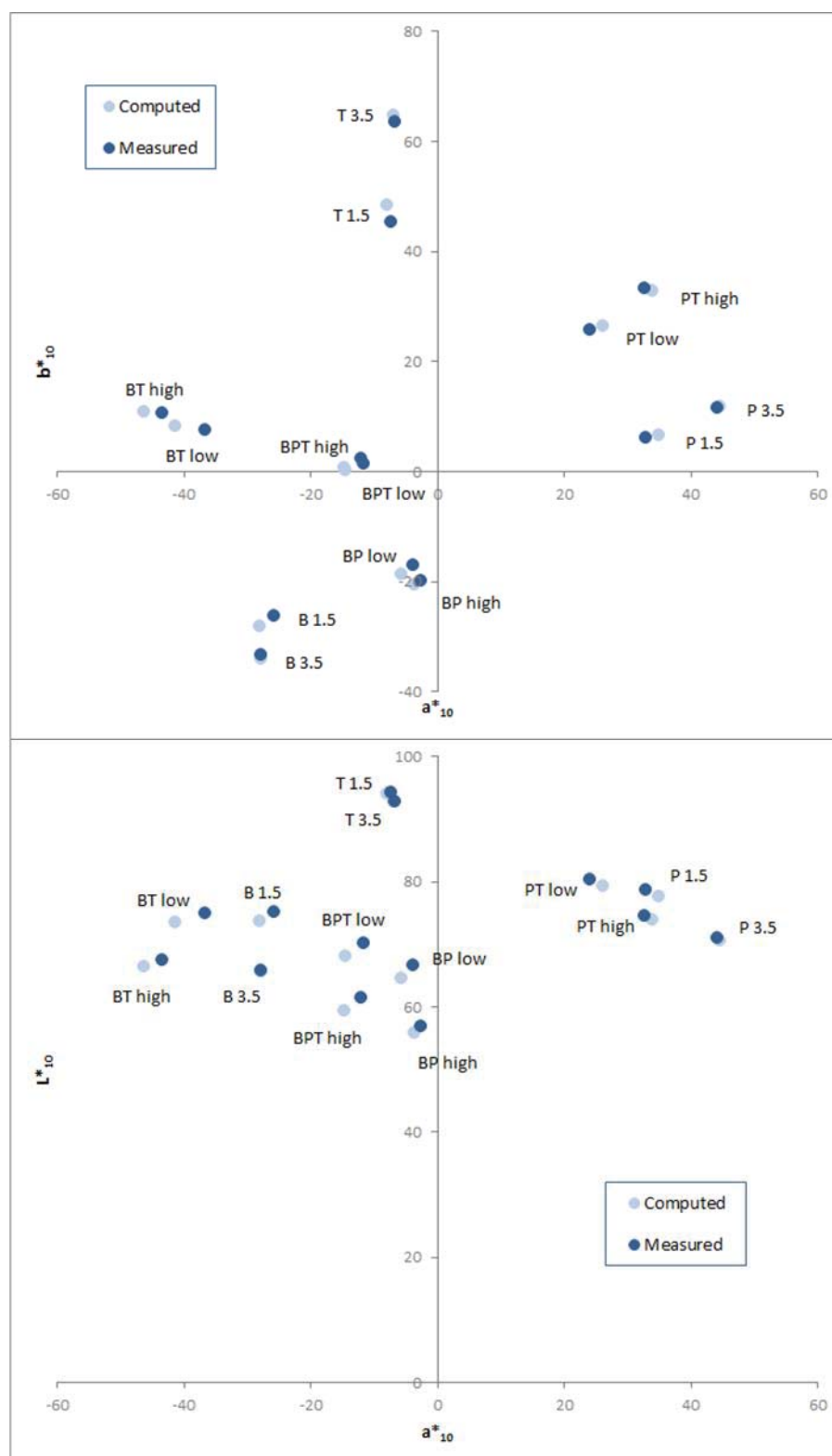


Figure 5.9 Positions in colour space of $L^*_{10}a^*_{10}b^*_{10}$ gamut boundary colours computed using the Kubelka-Munk blending model for the White gel containing selected dye blends and additional single dye levels, and those of the measured colours of the gel prepared using the same single dyes and dye blends. Top: chromatic a^*b^* view. Bottom: 'frontal' a^*L^* view.

5.5.2. Gamut boundary sampling technique: density of sampling points

For computed colours, an even sampling of the gamut surface was desired, that is, an even coverage of the gamut as well as even spacing between sampling points. The aim was to achieve a sufficiently dense sampling of the gamut to avoid false concavities, and at the same time to devise and impose a rule on the (minimum) number of points needed. The combination of the three-unit $\Delta E^*_{ab,10}$ spacing rule, and the Kubelka-Munk-based colour prediction model yielded a well-defined gamut boundary. The boundary comprised over 4,000 individual points, which is a large number compared to the number of points used to describe the gamut boundaries in other methods. In the Segment Maxima Gamut Boundary Descriptor (SMGBD) method, the gamut boundary can be comprised of hundreds, rather than thousands, of colours, depending on the number of segments chosen (Morovic and Luo, 2000), and an example of a primary data set to which the method can be applied is a colour reproduction device gamut ranging from 3,750 to 15,000 colours.

The gamut boundaries in this study could potentially have been computed from a smaller subset of points. Whereas the $\Delta E^*_{ab,10}$ spacing rule applied to each and every point in the canopy of colours from single dyes and two-dye blends, it was not applied to colours in adjacent series which formed the bottom surface, and without any apparent loss of definition. This was an attempt to avoid over-sampling of points on a surface which was already partly defined by the rim of the canopy, and in the knowledge that every point would be a bottom surface point. The SMGBD method could be used to select the points for a sub-sample. These points, in turn, will correspond to a set of dye blends which can be used to compute standard, or ‘base’ gamuts (similar to the gamut computed for the whitened starch gel) for substrates other than the gels. For the whitened gel, the gamut boundary based on the full set of points could be used to evaluate or validate the boundary that is based on any sub-set of the points.

5.6. Conclusions

Because colour gamut boundary computation in this study relied on the prediction of colours from dye blends, there was a need to know how good these predictions were of actual, measured colours. Although there were good indications of a linear relationship between absorption coefficients and concentration for each individual dye (at each wavelength), the ability of the linear, additive model to predict the actual $L^*_{10}a^*_{10}b^*_{10}$ colours appears to depend on the dye blend. In the computation of a gamut boundary comprised of colours generated by using the Kubelka-Munk model, this means that the actual size and shape of the gamut may differ slightly from the one computed. If the difference between computed and measured colours were to prove consistent for given dye blends, then the corresponding regions of the computed gamut boundary could be adjusted by a known set of ‘rules’ to give something closer to the actual shape.

The finding that the unit absorption coefficients for each dye remained largely consistent with a change in substrate colour from white and brown allowed for the effect of substrate browning, which was to decrease progressively the size of the colour gamut, to be seen quickly; all that was needed was the simple substitution of the brown for the white substrate absorption spectra in the blending model. However the possibility of dye unit absorption coefficients changing with increased browning of the (un-dyed) substrate needs further investigation, but will not be explored further in this thesis.

The well-defined colour gamut boundary that was computed using a combination of the three-unit $\Delta E^*_{ab,10}$ spacing rule, and the Kubelka-Munk-based colour prediction model provides a primary data set from which a smaller subset of sampling points could be drawn, and provides a method for the computation of colour gamut boundaries for substrates other than the dyed gels used in this study.

5.7. Appendix

5.7.1. Comparison of gel and microwave-baked cake substrate colours

without added primary dyes

Table 5.5. Computed $L^*_{10}a^*_{10}b^*_{10}$ colours, and computed chroma, $C^*_{ab,10}$, and hue angle, $h_{ab,10}$, of the four model gels used in this chapter, prior to the addition of primary dyes and their blends. For comparison the measured values of the un-dyed cake substrate from the study in the previous chapter. The results show that the computed Brown3 gel colour was found to be similar to the lightness and chroma of the cake colour (refer also Section 5.2.1.4).

Substrate	L^*_{10}	a^*_{10}	b^*_{10}	$C^*_{ab,10}$	$h_{ab,10}$
White	97.2	-0.4	0.4	0.6	135
Brown1	86.5	9.0	10.7	14.0	50
Brown2	81.8	12.3	14.3	18.8	49
Brown3	76.0	16.3	18.5	24.7	49
Cake	77.4	0.1	20.7	20.7	90

5.7.2. Unit absorption spectra at λ_{max} for each primary dye in the

Brown1 and Brown3 gel substrates

5.7.2.1. In the Brown1 gel

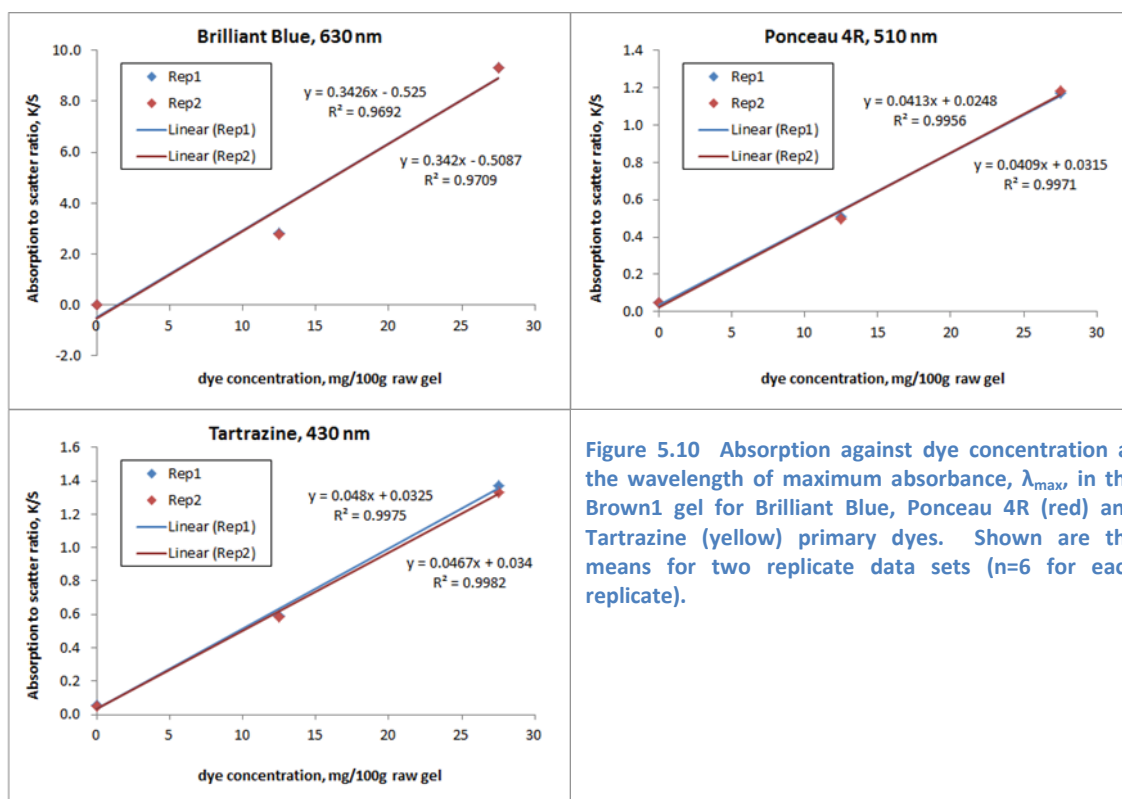


Figure 5.10 Absorption against dye concentration at the wavelength of maximum absorbance, λ_{max} , in the Brown1 gel for Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) primary dyes. Shown are the means for two replicate data sets ($n=6$ for each replicate).

5.7.2.2. In the Brown3 gel

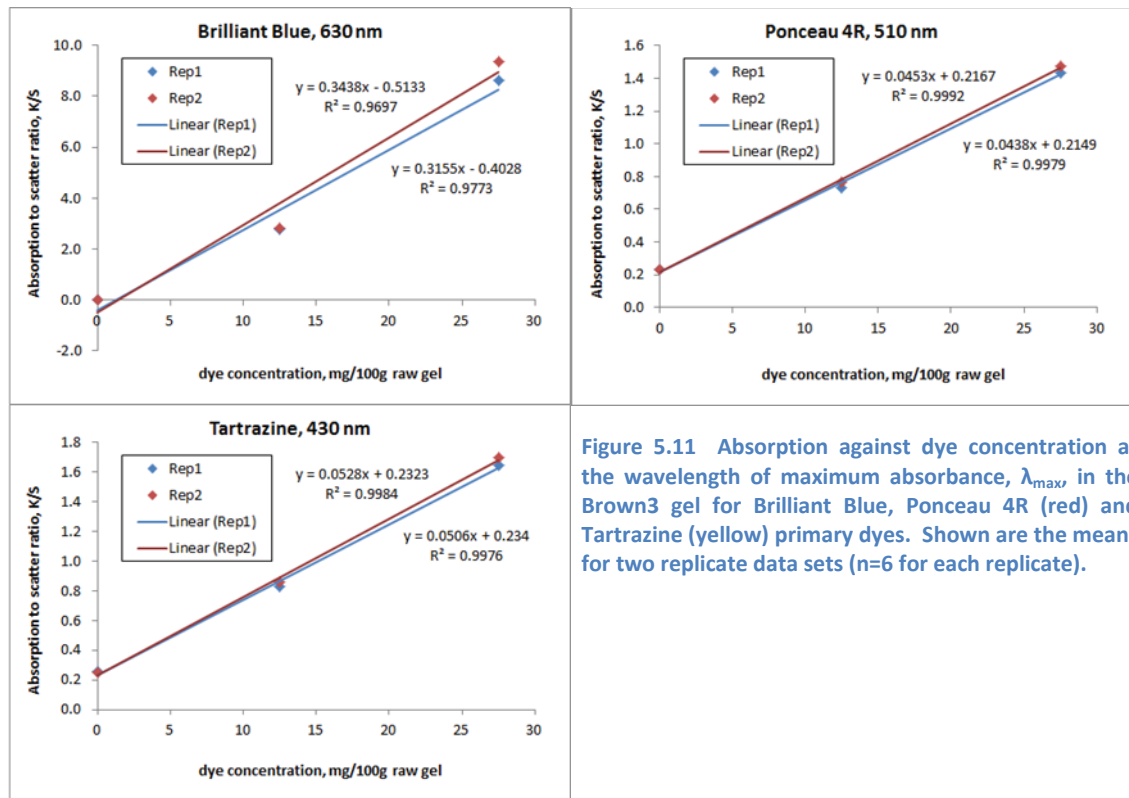


Figure 5.11 Absorption against dye concentration at the wavelength of maximum absorbance, λ_{max} , in the Brown3 gel for Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) primary dyes. Shown are the means for two replicate data sets ($n=6$ for each replicate).

5.7.3. MATLAB® code for the gamut boundary colour figures (Figure 5.8).

5.7.3.1. For the White gel:

```
clear;
close all;
clc;

data=colour_xyz_white();
x=data(:,2);
y=data(:,3);
z=data(:,1);

WP=whitepoint('d65');
lab=data;
cform=makecform('lab2srgb','AdaptedWhitePoint',WP);
srgb=applycform(lab,cform);

hold on
for i=1:4724
plot3(x(i),y(i),z(i),'o','MarkerFaceColor',srgb(i,:), 'MarkerEdgeColor',
srgb(i,:), 'MarkerSize',10)
end
hold off
xlabel('a*', 'FontSize',14);
```

```

ylabel('b*', 'FontSize',14);
zlabel('L*', 'FontSize',14);
xlim([-70,70]);
ylim([-50,80]);
zlim([50,100]);
axis equal
axis vis3d
daspect([1 1 1])

```

5.7.3.2. For the Brown3 gel:

```

clear;
close all;
clc;

data=colour_xyz_brown();
x=data(:,2);
y=data(:,3);
z=data(:,1);

WP=whitepoint('d65');
lab=data;
cform=makecform('lab2srgb','AdaptedWhitePoint',WP);
srgb=applycform(lab,cform);

hold on
for i=1:4724
plot3(x(i),y(i),z(i),'o','MarkerFaceColor',srgb(i,:),'MarkerEdgeColor',
,srgb(i,:),'MarkerSize',10)
end
hold off
xlabel('a*', 'FontSize',14);
ylabel('b*', 'FontSize',14);
zlabel('L*', 'FontSize',14);
xlim([-50,50]);
ylim([-50,80]);
zlim([50,100]);
axis equal
axis vis3d
daspect([1 1 1])

```

Chapter Six: Food coloration using colour gamut mapping

6.1. Introduction

For a novel food printing technology which aims to render complex colour images or designs in 3D within a variety of food matrices, any colour that the matrix itself has needs to be taken into consideration. For matrices modeled on baked goods, changes in formulation (made according to consumer specifications for nutritional composition, for example) might cause simultaneous changes in the lightness, yellowness and redness of crumb colour (Hicsasmaz *et al.*, 2003; Ronda *et al.*, 2005), as might thermal reactions during cooking. These will be referred to collectively as browning. In the previous chapter, the colour gamut boundary was computed for a model food substrate containing blends of primary dyes. This boundary represented the limit of the colours that could be produced using the dye blends, up to and including the maximum level permitted in foods. The model substrate, initially uncoloured, was also manipulated to display the browning characteristic, in isolation, to different degrees, to model the effects of increased browning on the boundary limits. As the level of browning in the substrate increased, the gamut decreased in both the lightness and chroma dimensions. Furthermore, the simple substitution of brown for white in the computation of individual gamut boundary colours was shown to be a quick and valid approach to computing the effects of browning.

The implication of the decrease in gamut size with substrate browning is that colours that are within the larger gamut from the white substrate, but outside the smaller gamut from the brown substrate, will not be able to be reproduced in the browned substrate. This is the type of issue that is routinely encountered, and handled, in the cross-media reproduction of colour images, as media such as computer and television screens, and print, will usually have different colour gamuts (Morovic, 2003). Colours that are within the gamut of the original medium but are outside the gamut of the reproduction medium need to be transformed into reproducible colours, in a process known as colour gamut mapping. There are two main types of mapping algorithm:

- *Clipping* algorithms transform only the out-of-gamut colours, replacing each with a colour on the boundary of the reproduction gamut. A replacement colour will have either:
 - the smallest ΔE difference between it, and the original colour, whether or not it shares the same hue angle as the original colour, or
 - is at the intersection of the reproduction gamut boundary and a vector drawn from the original colour to a nominated centre of gravity (for example, $L^*a^*b^*$ 50,0,0) in the reproduction gamut, within the hue angle plane for the original colour.
- *Compression* algorithms are applied to both out-of-gamut, and within-gamut colours, with all finishing inside the reproduction gamut, within its boundary. The *linear* type of compression algorithm maps colours either
 - *sequentially* (typically their lightness, followed by their chroma) within a plane of constant hue angle, or
 - *simultaneously* in both dimensions within the hue angle plane along lines pointing to a centre of gravity.

Clipping aims to maintain the accuracy of colours, while compression aims to maintain the relative spacing between them. The choice of algorithm to use depends on the properties desired in the reproduction, as specified in a *rendering intent*. The assessment of algorithm performance is made against this intent, and is specific to the image and media to which it is applied (Braun *et al.*, 1999; Morovic, 2003).

The desired, and novel, outcome of colour gamut mapping in this research is to use the results of mapping to develop a set of simple transformations that could be used by the 3D colour food printer to correct dye recipes very rapidly for the effects of substrate browning. It is envisaged that the printer would hold information on ‘standard’ dye quantities needed to render a given

colour in a particular voxel (for example, in a white substrate), and be able to predict the level of browning in the substrate for a given set of ingredients and processing conditions. Accordingly it will adjust the ‘standard’ dye quantities in order to produce the best equivalent of the colour for a given level of browning. The dose-response-like reduction in the lightness and chroma ranges of the colour gamut with increased gel browning suggests that such transformations should be possible. These transformations might form a part of an overall transformation ‘toolbox’ in which the step preceding mapping is the rapid computation of colour gamut boundaries for the printed food matrix by substitution of brown substrate spectral absorption values for the white substrate values in the Kubelka-Munk blending model, the approach that was validated in Chapter Five for the model food gel.

The objectives of the work in this chapter were:

- To map each tile colour from its original position (in the $L^*a^*b^*$ colour space) to a new ‘starting position’ in the colour gamut from the dyed, White gel substrate, and then to map the colour from here to each of the colour gamuts from the three, dyed, Brown gels, using clipping and compression methods;
- To compute the dye quantities for the mapped colours in each of the four substrates;
- To determine any relationships (i.e. those that can be fitted by a mathematical model) that exist between substrate colour and the dye quantities computed for a given tile colour within each mapping method, which might lead to the development of simple transformations between dye quantities with increase in substrate browning.

6.2. Materials and General Methods

6.2.1. Selection of appropriate methods

Colour gamut mapping was applied to the same tile colours that were used in Chapter Four, and utilised the gamut boundaries computed in Chapter Five. Mapping was specific to the D65 standard illuminant and 10° standard observer, the conditions under which tile colours were

measured and for which gamut boundary colours were computed. For this chapter, both gel gamut boundary colours and the tile colours being mapped were SCI colours.

Following trends identified in a survey of gamut mapping algorithms (Kang, 2006), in which most algorithms were found to be hue-preserving, and preceded by lightness compression, the algorithms developed in this study also aimed to preserve hue (that is, they were applied in a 2D plane defined by chroma, C^* , and lightness, L^* , at the hue angle of each tile colour), and began with lightness compression. In each hue angle plane clipping algorithms were limited to the minimum ΔE type, and compression algorithms to the linear, sequential type. Neither clipping nor compression was possible towards a centre of gravity, because the combined decrease and shifting of the lightness and chroma ranges with increased substrate browning made it difficult to set a common centre on the L^* axis. The use of simultaneous compression to investigate the effect of increased substrate browning on dye quantities would have relied on a common centre of gravity for all four substrate gamuts.

6.2.2. General procedure

1. At the hue angle of each tile colour, gamut boundary polygons were drawn for the White, Brown1, Brown2 and Brown3 gel substrates containing primary dye blends in a 180 degree, two-dimensional chroma-lightness (C^*L^*) plane.
2. Each tile colour was mapped to each gamut, as follows:
 - a. The lightness of the tile colour was compressed to fit within the lightness range of the colour gamut from the dyed, White gel, before the tile colour was clipped, or its chroma compressed linearly, to the boundary of the White gel gamut;
 - b. The lightness of the tile colour on the gamut boundary of the dyed, White gel, as well as the lightness of the White gel gamut boundary colours themselves, was compressed to fit within the lightness ranges of the colour gamuts of the dyed, Brown gels, before the colour was clipped, or had its chroma compressed, to the Brown gel gamuts.

3. Dye recipes were found corresponding to the new (clipped or compressed) colour in each reproduction gamut; dye recipes resulting from each mapping method (clipping or compression) were investigated for a possible relationship between increased substrate browning and the quantities of dye required to provide the best equivalent of the colour at each level of browning. Dye recipes from clipping and compression were also compared. Samples were not prepared using the computed dye recipes.

Figure 6.1 shows a schematic representation of the general procedure.

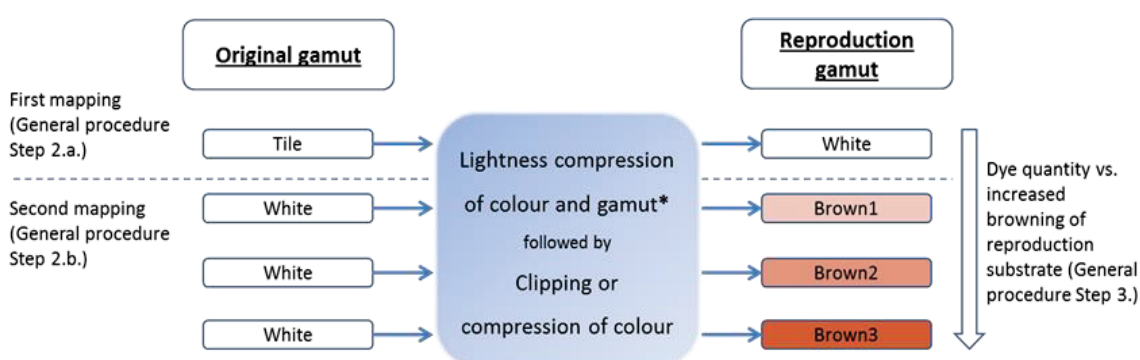


Figure 6.1 Schematic representation of the general procedure for mapping each tile colour to the colour gamuts for model food gels (substrates) which differ in their level of browning but contain the same blends of primary dyes. Tile colours were initially mapped to the gamut for the White gel containing primary dye blends, before being mapped to the gamuts for the Brown gels, which were the same as the White, except for having increasing levels of artificial browning. (*For the initial mapping of Tile to White, lightness compression applied to the tile colour only, and not also to the gamut of tile colours, which was not known.)

The following sections detail the methods and results for each step.

6.3. Gamut boundaries at planes of constant hue angle

6.3.1. Computation

To recap, each point on the gamut boundary represents a colour computed from blending two dyes (for the upper surface of the boundary) or from blending three dyes (for the bottom surface). Concentration totals for the two-dye blends ranged from zero, to the legally permitted maximum. The permitted maximum concentration was needed only for the three-dye blends. The choice of blends ensured that the distance between boundary colours was three $\Delta E^*_{ab,10}$ units or less.

Chroma, $C_{ab,10}^*$ and hue angle, $h_{ab,10}$, were calculated for each individual gamut boundary colour (in each substrate), and for each SCI tile colour:

$$C_{ab,10}^* = \sqrt{a_{10}^{*2} + b_{10}^{*2}}$$

Equation 6.1

$$h_{ab,10} = \tan^{-1} \left(\frac{b_{10}^*}{a_{10}^*} \right)$$

Equation 6.2

The formula above for hue angle, returns a result in radians, which was subsequently converted to a result in degrees, anti-clockwise from the $+a_{10}^*$ axis (i.e. from zero, to 360 degrees).

At the hue angle of each tile colour, the gamut boundary points from each substrate having the same hue angle as that of the tile were plotted in a two dimensional chroma-lightness (C^*-L^*) plot. To provide adequate detail, gamut boundary points and tile colour were regarded as having the same hue angle, X degrees, if their hue angles ranged from X.0 to X.9 degrees. To help visualise the boundaries, and their intersections with the L^* axis, the gamut boundary points in the opposite hue angle plane, located at 180 degrees from the hue angle of the tile colour, were also plotted, and their chroma assigned as negative values. This then provided an outline of a polygon cross-section through each gamut in a 180 degree plane.

To ensure that the gamut boundaries in each plane extended to the rim of the chromatic boundary on either side, the boundaries needed to include points corresponding to a two-dye blend containing the maximum dye quantity. If these were not already available from the gamut boundary computation in Chapter Five, they were interpolated from the two nearest available points, each from a hue angle either side of the tile hue angle, and each corresponding to a two-dye blend containing the maximum dye quantity. The boundary rim point in the tile hue angle plane was taken as the intersection of the line connecting the neighbouring points with the hue angle plane. The method used here for computing line-plane intersections in three dimensions is given in Morovic (2008).

6.3.2. Results

Figure 6.2 shows the colour gamut boundaries for the four gels (each containing the same primary dye blends) at the hue angle of each tile colour; each boundary extends to the opposite hue angle to form a polygon in a plane spanning 180 degrees. Also shown are the original positions of each tile colour. Results are shown for ten out of the twelve tiles. Very little difference was found between the gamut boundary plots for Green and Difference Green, and between those for Mid Grey and Difference Grey (results not shown). The purpose of the Difference tiles, which are manufactured to differ by only a small amount to the main tiles, is to assess the sensitivity of colour measuring instruments to detecting these small differences (Lucideon, 2014). Only Green and Mid Grey were included as colours for gamut mapping in this chapter.

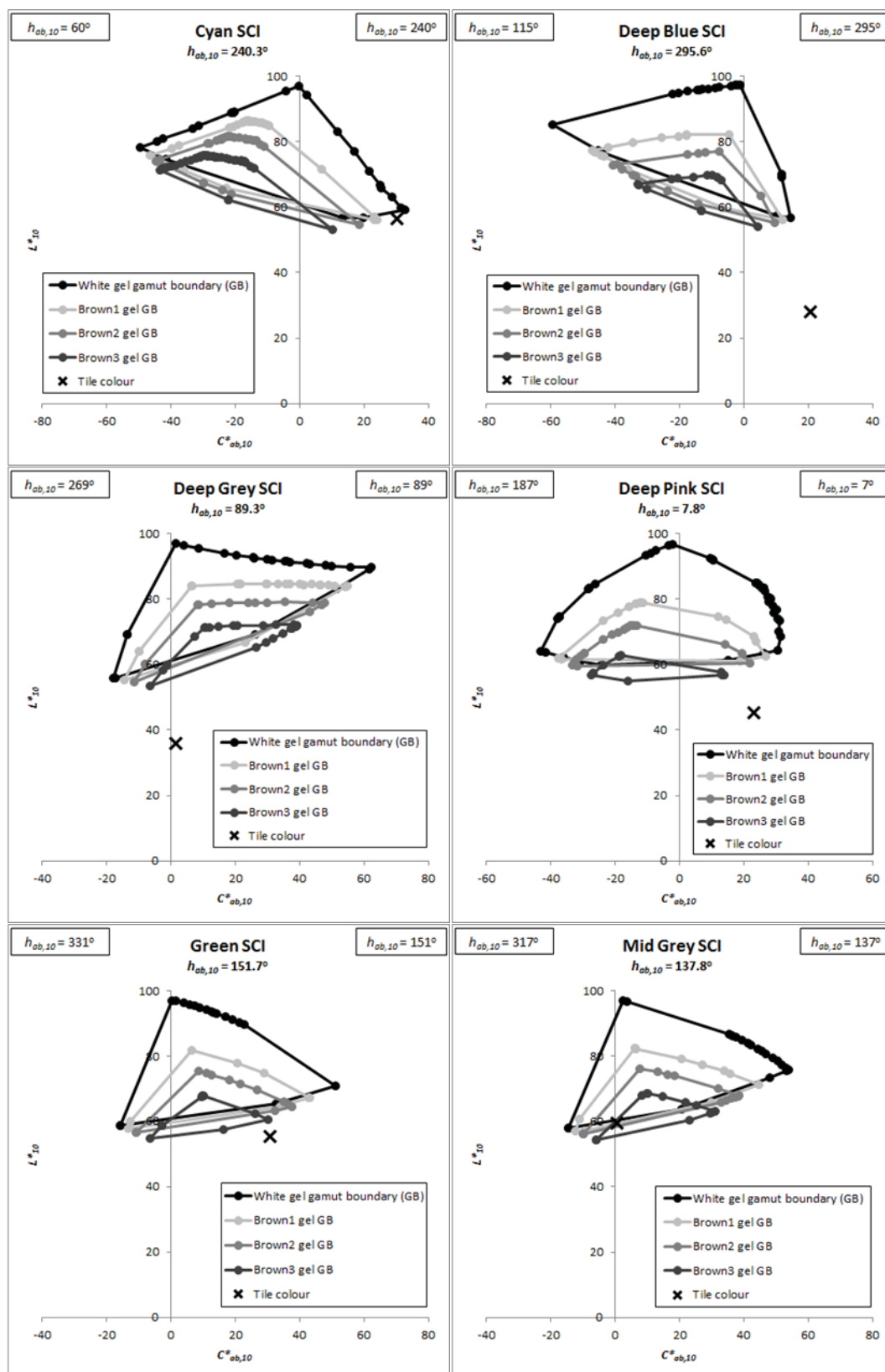
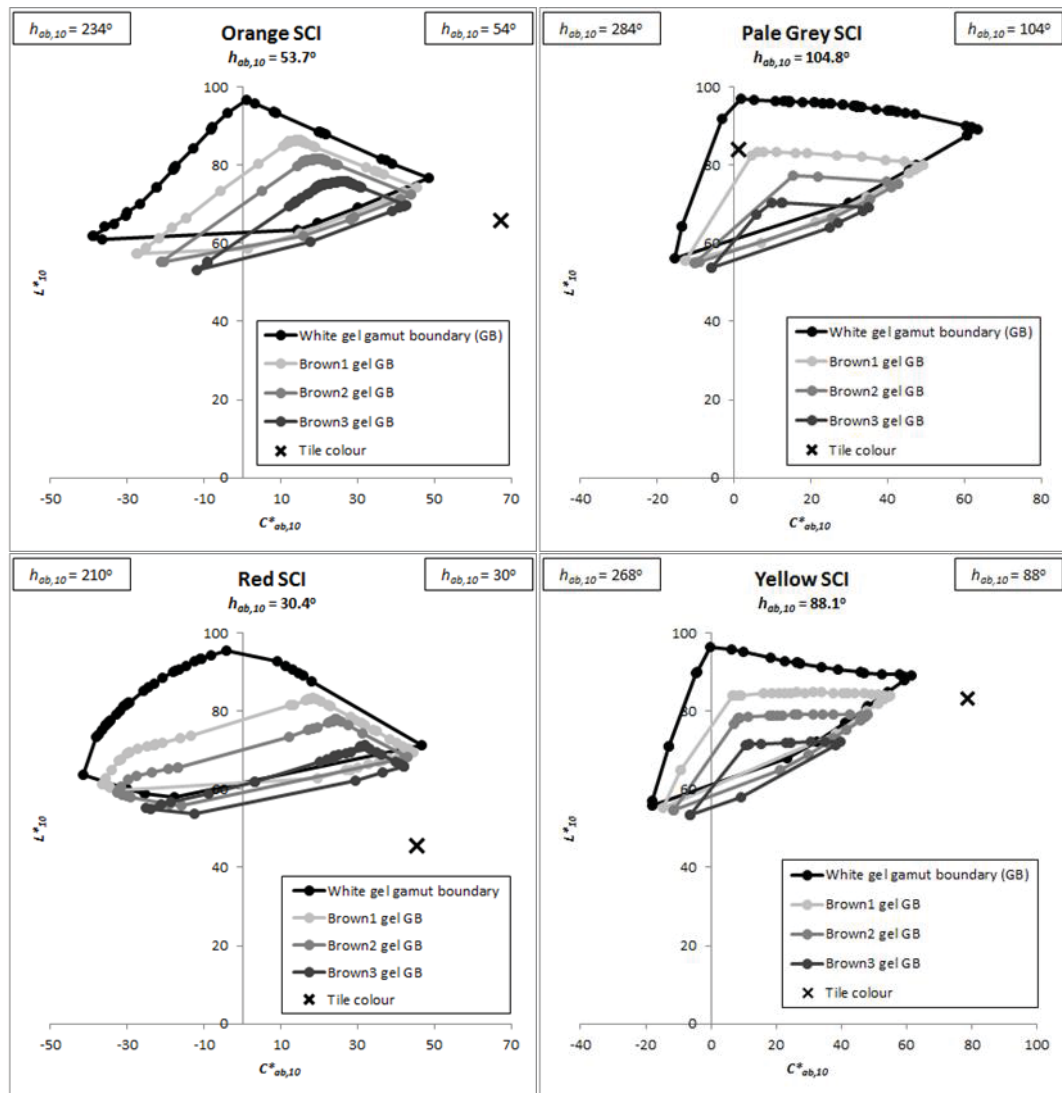


Figure 6.2 Colour gamut boundary polygons at the hue angle of each SCI tile colour for the White, Brown1, Brown2 and Brown3 gel substrates containing the same primary dye blends to the maximum level allowable in foods. Also shown are the original positions of each tile colour, prior to gamut mapping (continued on the next page).



At individual hue angles, the plots provide a more detailed view of the dose response-like effect of substrate browning first discussed in Chapter Five. Each gamut boundary polygon is shown in full detail, with the points (colours) that were computed in Chapter Five, as well as the lines joining the points. The number of computed points available differed between hue angles and between the four gamuts. There was also a need to interpolate colours at the chromatic extremes (the rim) of the boundaries at some hue angles. Even though sampling was sufficiently dense and evenly spread to visualise entire gamut boundaries, the positions of the individual colours meant that they were not necessarily aligned along each hue angle in equal

number. However the combination of available points and interpolated rim points, gave reasonable definition to the boundaries at the individual hue angles.

6.4. General colour gamut mapping procedures

6.4.1. Lightness compression

In the C*-L* plane at the hue angle of the tile, the lightness of the (points in the) original gamut boundary, and the lightness of the original colour, was compressed by linear scaling, using Equation 6.3. This is the same equation as given in Morovic (2003), but has lightness, J , replaced by lightness, L , in accordance with the use of CIELAB in place of CIECAM97s as the colour appearance space for mapping:

$$L_R = L_{Rmin} + (L_O - L_{Omin}) \times \frac{(L_{Rmax} - L_{Rmin})}{(L_{Omax} - L_{Omin})}$$

Equation 6.3

Where:

L_O is the lightness of the original colour;

L_R is the lightness of the reproduction colour;

L_{Omax} and L_{Omin} are maximum and minimum lightness values respectively of the original gamut; and

L_{Rmax} and L_{Rmin} are maximum and minimum lightness values respectively of the reproduction gamut.

6.4.2. Chroma compression

Chroma compression followed lightness compression. The chroma of the colour was compressed linearly at its compressed lightness, by the following equation (Morovic, 2003):

$$C_R = C_O \times \frac{G_R}{G_O}$$

Equation 6.4

Where all points are distances (equivalent to the chroma value) along a horizontal line from the lightness axis:

C_R is the distance to the reproduction (mapped) colour;

C_O is the distance to the lightness-compressed original colour;

G_R is the distance to the reproduction gamut boundary;

G_O is the distance to the lightness-compressed original gamut boundary.

6.4.3. Clipping

Clipping also followed lightness compression. Specifically, a hue-preserving nearest-point clipping approach was used, as distinct from geometric nearest-point clipping which maps out-of-gamut colours to the closest point on the reproduction gamut boundary (Morovic, 2003), which might not be necessarily at the same hue angle as that of the out-of-gamut original colour.

The hue-preserved nearest-point clipped colour was located on the line segment of the reproduction gamut boundary from which a line could be drawn at 90 degrees to the out-of-gamut original colour. The clipped colour was at the intersection of these two lines (Morovic, 2008). The chroma of the clipped colour on the reproduction boundary needed to be within the chroma values of the points at each end of the line segment.

6.5. Colour gamut mapping to a 'standard' colour gamut

6.5.1. Lightness compression

For mapping of each Tile colour to the White substrate gamut, lightness compression was applied to the original tile colour only, and not also to the tile gamut boundary colours because these were not available. For lightness compression of the tile colour itself, the lightness range

of the tile colour gamut was assumed to be from 0 (L_{Omin}) to 100 (L_{Omax}), assuming there was no restriction on the level of dye used in the manufacture of the tiles.

6.5.2. Chroma compression

Lightness-compressed tile colours were either already inside the White (reproduction) gamut and did not require chroma compression, or remained outside the White substrate gamut. The chroma of the latter colours was not able to be compressed to *inside* the White (reproduction) gamut using Equation 6.4, in the absence of the tile colour gamut and therefore the absence of the G_O term. Instead, these colours were mapped to as far as the White gamut *boundary*.

Following the method given in Morovic (2008) to compute line-line intersections in two dimensions, lightness-compressed colours were located by calculating the intersection of the two lines defined by:

- the light-compressed tile colour and the point on the lightness axis having the same L^* value as that colour, and
- the line segment on the White substrate gamut boundary defined by the points having L^* values immediately above, and immediately below, that of the light-compressed tile colour.

If the chroma at the intersection was greater than the chroma of the lightness-compressed tile colours, this indicated that the colour was already within the White gamut boundary. Otherwise the colour was compressed to the intersection point. Examples of both type of scenario are depicted in Figure 6.3.

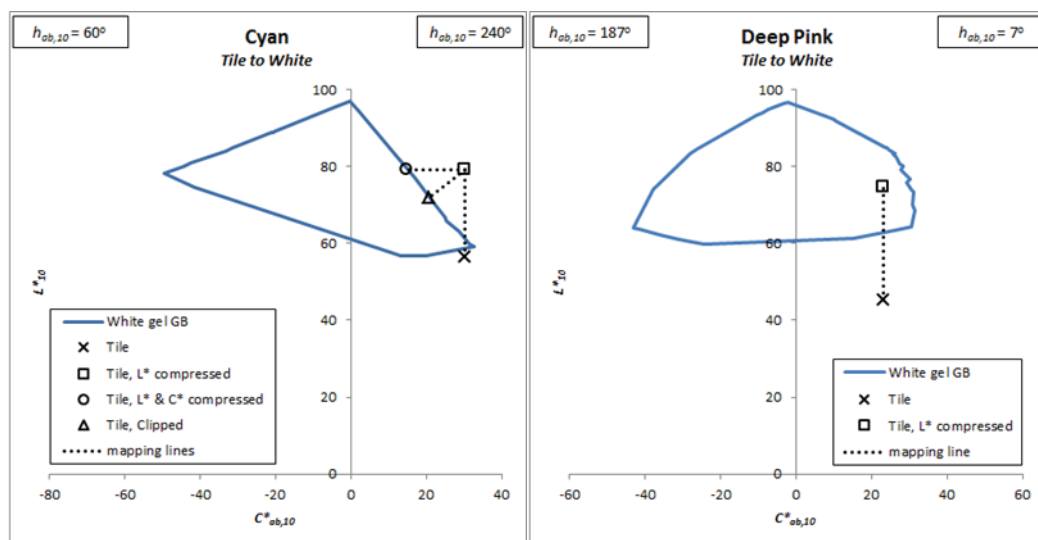


Figure 6.3 Examples of colour gamut mapping of tile colours to a 'standard' colour gamut (computed for a 'White' gel containing dye blends). Left: Mapping to the White gamut boundary by lightness compression, followed by clipping or chroma compression. Right: Mapping to inside the boundary by lightness compression only.

6.5.3. Clipping

Lightness-compressed colours were also clipped, where possible, to the White substrate gamut boundary following the procedure given in Section 6.4.3 (Figure 6.3). Clipping was not required if line-boundary intersections (see 6.5.2 above) had indicated that the lightness-compressed colour was already within-gamut.

6.6. Colour gamut mapping: effects of browning

6.6.1. Lightness compression

For mapping of colours from the White gamut to each of the Brown gamuts, lightness compression was applied to both the original colour, and to the original White gamut boundary colours. Lightness of both the original colour and the original gamut boundary colours was compressed to fit within the lightness range for the relevant Brown substrate.

6.6.2. Chroma compression

As a result of lightness compression, colours were moved to one of four possible locations relative to the Brown gamut boundary, which are described in Table 6.1, and for which

examples are shown Figure 6.4. The exact location depended on the original position of the colour in the White gamut boundary (following the steps described in 6.5), prior to lightness compression, and the degree of lightness compression required (6.6.1). Colours were located by calculating the intersection of the line at the colour's lightness, and the appropriate line segment on the Brown gamut boundary (with the line segment defined in the same way as described in 6.5.2, for the mapping of the Tile colour to the White gamut). Depending on the location, the lightness-compressed colour either did not require chroma compression, or was chroma-compressed using Equation 6.4 (Table 6.1).

Table 6.1 Description of the different methods used to compress the chroma of tile colours from a 'standard' colour gamut (computed for a 'White' gel containing dye blends) to the colour gamut for the same gel containing different levels of artificial browning ('Brown'); methods differed according to the location of the colour in the 'White' colour gamut following initial lightness compression.

Location following lightness compression	Action to compress chroma
On the lightness-compressed White gamut boundary and outside the Brown gamut boundary (Figure 6.4 , Cyan)	Chroma compressed to the Brown gamut boundary using Equation 6.4, where $C_O = G_O$, and therefore $C_R = G_R$
On the lightness-compressed White gamut boundary and inside the Brown gamut boundary (Figure 6.4 , Orange)	Chroma compression not required
Inside the light-compressed White gamut boundary but outside the Brown (Figure 6.4 , Deep Pink)	Chroma compressed to inside the Brown gamut boundary using Equation 6.4, where G_O is the intersection of the horizontal line at the original colour's lightness with the appropriate line segment on the White gamut boundary, and G_R the intersection with the Brown gamut boundary
Inside the Brown gamut boundary (Figure 6.4 , Green)	Chroma compression not required

6.6.3. Clipping

Lightness-compressed colours were also clipped, where possible, to each of the Brown gamuts, following the procedure given in Section 6.4.3. Again, clipping was not required if line-boundary intersections (see 6.6.2 above) had indicated that the lightness-compressed colour was already within-gamut.

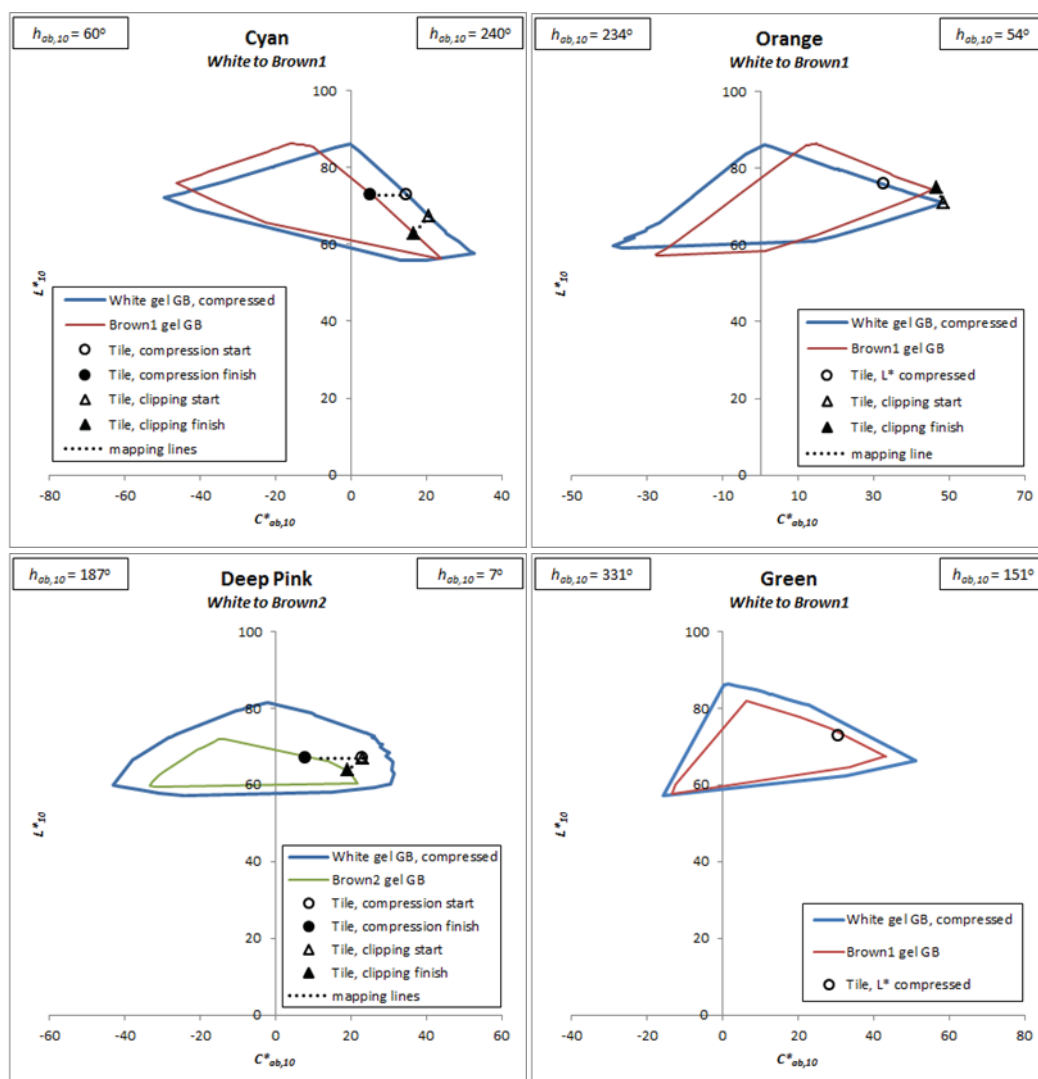


Figure 6.4 Examples of colour gamut mapping of tile colours from a 'standard' colour gamut (computed for a 'White' gel containing dye blends) to the colour gamut for the same gel containing different levels of artificial browning ('Brown'). Left: Mapping to the Brown gamut boundary by lightness compression, followed by clipping or chroma compression. Right: Mapping to inside the boundary by lightness compression only.

6.7. Results from colour gamut mapping

Figure 6.5 to Figure 6.9 show the final $C^*ab,10$ - $L^*,10$ positions of the mapped tile colours in each of the four gel gamuts. For clarity, individual gamut boundary points have been removed. These figures indicate the extent to which the full mapping algorithms of lightness compression, followed by either clipping, or chroma compression, could be applied. Not only is lightness compression a feature of the majority of gamut mapping algorithms surveyed (Kang, 2006) it was particularly useful in this study in that the notable effect of increased gel browning was to decrease the lightness range of the gel colour gamut. The degree of gel browning set the degree

of lightness compression necessary for both the colour being mapped (located in the White gel gamut) and the White gel gamut boundary colours themselves, thereby setting the distances for mapping from White to Brown. More details on the extent of mapping that was possible are given in Appendix Figure 6.15, which illustrates the mapping of each tile colour between each pair of original and reproduction gamuts, and in Appendix Table 6.2, which lists the $C^*_{ab,10}$ and L^*_{10} values for the mapped colours. These should be referred to also when reading the following discussion.

Although compression algorithms would normally have colours positioned inside the reproduction gamut boundary following mapping, for some tile colours (Cyan, Deep Blue, Orange, Red and Yellow) only ‘partial’ compression was possible, to as far as the White gamut boundary in the initial mapping step (Figure 6.5, Figure 6.7 and Figure 6.8). This was due to the absence of a chromatic boundary for the tiles (and therefore of the G_O term in Equation 6.4) which would have been needed for the compression of chroma to within the reproduction boundary, following lightness compression. In lieu of chroma compression proper, the colour was ‘clipped’ horizontally until the mapping line intersected the White gel gamut boundary (see Section 6.5.2). Other colours (Deep Grey, Deep Pink, Green, Mid Grey and Pale Grey), were mapped to inside the White gel gamut by lightness compression alone, without the need for chroma compression (Figure 6.6 and Figure 6.9). All subsequent compressions of Cyan and Deep Blue from White to Brown gel gamuts were also partial compressions (from boundary to boundary), while those for Orange, Red and Yellow were either partial compressions, or lightness-only compressions. For the remaining colours, compressions to the Brown gel gamuts were either possible by full compressions or lightness only compressions, or not at all possible. Solutions were not always available from compression algorithms because some chroma mapping lines were seen to not reach the reproduction gamut boundary (in the compression of Deep Pink to Brown3), or intersected the boundary in the plane which was 180 degrees from the hue angle of the tile colour (in the compression of Cyan to Brown2 and to Brown3) (Appendix Figure 6.15). Mid Grey could not be compressed to Brown2 and to Brown3, nor Pale Grey to

any of the Brown gel gamuts; the sections of the original and reproduction gamut boundaries closest to the colour in the original gamut that would define the G_R and G_O terms for Equation 6.4 are located on opposite sides of the lightness axis, rather than on the same side (Appendix Figure 6.15). The colours could have instead been ‘clipped’ horizontally to the reproduction gamut boundary, but this technique was defined only for the mapping of the colour to the White gel gamut (see Section 6.5.2).

The full algorithms of lightness compression, followed by clipping, were able to be applied to the mapping of Cyan, Deep Blue, Orange, Red and Yellow to the White gel gamut and to their subsequent mapping to each of the Brown gel gamuts. The full algorithm was not required for Deep Pink, Green, Mid Grey and Pale Grey until their mapping to some or all of the Brown gel gamuts, as lightness compression alone otherwise provided the solution. For Cyan, Deep Blue, Deep Pink, Orange, Red and Yellow, clipping mapped the colour to a point outside some or all of the colour gamuts for the gels. These are indicated by a shaded symbol in Figure 6.5 to Figure 6.8, and noted also in Figure 6.15 and Table 6.2 in the Appendix. These out-of-gamut points were replaced by the outermost point on the relevant gel gamut boundary (the point with the highest chroma, and the nearest achievable colour) which was taken to be the final solution. Deep Grey could not be clipped to any of the four gamuts from its position within these gamuts following lightness compression, meaning the only mapping solutions for Deep Grey were those from (lightness) compression.

6.7.1. Description of the changes in C^* and L^* across the mapped colours

The following discussion is divided into different groups of tile colours. The colours in each group display similar patterns of mapping, and similar relative positioning of original and reproduction gamuts at their respective hue angles. These same groupings are used later when discussing the quantities of dye needed in the reproduction gel substrates to produce the mapped colours, in Section 6.9.2.

6.7.1.1. Cyan, Deep Blue, Deep Pink and Green

For **Cyan and Deep Blue**, mapping of the original colour to the White gel gamut boundary resulted in two new different starting positions, with the clipped colour darker and more chromatic than the compressed colour (Figure 6.5). For **Deep Pink and Green**, there was only one new position, resulting from lightness compression only of the original colour (Figure 6.6). As the level of browning in the reproduction gel substrate increases, the gamut shrinks with respect to its lightness and chroma ranges, and gamut mapping replaces gradually each original tile colour with a darker and less chromatic colour. In most of the substrates the clipped colour is darker and more chromatic than the compressed colour; increased browning of the gel substrate increases the distance between the compressed and clipped colours because (following initial lightness compression of the White gamut boundary) compression has occurred in a single dimension (chroma) whereas clipping has occurred simultaneously in two dimensions (lightness and chroma) (Appendix Figure 6.15).. The exceptions are Deep Pink in White, and Green in White and in Brown1, which were neither clipped nor compressed further following lightness compression.

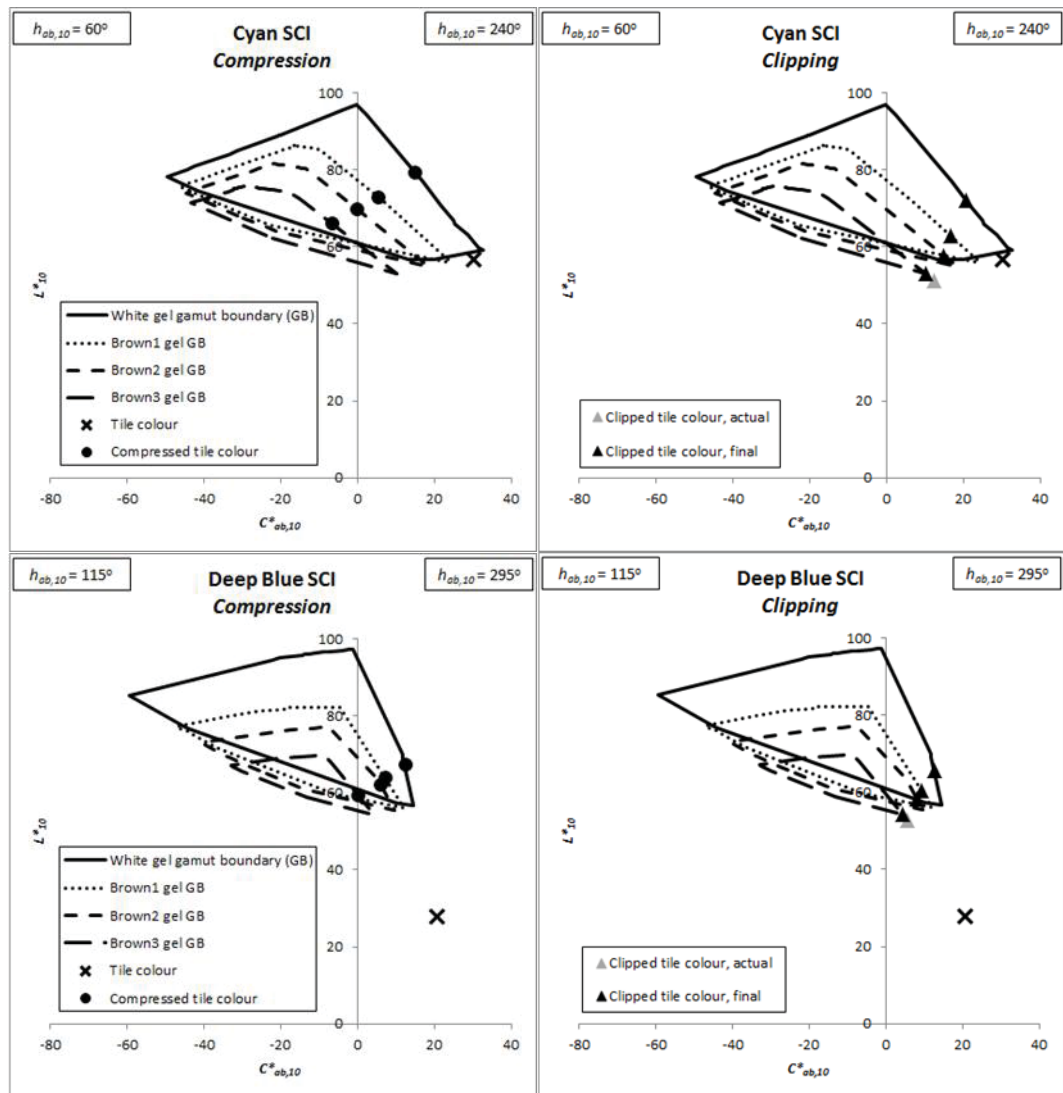


Figure 6.5 The original positions of each Cyan and Deep Blue SCI tile colour in its hue angle plane, and its position in each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels) following mapping by compression and clipping algorithms. Lightness compression preceded clipping or chroma compression.

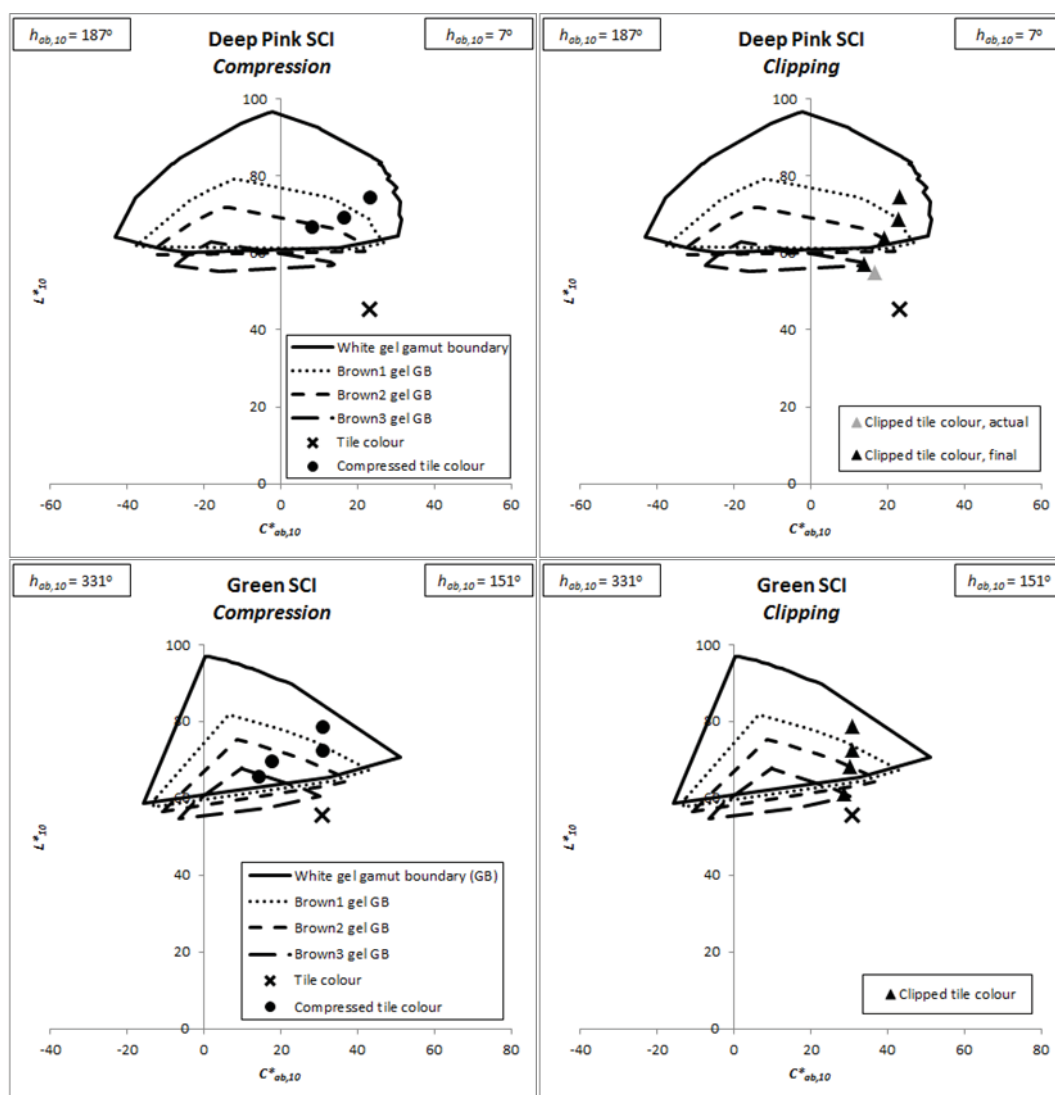


Figure 6.6 The original positions of each Deep Pink and Green SCI tile colour in its hue angle plane, and its position in each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels) following mapping by compression and clipping algorithms. Lightness compression preceded clipping or chroma compression.

6.7.1.2. Orange and Yellow

Clipped colours are again more chromatic than the compressed colours on the colour gamut boundary for the White gel, a trend that largely continues with increased browning of the gel (Figure 6.7). As the level of browning in the reproduction gel substrate increases, compressed colours become darker, but their chroma remains unchanged due to lightness compression alone placing the colours within each Brown gel colour gamut boundary. The exception to this was Yellow in Brown3 for which chroma also needed to be compressed, but only over a very short distance (Appendix Figure 6.15). The outermost chromatic point in each reproduction gel

gamut boundary was used in place of all clipped colours, and became darker and less chromatic with substrate browning. Although the lightness of the compressed colours is initially higher than that of the clipped colours, increased browning sees a reversal of this trend (Appendix Figure 6.15 and Appendix Table 6.2).

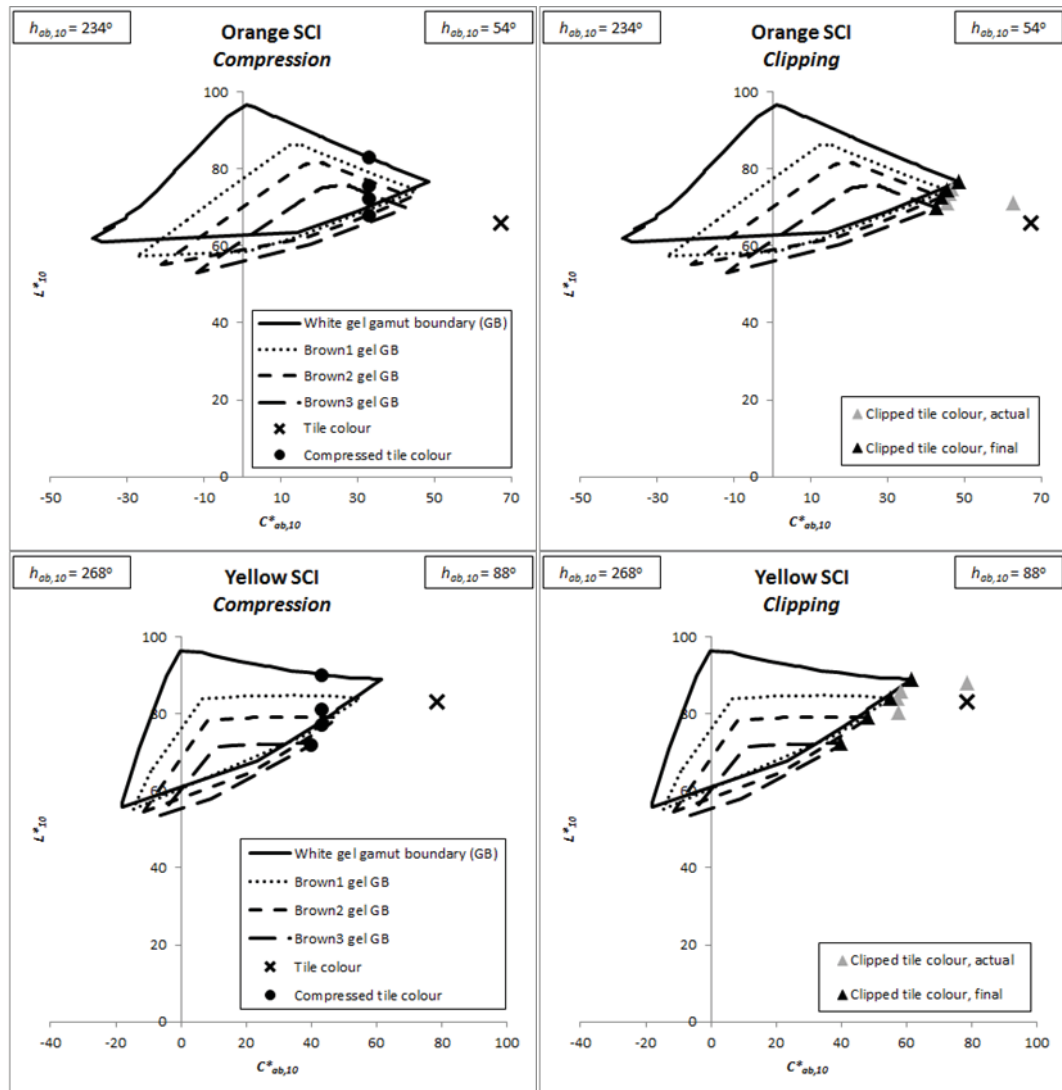


Figure 6.7 The original positions of each Orange and Yellow SCI tile colour in its hue angle plane, and its position in each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels) following mapping by compression and clipping algorithms. Lightness compression preceded clipping or chroma compression.

6.7.1.3. Red

As the level of browning in the reproduction gel substrate increases, the chroma and lightness of both the clipped and the compressed colours decreases, with the exception of no change in the chroma of the compressed colour when the gel substrate changes from white to the lowest level of browning (Figure 6.8). In each substrate the clipped colours are more chromatic than the compressed colours. Compressed colours are initially the lighter but clipped colours have become the lighter by the time the highest level of browning in the gel has been reached.

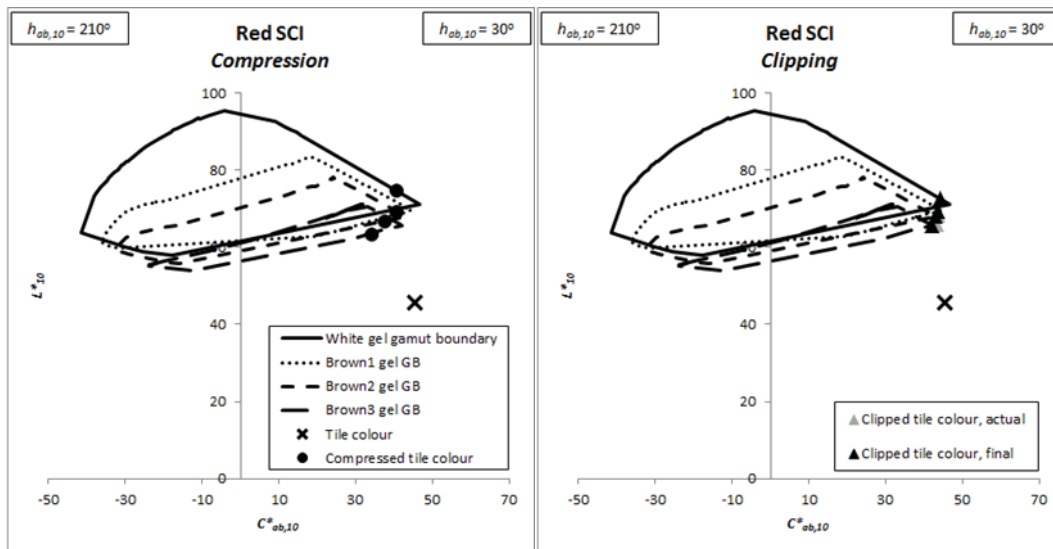


Figure 6.8 The original position of the Red SCI tile colour in its hue angle plane, and its position in each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels) following mapping by compression and clipping algorithms. Lightness compression preceded clipping or chroma compression.

6.7.1.4. Deep Grey, Mid Grey and Pale Grey

The Deep Grey colour was able to be mapped to each of the reproduction gamuts by lightness compression only (Figure 6.9). As the level of browning increased in the reproduction gel, the lightness of the mapped Deep Grey colour decreased while chroma remained unchanged. Mid Grey become darker with increased gel browning, as well as more chromatic at the higher levels of browning (Figure 6.9). Lightness of Pale Grey also decreased with substrate browning, together with an overall increase in chroma (Figure 6.9).

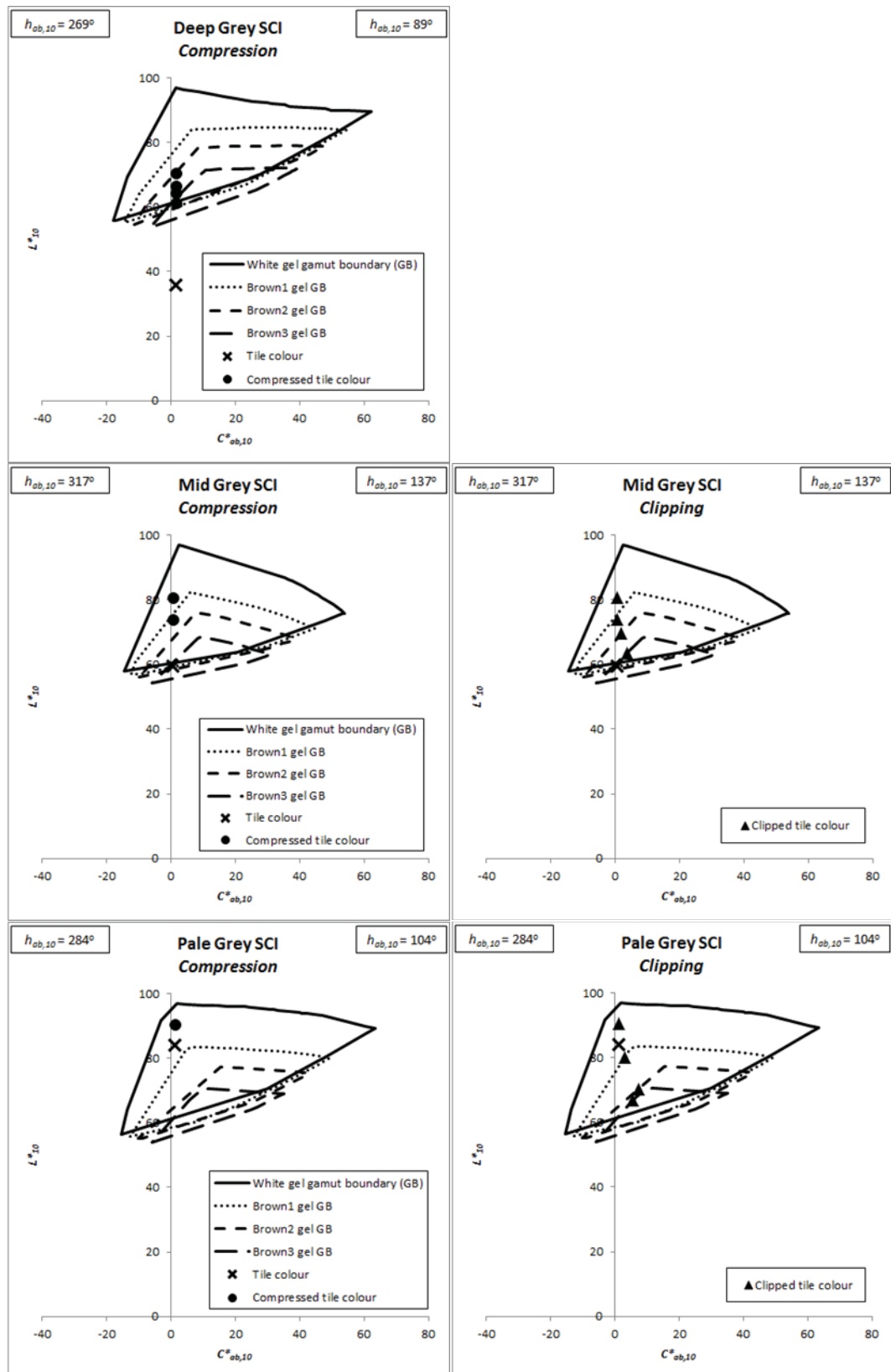


Figure 6.9 The original positions of each Deep Grey, Mid Grey and Pale Grey SCI tile colour in its hue angle plane, and its position in each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels) following mapping by compression and clipping algorithms. Lightness compression preceded clipping or chroma compression.

6.8. Computing dye recipes for mapped colours

6.8.1. Recipe correction method

The results from gamut mapping were the L^*_{10} and $C^*_{ab,10}$ values of the new colours in the reproduction gamuts. The process of obtaining the dye recipe that corresponds to each new colour made use of the high density of points (colours) computed for the gamut boundaries and of their corresponding dye blends (Chapter Five). A gamut boundary point, if sufficiently close to the mapped colour, could be used as the starting point for convergence towards the mapped colour. Because the mapped colour was computed and therefore not a measurable target, the dye recipe could not be obtained by the colour matching techniques used previously, in Chapter Four.

Procedure:

1. The a^*_{10} and b^*_{10} values of each mapped colour were calculated from its $C^*_{ab,10}$ value, and from the hue angle of the tile colour, using the following formulae:

$$a^*_{10} = C^*_{ab,10} \cos(h_{ab,10})$$

Equation 6.5

$$b^*_{10} = C^*_{ab,10} \sin(h_{ab,10})$$

Equation 6.6

2. The colour on the reproduction gamut boundary with the smallest $\Delta E^*_{ab,10}$ difference between it, and the $L^*_{10}a^*_{10}b^*_{10}$ values of the mapped colour was found
3. The X_{10} , Y_{10} and Z_{10} values of the mapped colour, and of the gamut boundary colour closest to the mapped colour, were calculated from their L^*_{10} , a^*_{10} and b^*_{10} values, as follows:

$$X_{10} = X_n \left(\frac{L^*_{10} + 16}{116} + \frac{a^*_{10}}{500} \right)^3$$

$$Y_{10} = Y_n \left(\frac{L^*_{10} + 16}{116} \right)^3$$

$$Z_{10} = Z_n \left(\frac{L^*_{10} + 16}{116} - \frac{b^*_{10}}{200} \right)^3$$

Equation 6.7

for $\frac{Y}{Y_n} > 0.008856$; in other words, if $L^*_{10} > 7.9996$ (Kang, 2006)

4. The (recipe) correction matrix was used to reduce the difference between the target colour (the mapped colour), and the nearest colour.

The correction matrix is the inverse of the influence matrix (McDonald, 1987). The influence matrix is:

$$\Delta X = \left(\frac{\partial X}{\partial c_1} \right) \Delta c_1 + \left(\frac{\partial X}{\partial c_2} \right) \Delta c_2 + \left(\frac{\partial X}{\partial c_3} \right) \Delta c_3$$

$$\Delta Y = \left(\frac{\partial Y}{\partial c_1} \right) \Delta c_1 + \left(\frac{\partial Y}{\partial c_2} \right) \Delta c_2 + \left(\frac{\partial Y}{\partial c_3} \right) \Delta c_3$$

$$\Delta Z = \left(\frac{\partial Z}{\partial c_1} \right) \Delta c_1 + \left(\frac{\partial Z}{\partial c_2} \right) \Delta c_2 + \left(\frac{\partial Z}{\partial c_3} \right) \Delta c_3$$

Equation 6.8

Where the following are the partial derivative coefficients:

$$\left(\frac{\partial X}{\partial c_n} \right) = \sum E_\lambda \bar{x}_\lambda \left(\frac{2R_\lambda^2}{R_\lambda^2 - 1} \right) \left(\frac{k}{s} \right)_{\lambda,n}$$

$$\left(\frac{\partial Y}{\partial c_n} \right) = \sum E_\lambda \bar{y}_\lambda \left(\frac{2R_\lambda^2}{R_\lambda^2 - 1} \right) \left(\frac{k}{s} \right)_{\lambda,n}$$

$$\left(\frac{\partial Z}{\partial c_n} \right) = \sum E_\lambda \bar{z}_\lambda \left(\frac{2R_\lambda^2}{R_\lambda^2 - 1} \right) \left(\frac{k}{s} \right)_{\lambda,n}$$

Equation 6.9

And:

E_λ is the relative spectral power of the standard illuminant (D65);

$\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{z}_\lambda$ are the colour matching functions of the standard observer (here the 10 degree observer);

R_λ is the reflectance of the target, which in this case was the mapped colour; however, because the mapped colour was not a measureable target, the computed R_λ of the nearest colour (from its dye recipe that was used in gamut boundary computation) to the mapped colour was used at the beginning of the loop (McDonald, 1987); subsequently the computed R_λ from the recipe at the end of each iteration loop was used;

$\left(\frac{k}{s}\right)_{\lambda,n}$ is the unit absorption coefficient for dye n at wavelength λ .

The influence matrix is inverted by standard matrix algebra to give the correction matrix:

$$\begin{aligned}\Delta c_1 &= \left(\frac{\partial c_1}{\partial X}\right)\Delta X + \left(\frac{\partial c_1}{\partial Y}\right)\Delta Y + \left(\frac{\partial c_1}{\partial Z}\right)\Delta Z \\ \Delta c_2 &= \left(\frac{\partial c_2}{\partial X}\right)\Delta X + \left(\frac{\partial c_2}{\partial Y}\right)\Delta Y + \left(\frac{\partial c_2}{\partial Z}\right)\Delta Z \\ \Delta c_3 &= \left(\frac{\partial c_3}{\partial X}\right)\Delta X + \left(\frac{\partial c_3}{\partial Y}\right)\Delta Y + \left(\frac{\partial c_3}{\partial Z}\right)\Delta Z\end{aligned}$$

Equation 6.10

And the corrected recipe:

$$\text{New } c_1 = \text{original } c_1 + \Delta c_1$$

$$\text{New } c_2 = \text{original } c_2 + \Delta c_2$$

$$\text{New } c_3 = \text{original } c_3 + \Delta c_3$$

Equation 6.11

Where:

c is dye concentration in the gel prior to heating, in mg dye/100g gel;

1, 2 and 3 denote the dyes.

5. The $R_{\lambda,m}$ and $L^*_{10}a^*_{10}b^*_{10}$ values for the gel colour corresponding to the corrected recipe were computed, using the methods described previously in Chapter Five.
6. The iteration loop was repeated, using computed $R_{\lambda,m}$ from Step 5, and stopped when one or more negative dye concentrations were computed for a recipe (McDonald, 1987), or when the total dye quantity in the recipe exceeded the legal maximum. The dye recipe for the colour with the smallest predicted (computed) $\Delta E^*_{ab,10}$ difference, and the smallest hue angle difference, to the target (the mapped colour) was taken to be the recipe for the mapped colour. The criteria for a satisfactorily close match between the two colours were:
 - a. a $\Delta E^*_{ab,10}$ difference of three units or less (the same criterion used previously in Chapter Four), and
 - b. a hue angle difference of one degree or less, given that the mapping algorithms used in this study were hue-preserving.

6.8.2. Effect of browning on computed dye quantities

The changes in dye quantities that were required to clip or compress each tile colour as the degree of browning was increased in the reproduction gel substrate, were examined. In Chapter Five, the measured lightness, L^*_{10} , of the substrate itself (without any primary dye blends added) was found to decrease, and its chroma, $C^*_{ab,10}$, to increase, with increased artificial browning, while its hue angle remained virtually unchanged (at either 50 or 49 degrees, see Figure 5.7 and Table 5.5, from Chapter Five). Visually, these changes were perceived as a simultaneous darkening and reddening of the gel colour, relative to the un-dyed White gel. Potentially then, either L^*_{10} or $C^*_{ab,10}$ of the substrate could be used as a simple index of browning. L^*_{10} was chosen as the browning index in this study because it might be regarded as

a more obvious description of the change in visual appearance of the gels, and because potentially it could be used as a common index of changes in several substrate characteristics, in addition to browning, such as the light scattering effects of surface texture. Linear and non-linear models were fitted to dye quantity data against decreasing substrate lightness, for each tile colour. Dye quantity data included total quantity, and quantities for the individual primary dyes in the recipes.

6.9. Dye recipes for mapped colours: Results and discussion

6.9.1. Extent of recipe correction

Because the mapped colours in each of the reproduction gamuts were not measurable targets the dye recipes required to produce them could not be obtained directly by the colorimetric matching technique used in Chapter Four; instead the dye recipes and dye totals shown in graphical form in Figure 6.10 to Figure 6.13 and in Appendix Figure 6.16 are for colours with the smallest $\Delta E^*_{ab,10}$ and $\Delta h_{ab,10}$ differences to the mapped colours by the end of iterative dye recipe correction. The computation of negative dye quantities was the reason for stopping the correction loop in the majority of cases. The loop was also stopped when the $\Delta E^*_{ab,10}$ and/or $\Delta h_{ab,10}$ differences between the closest colour and the mapped colour reached zero. For the clipped Mid Grey and Pale Grey colours in Brown2, and the clipped Yellow in Brown3, the correction loop was stopped when it became clear that recipe correction, rather than converging to the mapped colour, appeared to alternate between two sets of recipes, with the recipes in each set having similar dye proportions. The two sets of recipes were for colours located either side of the mapped colour.

Appendix Table 6.3 shows the smallest $\Delta E^*_{ab,10}$ and $\Delta h_{ab,10}$ differences reached between the closest and mapped colours by the end of iterative recipe correction. In most cases, the condition that the closest and mapped colours are within three $\Delta E^*_{ab,10}$ units, and within one degree, of each other, was satisfied. One notable exception to this was the Deep Grey colour compressed to the White and Brown1 gamuts, for which the $\Delta E^*_{ab,10}$ distances to the closest

colours were 11.0 and 7.7 units respectively. The Deep Grey colour was located well inside these reproduction gamuts following (lightness only) compression (Appendix Figure 6.15), and clearly not near enough to a starting colour on the gamut boundary for recipe correction to converge to a satisfactorily close solution. Therefore for colours that have undergone full compression, and which lie within the reproduction gamut boundary, gamut boundary points cannot solely be relied upon for starting dye recipes; more detail is needed within the boundary to increase the number and proximity of starting recipes.

In some cases the closest possible hue angle difference between colours from iterative recipe correction and mapped colours was more than one degree. This was found for the Cyan and Deep Pink tile colours compressed to the White gel gamut, and for the Cyan and Deep Blue colours compressed from the White to the Brown1 gamuts, as soon as after the first iteration step. The starting colour however, was also found to be the same angular distance from the mapped colour, but in the opposite direction (Appendix Table 6.4), as well as being a similar $\Delta E^*_{ab,10}$ distance from the mapped colour. The colours from the two ‘consecutive steps’ also had similar dye recipes; with both recipes producing a colour within similar range of the mapped colour, either would have been an acceptable solution. For Mid Grey mapped to the White gel gamut, and from the White to the Brown1 and Brown2 gel gamuts, and for Pale Grey mapped to the White, and then to the Brown1 gel gamuts, the hue angle differences between closest and mapped colours were large, ranging from 11 to 47 degrees (Appendix Table 6.3). However, the low chroma of these colours (and therefore their close proximity to the lightness axis) meant that the mapped and nearest colours were much closer to each other than suggested by the $\Delta h_{ab,10}$ differences. As indicated in Chapter Five, Section 5.5.1, colours low in chroma are subject to relatively large angular variation from small errors. For these colours, $\Delta E^*_{ab,10}$ should be a more useful indicator than $\Delta h_{ab,10}$ of the proximity of the colours from recipe correction to mapped colours.

Some of the differences between mapped colours and closest colours in Appendix Table 6.3 are differences between the outermost gamut boundary point in the hue angle plane, which replaced

the mapped colour, and *its* closest colour. The replacement of mapped colours with outermost gamut boundary points (the point with the highest chroma, at the ‘rim’ of the boundary) applied to colours which were clipped to a point outside the reproduction gamut boundary. Recipe correction for an out-of-gamut clipped colour would have begun with a starting recipe for a colour on the reproduction gamut boundary and converged (back) to the out-of-gamut colour.

6.9.2. Relationships between gel browning and computed dye quantities

Figure 6.10 to Figure 6.13 show the changes in computed *total* quantities of dye required to produce the best equivalent of each tile colour in the gel with decreasing measured lightness of the gel (as an indicator of increasing gel browning). The traces for the individual dyes in each recipe can be found in Appendix Figure 6.16. In the following sections, the full impact of gel browning is discussed for those tile colours for which a recipe is available for each reproduction gamut.

6.9.2.1. Cyan, Deep Blue, Deep Pink and Green

Figure 6.10 shows that for Cyan, Deep Blue, Deep Pink and Green, the (computed) total quantity of dye needed to produce the clipped colour in most of the reproduction gel substrates is more than that needed to produce the compressed colour. More dye is needed to produce clipped colours because they are darker and more chromatic than the compressed colours. The exceptions are Deep Pink in White, and Green in White and in Brown1, where the quantity of dye needed for the clipped and compressed colours is the same. As the lightness of the reproduction gel substrate decreases, the total quantity of dye in the recipes needed to produce the clipped colours increases, whereas the quantity needed to produce the compressed colours increases comparatively less (for Deep Blue), or not at all (for Green). The relatively small change in dye quantity needed to achieve compressed colours with increased substrate browning indicates that browning itself makes a larger contribution to these colours than it does to the clipped colours. For clipping, an increasing amount of dye is needed to achieve an increasingly

darker and more chromatic result with substrate browning, relative to compression, as indicated by the increasing distance between compressed and clipped colours.

For **Deep Blue, Deep Pink and Green**, in addition to an increasing total amount of dye, an increasing proportion of Brilliant Blue dye is needed in the recipes, relative to the other dyes, to produce the clipped colours as they darken with increased browning of the substrate (Appendix Figure 6.16). Though accounting for a lower proportion of the predominant dyes in the recipes, Brilliant Blue is the darkest of the three dyes, on a unit concentration basis. For the clipped **Cyan** colour, the proportion of blue to red dye decreased with substrate browning, however the blue dye already accounted for a higher proportion of total dye in the recipes for this colour than it did in the recipes for the other three colours. For the compressed Deep Blue colour, the patterns observed for its clipped equivalent are also seen: an increasing proportion of blue to red dye in addition to the increase in total dye quantity, which together should achieve the increasingly darker, compressed colours with substrate browning. The lack of apparent change in total dye quantity for the compressed Green colour follows the pattern observed for the predominant, yellow dye.

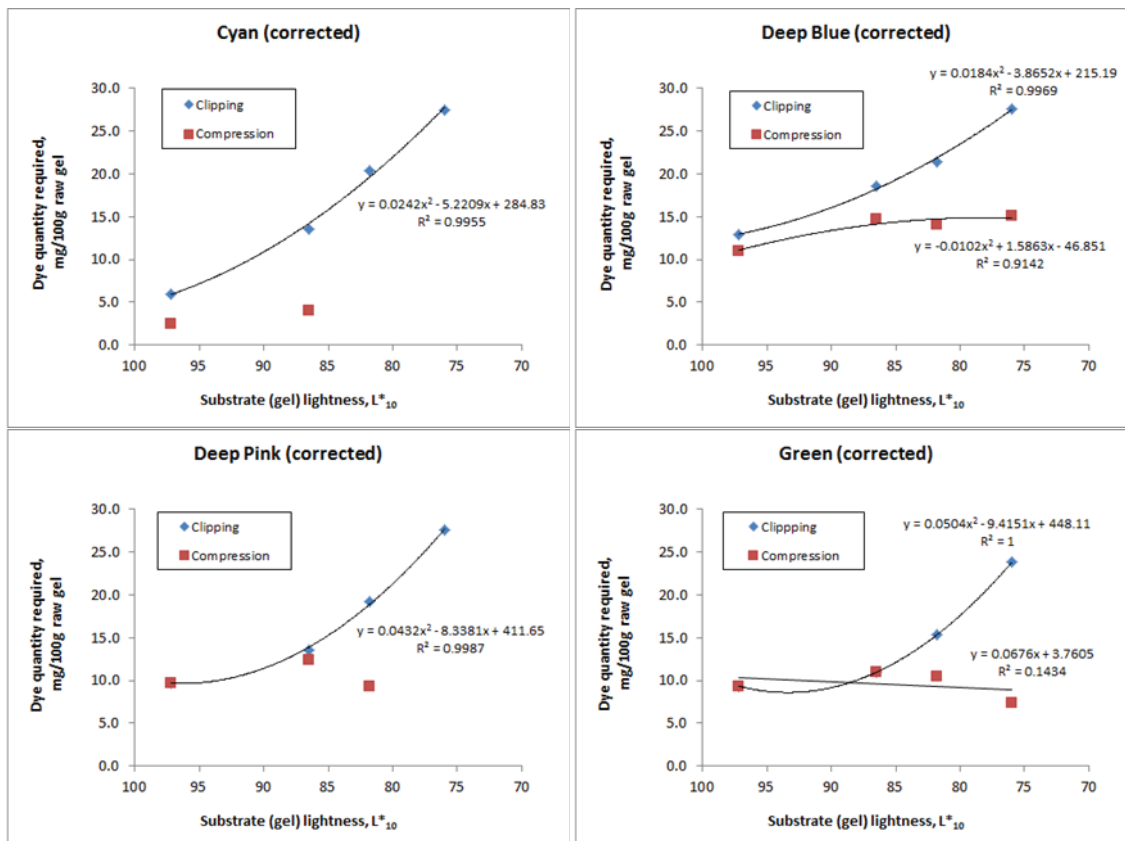


Figure 6.10 The total quantities of dye needed to produce the best equivalent of the Cyan, Deep Blue, Deep Pink and Green tile colours in each of the four reproduction gel substrates, according to the increase in the measured lightness of the substrate. Each dye recipe total is for the colour in the reproduction gamut that was closest to the mapped (clipped or compressed) colour after iterative dye recipe correction.

6.9.2.2. Orange and Yellow

For **Orange and Yellow**, more total dye is needed to produce clipped colours than to produce compressed colours in most of the gel substrates, as clipped colours are more chromatic than the compressed colours. However, opposite to what was observed for Cyan, Deep Blue, Deep Pink, and Green, as substrate lightness decreases, it is the quantity of dye needed to produce the compressed colours that increases, and the quantity of dye for the clipped colours that is unchanged, remaining at the permitted maximum (Figure 6.11). Compressed colours did become darker with increased substrate browning, but chroma remained unchanged (with the small exception of Yellow in Brown3); the necessary increase in dye quantity was likely due to the combined need to darken the colour, and to maintain the chroma at the same level. For Orange, the need to darken the compressed colour with substrate browning can also be met by an increasing proportion of Red dye (the darker dye) in the recipe (Appendix Figure 6.16).

Clipped colours, located at the outermost chromatic point in each substrate gamut boundary, became darker and less chromatic with substrate browning. The same (or similar) total dye quantities can be used for each of these colours; the difference between them is due largely to the decreases in *substrate* lightness and chroma. The quantities of the predominant dyes in the recipes for the clipped colours also show little or no change with substrate browning (Appendix Figure 6.16). The total dye quantities needed for clipping and compressing the colours converge as the substrate darkens, and the reason for this can be seen in Appendix Figure 6.15: in moving from the White through to the Brown3 gamuts, the compressed colour moves gradually towards the bottom surface of the Brown3 gamut; as with outermost (rim) points, bottom surface points were computed from recipes containing the maximum permitted dye level.

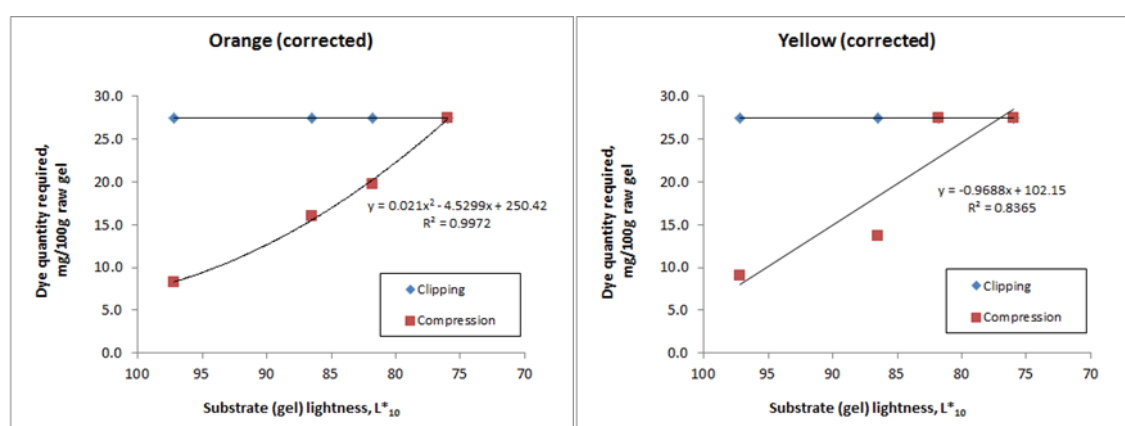


Figure 6.11 The total quantities of dye needed to produce the best equivalent of the Orange and Yellow tile colours in each of the four reproduction gel substrates, according to the increase in the measured lightness of the substrate. Each dye recipe total is for the colour in the reproduction gamut that was closest to the mapped (clipped or compressed) colour after iterative dye recipe correction.

6.9.2.3. Red

For **Red**, there is a more marked increase in the total quantity of dye needed to produce the compressed colour when moving from the White substrate to the Brown1 substrate, compared with the increase in dye needed to produce the clipped colour (Figure 6.12). Not only is the compressed colour in the White substrate lighter and less chromatic than the clipped colour, therefore requiring less dye to begin with, the increase in dye quantity in moving to Brown1 needs to cause both a darkening in colour, and to maintain the chroma that is unchanged in

moving from White to Brown1. This is the same as what was observed for the compressed Orange and Yellow colours. In moving from Brown1 to Brown3 comparatively smaller changes are seen in the quantity of dye needed to produce both clipped and compressed colours. Similar to the clipping of Orange and Yellow, and the compression of Cyan, Deep Blue, Deep Pink and Green, the change in the mapped colour is due largely to the effects of the substrate. As the substrate darkens from Brown1, the dye quantities needed for the clipped and compressed colours converge to similar levels because, as was observed for Orange and Yellow, the Red colour is replaced by a boundary rim point or by a bottom surface point on the relevant Brown substrate gamut, and both require the same amount of dye. The changes in total dye quantity that are needed to produce the clipped and compressed colours with substrate browning are due to changes in the quantity of red dye; no change is observed for the other dye in the recipe, the yellow dye (Appendix Figure 6.16).

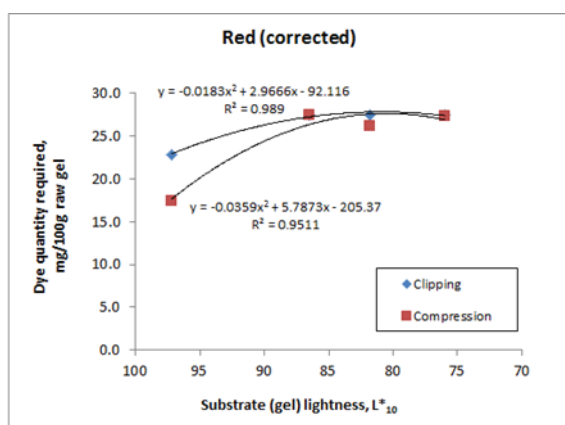


Figure 6.12 The total quantities of dye needed to produce the best equivalent of the Red tile colour in each of the four reproduction gel substrates, according to the increase in the measured lightness of the substrate. Each dye recipe total is for the colour in the reproduction gamut that was closest to the mapped (clipped or compressed) colour after iterative dye recipe correction.

6.9.2.4. Deep Grey, Mid Grey and Pale Grey

Of the **Grey** colours, full dye quantity data are available only for the clipped Mid Grey and Pale Grey colours. The total quantity needed for these colours increases with substrate browning, in line with their decreasing lightness and increasing chroma, though for Pale Grey the trace is less clear cut (Figure 6.13). Overall, less dye is needed for these colours than for other mapped colours which will be due to their comparatively low chroma. Although not the predominant dye in the recipes for the clipped Mid Grey colour, the relative proportion of Brilliant Blue

increases with substrate browning, which likely contributes to the progressive darkening of the colour. Conclusions were not able to be drawn about the dye quantities needed for the lightness-compressed Deep Grey colour, due to the relatively large distances between the closest colours computed from iterative dye recipe correction and the mapped colours in the White and Brown1 substrates (Appendix Table 6.3).

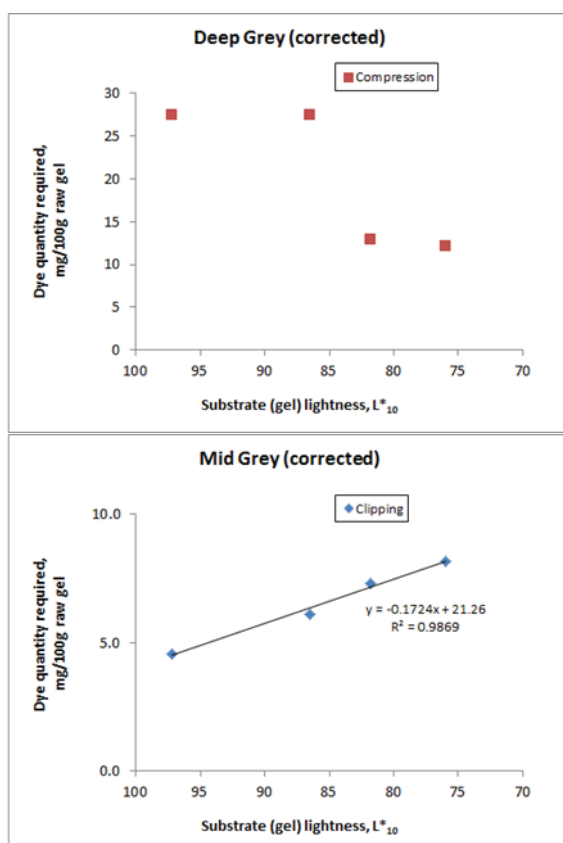


Figure 6.13 The total quantities of dye needed to produce the best equivalent of the Deep Grey, Mid Grey and Pale Grey tile colours in each of the four reproduction gel substrates, according to the increase in the measured lightness of the substrate. Each dye recipe total is for the colour in the reproduction gamut that was closest to the mapped (clipped or compressed) colour after iterative dye recipe correction.

6.9.3. Models fitted to the relationships between gel browning and computed dye quantities for mapped colours

Linear and non-linear models were fitted to the computed dye quantity data only where they were available for all four substrates. According to the squared Pearson correlation coefficients, R^2 , for the models fitted to the dye quantity data (Appendix Table 6.5), the increase seen in *total* quantity with increasing substrate browning in the clipping of Deep Pink and Green is best described as non-linear (quadratic). For the number of observations for these dyes ($n=4$), the R^2

values exceed the thresholds for significance at 5% for quadratic models (that is, $R^2 \geq 0.994$) (Lindley and Scott, 1984). For clipped Cyan and Deep Blue, and for compressed Orange, the relationship between total dye quantity and substrate browning can be described as either quadratic or linear, with the R^2 values for the fitted linear models also exceeding the threshold (of 0.903) for significance at 5%. However, similar to the traces for Deep Pink and Green, the traces for Cyan, Deep Blue and Orange display some curvature, and therefore a quadratic model is deemed more appropriate. A significant increase in total dye quantity with increased substrate browning is also found for the clipping of Mid Grey, where the relationship is linear. For significance at 10%, threshold values for R^2 are 0.810 and 0.976 respectively for linear and quadratic models. These see the traces for the compression of Deep Blue and Yellow as being fitted best by a linear model and that for the clipping of Red by a quadratic model, while at 0.951 the R^2 value for the quadratic model fitted to the compressed Red data approaches significance. The relationship between dye quantity and substrate browning is not significant for Pale Grey, due to noisy data (Figure 6.13). Models were not fitted to the dye quantity data for Deep Grey.

Examining the quadratic models further, the trends for the individual dyes in the recipes for the clipped Cyan, Deep Blue, Deep Pink, Green colours, and the compressed Orange colour, follow the significant non-linear trends for the recipe totals, with the exception of Brilliant Blue in Cyan, for which a linear model is the better fit (Appendix Table 6.5). The trends observed for the predominant dyes in the recipes for the mapped Red and Yellow colours (quadratic and linear respectively) follow those observed for the corresponding dye totals, at 10% significance. The linear increase in total dye quantity required to produce the clipped Mid Grey colour with substrate browning is mirrored by the significant, linear trend for the predominant, red dye.

Caution is needed when applying quadratic models; owing to their flexibility they can be made to fit most data. While R^2 values were either significant or high for the quadratic models fitted to the red dye data in the compression of Deep Blue, to the total and yellow dye data in the compression of Green, and to the yellow dye data in both the clipping and compression of Red

and in the clipping of Mid Grey (ranging from 0.93 to 0.99), R^2 values for the linear models fitted to the same data were comparatively low, and not significant, ranging from 0.1 to 0.6. The attempts to fit the linear model support the observation that the levels of these dyes in these recipes do not appear to change markedly with browning of the substrate, for the number of data points available. The fitted equations shown in Figure 6.10 to Figure 6.13 and in Appendix Figure 6.16 are the ones regarded the most appropriate, based on the above discussion.

The fitted models, linear or quadratic, for the relationships between dye quantity and decreasing substrate lightness were not intended as absolute or final solutions; rather they were intended to show the pattern of changes in dye recipe, not only with substrate browning, but also with target (tile) colour. The 'relationships' between target colours and mapping outcomes are discussed further in the following section.

6.10. General Discussion

Colour gamut boundaries provide information on the limits of viewable or printable colours in different media, and are used to determine the degree of mapping of colours that is required from one gamut to another, so that they can be displayed or reproduced by different media. In 3D colour food printing, colour images from an original medium such as a computer screen or smartphone device will be rendered within a food matrix using the reproduction medium of printer, food dyes and food substrate. In terms of its characteristics the food substrate will not be a fixed, nor small range, commodity. Gamuts of coloured foods are expected to vary according to the formulation and processing of the substrate.

In this study the model systems of coloured tiles and conventionally cooked food gels represented original and reproduction media respectively. A single food gel was manipulated to display the browning characteristic to different degrees, starting with white. Gamut boundary colours resulting from the addition of the same primary-dye blends to each gel variant were computed. The tile colours were mapped to each gel colour gamut, starting with mapping to the gamut from the dyed, White gel, before being mapped from here to each of the colour gamuts

from the dyed, Brown gels. The aim was devise an algorithm for rapid computation of dye quantities in order to render the best equivalent of a target colour for a given level of substrate browning, which could be used by the 3D food printer.

6.10.1. Observed trends in the lightness, chroma and dye recipes of the mapped colours

For all tile colours, the results provide information on the limits of available replacement colours. The hue angle range covered by the Orange, Red and Yellow tile colours (30 to 88 degrees, anti-clockwise from the $+a^*$ axis) coincides with the regions of the gamuts from the dyed, Brown gels having a larger population of colours available for replacing the original colours (see also Figure 5.7 in Chapter Five). At these hue angles the (light-compressed) White substrate gamut boundary appears to fit more tightly around the Brown substrate gamut boundary, and the resulting overlap increases the chances of light compression alone placing the tile colour inside the reproduction gamut.

At the hue angles for Cyan, Deep Blue, Deep Pink, and Green (ranging from seven to 151 degrees in the clockwise direction from the $+a^*$ axis), the range of colours available to replace the original colours shrinks with substrate browning. When this occurs, compression may not always provide a solution because compression lines may not be able to reach the reproduction gamut boundary.

Larger increases in dye quantities with substrate browning were observed when the decrease in lightness of the mapped colour was large, relative to the change in chroma. Again, this is where the Cyan/Deep Blue/Deep Pink/Green and Orange/Yellow/Red groupings displayed differences; for Cyan, Deep Blue, Deep Pink and Green the trend was observed for the clipped colours, while for Orange, Yellow and Red it was found for the compressed colours.

6.10.2. Effects of gamut boundary detail and choice of mapping algorithm

In this chapter, colour gamut mapping utilised the colour gamut boundaries for the dyed substrates that were computed in Chapter Five, which in their entirety were computed in great detail with a very high density of points. The rationale for this level of detail was to allow mapping of tile colours to the required gamut boundary with relative ease, but this came at the expense of not being able to obtain dye recipes for colours that were mapped to *within* a reproduction boundary by compression. Therefore it is recommended that some of the detail in the computed gamut boundaries be sacrificed, and to instead fill the inside of the boundary with some detail. This should increase the range of starting recipes for iterative recipe correction, which are closer to colours that have undergone full compression and which therefore lie within the gamut boundary. Full compression can take place when the original gamut boundary is available, as would normally be the case; in this study the gamut boundary of the tile colours, which would have enabled initial, full compression to the White gel gamut boundary, was not known. Any further detail needed at individual hue angles could be filled by interpolation of boundary points, in the same way that some of the outermost boundary points were derived by interpolation in this study.

The choice of hue-preserving gamut mapping placed a heavy constraint on the accuracy of the results, and there may not be a need for this level of accuracy for a printed food application. For consistency, recipe correction was used to find solutions for *all* mapped colours. For many of these colours however, the closest colour on the gamut boundary (the source of the starting recipe) was already within three $\Delta E^*_{ab,10}$ units and one degree of the mapped colour. For the Deep Blue colour clipped from the White to the Brown1 and Brown2 gamuts hue angle differences between the clipped colour and the starting colour exceeded the one degree limit before recipe correction, ranging from five to seven degrees; recipe correction reduced these differences to between zero and two degrees, and yet the dye quantity traces before and after recipe correction appear similar (Figure 6.14). The dye quantity traces for the clipped Mid Grey

colour before and after recipe correction show more obvious differences (Figure 6.14). Although the large hue angle differences (31 to 114 degrees) in the Brown1 and Brown2 gamuts indicated the need for recipe correction, again this should not have been necessary due to the low chroma of the colours. To save on computational load a suggested approach for the 3D colour food printer is to keep to a minimum ΔE^* mapping approach in a constant hue angle plane, but to either relax the constraint on the hue angle of the nearest colour (removing the need for dye recipe correction), or impose a chromatic threshold above which the hue angle differences are deemed too large, therefore making recipe correction necessary; a given hue angle difference might be more problematic at a higher chroma than at a lower chroma. Such an approach would combine aspects of minimum ΔE^* clipping proper, which clips to the nearest point *per se*, with those of hue-preserving minimum ΔE^* clipping. The application of ΔH^* , the Euclidean hue difference, alongside the angular difference might prove useful here.

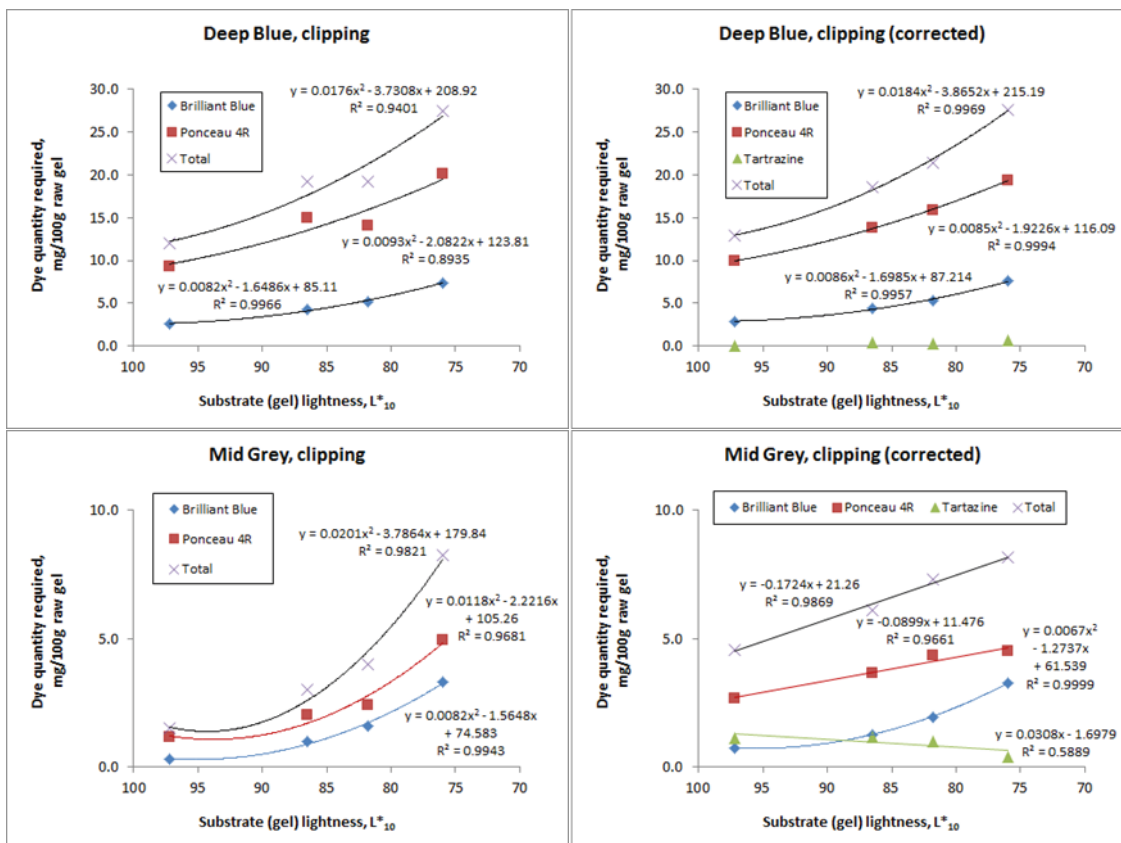


Figure 6.14 Comparison of dye recipes for colours closest to the clipped Deep Blue and Mid Grey tile colours before (left) and after (right) iterative dye recipe correction. Each dye recipe is for a colour in each of the four reproduction gel substrates, which differ in their level of measured lightness.

6.10.3. Implications for 3D colour food printing

The findings in this study were as much a function of using the tile colours as models of original colours, as they were of using the gels and food dyes for reproducing the colours. The chromatic boundaries of the tile colours was not known, and colour gamut mapping in this study worked to assumed lightness range of zero to 100 units for tile colours. In actual 3D printing of colour in food, it is expected that the full gamut of the original image or medium would be known, as they are in conventional colour printing. Therefore all sequential lightness-chroma compressions of original colours to the gamut of a dyed, white substrate would be full compressions, placing the compressed colours within the gamut boundary, rather than partial compressions placing the colours on the boundary itself. For colours similar to the Cyan, Deep Blue, Deep Pink and Green colours in this study, full compressions would have resulted in steeper increases in dye quantities with substrate browning (compared to the very small increases that were observed for their partially compressed counterparts) if the overlap of light-compressed White gamuts and Brown gamuts meant that the chroma of the compressed colours with browning remained unchanged, similar to what was found for the Orange, Red and Yellow compressions in this study.

For 3D colour food printing also, a decision needs to be made on whether clipping or compression should be used as the basis of the algorithm which will compute dye quantities in response to changes in characteristics of the food substrate. Compression algorithms are regarded as working better than clipping algorithms when the differences between media and/or gamuts are large (Morovic, 2003). In this study, original and reproduction media were either the same (as in the mapping of colours from White to Brown gamuts) or had similar properties (the smooth surfaces of the tiles and gels for the initial mapping of the tile colour to White), which means that the clipping algorithm should have given the better results. For the food printer, we would expect very large differences between image gamuts and food substrate gamuts, and therefore compression might be the favoured approach.

6.11. Appendix

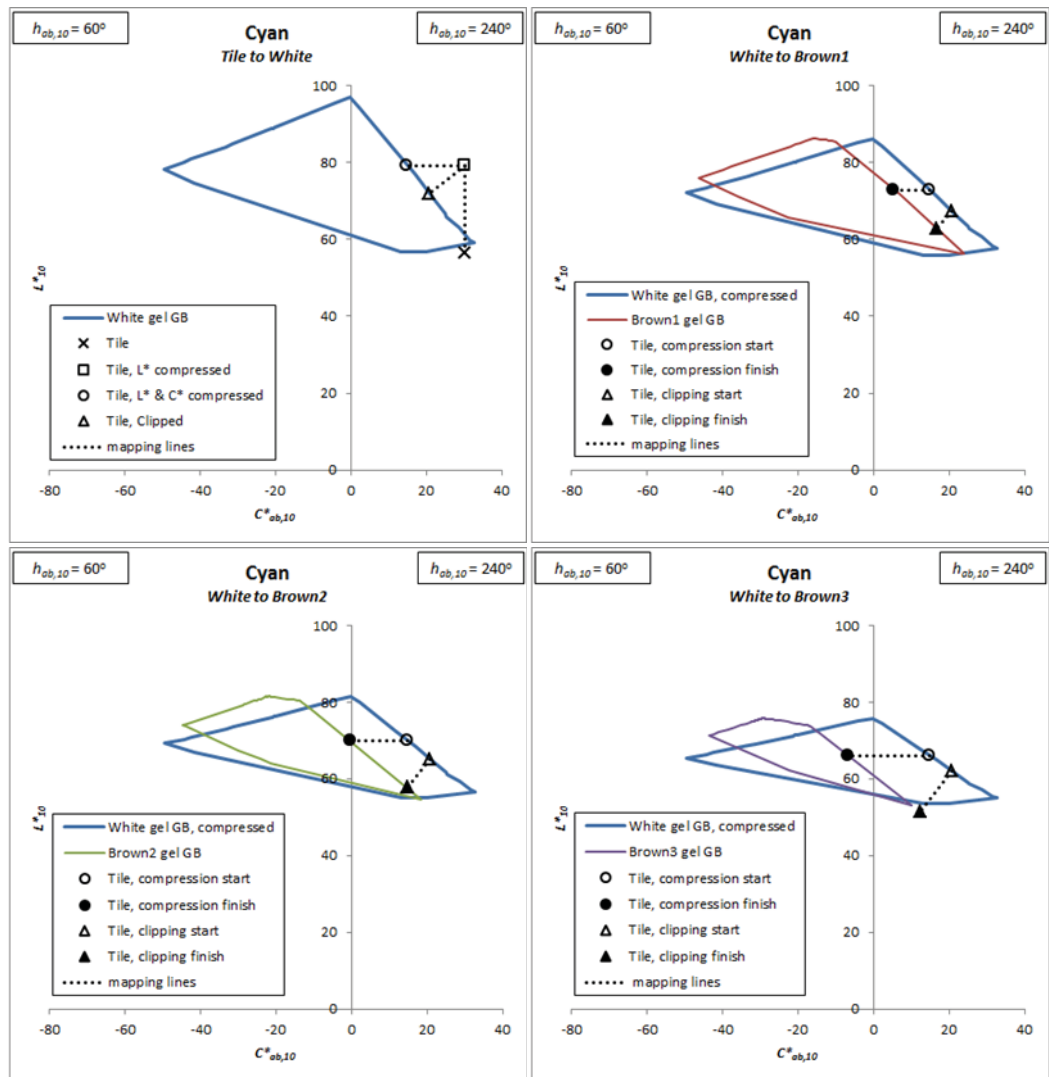
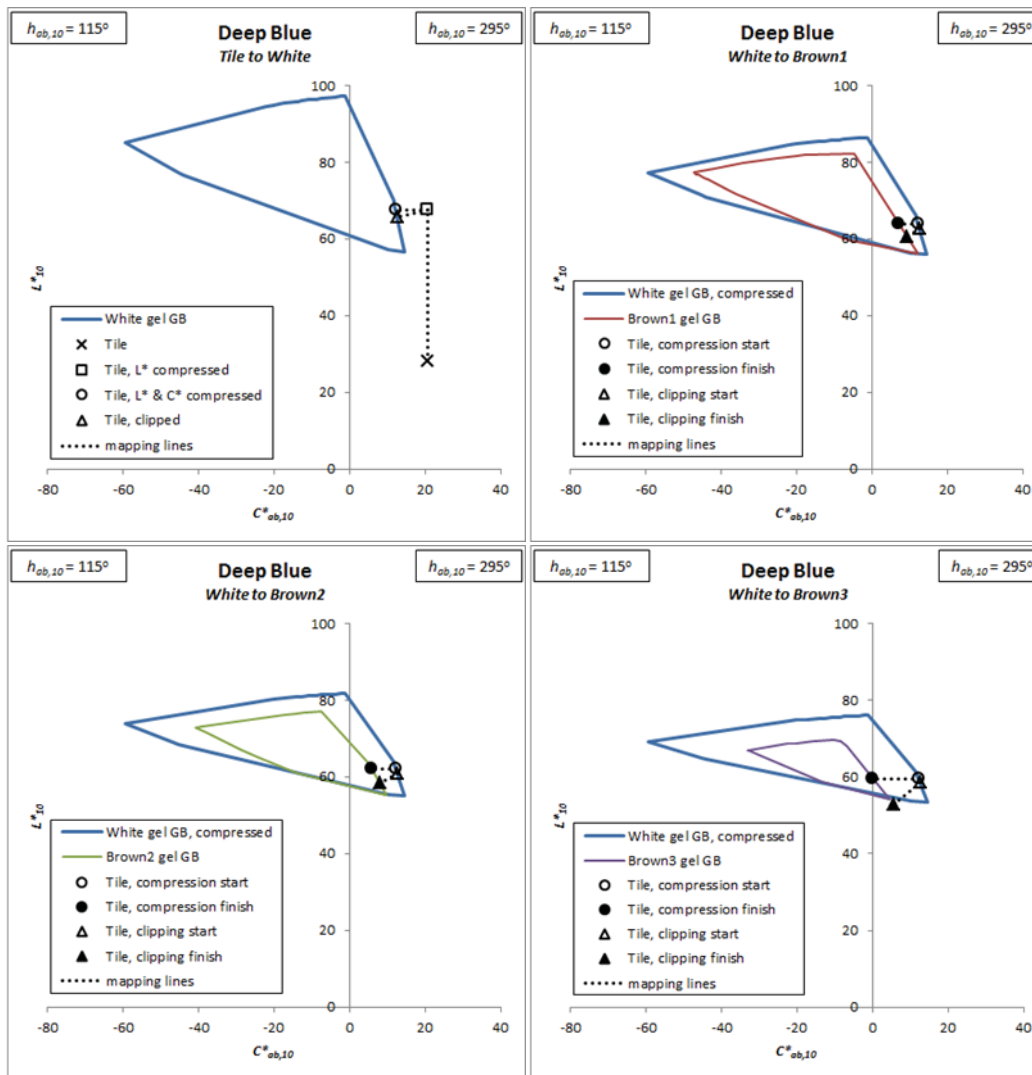
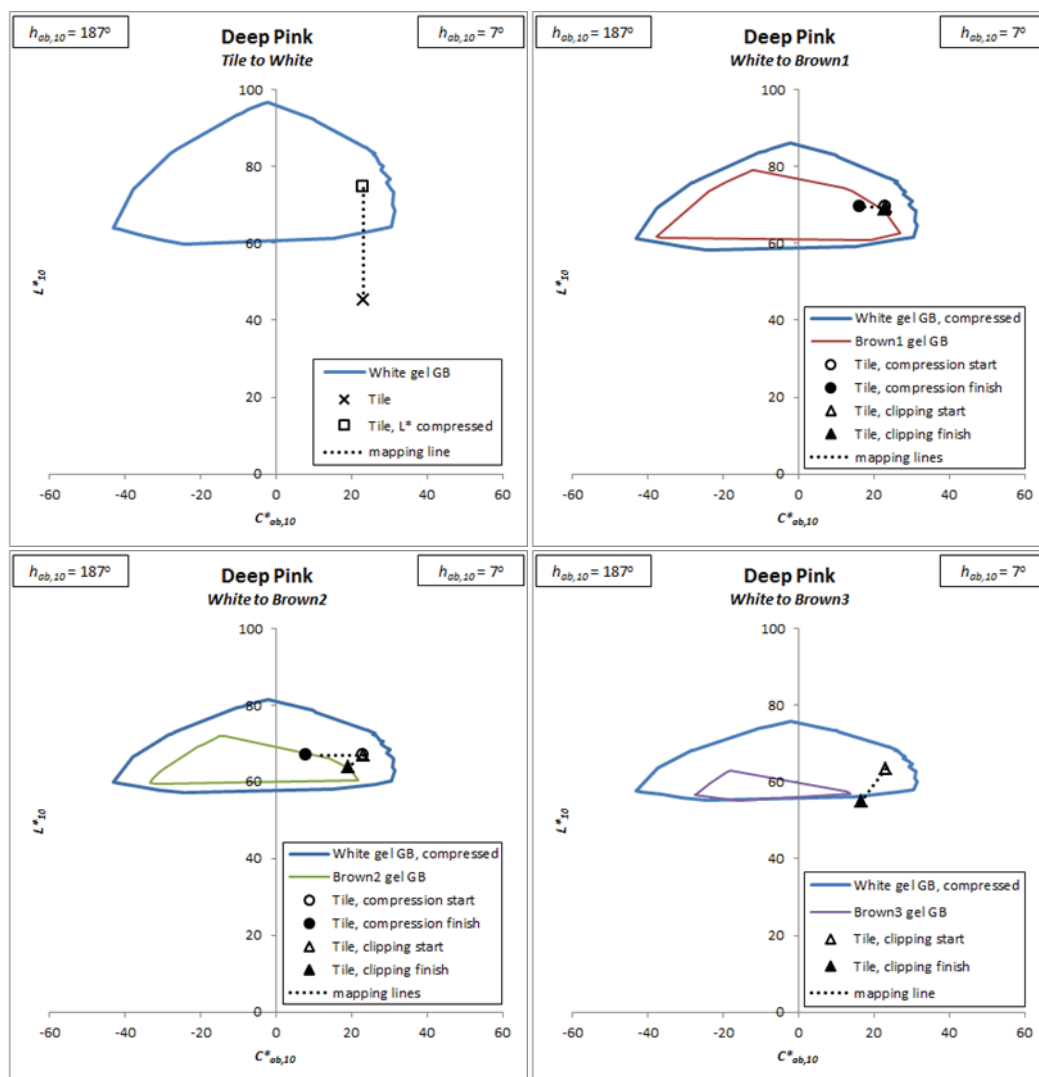
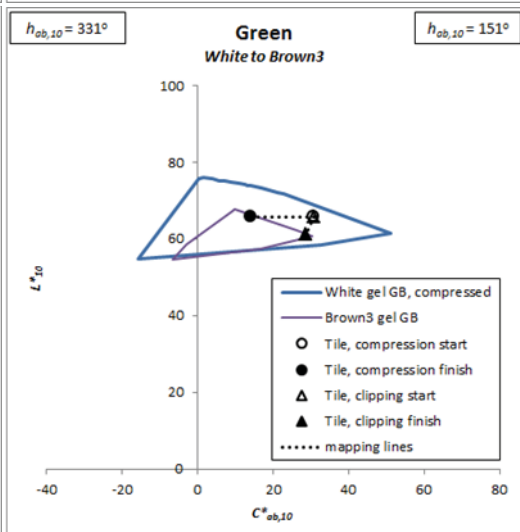
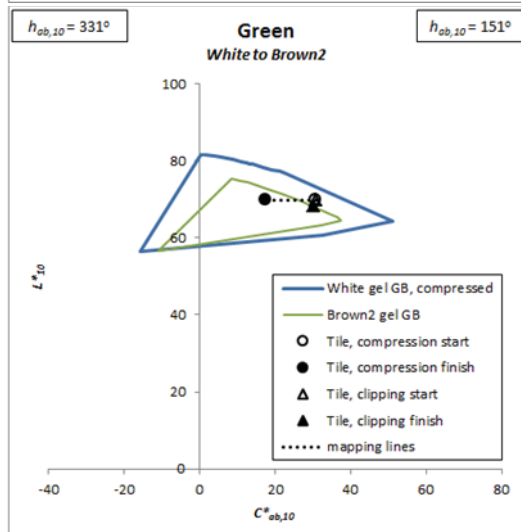
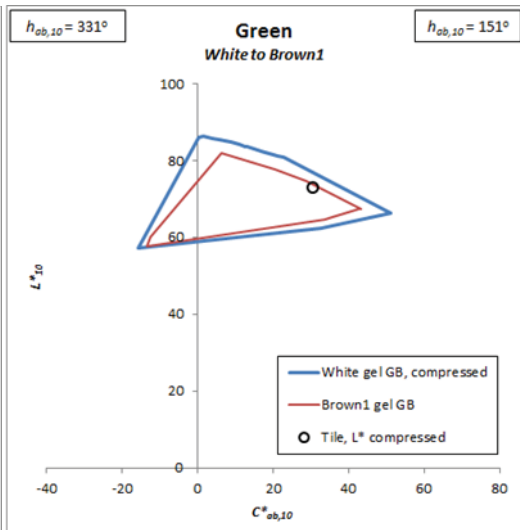
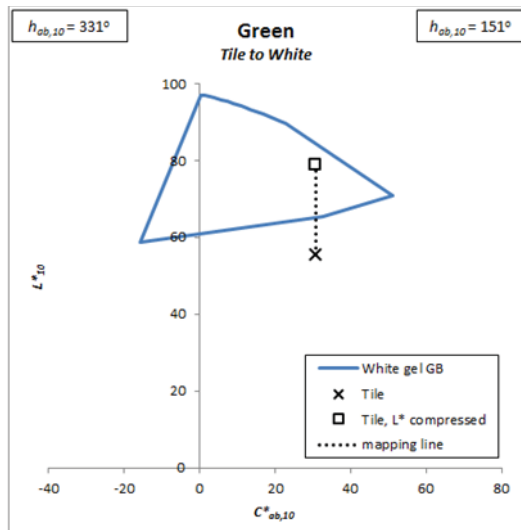
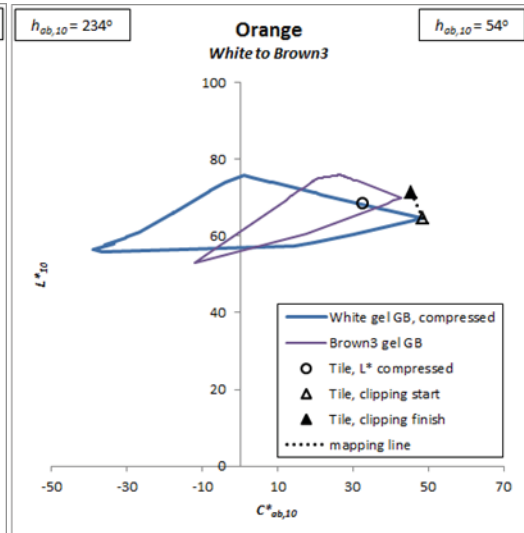
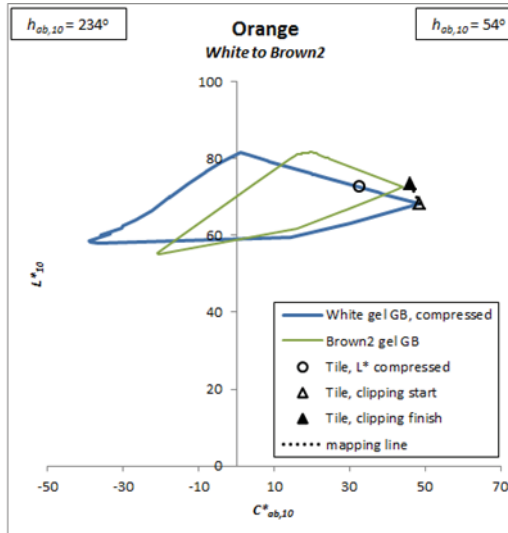
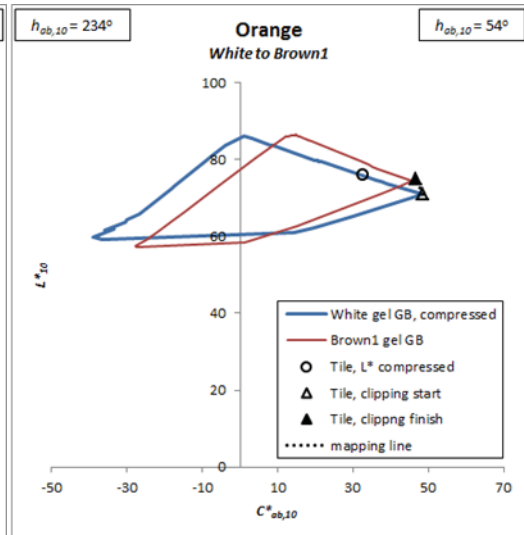
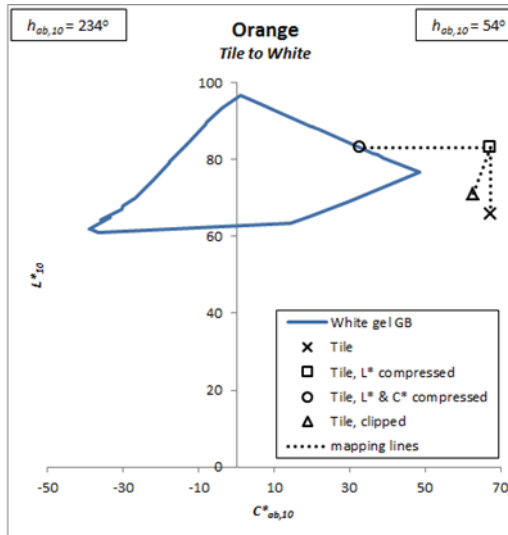


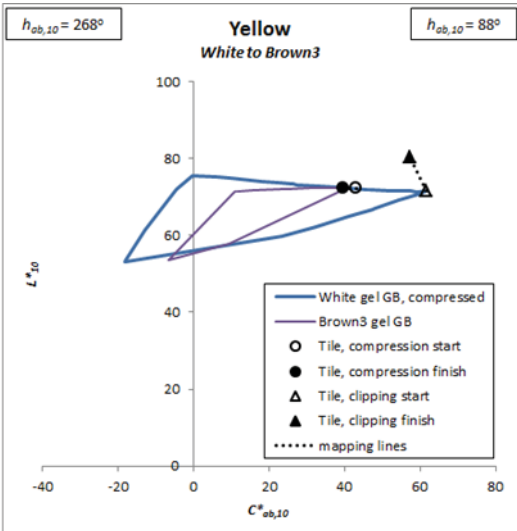
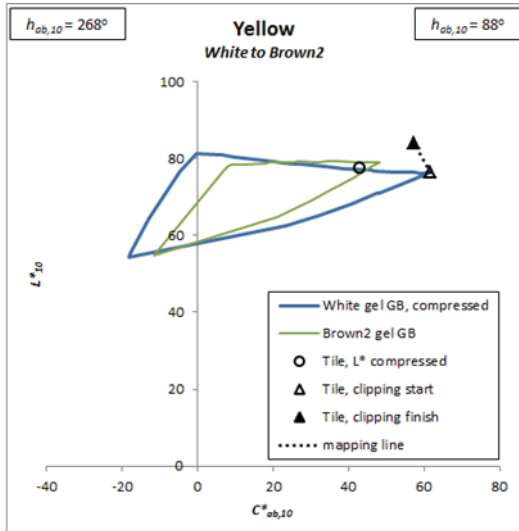
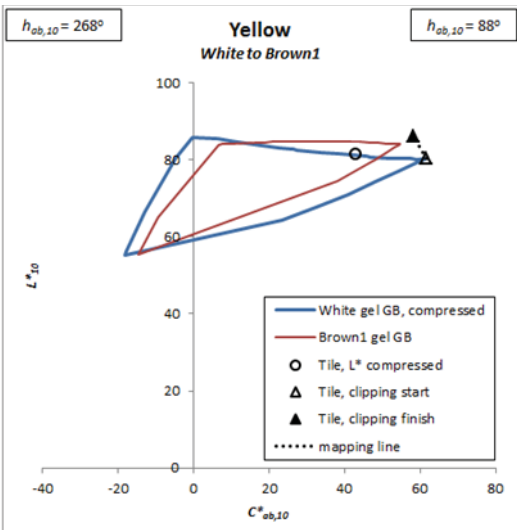
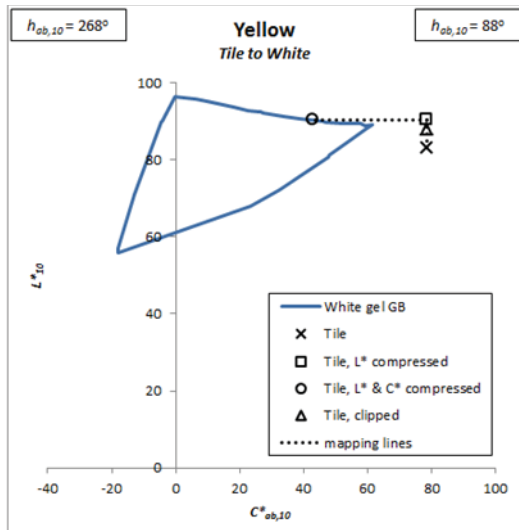
Figure 6.15 Plots showing the mapping of each SCI tile colour, by compression and clipping algorithms, to each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels), in more detail than is shown in Figure 6.5 to Figure 6.9 in which the original and final positions only of the tile colours are shown. In the present figure, results are separated into individual plots for each reproduction gamut and show the positions of the lightness-compressed original colours prior to clipping or chroma compression (continued on the following pages).

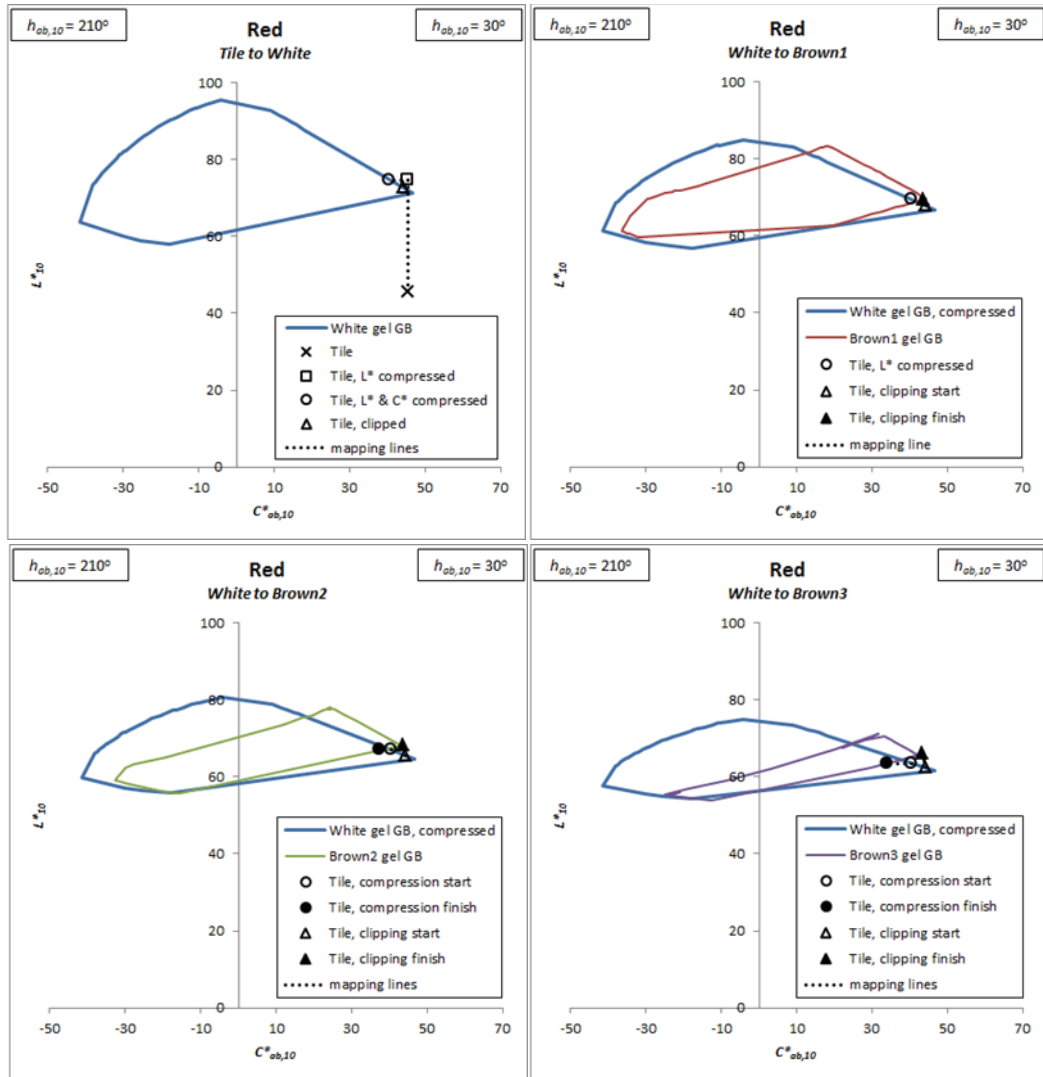


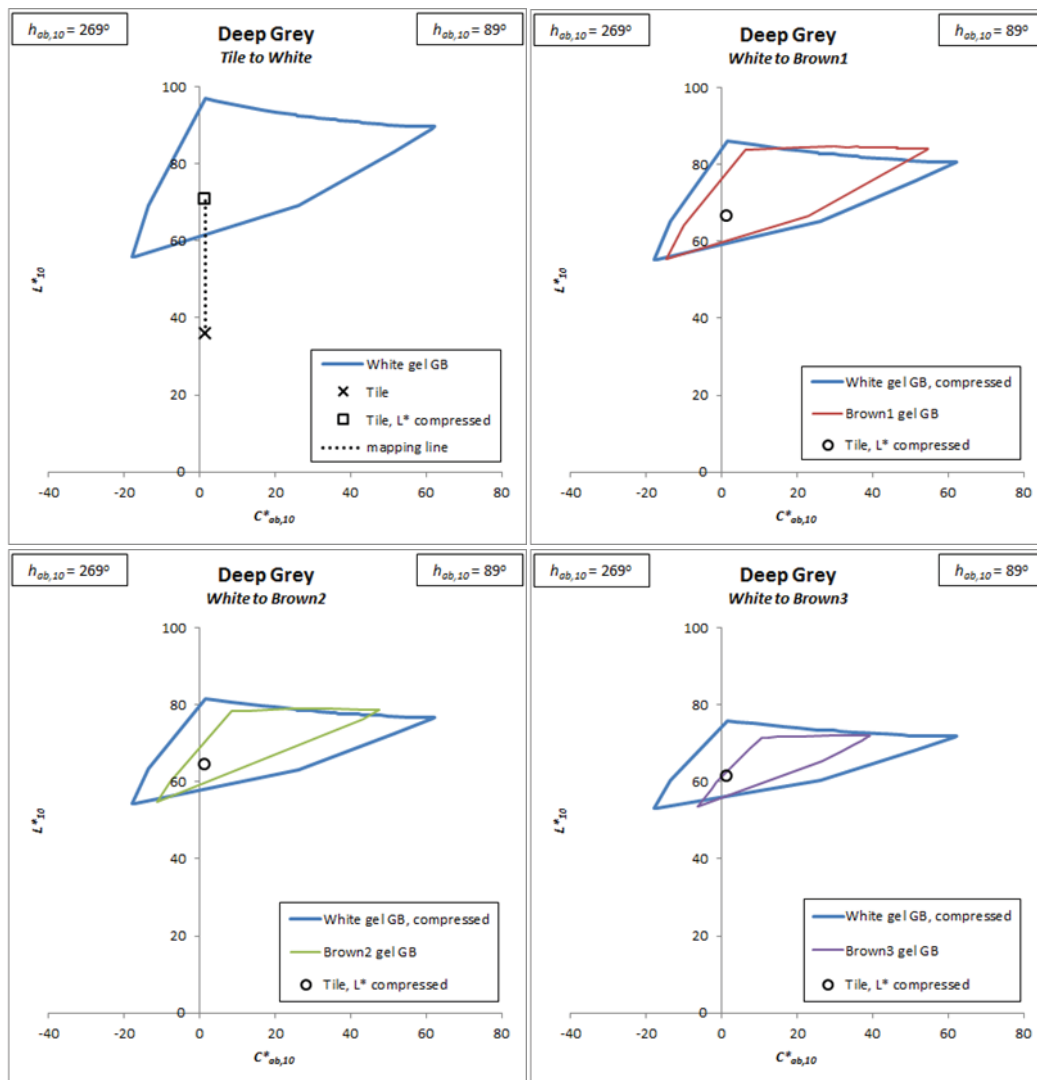


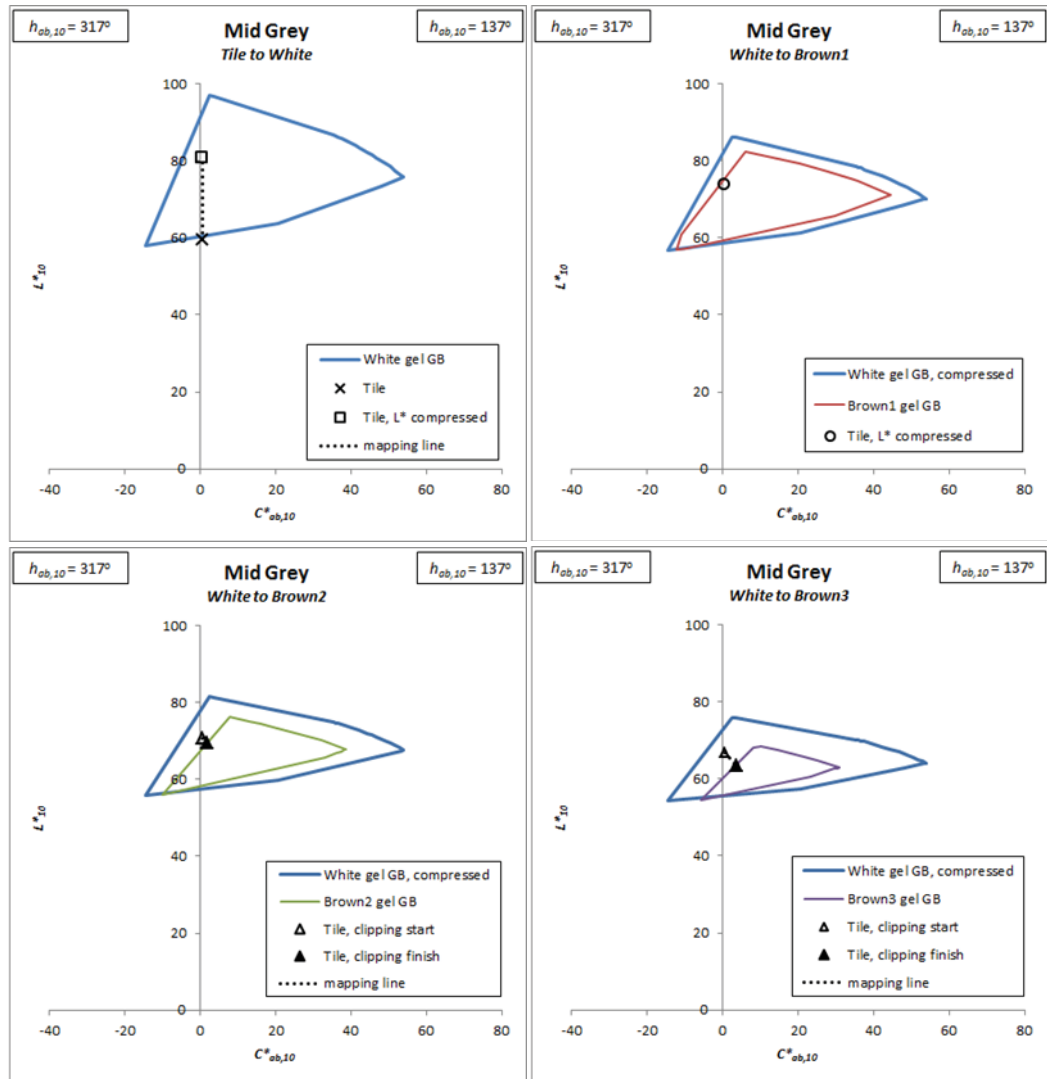












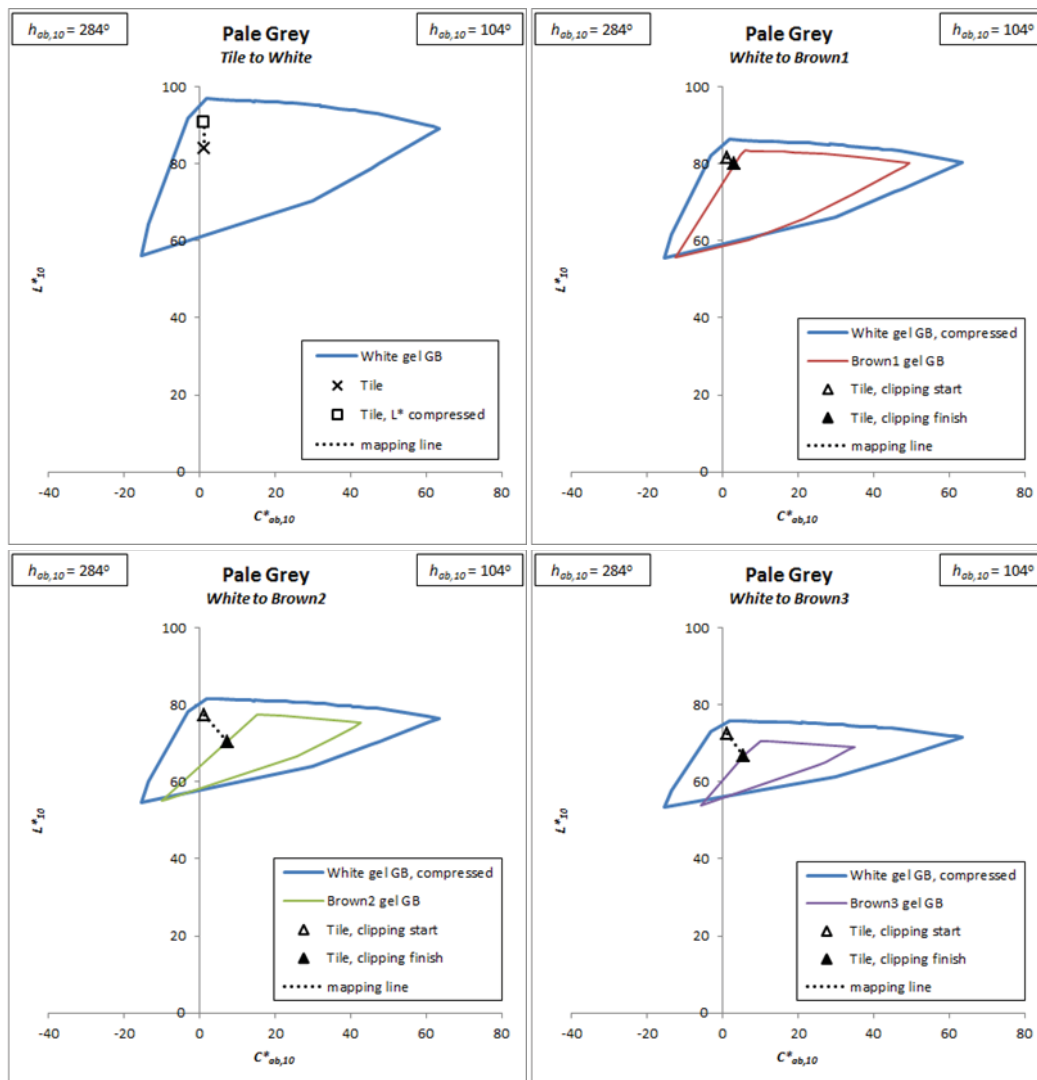


Table 6.2 Computed chroma, $C^*_{ab,10}$, and lightness, L^*_{10} , values of each SCI tile colour following mapping by clipping or compression algorithms to each of the four reproduction colour gamuts (for the White, Brown1, Brown2 and Brown3 gels) (see also Figure 6.5 to Figure 6.9 and Appendix Figure 6.15). Letter labels refer to the extent to which mapping was possible; key to labels is shown below table.

Original Tile Colour $C^*_{ab,10}$, L^*_{10}	Mapping Algorithm	Original gamut to Reproduction gamut							
		Tile to White		White to Brown1		White to Brown2		White to Brown3	
		$C^*_{ab,10}$	L^*_{10}	$C^*_{ab,10}$	L^*_{10}	$C^*_{ab,10}$	L^*_{10}	$C^*_{ab,10}$	L^*_{10}
Cyan 30.3, 56.6	Clipping	20.7	71.9	16.7	62.8	14.8	57.7	12.5	51.3
								BP 10.2	53.1
	Compression	PC 15.0	79.3	PC 5.3	72.9	OP -0.4	69.9	OP -6.7	66.1
Deep Blue 20.7, 28.0	Clipping	12.6	65.7	9.3	60.5	8.0	58.3	5.6	52.8
								BP 4.5	54.1
	Compression	PC 12.3	67.4	PC 7.1	63.9	PC 5.9	62.1	PC 0.1	59.5
Deep Grey 1.5, 35.8	Clipping	LC 1.5	70.7	LC 1.5	66.4	LC 1.5	64.2	LC 1.5	61.3
	Compression	LC 1.5	70.7	LC 1.5	66.4	LC 1.5	64.2	LC 1.5	61.3
Deep Pink 23.1, 45.4	Clipping	LC 23.1	74.6	22.8	68.8	19.2	63.8	16.7	54.8
								BP 13.9	56.9
	Compression	LC 23.1	74.6	16.2	69.4	8.0	66.8	NO	
Green 30.7, 55.5	Clipping	LC 30.7	78.8	LC 30.7	72.6	30.1	68.2	28.7	61.3
	Compression	LC 30.7	78.8	LC 30.7	72.6	17.4	69.6	14.3	65.8
Mid Grey 0.5, 59.6	Clipping	LC 0.5	80.5	LC 0.5	73.8	1.9	69.5	3.6	63.6
	Compression	LC 0.5	80.5	LC 0.5	73.8	NO		NO	
Orange 67.3, 65.8	Clipping	62.6	71.1	46.8	74.9	46.1	73.5	45.6	71.2
		BP 48.5	76.6	BP 45.6	74.4	BP 44.0	72.6	BP 42.7	69.9
	Compression	PC 32.8	83.1	LC 32.8	75.8	LC 32.8	72.4	LC 32.8	68.2
Pale Grey 1.1, 84.0	Clipping	LC 1.1	90.6	3.2	80.1	7.3	70.3	5.4	66.9
	Compression	LC 1.1	90.6	NO		NO		NO	
Red 45.3, 45.6	Clipping	44.2	72.7	43.7	69.3	43.5	68.2	43.2	66.0
						BP 43.2	68.2	BP 42.1	65.7
	Compression	PC 40.6	74.7	LC 40.6	69.4	PC 37.4	66.9	PC 33.9	63.6
Yellow 78.7, 83.2	Clipping	78.6	88.0	58.2	86.0	57.2	84.1	57.3	80.4
		BP 61.5	89.1	BP 54.8	84.1	BP 48.2	79.0	BP 39.8	72.2
	Compression	PC 43.0	90.3	LC 43.0	81.2	LC 43.0	77.2	PC 39.7	72.2

BP: boundary rim point, replacing original mapping solution in row immediately above;
PC: partial compression i.e. compression from one gamut boundary to the other;
OP: solution located in opposite hue angle plane (not used);
LC: lightness compression only, without subsequent chroma mapping;
NO: no solution possible.

No label indicates that a full algorithm could be applied (lightness compression, followed by clipping or chroma compression), and that the mapped colour was located within the reproduction gamut boundary in the hue angle plane of tile without it having to be replaced by an alternative listed above.

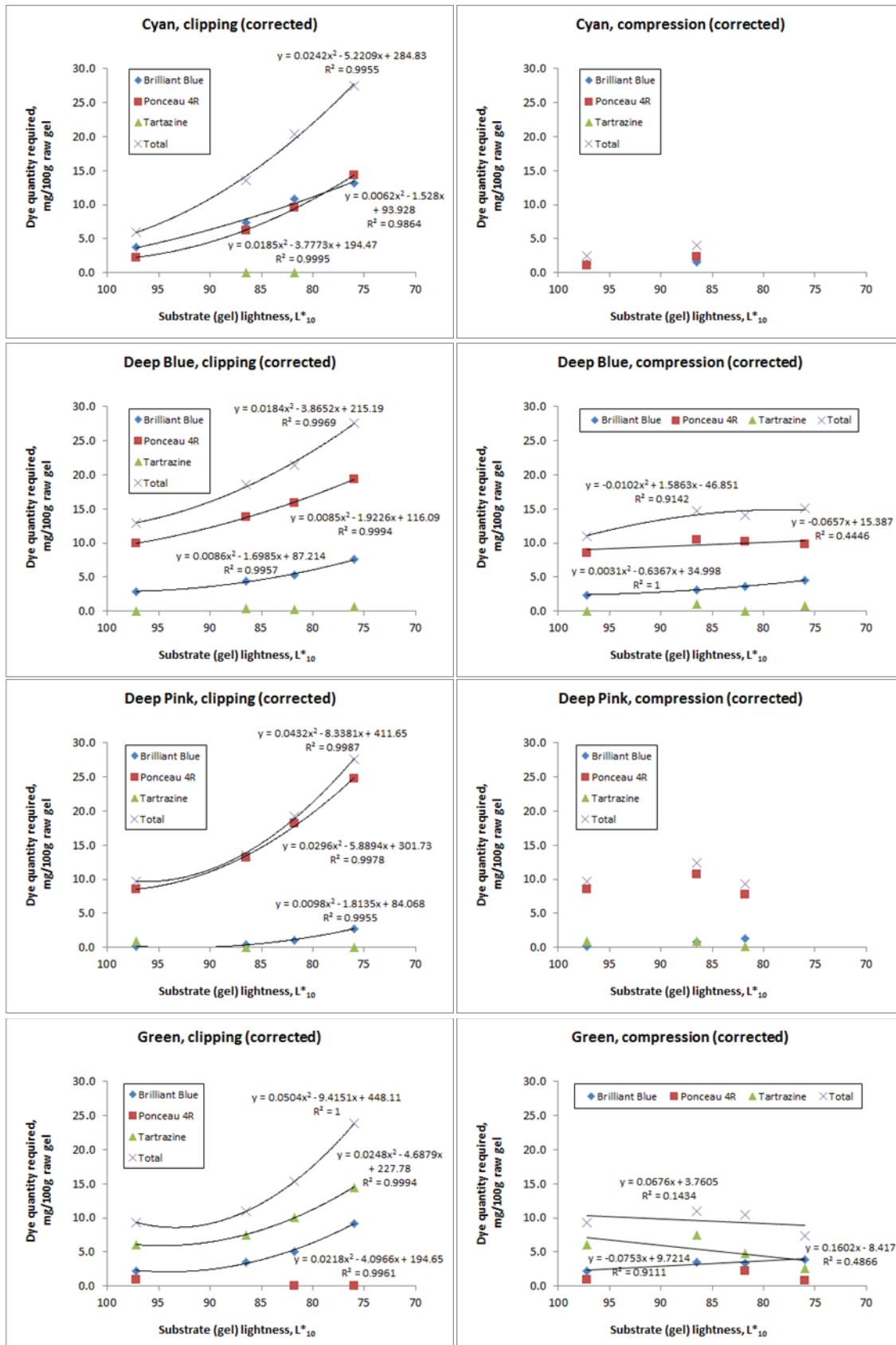
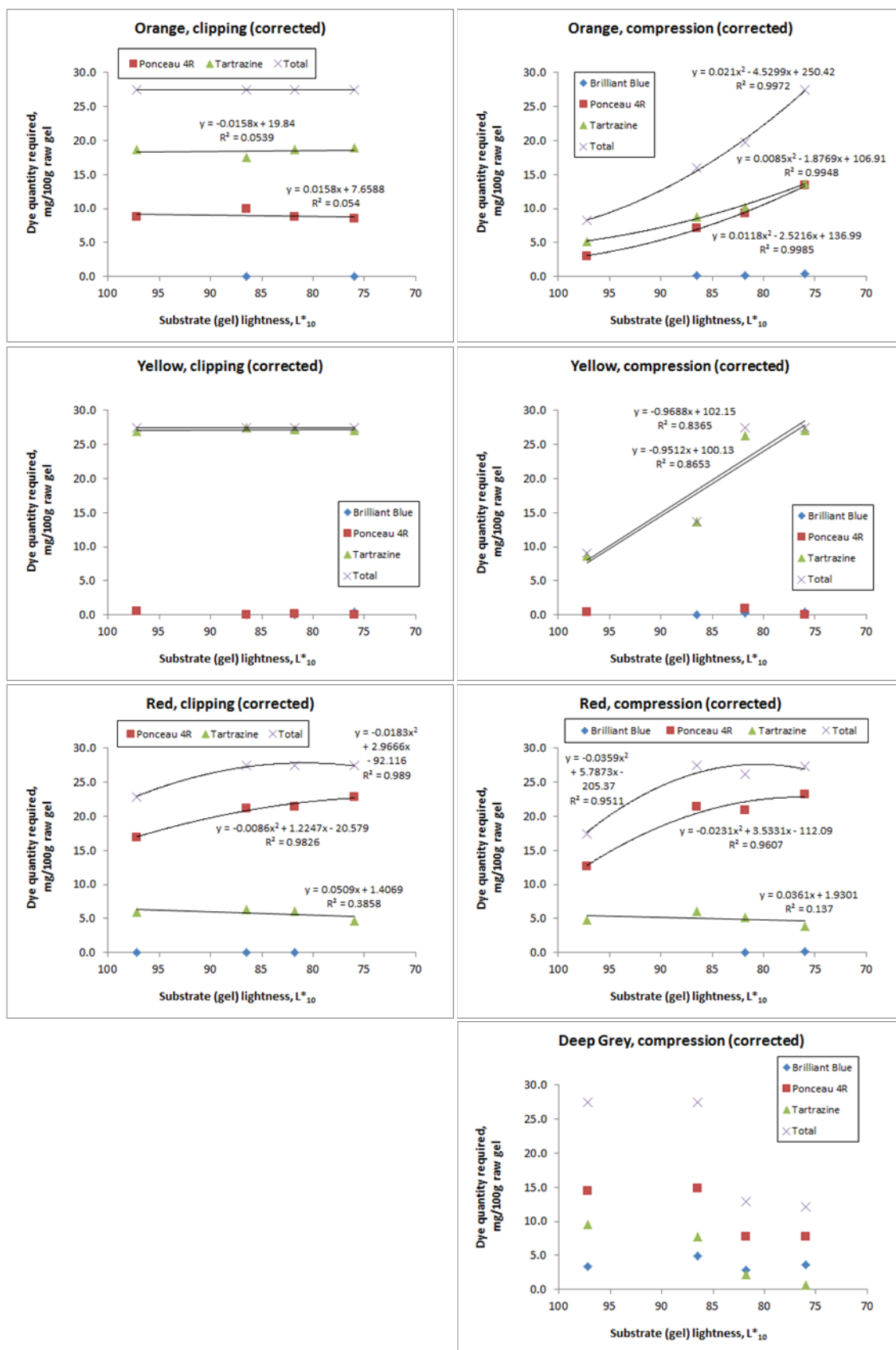


Figure 6.16 Full details of the dye recipes (total quantity and quantities of the constituent dyes) needed to produce the best equivalent of each SCI tile colour in each of the four reproduction gel substrates, according to the increase in the measured lightness of the substrate. Each dye recipe is for the colour in the reproduction gamut that was closest to the mapped (clipped or compressed) colour after iterative dye recipe correction (continued on the following pages).



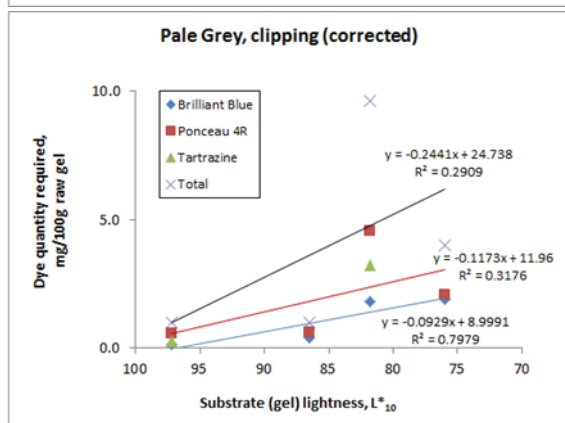
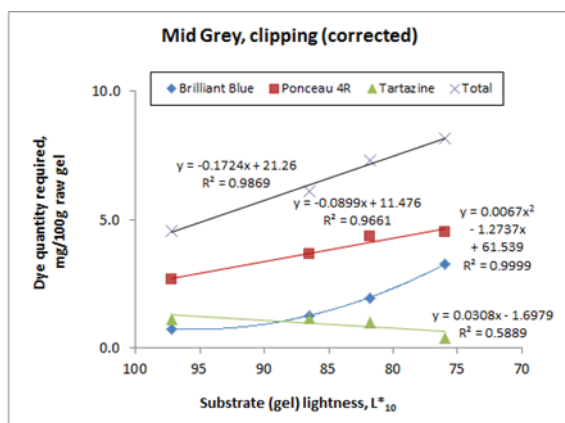


Table 6.3 Overall differences, $\Delta E^*_{ab,10}$, and hue angle differences, $\Delta h_{ab,10}$, between mapped (clipped or compressed) tile colours and the closest colours to the mapped colours following iterative dye recipe correction. Refer letter labels, and key to labels given below table for more details.

Original Tile Colour	Mapping Algorithm	Original gamut to Reproduction gamut							
		Tile to White		White to Brown1		White to Brown2		White to Brown3	
		$\Delta E^*_{ab,10}$	$\Delta h_{ab,10}$	$\Delta E^*_{ab,10}$	$\Delta h_{ab,10}$	$\Delta E^*_{ab,10}$	$\Delta h_{ab,10}$	$\Delta E^*_{ab,10}$	$\Delta h_{ab,10}$
Cyan	Clipping	S 0.5	0.7	0.4	-0.9	0.4	-0.7	B	
	Compression	S 0.8	1.8	S 0.7	5.7	n/a		n/a	
Deep Blue	Clipping	0.4	0.6	0.2	0.0	0.5	-2.2	C 0.0	0.0
	Compression	0.4	-0.5	1.7	-9.1	0.2	-1.4	0.0	0.0
Deep Grey	Clipping	n/a		n/a		n/a		n/a	
	Compression	S 11.0	2.9	S 7.7	-23.1	0.0	-0.3	0.0	0.5
Deep Pink	Clipping	2.5	-6.0	0.2	-0.1	S 0.6	-0.1	C 0.0	-0.1
	Compression	2.5	-6.0	1.4	-3.7	1.1	-0.1	n/a	
Green	Clipping	3.3	1.0	S 1.8	-0.9	0.5	0.7	0.5	-0.7
	Compression	3.3	1.0	S 1.8	-0.9	2.6	0.7	0.7	0.3
Mid Grey	Clipping	2.9	36.4	2.1	46.6	1.4	21.0	0.0	-0.1
	Compression	2.9	36.4	2.1	46.6	n/a		n/a	
Orange	Clipping	B		CS 1.1	1.1	B		CS 0.2	-0.3
	Compression	S 1.3	-2.2	2.1	-0.3	2.6	1.2	S 3.3	2.3
Pale Grey	Clipping	2.5	13.6	S 1.0	11.1	2.2	1.5	S 0.6	0.6
	Compression	2.5	13.6	n/a		n/a		n/a	
Red	Clipping	0.6	-0.7	S 0.7	-0.1	B		B	
	Compression	1.0	-1.3	S 0.9	50.2	0.2	0.2	0.7	0.5
Yellow	Clipping	CS 1.0	0.3	CS 0.3	0.3	CS 0.7	0.3	CS 0.3	0.3
	Compression	S 1.2	-1.5	S 3.4	-1.1	S 1.4	-1.3	S 0.3	0.3

- S: differences between the mapped colour and the starting colour for recipe correction on the reproduction gamut boundary, which was already the closest colour to the mapped colour;
- B indicates that a colour on the chromatic rim of the reproduction gamut boundary replaced the mapped colour, and that the rim colour was derived from a dye recipe during gamut boundary computation, removing the need for iterative recipe correction;
- C also indicates that a chromatic rim colour replaced the mapped colour, but recipe correction was needed because the rim colour had been interpolated and therefore did not have an associated dye recipe;
- n/a indicates that mapping was not possible.

Table 6.4 Overall differences, $\Delta E^*_{ab,10}$, and hue angle differences, $\Delta h_{ab,10}$, between selected compressed colours and their starting colours for iterative dye recipe correction, and between the compressed colour and the colour from the first recipe correction iteration step. The table also compares the dye recipes for the colours from the two steps, for a given compression. The dye recipes indicated in bold are those that were selected as the dye recipe for the mapped colour.

Original Tile Colour	Recipe correction iteration step	Compression from Tile gamut to White gamut				
		Distance of solution from mapped colour		Dye quantities, mg dye/100 g raw gel		
		$\Delta E^*_{ab,10}$	$\Delta h_{ab,10}$	Blue	Red	Yellow
Cyan	Starting colour (closest available)	0.8	1.8	1.4	1.1	
	1	1.1	-2.0	1.3	1.4	0.0
Deep Pink	Starting colour (closest available)	2.7	6.6	0.2	8.0	
	1	2.5	-6.0	0.2	8.6	0.9
Original Tile Colour	Recipe correction iteration step	Compression from White gamut to Brown1 gamut				
		Distance of solution from mapped colour		Dye quantities, mg dye/100 g raw gel		
		$\Delta E^*_{ab,10}$	$\Delta h_{ab,10}$	Blue	Red	Yellow
Cyan	Starting colour (closest available)	0.7	5.7	1.6	2.4	
	1	0.8	-6.0	1.6	2.9	0.0
Deep Blue	Starting colour (closest available)	2.2	9.3	3.2	8.8	
	1	1.7	-9.1	3.1	10.5	1.1

Table 6.5 Squared correlation coefficients, R^2 , for linear and quadratic models fitted to total and individual primary dye quantity data against increased artificial browning of the gel substrate colour, for clipped and compressed tile colours. Statistical significance is indicated for the number of observations for each dye and dye total (n=4).

Original Tile Colour	Dye quantity	R^2 for fitted model			
		Clipping		Compression	
		Linear	Quadratic	Linear	Quadratic
Cyan	Total	0.9719 ^a	0.9955 ^c	n<4	
	Brilliant Blue	0.9788 ^a	0.9864 ^d		
	Ponceau 4R (red)	0.9544 ^a	0.9995 ^c		
Deep Blue	Total	0.9661 ^a	0.9969 ^c	0.8113 ^b	0.9142
	Ponceau 4R	0.9833 ^a	0.9994 ^c	0.4446	0.9847 ^d
	Brilliant Blue	0.9304 ^a	0.9957 ^c	0.9584 ^a	1.000 ^c
Deep Grey	Total	n/a		n/a	
	Ponceau 4R				
	Tartrazine (yellow)				
	Brilliant Blue				
Deep Pink	Total	0.8921 ^b	0.9987 ^c	n<4	
	Ponceau 4R	0.9354 ^a	0.9978 ^c		
	Brilliant Blue	0.7516	0.9955 ^c		
Green	Total	0.7922	1.000 ^c	0.1434	0.9869 ^d
	Tartrazine	0.8458 ^b	0.9994 ^c	0.4866	0.9286
	Brilliant Blue	0.8189 ^b	0.9961 ^c	0.9111 ^a	0.9424
Mid Grey	Total	0.9869 ^a	0.9896 ^d	n/a	
	Ponceau 4R	0.9661 ^a	0.9764 ^d		
	Brilliant Blue	0.8714 ^b	0.9999 ^c		
	Tartrazine	0.5889	0.9854 ^d		
Orange	Total	n/a		0.9736 ^a	0.9972 ^c
	Tartrazine	0.0539	0.6845	0.9749 ^a	0.9948 ^c
	Ponceau 4R	0.0540	0.6846	0.9730 ^a	0.9985 ^c
Pale Grey	Total	0.2909	0.3278	n/a	
	Ponceau	0.3176	0.3486		
	Brilliant Blue	0.7979	0.8227		
Red	Total	0.7712	0.9890 ^d	0.7588	0.9511
	Ponceau 4R	0.9434 ^a	0.9826 ^d	0.8781 ^b	0.9607
	Tartrazine	0.3858	0.9831 ^d	0.1370	0.9756 ^d
Yellow	Total	n/a		0.8365 ^b	0.8405
	Tartrazine	n/a		0.8653 ^b	0.8700

a: significant at 5% for linear model (threshold critical value for R^2 of 0.903);

b: significant at 10% for linear model ($R^2 \geq 0.810$);

c: significant at 5% for quadratic model ($R^2 \geq 0.994$);

d: significant at 10% for quadratic model ($R^2 \geq 0.976$);

n/a: mapping was not possible (Deep Grey clipping; Mid Grey and Pale Grey compression), or no change in dye quantity with substrate browning (total quantities for clipped Orange and Yellow), or iterative dye recipe correction unsuccessful (Deep Grey compression).

Chapter Seven: Comparing colorimetric matching and colour gamut mapping

7.1. Introduction

This chapter revisits the problem of matching the colours of the tile standards with coloured microwave-baked cakes containing blends of primary dyes, which was the subject of Chapter Four, but now incorporates the colour gamut boundary computation, and colour gamut mapping approaches developed in the intervening chapters. This chapter will consolidate the two different methodologies, colorimetric matching and colour gamut mapping, and in doing so compare their performance in finding the best equivalents of each original tile colour within the gamut of (possible) cake colours. This chapter does not include methods which adjust for substrate characteristics because the cake was taken to be a single substrate of mixed characteristics.

In Chapter Four, a predictive colour matching model was developed which combined Kubelka-Munk linear absorption coefficients that were derived for each primary dye in the cake, with the colorimetric matching technique based on the Allen algorithm. This model computed dye recipes for the cakes which were good first solutions in that cake colours computed using these recipes were largely within the numerical limit of a good visual match to the corresponding tile colours. Differences in the physical properties of the tiles and cakes meant that the solutions were much better when matching was targeted at the measured reflectance of the tile colour, rather than to its measured reflectance corrected for surface effects. However, for some tile colours, the computed recipes called for negative dye concentrations, or concentration totals that exceeded the legal maximum. On the basis of an approximate cake colour gamut boundary it was seen that those tile colours for which out-of-range concentrations were computed lay outside this boundary. As expected, for out-of-gamut colours much larger differences between tile colour and cake colour resulted from having to adjust computed dye quantities to keep the total to within the legal limit. The computation of a more detailed gamut boundary for cake

colours should allow colour gamut mapping techniques to be applied to provide potentially more satisfactory solutions, which are closer to the tile colours and to possibly allow more efficient use of dyes. The comparison of colorimetric matching and colour gamut mapping outputs for each tile colour will help to decide which colour rendition technology will be more suitable for use by the 3D colour food printer being developed.

The aims of this work in this chapter were:

- To compute the detailed colour gamut boundary for the range of colours possible by adding Brilliant Blue, Ponceau 4R red and Tartrazine yellow dyes, and their blends, in quantities up to the legal maximum, to the microwave-baked cake substrate;
- To apply colour gamut mapping to all tile colours, mapping these colours to the reproduction (cake) gamut;
- To compute the dye quantities needed to produce the mapped colours in the cake;
- To compare the solutions for each tile colour from the two approaches, colorimetric matching and colour gamut mapping, and then to make a recommendation on whether one method is favoured over the other in providing the best equivalent of the tile colour in the cake; and should colour gamut mapping be favoured, to specify whether a compression or clipping algorithm provides the better solution.

Returning to the cake substrate also leads to the following supplementary aims:

- For each tile colour, to map both its specular component included (SCI) and specular component excluded (SCE) colours, to allow comprehensive comparisons with colorimetric matching results (previously, only the SCI tile colours were mapped to the gel colour gamut boundary, due to the tiles and gels having similar surface properties, as discussed in Chapter Six);
- To map each colour both with and without initial lightness compression (previously all mapping to the gel gamuts was done with lightness compression, due to the effects of increased gel browning on decreasing the lightness range of the gamuts).

7.2. Materials and Methods

The analyses presented in this chapter are based on the methods reported in Chapters Five and Six for colour gamut boundary computation and colour gamut mapping respectively, as they are applied to the cake-derived data from Chapter Four. These chapters can be referred to for more information. The steps are described here again in only general detail, with an emphasis on any differences to previous methods.

For convenience colorimetric matching will often be referred to simply as ‘matching’ and colour gamut mapping as ‘mapping’. The mention of any colour refers to both its SCI and SCE versions, unless otherwise specified.

7.2.1. Boundary for the entire cake gamut

The basis for computing the colour gamut boundary for the microwave-baked cake containing blends of primary dyes was the computation of individual $L^*_{10}a^*_{10}b^*_{10}$ colours using the Kubelka-Munk model (Equation 4.10 below, from Chapter Four), which is the same method as was reported in Chapter Five for computing the colour gamut boundary resulting from the addition of primary dye blends to the initially White gel.

$$\left(\frac{K}{S}\right)_{\lambda,blend} = \left(\frac{K}{S}\right)_{\lambda,substrate} + c_1 \left(\frac{k}{s}\right)_{\lambda,1} + c_2 \left(\frac{k}{s}\right)_{\lambda,2} + c_3 \left(\frac{k}{s}\right)_{\lambda,3}$$

For each blend, the spectrum of absorption values for the cake substrate, $\left(\frac{K}{S}\right)_{\lambda,substrate}$ and the cake-derived spectral unit absorption coefficients for each dye, $\left(\frac{k}{s}\right)_{\lambda,n}$ (from Chapter Four), together with dye concentrations, c_n , were substituted into the equation to compute a spectrum for the blend. The dye blends were the same as those used to compute the colour gamut boundaries for the gels in Chapter Five. For the cake gamut boundary $L^*_{10}a^*_{10}b^*_{10}$ values were computed from $\left(\frac{K}{S}\right)_{\lambda,blend}$ via direct conversions to computed, measured $R_{\lambda,m}$ and then to X_{10} ,

Y_{10} , Z_{10} , as explained in Chapter Four, whereas for the gels, $\left(\frac{K}{S}\right)_{\lambda,blend}$ was converted first to computed internal reflectance, $R_{\lambda,i}$ before being converted to computed $R_{\lambda,m}$.

7.2.2. Gamut boundaries at planes of constant hue angle

From the computed cake gamut boundary colours, gamut boundary polygons were drawn in the 180 degree, two dimensional chroma-lightness (C^*L^*) plane at the hue angle of each tile colour, following the method reported in Chapter Six. In the present chapter two polygons were drawn for each tile colour, one for each of the hue angles of the SCI and SCE tile colours, whereas in Chapter Six a single polygon was drawn, for the SCI colour only.

7.2.3. Gamut mapping

At the hue angle of each tile colour (SCI and SCE), the tile colour was mapped to the cake gamut boundary (see also Chapter Six for methodology). In the present chapter colours were clipped and compressed with *and* without initial lightness compression, whereas previously, in Chapter Six, lightness compression always preceded clipping or chroma compression to the gel gamuts. Although lightness compression features in many gamut mapping algorithms, gamut mapping is possible also without lightness compression (Kang, 2006). Again, lightness compression was defined by an assumed range of zero to 100 L^* units for the tile colours, and the lightness range for the entire reproduction (cake) colour gamut.

7.2.4. Dye quantities for mapped colours

The dye quantities needed to produce the mapped colours in the cakes were computed using iterative dye recipe correction, with the nearest available gamut boundary point to the mapped colour as the starting colour, following the methods described previously in Chapter Six.

7.2.5. Comparison of outputs from colour gamut mapping and from colorimetric matching

$\Delta E^*_{ab,10}$ differences, as well as the lightness, chroma and Euclidean hue differences, ΔL^*_{10} , $\Delta C^*_{ab,10}$ and $\Delta H^*_{ab,10}$ respectively, between the tile colours and their mapped counterparts were

computed. These differences, along with the dye recipes, were compared to those previously computed from colorimetric matching in Chapter Four.

7.3. Results and Discussion

7.3.1. Gamut boundaries

7.3.1.1. Boundary for the entire cake gamut

Figure 7.1 shows the gamut boundary for the range of computed colours resulting from the addition of the three primary dyes and their various blends to the cake substrate. The same dye blends that had been used to compute the gamut boundary colours for the dyed, White gel in Chapter Five were used for the cake. For gel colours, dye blends (i.e. their total concentration and relative dye proportions) had been designed so that the $\Delta E^*_{ab,10}$ spacing between colours on the computed gamut boundary was no more than three units; by using the same dye blends for the cake colours, it was not guaranteed that the spacing between the computed colours on the cake colour gamut boundary would be the same. While the three-unit $\Delta E^*_{ab,10}$ spacing condition was met by the vast majority of the computed cake colours, a small number of the differences between colours rose to between four and five units.

Also shown superimposed in Figure 7.1 is the less-detailed gamut boundary that was drawn for the cake colours in Chapter Four. This clearly shows the impact that a lack of boundary detail would have on the mapping of tile colours to this reproduction gamut. In general terms, out-of-gamut colours in the chromatic green-yellow quadrant would be clipped further than is necessary towards less chromatic replacement colours, and some within-gamut colours clipped unnecessarily. Similarly, dark colours located to the right (redder) side of the lightness axis might become much lighter than they need to be as a result of mapping to the less-detailed boundary. At individual hue angles a lack of gamut boundary detail will be more evident.

Although the comparison between the cake colour gamut and the White gel colour gamut was not a focus of this work, it is still interesting to note the differences between them. The gamut

of colours from the cake and White gel substrates are similar in shape, but differ in their lightness and chroma ranges (Figure 7.1). The chroma range of the cake gamut is more extended in the $+a^*$ and $+b^*$ directions (i.e. towards redder and more yellow colours), but reduced in the $-b^*$ (blue) region. This is consistent with the cake itself having a yellow colour when it does not contain any added dye. The lightness range of the cake gamut is a similar size to the lightness range of the White gel gamut, but occurs at a lower region of the lightness axis. It might be harder therefore to achieve matches in the cake for lighter tile colours, and for blue- and purple- type colours, without colour gamut mapping. Although the un-dyed cake may be darker *per se* than the un-dyed White gel, it may be darker also by virtue of it being a more porous sample, and therefore of more light being lost during colour measurement (Negueruela, 2010).

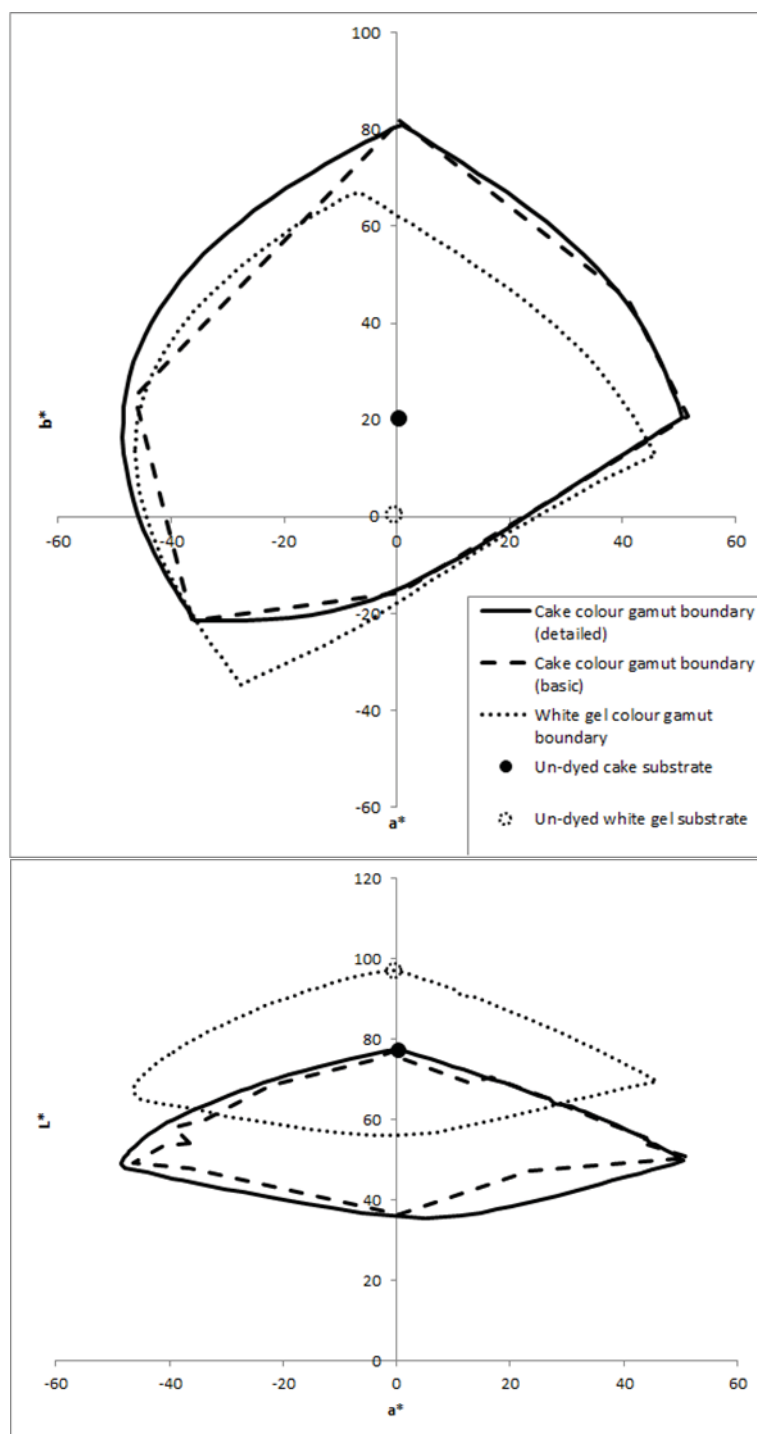


Figure 7.1 Plots showing the chromatic (top) and lightness (bottom) ranges of the colour gamut boundaries for the microwave-baked cake and whitened starch gel containing primary dye blends to the maximum level allowed in foods. Also shown is the less-detailed gamut boundary for the cake colours from Chapter Four.

7.3.1.2. Gamut boundaries at planes of constant hue angle

Figure 7.2 shows the cake gamut boundary polygons in a 180 degree plane originating at the hue angle of each tile colour (SCI and SCE), and the original positions of the tile colours. The detailed gamut boundary has the Deep Pink SCI colour located within the gamut of cake colours, rather than being out-of-gamut as was found in Chapter Four (Figure 4.7), and the Deep Pink SCE and Red SCI colours only slightly out-of-gamut, rather than being further away. Mid Grey SCI, which was shown previously to be within-gamut according to the less-detailed boundary, is also shown to be slightly outside the detailed boundary.

In fact, while colorimetric matching in Chapter Four returned mostly positive, within-range concentrations for Deep Pink SCE and Red SCI, at 30.3 mg/100 g batter the computed dye total for Deep Pink SCE was slightly more than the legal maximum of 27.4 mg/100 g batter, as was the computed total for Red SCI (of 28.9 mg/100 g batter). The computed dye recipe for Mid Grey SCI from colorimetric matching included a small, negative concentration for the yellow dye (-0.1 mg/100g). These dye quantities provide another indication of the colours being only slightly out-of-gamut, and clearly demonstrates the accuracy of the detailed gamut boundary computation.

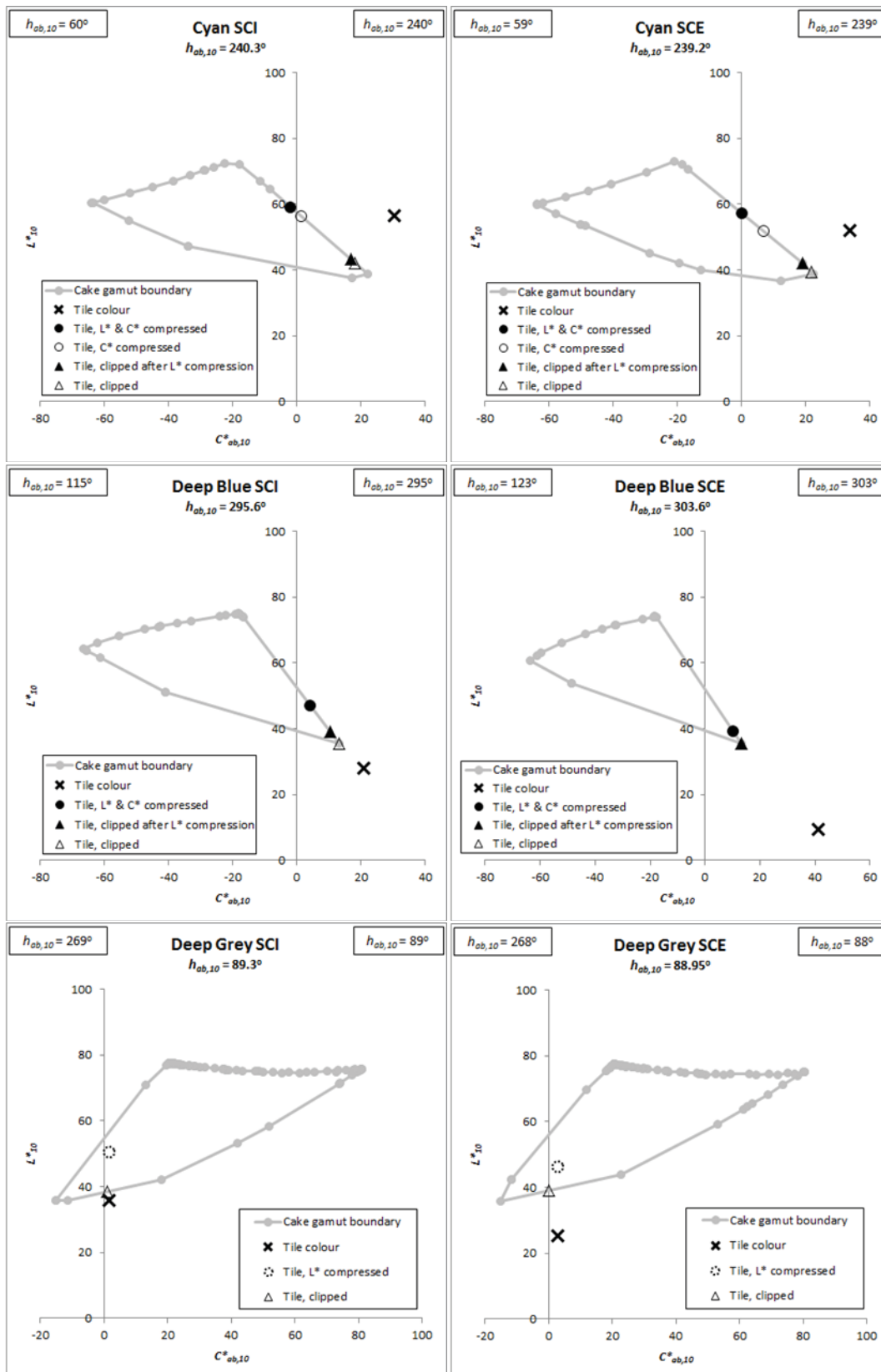
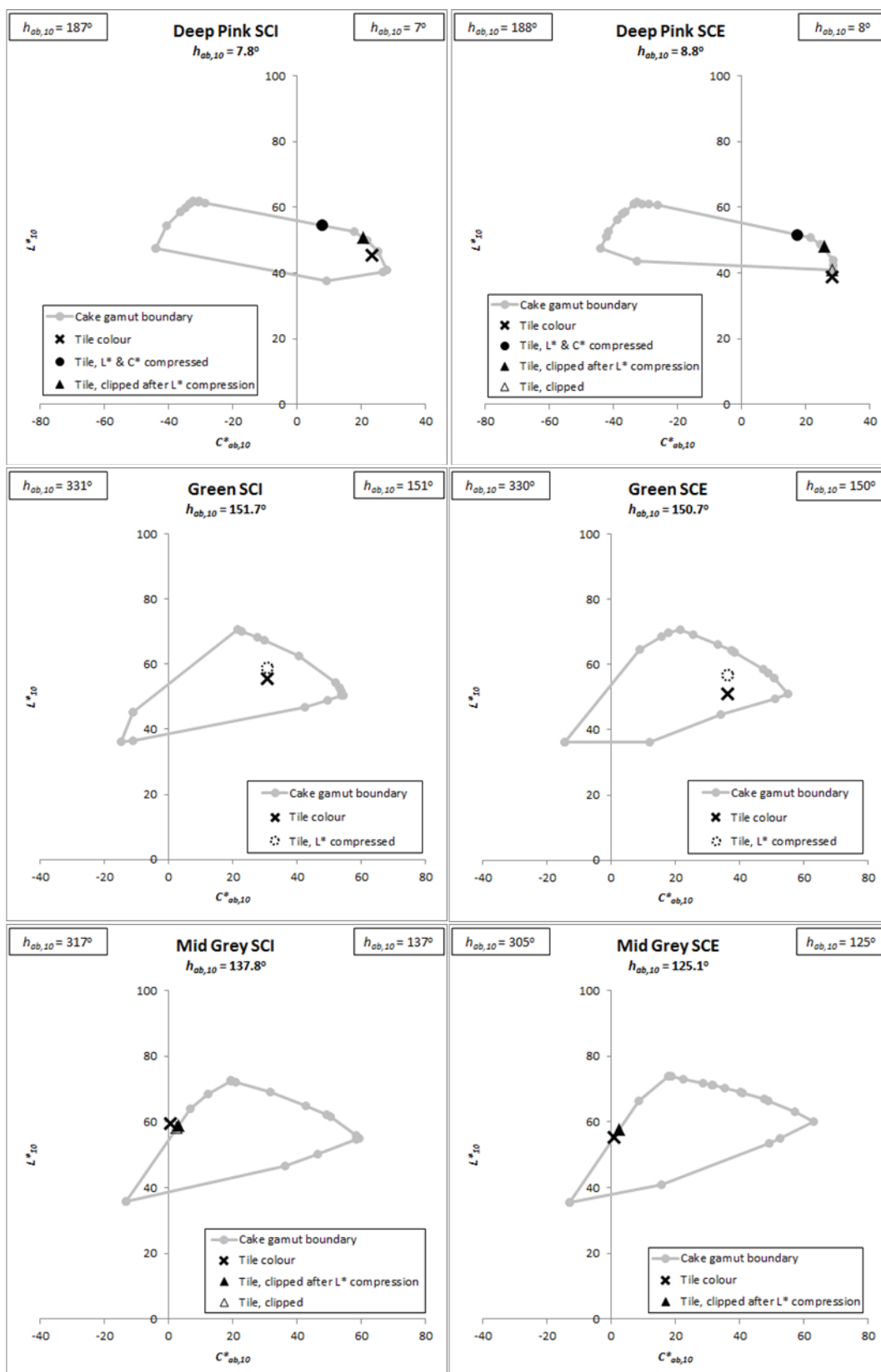
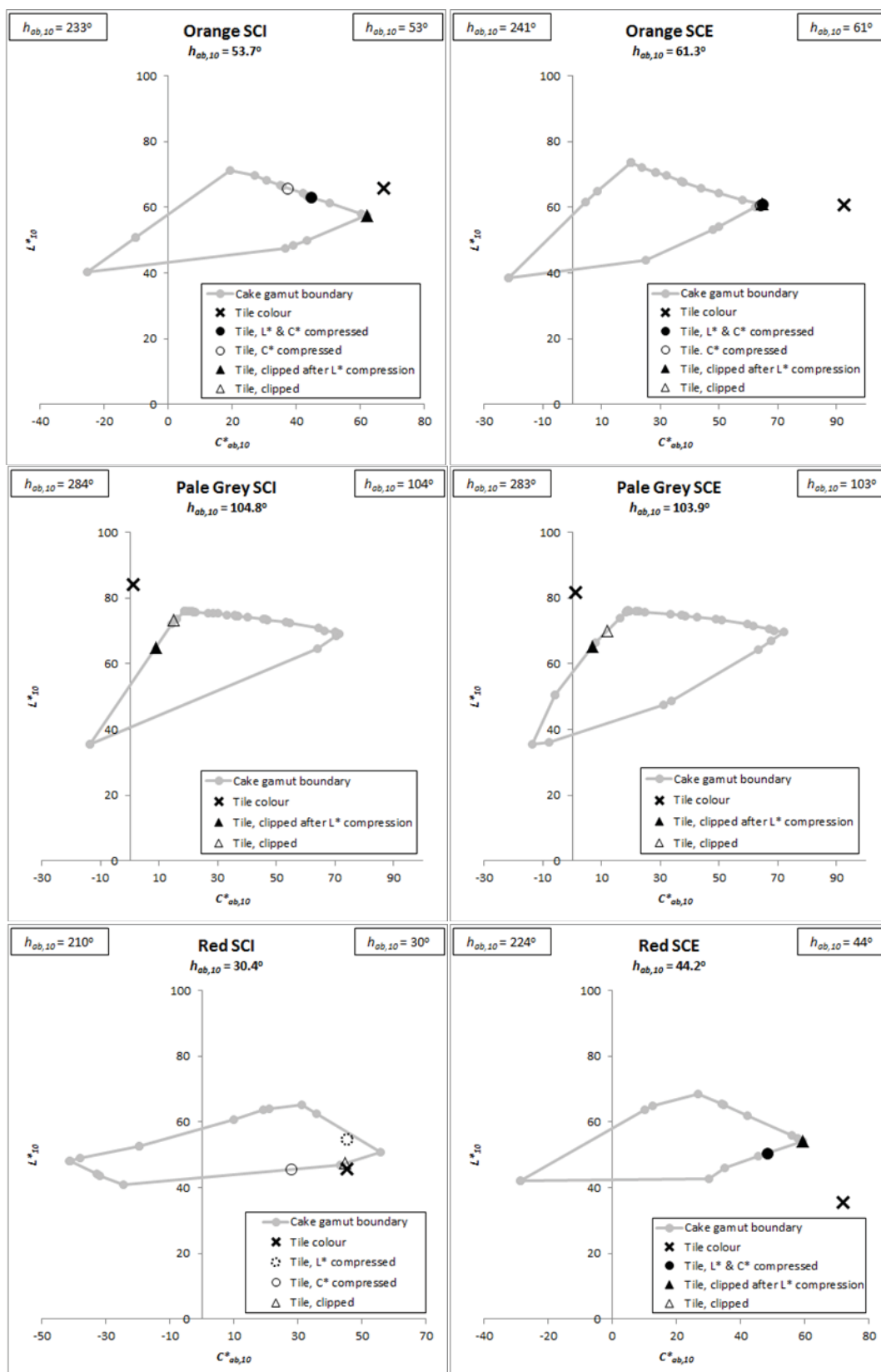
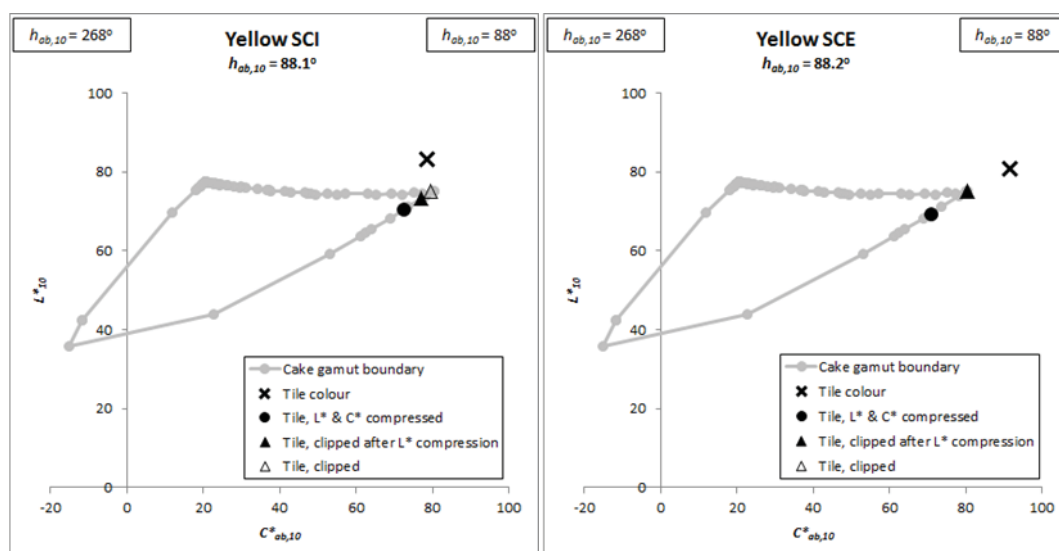


Figure 7.2 Plots showing the original position of each tile colour (SCI and SCE) in its hue angle plane, and its positions following mapping by various gamut mapping algorithms (continued on the following pages).







7.3.2. Gamut mapping

In addition to the original positions of the SCI and SCE tile colours in their hue angle planes, Figure 7.2 also shows their positions in the cake colour gamut following mapping. Appendix Figure 7.13 illustrates each individual mapping. As in Chapter Six, clipping or chroma compression was preceded by lightness compression, for the colour to fit within the lightness range of the cake gamut. However the work in this chapter differs from that in Chapter Six, in that clipping and compression were also done without initial lightness compression, where possible.

In accordance with the explanation given previously in Chapter Six, Mid Grey and Pale Grey colours were only clipped (with or without initial lightness compression) and not chroma-compressed.

7.3.2.1. Mapping with initial lightness compression

For all colours except Orange (SCI only), Pale Grey and Yellow, initial lightness compression (prior to clipping or chroma compression) increased the lightness of the original tile colours (Figure 7.2). The largest increases in lightness were for Deep Blue, Deep Grey, Deep Pink and Red (ranging from nine to 30 L^*_{10} units across SCI and SCE colours). Comparing SCI and SCE colours, the larger increases in lightness were for the SCE colours. The degree of increase in

lightness for a given tile colour was related to how much darker the colour was relative to the darkest possible cake colour having a computed L^*_{10} of 36 units. The original Orange SCI, Pale Grey and Yellow colours were lighter than the lightest possible cake colour (with a computed L^*_{10} of 78 units), and were darkened by initial lightness compression; as a result the lightness of Pale Grey and Yellow was decreased by more than 10 L^* units, ranging from 11.3 to 13.3 units across the SCI and SCE colours.

For Deep Pink SCI, which was already within the gamut of cake colours, lightness compression pushed this colour out-of-gamut, in addition to increasing its lightness. An alternative approach would have been to apply lightness compression only to those colours that were out-of-gamut, or, if applying lightness compression to all colours, to use the lightness range of the reproduction (cake) gamut at the hue angle of the colour to be mapped, rather than to use the lightness range for the entire reproduction gamut.

When lightness compression preceded clipping or chroma compression, a result was always returned, however following sequential compression of lightness and chroma, the Cyan SCI colour was mapped to the section of the gamut boundary which was 180 degrees from the hue angle of the tile colour (Figure 7.2). As in Chapter Six, in the absence of full (chromatic) gamut information for the tile colours, sequential lightness-chroma compressions were not full compressions, but only partial compressions, placing colours on to the cake gamut boundary, rather than inside the boundary. Again, for some colours, lightness compression alone placed the colour inside the boundary and therefore further clipping or chroma compression was not necessary (Deep Grey, Green, and Red SCI). When lightness compression followed by clipping placed the colour outside the cake gamut boundary, it was replaced by the outermost chromatic point (Deep Blue SCE, Orange SCI, Red SCE and Yellow SCE) (Appendix Figure 7.13).

7.3.2.2. Mapping without initial lightness compression

Without initial lightness compression, chroma compression alone was possible only for Cyan, Orange, and Red SCI. Chroma compression alone was not possible if the lightness of the tile

colour was outside the lightness range of the cake gamut (Deep Blue, Deep Grey, Deep Pink SCE, Red SCE and Yellow) meaning the chroma compression line would not have been able to reach the gamut boundary, or if the original position of the tile colour was already within the cake gamut (Deep Pink SCI and Green). Chroma compression alone could still have been applied to the latter colours if the chroma range of the tile colours were known. Without initial lightness compression, clipping was possible for most tile colours, except for those already inside the cake gamut boundary (Deep Pink SCI, Green, and Mid Grey SCE). The clipping-only ‘solution’ was replaced by the outermost chromatic boundary point for Deep Blue, Orange, Red SCE and Yellow SCE.

7.3.2.3. Final L^* and C^* after mapping

When initial lightness compression increased the lightness of a given SCI or SCE tile colour, the colour following subsequent clipping or chroma compression was lighter than its counterpart that was clipped or compressed without lightness compression. These conclusions were able to be drawn for the following colours: Cyan (clipped and compressed), Deep Blue SCI (clipped only), Deep Pink SCE (clipped only), and Mid Grey SCI (clipped only). When initial lightness compression darkened the tile colour, clipped or compressed colours were darker than they were without initial lightness compression: Orange SCI (compressed only), Pale Grey (clipped only), and Yellow SCI (clipped only).

If a given colour (SCI or SCE) was able to be *both* compressed *and* clipped (with or without initial lightness compression), the compressed and clipped colours differed in one of the following ways:

- the clipped colour was darker and more chromatic than the compressed colour (Cyan, Deep Blue, Deep Pink, Orange SCI);
- the clipped colour was the lighter and more chromatic (Red and Yellow);
- the clipped and compressed colours were the same (Orange SCE).

7.3.3. Dye quantities for mapped colours

As in Chapter Six, the source of the dye recipe for the mapped colour was the colour having a computed $\Delta E^*_{ab,10}$ difference of up to three units, and a hue angle difference of one degree or less, to the mapped colour. In the majority of cases, dye recipe correction converged to a solution with zero $\Delta E^*_{ab,10}$ difference to the mapped colour. Otherwise, with the exception of the lightness-compressed Deep Grey SCE colour, the $\Delta E^*_{ab,10}$ difference was 0.9 units or less. These small or null differences were achieved for a hue angle difference of 0.5 of a degree or less, with the exception of the lightness- and chroma-compressed Cyan SCE and clipped Deep Grey SCE colours, for which the differences between the colours from recipe correction and the mapped colours were 188 and 181 degrees respectively. The mapped colours however, are located very close to the L^* axis, and therefore the colours from recipe correction and the mapped colours are likely to be much closer than is suggested by their hue angle differences. For lightness-compressed Deep Grey SCE the computed $\Delta E^*_{ab,10}$ difference between the colour from recipe correction and the mapped colour was eight units, due largely to the difference in lightness between the two colours (7.9 units), while the hue angle difference was only 1.5 degrees. As with the findings reported in Chapter Six, the nearest available gamut boundary colour providing a starting point for recipe correction was likely too far away from the mapped colour for recipe correction to have converged to a satisfactorily close solution.

Dye recipes are shown in graphical form in the next Section (7.3.4), in Figure 7.3 to Figure 7.12, where outputs from colour gamut mapping and colorimetric matching are compared. The effect of initial lightness compression is evident in the dye recipes for colours that were subsequently clipped or compressed (i.e. colours other than Deep Grey, Green and Red SCI). As a result of initial lightness compression, some of the clipped or chroma-compressed colours required either less total dye (Cyan, Deep Blue SCI, Deep Pink SCE, clipped Mid Grey SCI) or more dye (compressed Orange SCI and clipped Pale Grey) than their non-lightness-compressed counterparts, due to the former colours being lighter or darker respectively. Dye recipes for other clipped or compressed colours were unaffected by lightness compression; with or without

initial lightness compression, these colours were mapped eventually to an outermost chromatic point (clipped Orange SCI, Deep Blue SCE, Red SCE, and Yellow SCE colours, and clipped and compressed Orange SCE), and also to a bottom surface point (clipped Yellow SCI) which all require the maximum dye amount.

Irrespective of whether or not initial lightness compression was applied, **either**

- the clipped version of a given colour (SCI or SCE) demanded higher total dye quantities to be used than did the compressed counterpart, consistent with clipping solutions being darker *and* more chromatic (Cyan, Deep Blue, Deep Pink, and Orange SCI) *or* simply more chromatic (Red SCI), **or**
- clipped colours needed the same total quantity of dye as did the compressed colours, because both are among colours in the cake gamut which require the maximum dye quantity (Orange SCE, Red SCE, and Yellow); however the relative proportions of the different dyes within each recipe differed according to whether the colour had been clipped or compressed (Red SCE, and Yellow).

7.3.4. Differences between outputs from colorimetric matching and colour gamut mapping, in providing the best equivalents of the original tile colours

7.3.4.1. Rationale

A key focus of this chapter, which sets it apart from the previous chapter on colour gamut mapping, is that as well as comparing the performance of the different mapping algorithms to each other (in the L^* and C^* values and dye recipes of the mapped colours), the mapped colours are also compared to the original tile colours. In the previous chapter on colour gamut mapping, Chapter Six, the aim was to find the best equivalent of each tile colour in a set of gel substrates which differed only in their level of browning. Therefore it was *expected* that each new, replacement colour would be different to the original tile colour. However, for the purpose of

directly comparing the relative merits of colorimetric matching (Chapter Four) and colour gamut mapping, the differences between the colour outputs from each method and the original colours needed to be investigated. For Pale Grey, the discussion below compares the different outputs from colour gamut mapping only; these were not able to be compared with an output from colorimetric matching, which was unavailable due to the computed quantities for all three dyes being negative.

To recap, the dye recipes computed from colorimetric matching in Chapter Four, were scaled back to within legal range if negative concentrations were called for, or if the total exceeded the legal maximum. This occurred if the tile colour was out-of-gamut, on the basis of an approximate gamut boundary. Any negative concentrations for individual dyes were increased to zero, and recipe totals were scaled to within 27.4 mg/100g batter, whilst retaining the relative proportions of the non-zero-quantity dyes. The exceptions were Deep Pink (SCI), Green (SCI and SCE), and Mid Grey (SCE), which were within-gamut.

7.3.4.2. Magnitude of differences between mapped or matched colours, and the (original) tile colours, and in their corresponding dye quantities

Figure 7.3 to Figure 7.12 show the computed $\Delta E^*_{ab,10}$ total colour differences between the tile colours (SCI or SCE) and the outputs from colorimetric matching and colour gamut mapping. It also shows the total colour difference expressed in terms of individual lightness, chroma and Euclidean hue differences ($\Delta H^*_{ab,10}$). Because these differences are the values from colorimetric matching or gamut mapping subtracted from the values for the tiles, positive values indicate that the tile was the lighter and more chromatic; conversely, negative values indicate that the colour from matching or mapping was lighter and more chromatic than the tile colour was originally. Figure 7.3 to Figure 7.12 also show the total dye quantities and the dye recipes required to achieve the colours from the different methods.

7.3.4.2.1. Observations for each tile colour

Cyan: For both the SCI and the SCE colours (Figure 7.3), $\Delta E^*_{ab,10}$ differences between clipped colours (with and without lightness compression) and the tile colour were of similar magnitude to the $\Delta E^*_{ab,10}$ differences between the colours from colorimetric matching and the tile colours (19.1 or 19.0, vs. 20.1 for SCI; 17.7 or 17.3, vs. 17.2 for SCE). The colours from matching however needed less total dye than the colours from clipping. The colours from mapping algorithms involving chroma compression have the largest $\Delta E^*_{ab,10}$ differences to the tile colours, due to relatively larger shifts (i.e. decrease) in chroma, but these colours require the least amount of dye. The main, and potentially most important, difference between the matching and mapping outcomes is the relative contribution of lightness, chroma and hue differences to the $\Delta E^*_{ab,10}$ differences. In matching, hue difference is predicted to be by far the main contributor (by 19.3 $\Delta H^*_{ab,10}$ units for SCI and 16.3 $\Delta H^*_{ab,10}$ units for SCE), with comparatively less input from lightness and chroma differences, whereas in mapping, lightness and chroma differences are the main contributors, with hue differences contributing comparatively little (zero to 2.6 $\Delta H^*_{ab,10}$ units across SCI and SCE). Visually, the match between the Cyan SCI tile colour and the cake match from Chapter Four was one of the least satisfactory (Figure 4.8), which might have been due to the large hue difference between them. These observations suggest that for this colour, clipping is preferable to matching and compression, and that as much dye as possible, plus a lower proportion of blue to red dye in the recipe (down from the 86% blue to 14% red (SCI), and the 88% blue to 12% red (SCE), for the colours from matching) is needed to produce the most chromatic colour of the correct hue.

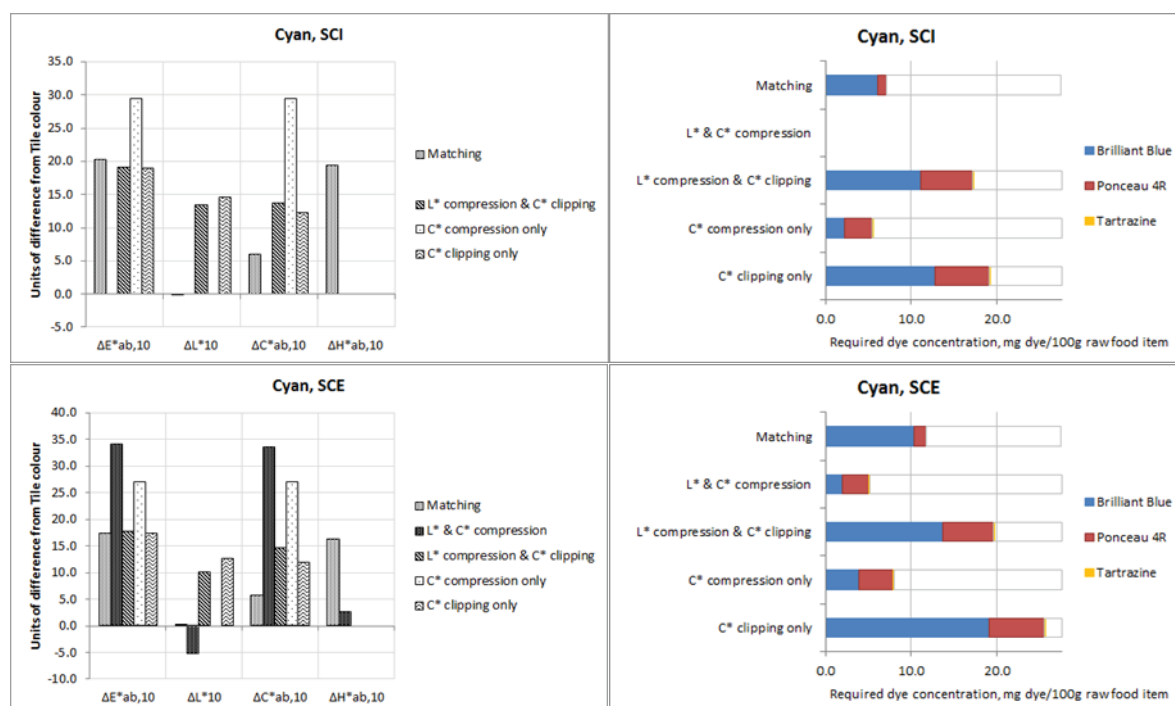


Figure 7.3 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Cyan SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Deep Blue: For the SCI colour (Figure 7.4), the colours from mapping algorithms involving lightness compression were the most different to the original tile colour ($\Delta E^*_{ab,10}$ values of 25.5 and 15.3 units) than were the colours from matching, or from clipping alone, which differed to the tile colour by 11.1 and 10.6 $\Delta E^*_{ab,10}$ units respectively. The lightness-compressed colours also needed less dye than did the colours from either matching, or clipping alone. The colours from both matching, and clipping only, required the maximum possible dye quantity; the total dye quantity computed from colorimetric matching exceeded the legal limit and was scaled back to this limit, while the quantity for the clipped-only colour was for an outermost chromatic point, defined by the legal limit. For the SCE colour, the colours from matching and clipping only are again closest to the original tile colour (by 38.7 and 38.4 $\Delta E^*_{ab,10}$ units respectively), and require the maximum amount of dye possible, for the same reasons as for the SCI colour, and are this time joined by the colour clipped with initial lightness compression, which is an outermost chromatic point. At a $\Delta E^*_{ab,10}$ of 43.4 units, the colour from sequential lightness-

chroma compression has the largest difference to the original tile colour, and needs the least amount of dye, due to it being slightly lighter and less chromatic. Recipes for colours needing the maximum total dye quantity have in common an absence of yellow dye. ΔL^*_{10} and $\Delta C^*_{ab,10}$ differences between the colours from matching or mapping, and the original tile SCI and SCE colours mirror the $\Delta E^*_{ab,10}$ differences. Gamut mapping reduced the $\Delta H^*_{ab,10}$ difference between the colours from matching and the original tile colours from 2.6 or 5.9 units, to zero, for SCI and SCE respectively.

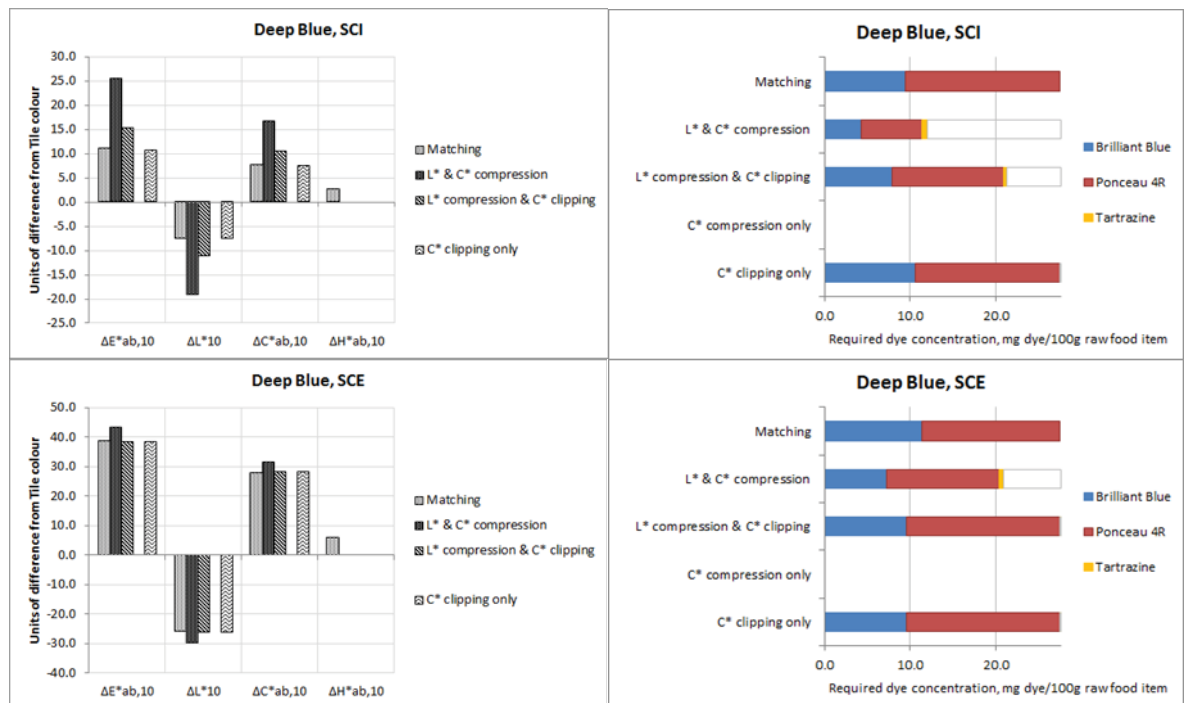


Figure 7.4 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Deep Blue SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Deep Grey: Lightness compression (only) of both the SCI and SCE colours produced much lighter colours than did either clipping alone or matching, which contributed to the larger $\Delta E^*_{ab,10}$ differences between the lightness-compressed colours and the original tile colours (14.8 and 20.8 units for SCI and SCE respectively); $\Delta E^*_{ab,10}$ differences between the colours from

matching and the tile colours were 3.8 and 13.8 units for SCI and SCE respectively, and between clipped-only colours and tile colours they were 2.9 units for SCI and 14.0 units for SCE (Figure 7.5). Because lightness compression had lightened the original tile colours, it was expected that the resulting colours would require the least amount of dye; this was found for Deep Grey SCI, but harder to conclude for Deep Grey SCE, as the dye recipe from recipe correction was for a colour that was eight $\Delta E^*_{ab,10}$ units from the mapped colour. As with Deep Blue, the colours from matching required the most dye – the maximum amount – as the result of having to scale back the computed dye quantities for these colours. The clipped-only colours were expected to need the same amount of dye, having been mapped to the bottom surface of the boundary, but the quantities fell short of the maximum suggesting more detail may have been needed to fill the boundary at these locations. Mapping reduced the $\Delta H^*_{ab,10}$ difference between the colours from matching and the original tile colours from 1.6 to zero (SCI) or from 1.5 to 0.7 (SCE) units.

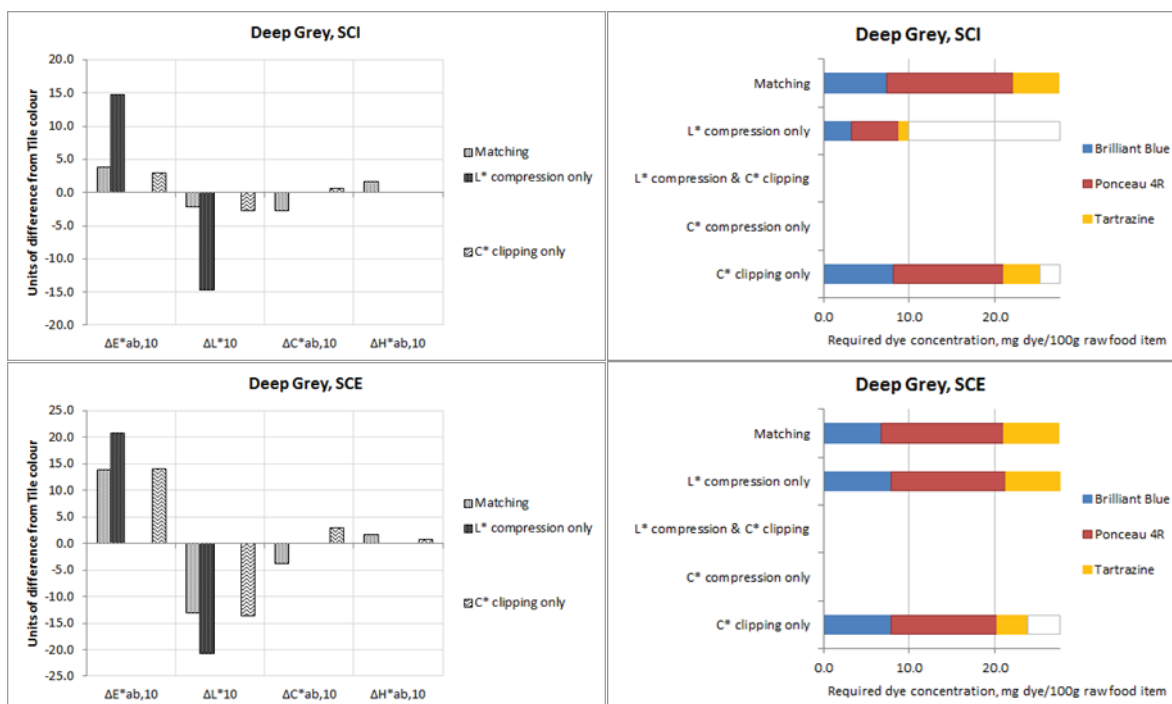


Figure 7.5 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Deep Grey SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Deep Pink: For both the SCI and SCE colours, the $\Delta E^*_{ab,10}$ differences between the colours from sequential lightness-chroma compression and the original tile colours (18.2 and 17.1 units for SCI and SCE respectively) were much larger than those between the colours clipped with or without initial lightness compression and the tile colours (ranging from 2.2 to 9.6 across SCI and SCE) and between the colours from matching and the tile colours (4.3 and 5.5 for SCI and SCE respectively) (Figure 7.6). Originally, the tile colours were either already within the cake gamut (SCI) or very close to the gamut boundary (SCE), so therefore matching had already provided a satisfactory solution in the form of a dye recipe. Sequential lightness-chroma compression only served to move the colour furthest away from this ‘best’ position, and it is seen that the resulting $\Delta E^*_{ab,10}$ differences are due to changes in both lightness and chroma. Lightness-compressed colours, whether subsequently clipped or chroma compressed, do however need less dye than the colours from matching. Only clipping alone (without initial lightness compression) of the SCE colour resulted in the smallest $\Delta E^*_{ab,10}$ difference to the tile (2.2 units), and this colour could be achieved by using the same amount of dye, and a similar dye recipe, as was needed for the colour from matching. Because the SCE colour was already close to the cake gamut, it was expected that, in the absence of lightness compression, clipping would provide a similar outcome to matching. There is zero $\Delta H^*_{ab,10}$ difference between mapped colours and the original tile colours, though the colours from matching differ from the tile colours by only 2.7 and 3.1 $\Delta H^*_{ab,10}$ units for SCI and SCE respectively.

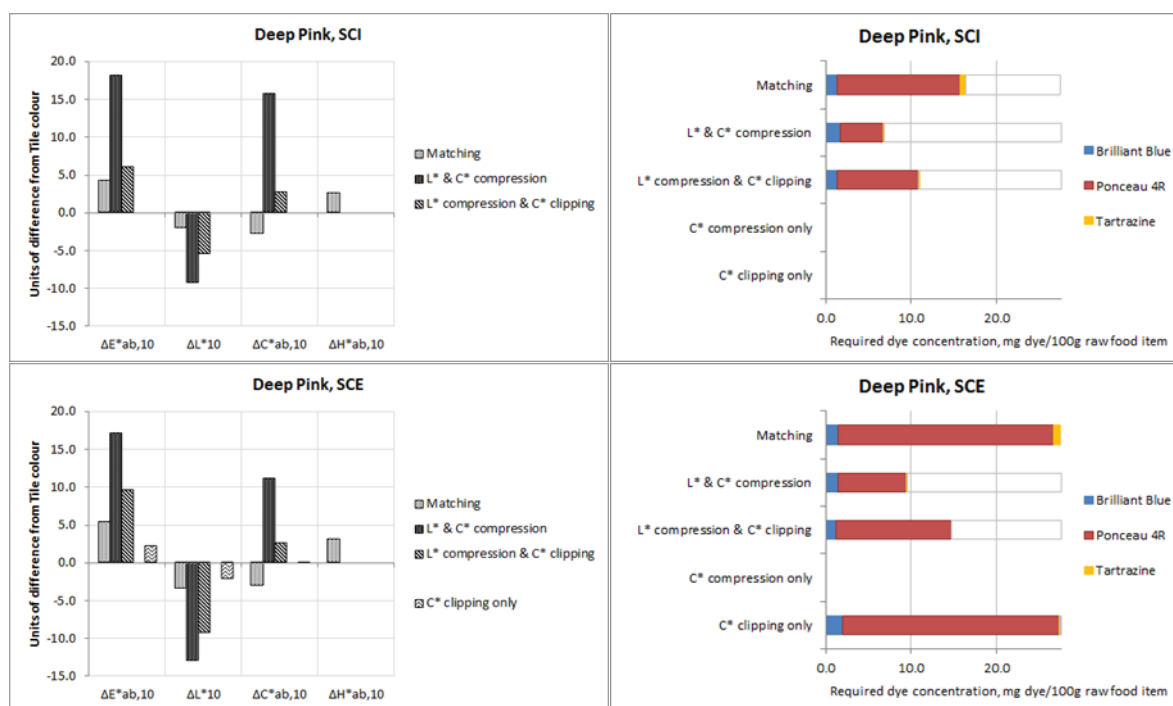


Figure 7.6 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Deep Pink SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Green: Like the Deep Pink SCI colour, the positions of the Green SCI and SCE colours were already within the cake colour gamut, before mapping. Therefore any attempt at mapping was going to increase the $\Delta E^*_{ab,10}$ differences between the tile colours, and their replacement colours, relative to the differences between the tile colours and the solutions from matching. Lightness compression, the extent to which mapping was possible, did increase the differences relative to the original colours, and because the colours became lighter, required less dye overall. These effects were observed for both the SCI and SCE colours with the SCE outcomes needing more dye than the SCI outcomes. Mapping reduced the $\Delta H^*_{ab,10}$ difference between the colours from matching and the original tile colours from 1.9 (SCI) or 1.8 (SCE) units, to zero (Figure 7.7).

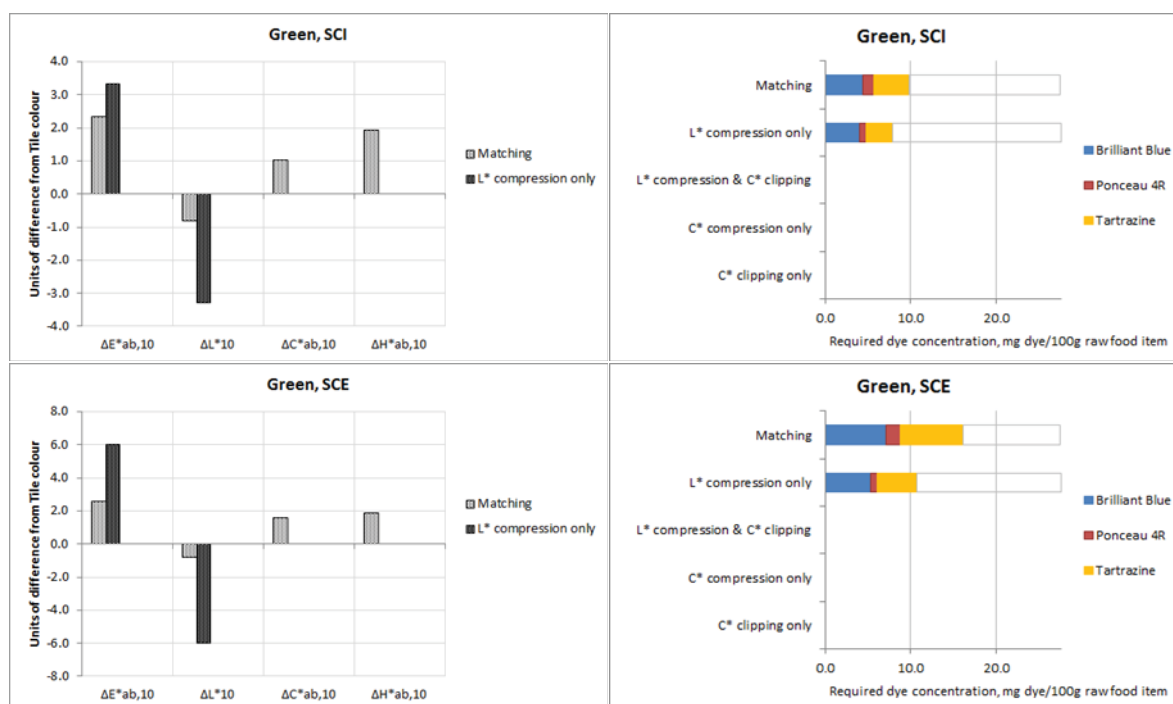


Figure 7.7 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Green SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Mid Grey: The largest differences are found here between the colours from clipping and the tile colours (2.5 to 2.8 $\Delta E^*_{ab,10}$ units across SCI and SCE), relative to the differences between the colours from matching and the tile colours (2.0 and 2.1 units) (Figure 7.8). This is due to the larger relative differences in lightness and chroma seen with clipping. There is however zero $\Delta H^*_{ab,10}$ difference between clipped colours and the original tile colours, though the colours from matching do differ from the tile colours by only 1.3 $\Delta H^*_{ab,10}$ units or less. Overall, $\Delta E^*_{ab,10}$, $\Delta H^*_{ab,10}$, $\Delta C^*_{ab,10}$ and ΔL^*_{10} differences are small, relative to what was found for other tile colours; this was due to a combination of the close proximity of the original Mid Grey tile colours to the cake gamut boundary, and to these colours being among the least affected by initial lightness compression. For the SCI colour, clipped colours needed the most dye. For SCE, originally a within-gamut colour, the colour from matching needed the most dye; lightness compression moved the colour out-of-gamut, and also lightened the colour, and therefore the colour from subsequent clipping needed less dye than the colour from matching.

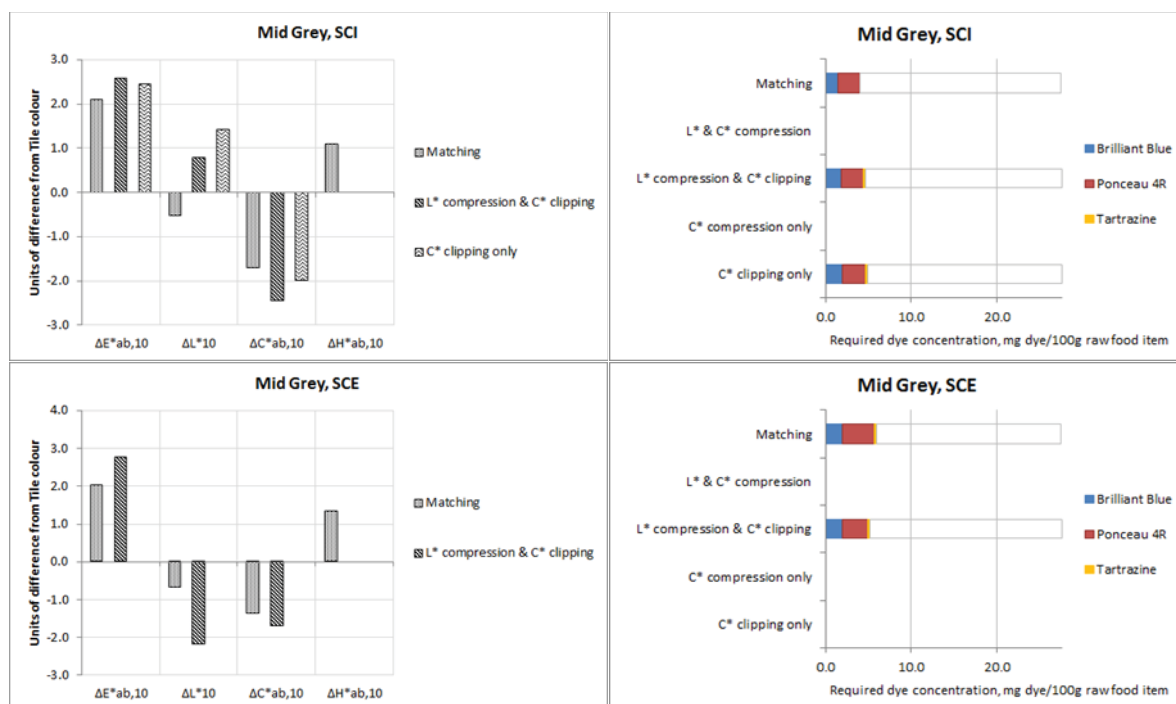


Figure 7.8 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Mid Grey SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Orange: The outermost chromatic boundary point was the solution for the SCI colour clipped with or without initial lightness compression. This colour is closest overall to the original colour, by 10 $\Delta E^*_{ab,10}$ units. The compressed SCI colours (with or without lightness compression) are furthest from the original colour (by 23.0 and 30.1 $\Delta E^*_{ab,10}$ units), due predominantly to the decrease in chroma, and are followed by the colour from matching (17.2 units). Whereas the colour from matching had a high contribution of hue difference (11.2 $\Delta H^*_{ab,10}$ units) to its overall difference to the tile colour, the predicted $\Delta H^*_{ab,10}$ differences between the mapped colours and the original colour are zero (Figure 7.9). As with Cyan, the visual match between the cake colour from matching and the SCI colour was one of the least satisfactory, which might have been due to the hue difference between them. Unlike Cyan though, the $\Delta E^*_{ab,10}$ between the colour from matching and tile colour also had a large contribution from their difference in chroma. The clipped colours, in addition to being the same hue as the original colour, have the smallest differences in chroma to the original tile colour (5.4

$\Delta C^*_{ab,10}$ units). This suggests that the clipped colour might be the best match visually to the original colour, but the clipped colours also require the highest dye quantity (the maximum possible). The colours from the compressions require the least amount of dye.

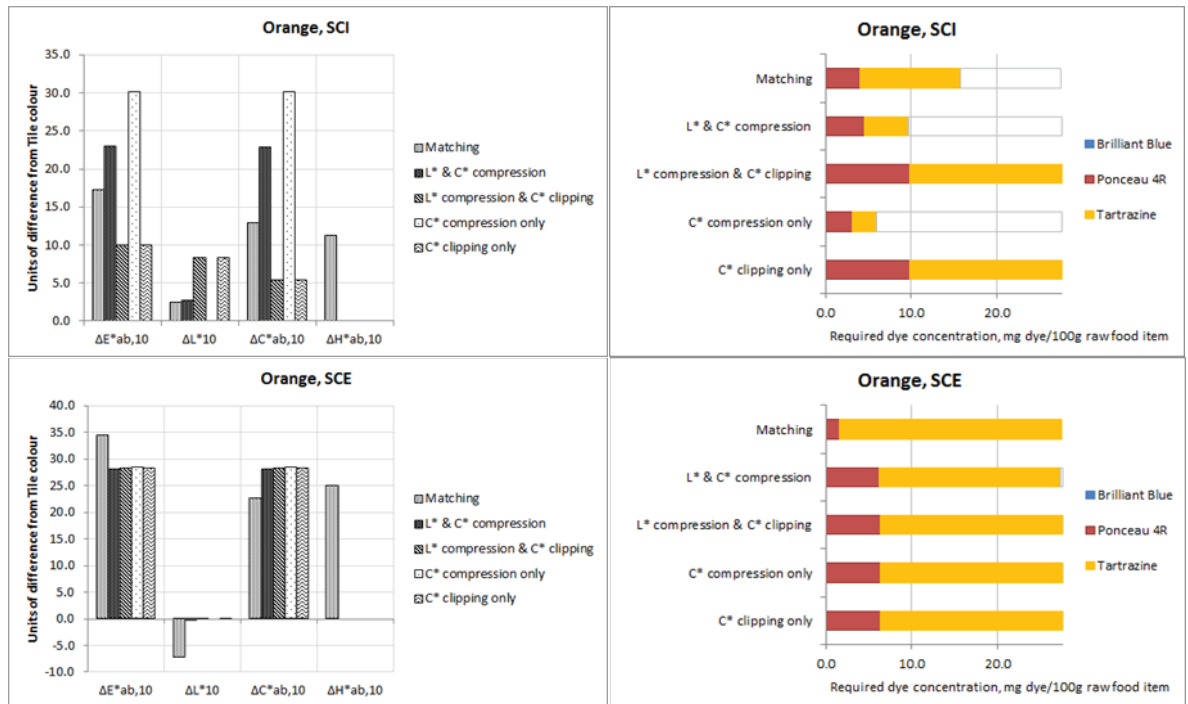


Figure 7.9 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$ and $\Delta H^*_{ab,10}$ respectively) between the measured Orange SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

For the SCE colours, where all mapping algorithms return virtually the same solution – the outermost boundary rim point – the $\Delta E^*_{ab,10}$ differences to the original colour (ranging from 28.1 to 28.4 units) are due entirely to $\Delta C^*_{ab,10}$ differences. The colour from matching has the largest difference to the original colour (by 34.5 $\Delta E^*_{ab,10}$ units), due predominantly to hue difference (25.0 $\Delta H^*_{ab,10}$ units) and to $\Delta C^*_{ab,10}$ (22.7 units). Again, mapping decreases $\Delta H^*_{ab,10}$ to zero. All mapping and matching solutions require the maximum level of dye allowable, but the relative proportions of red and yellow dyes in the matching recipe is different to those in the mapping recipes, with a higher proportion of yellow to red needed for the colour from matching.

This might in part explain the large overall difference between the colour from matching and the original SCE colour.

Pale Grey: Discussion here is limited to comparing the colours clipped with and without initial lightness compression, with the tile colours. Solutions from matching were not available, due to the computation of negative quantities for all three dyes. In addition, chroma compressions were not applied to this colour. For both the SCI and SCE colours, the colours clipped without lightness compression are closest to the tile colours (by 17.5 $\Delta E^*_{ab,10}$ units for SCI, and by 15.7 units for SCE), than are the colours clipped with lightness compression. This is due mainly to the larger decrease in lightness of the lightness-compressed colours; as a result, these colours also require the higher total dye quantity. These colours are however, closer in chroma to the original colour. All clipped colours do not differ in hue to the original colour (Figure 7.10).

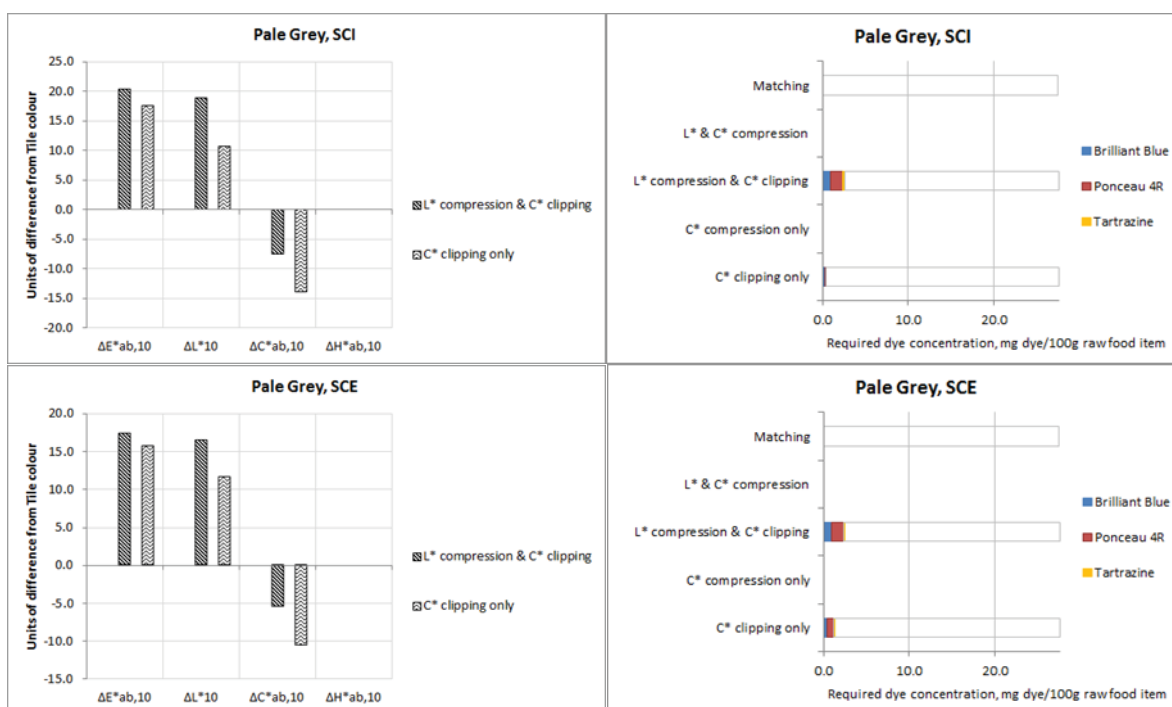


Figure 7.10 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Pale Grey SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Red: In order of decreasing overall colour difference to the original SCI colour, the colour from chroma-only compression was the most different (by 17.5 $\Delta E^*_{ab,10}$ units), followed by the colours from lightness compression only (9.1 units), matching (7.8 units), and clipping only (2.0 units) (Figure 7.11). Contributions to these $\Delta E^*_{ab,10}$ differences reflect the particular type of mapping: for the lightness-only and chroma-only compressions, ΔL^*_{10} and $\Delta C^*_{ab,10}$ differences are respectively the sole contributors to $\Delta E^*_{ab,10}$, while for the clipped-only colour, $\Delta E^*_{ab,10}$ is due to a combination of ΔL^*_{10} and $\Delta C^*_{ab,10}$ differences. There is no difference in hue between the mapped colours and original SCI colour. For the colour from matching, the $\Delta E^*_{ab,10}$ difference to the tile colour is the result of a combination of ΔL^*_{10} (4.3 units), $\Delta C^*_{ab,10}$ (5.5 units) and $\Delta H^*_{ab,10}$ (3.5 units). The colour from matching needs as much dye as the colour from clipping only, but as the original colour was already very close to the cake gamut, either method would have been expected to provide a satisfactory solution. The compressed colours were lighter and less chromatic and thus needed comparatively less dye.

Like the Orange SCI colour, the colour from clipping the Red SCE colour with or without initial lightness compression, yields the same solution (the outermost chromatic point) and is closest overall to the original colour, this time by 22.6 $\Delta E^*_{ab,10}$ units. Then, in order of increasing distance from the original colour, are the colours from matching (24.2 units), followed by the colour from sequential L*-C* compression (28.1 units) (Figure 7.11). All findings are due to combined contributions from lightness and chroma differences, with hue differences making a contribution to the colour from matching only. The colours from both matching and gamut mapping needed the maximum amount of dye, having been scaled back to the legal maximum (for matching) or being located on the chromatic rim or bottom surface, but differed in the relative proportions of red and yellow in their dye recipes (red being 56%-59% of the recipes for the mapped colours, and 47% of the recipe for the colour from matching). Mapping reduced the $\Delta H^*_{ab,10}$ difference between the original SCE colour and the colour from matching, from 5 units to zero.

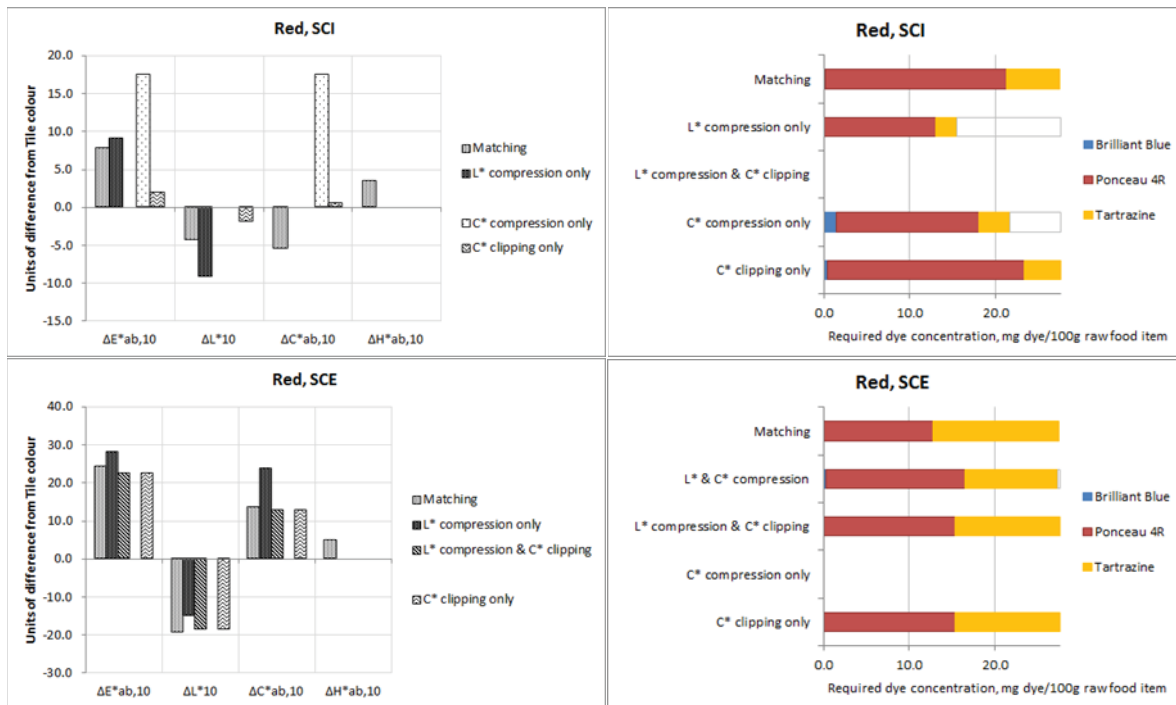


Figure 7.11 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Red SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

Yellow: For the SCI colour, the colour from matching had the largest difference to the original colour (by $15.9 \Delta E^*_{ab,10}$ units), followed by the colour from sequential L*-C* compression (14.1 units) and then the colours from clipping (10.1 and 8.1 units). For the colours from mapping, these differences are due to ΔL^*_{10} and $\Delta C^*_{ab,10}$ differences only, but the colour from matching is due to a combination of ΔL^*_{10} and $\Delta C^*_{ab,10}$ differences, as well as to a hue difference of $5.2 \Delta H^*_{ab,10}$ units (Figure 7.12). The colour from matching needed around half the amount of dye as did the colours from mapping; most likely due to the colour from matching being the least chromatic, relative to the original SCI colour (by $12.7 \Delta C^*_{ab,10}$ units). This implies more dye is needed to obtain the best result, meaning a colour of the correct hue which is also more chromatic. For the SCE colour, the colour from sequential L*-C* compression had the largest difference to the original tile colour (by $23.5 \Delta E^*_{ab,10}$ units), due to it having the largest ΔL^*_{10} and $\Delta C^*_{ab,10}$ differences to the original colour. This was followed by the colours from matching ($15.0 \Delta E^*_{ab,10}$ units), and the colour(s) from clipping (12.5 units). Mapping reduced the $\Delta H^*_{ab,10}$

difference between the original SCE colour and the colour from matching, from 3.6 units to zero. All mapped SCE colours needed the maximum amount of dye, due to their being located at the most chromatic point or at the bottom surface of the gamut boundary.

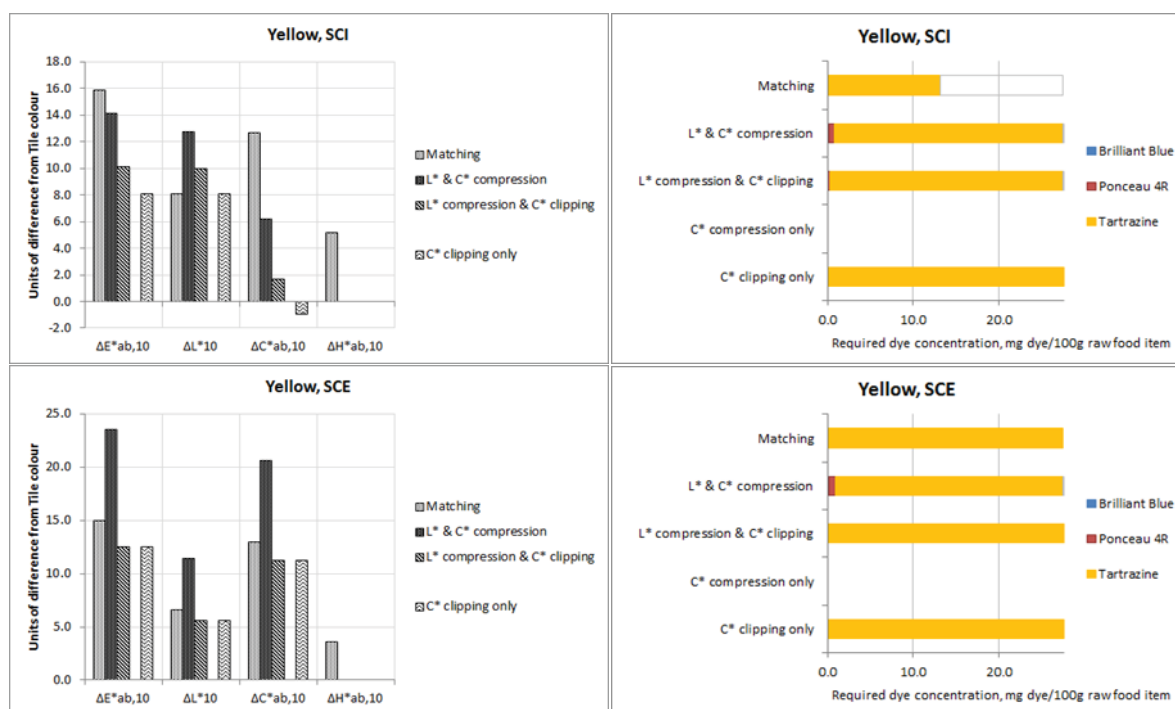


Figure 7.12 Left: Differences in overall colour ($\Delta E^*_{ab,10}$) and in lightness, chroma and hue (ΔL^*_{10} , $\Delta C^*_{ab,10}$, and $\Delta H^*_{ab,10}$ respectively) between the measured Yellow SCI and SCE tile colours and their best equivalents in the microwave-baked cake computed using colorimetric matching and colour gamut mapping algorithms. Right: Corresponding dye recipes for the computed colours.

7.3.4.3. Summary of findings and general discussion

Table 7.1 lists, for each tile colour, the colour gamut mapping and colorimetric matching techniques in order of ascending $\Delta E^*_{ab,10}$ difference between the resulting computed cake colour and the tile colour. Table 7.2 lists the techniques in ascending order of total dye quantity needed in the cake to produce the resulting colours. These tables do not indicate the magnitude of the differences between the various techniques, which have already been discussed. Where useful, some of the discussion of the differences in the preceding sections is repeated here, with the exception of further discussion of the results for Pale Grey, for which comparisons between the

matching and mapping techniques could not be made, in the absence of a result from colorimetric matching.

As summarised in the Table 7.1, the colours from colorimetric matching and clipping are closest overall to the original tile colours, for the majority of these colours. Orange SCE and Yellow SCI were the exceptions in that the colours from matching had the largest $\Delta E^*_{ab,10}$ differences to the tile colour. For Cyan, Deep Blue and Deep Grey SCE, clipping (with or without initial lightness compression) produced similar results to matching. Clipping and matching might have been expected to produce the better results; clipping is a nearest point mapping approach, while the adjustment of out-of-range dye quantities computed by colorimetric matching for out-of-gamut original colours seeks to find the nearest workable dye recipe. If a tile colour was already within the gamut of cake colours, matching should already have provided the best result (Deep Pink SCI, Green, Mid Grey SCE). The colours from gamut mapping algorithms involving chroma compression (with or without initial lightness compression), or lightness compression alone, had the largest $\Delta E^*_{ab,10}$ differences to the original tile colours. This was due to the original colours being shifted longer distances along the lightness and chroma mapping lines. The impact of lightness compression on individual colours depended on their original position. Additionally, for the Deep Pink SCI, Green, and Mid Grey SCE colours which were within the cake gamut to begin with, lightness compression only served to move the solution away from this ‘already best position’.

Table 7.1 General summary comparing outputs from colorimetric matching and colour gamut mapping algorithms for their closeness to the original tile colours. For each tile colour (SCI or SCE) algorithms are ranked in ascending order of $\Delta E^*_{ab,10}$ difference between the computed cake colour and the tile colour (1 = smallest $\Delta E^*_{ab,10}$ difference).

Coloration algorithm	Ascending rank order of $\Delta E^*_{ab,10}$ difference between computed colour from algorithm and tile colour																	
	Cyan		Deep Blue		Deep Grey		Deep Pink		Green		Mid Grey		Orange		Pale Grey		Red	
	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE
Matching	2	3	3	=3	3	=2	3	=3	2	1	1	1	2	2		2	2	4
L* compression only																		
L*-C* compression			3	2	3	2	3	4	2	2			3	=1		3	3	3
C* compression only	2												4	=1		4		
Clipping with L* compression	=1		2	=1			2	3			=2	2	=1	=1	2	2	=1	=1
Clipping only	=1		=1		1	=1	1	1			=2		=1	=1	1	1	=1	=1

Table 7.2 General summary comparing colorimetric matching and colour gamut mapping algorithms for the computed total dye quantity needed in the microwave-baked cake for the cake colours to provide the best equivalents for the tile colours. For each tile colour (SCI or SCE) algorithms are ranked in ascending order of computed total dye quantity (1 = least dye).

Coloration algorithm	Ascending rank order of total dye quantity for cake colours computed to match tile colours																	
	Cyan		Deep Blue		Deep Grey		Deep Pink		Green		Mid Grey		Orange		Pale Grey		Red	
	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE
Matching	2	3	3	=3	3	=2	3	=3	2	2	1	2	3	=1		=3	=1	=1
L* compression only																		
L*-C* compression			1	1	1	=2	1	1	1	1			2	=1		1	=1	=1
C* compression only	1		2										1	=1		2		
Clipping with L* compression	3	4	2	=2			2	2			2	1	=4	=1	2	2	=1	=1
Clipping only	4	5	=3	=2	2	1	=3				3		=4	=1	1	1	=1	=1

Table 7.2 shows that the colours from colorimetric matching and clipping typically needed the highest total dye quantities than did the colours from compression, due to the former colours being darker and/or more chromatic. When the colours from matching and clipping shared a similar $\Delta E^*_{ab,10}$ difference to the original tile colour (Cyan SCI and SCE), these did not necessarily call for the same total dye quantity. Conversely, when clipped or compressed colours and the colours from matching called for the same, or similar total dye quantity, they did not necessarily share the same $\Delta E^*_{ab,10}$ difference to the original tile colour (Red SCI and SCE, Deep Pink SCE, Orange SCE and Yellow SCE). Solutions also differed in their dye recipes. For example, in addition to less total dye being needed for the Cyan colours from matching (compared to those from clipping), the recipes for the colours from matching had a higher proportion of blue to red dye (SCI – 86:14; SCE – 88:12) than did the recipes for the clipped colours (SCI – 65:35 and 67:33; SCE – 69:31 and 75:25). For Orange SCE, the recipe for the colour from matching had a higher proportion of yellow to red dye than did the colours from mapping.

The observed differences in dye recipe and in total dye quantity between the methods could be due to the different ways in which the two types of recipe were reached. Matching was targeted at the colours at their original positions, whether within- or out-of-gamut, and computed dye recipes ‘corrected’ in a rudimentary way where necessary for out-of-gamut colours by scaling back dye quantities to within legal range, conserving internal dye proportions. Iterative recipe correction was applied to colours which all should have been within-gamut as a result of mapping, thereby increasing the likelihood of computing within-range dye quantities. For both Cyan and Orange, the colours from matching were predicted to be substantially more different in hue to the original tile colours, than were the colours from mapping (by more than 10 $\Delta H^*_{ab,10}$ units), suggesting that a basic form of recipe adjustment cannot guarantee a colour of the correct hue. The mapping algorithms on the other hand were hue-preserving methods.

As discussed previously in Chapter Four, ΔE^* is an index of total colour difference, and while the numerical magnitude of the contributions from lightness, hue, and chroma differences to overall difference can be determined, these still do not indicate which of the differences are the most *important* determinants of overall difference. However in this study, there may be a more direct relationship between magnitude and importance of difference. For Cyan and Orange, the visual match between the colours of the cakes prepared with dye quantities computed from colorimetric matching and the SCI tile colours were the least satisfactory (see Figure 4.8, Chapter Four). These cake colours had a large contribution of $\Delta H^*_{ab,10}$ to $\Delta E^*_{ab,10}$, whereas the contribution of $\Delta H^*_{ab,10}$ to $\Delta E^*_{ab,10}$ is much smaller, or zero, for the colours from gamut mapping, which is consistent with the mapping approach being hue-preserving. This suggests the corresponding cakes prepared using dye recipes computed from gamut mapping might be the better matches visually and that for these cakes, the question then becomes one of whether lightness or chroma differences are the more important. An understanding of the importance of these differences for both tile colours and cake colours will aid selection of the best approach for dye recipe computation, whether it is based on colorimetric matching or colour gamut mapping.

The performance of the colour gamut mapping algorithms, and their performance relative to colorimetric matching, was also a function of the gamut boundary information that was available for each tile colour. The degree of lightness compression for the tile colours was based on an assumed lightness range of zero to 100 L^* units – black to white – for these colours. The manufacturer of the tile colour standards used in this study also offers a set of ‘Neutral Standards’ – a range of greys from white to black – with reflectance values ranging from 88% to 0.5% (using the 0/45 measurement geometry, which for glossy materials is equivalent to the specular excluded geometry used in this thesis), and also an opaque black glass with 0% reflectance (Lucideon, 2014). On this basis, using an assumed L^* of zero units as the bottom of the lightness range for the tile colours was reasonable, but the true maximum lightness of the range might be short of the 100 L^* units used. Lightness of the tile colours was compressed to

fit within the lightness range of the *entire* cake gamut. Using these lightness ranges for the tile and cake colours, lightness compression pushed within-gamut colours (Deep Pink, Mid Grey) out of gamut, requiring additional computation (clipping or chroma compression) to bring them back to within gamut. Colours might have been kept within-gamut had the lightness range of the cake gamut at the hue angle of the tile colour been used instead, which was often different to the range for the entire cake gamut.

Without knowing the chromatic limits for the tile colours, full chroma compressions were not possible. Therefore out-of-gamut colours, which could otherwise have been placed within the cake gamut boundary, were mapped to the boundary itself. Full compressions for all colours would have resulted in larger shifts in chroma, rendering most colours less chromatic than was possible in this study, and needing less dye. In turn, the $\Delta E^*_{ab,10}$ differences between the compressed colours and the original colours would have increased, thereby increasing the distance between the solutions from colorimetric matching and from compression.

The results from the clipping only of tile colours, without initial lightness compression, were unaffected by the level of detail about the tile colour gamut, as clipping alone involved simply the replacement of the tile colour with its nearest colour on the cake gamut boundary.

7.4. Conclusions

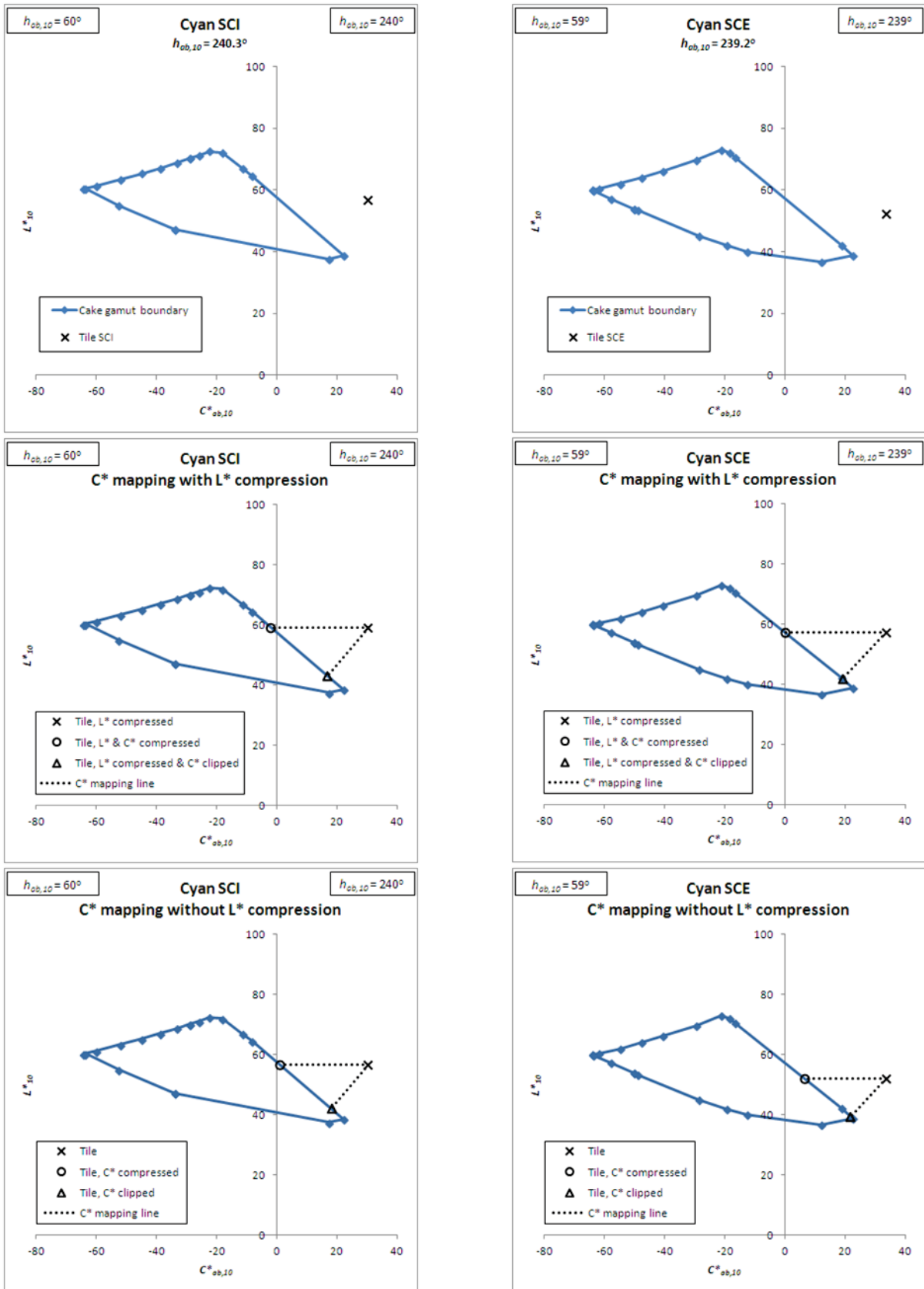
By using the same dye blends and dye quantities (for the same number of gamut boundary points) that were used for the model gel substrate, a colour gamut boundary can be computed for the range of colours achievable in the microwave-baked cake when blends of Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) dyes are added to the cake, which has greater definition and accuracy than the one previously computed using a much smaller number of points (Chapter Four). This allowed the mapping of out-of-gamut tile colours to take place, and the density of points located on the cake gamut boundary provided a useful source of starting recipes for iterative recipe correction, for most of the mapped colours.

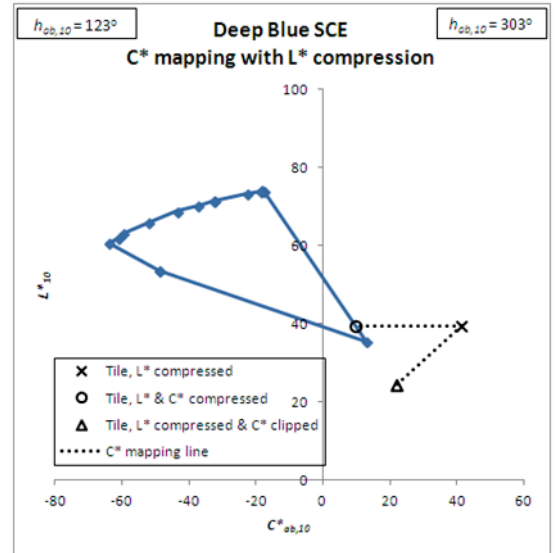
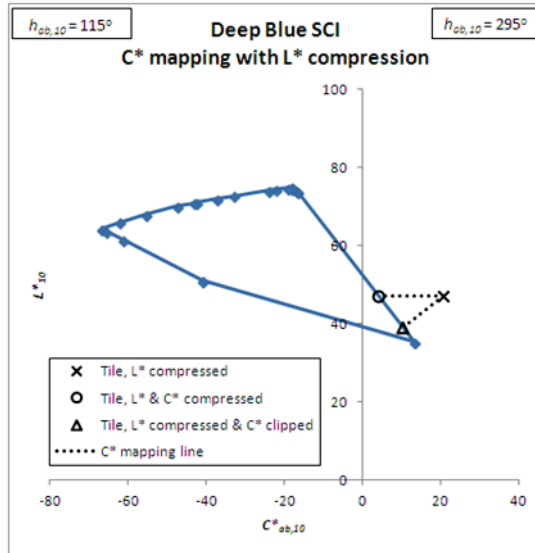
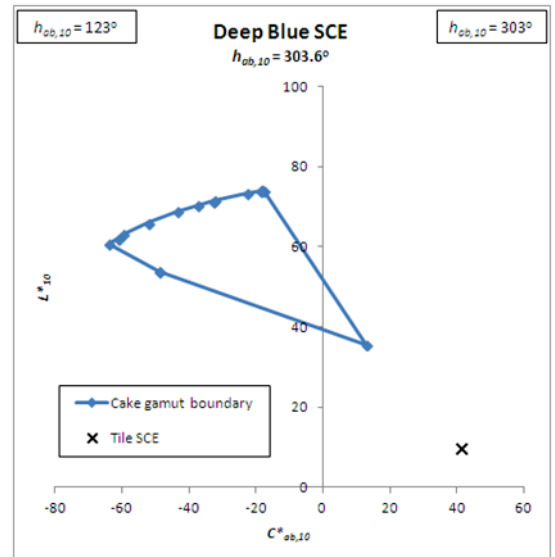
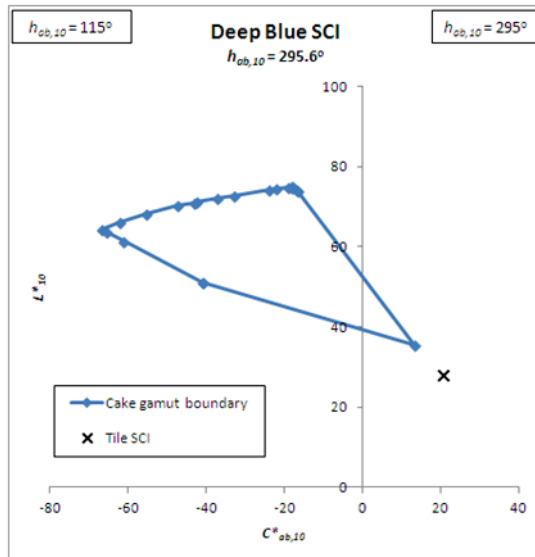
Of the two colour gamut mapping approaches, clipping of colours to the reproduction colour gamut could be favoured over compression in that the colours from clipping are predicted to be closer to the original colours, and more chromatic, than those provided by compression, but might require more total dye for some colours. Clipping should always return a solution for out-of-gamut colours, and will leave within-gamut colours untouched. Lightness and/or chroma compression may not always return a solution, or could move the colour away from the best possible solution. However, this does not preclude compression proper being applied should more information about the gamut of the original (target) colours be available. Based on computed dye quantities alone, it is difficult to favour the colour gamut mapping approach over the colorimetric matching approach, as one method does not consistently compute more or less dye than the other method. In this case the colorimetric matching approach might provide a fast, convenient method as it can produce similar $\Delta E^*_{ab,10}$ results to clipping, however clipping has the notable advantage (like compression), in that it can be a hue-preserving method, and therefore could produce a more visually acceptable result. Whether colorimetric matching or colour gamut mapping is selected should also be based on the:

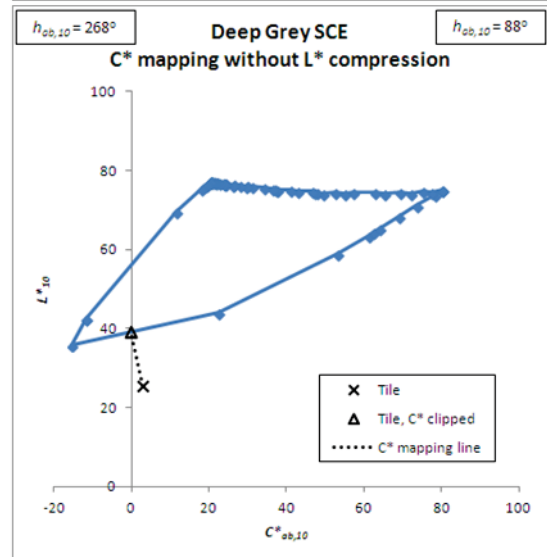
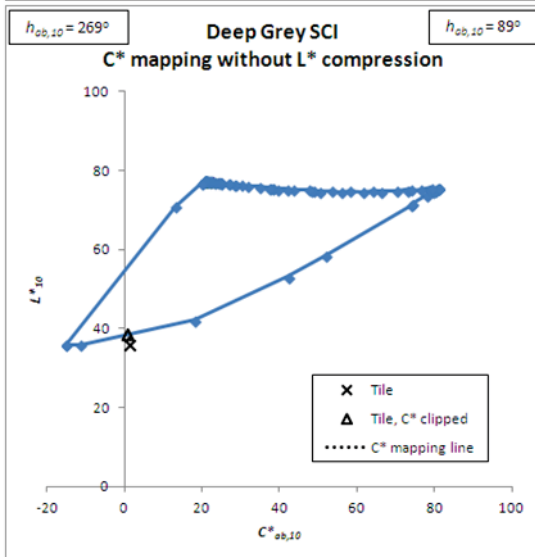
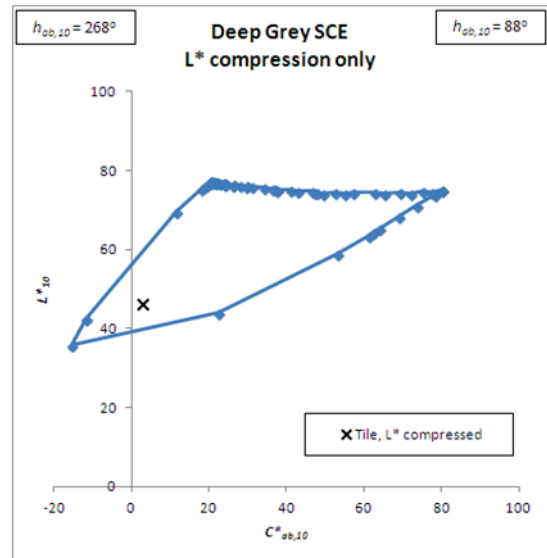
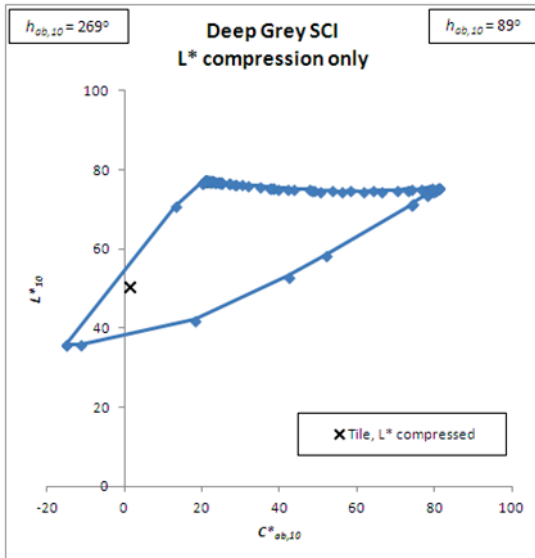
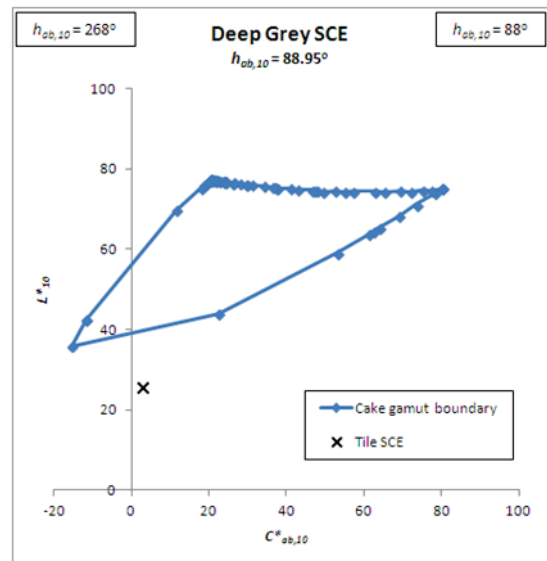
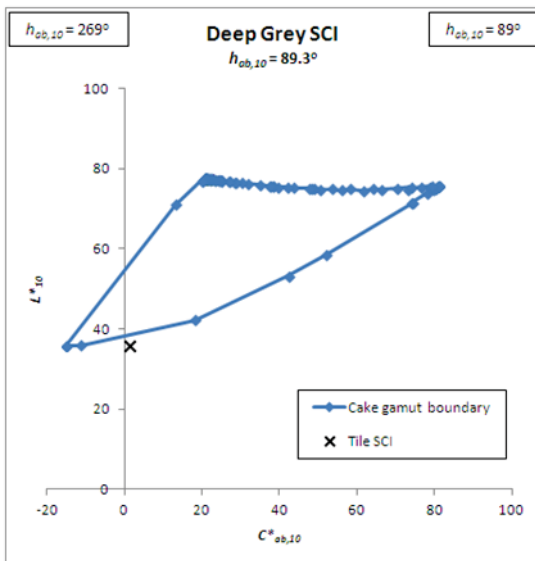
- proximity of the original colour to the reproduction gamut boundary (i.e. those tile colours already in close proximity to the reproduction gamut might be adequately catered for by colorimetric matching);
- relative importance of lightness, chroma and hue differences to the overall difference between the original colour and the computed colour reproduction;
- desired properties of the colours relative to each other, post matching.

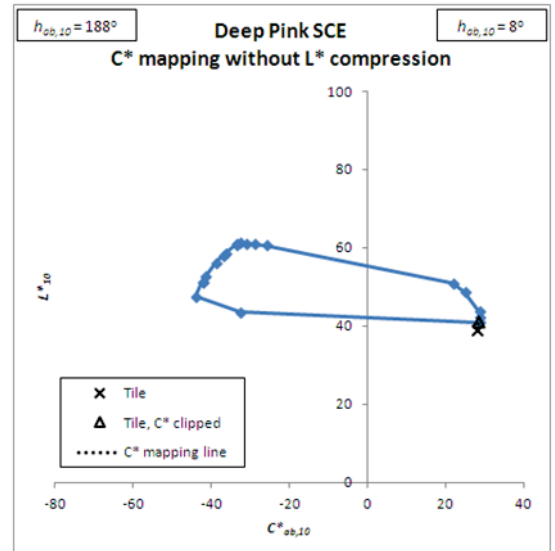
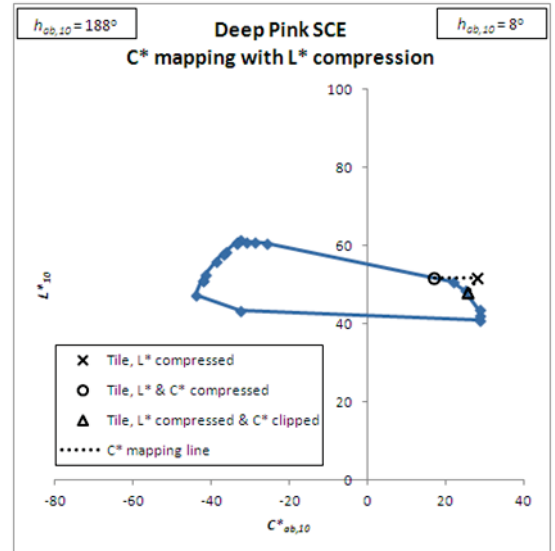
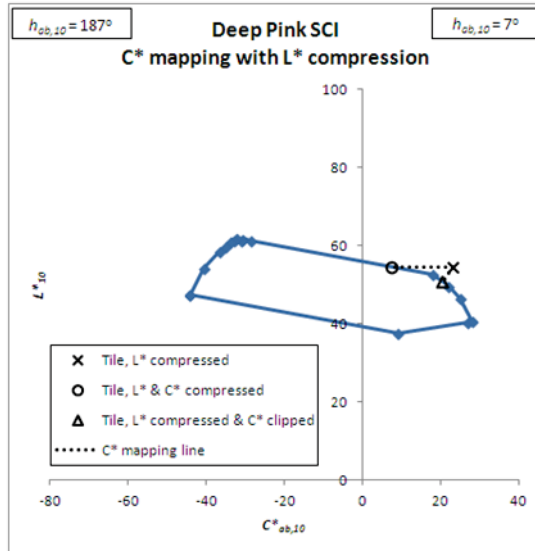
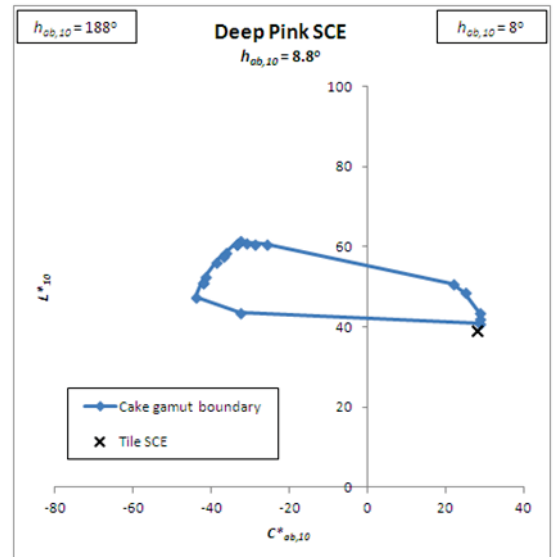
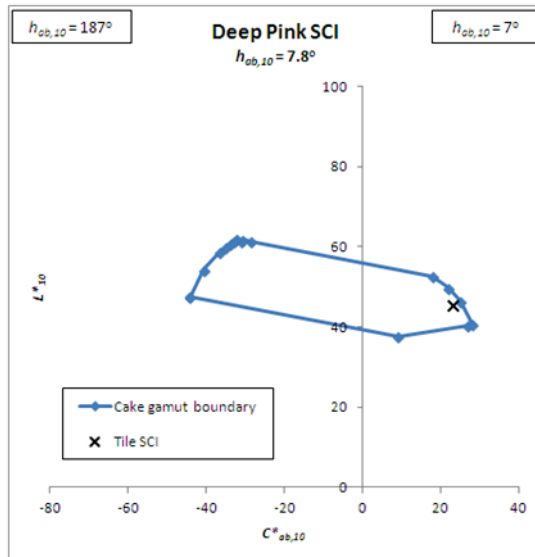
For the 3D colour food printer, multiple algorithms could be made available to the user and contained within the printer set-up, offering a choice of speed, economy of dye usage, or high computational capacity (for accuracy), or a combination of all three, depending on need.

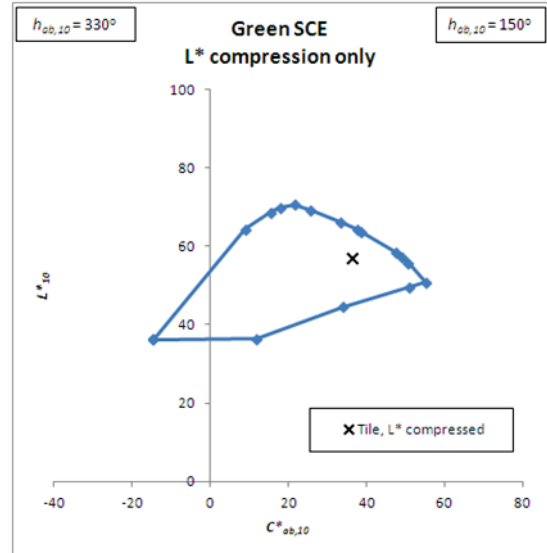
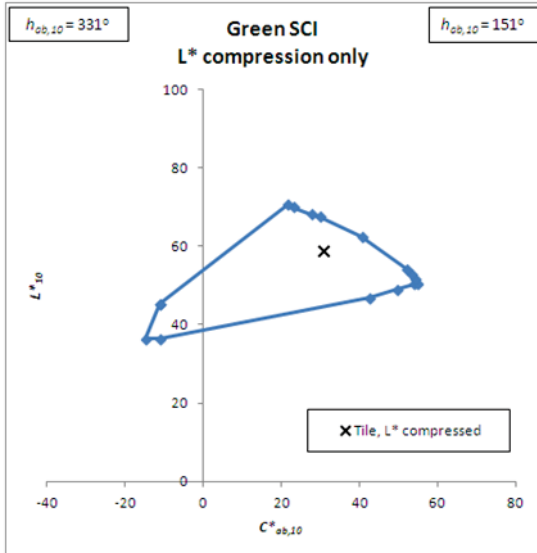
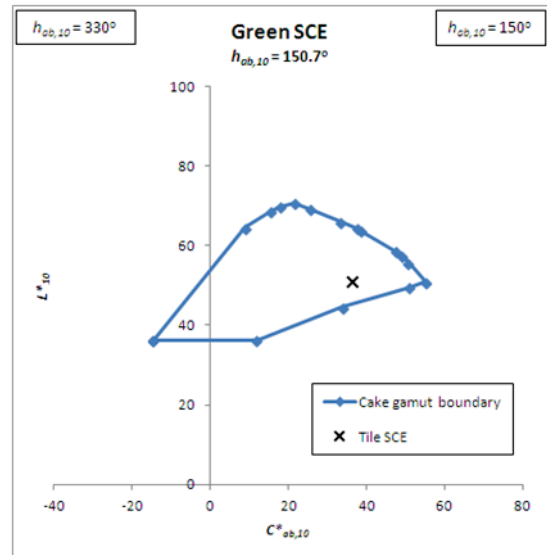
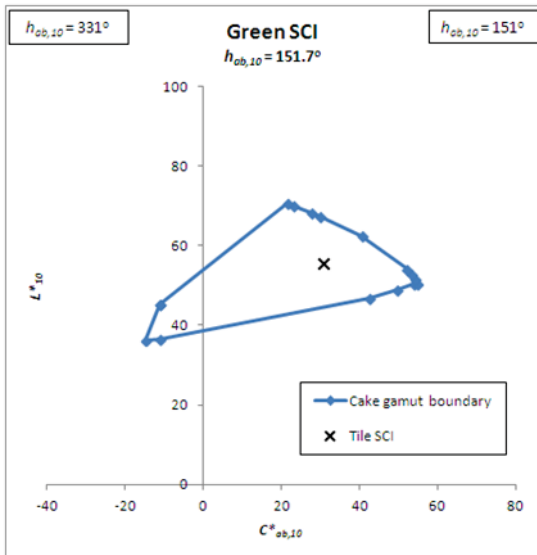
7.5. Appendix

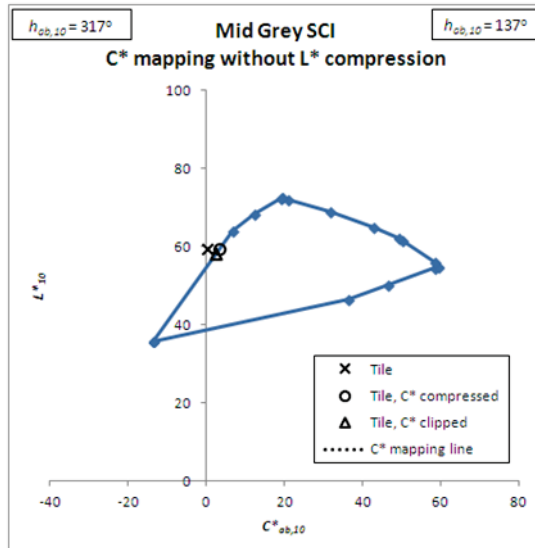
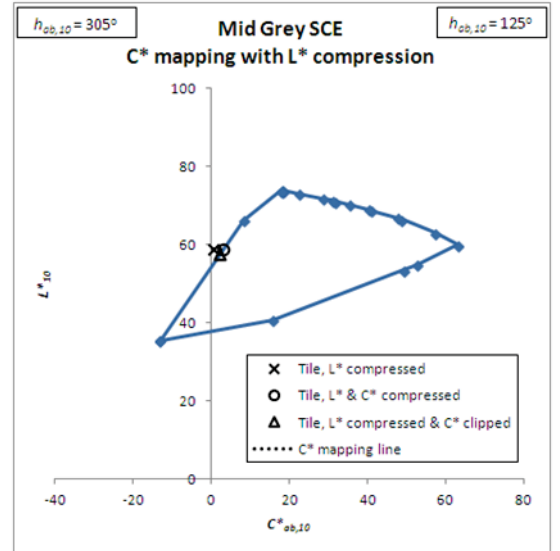
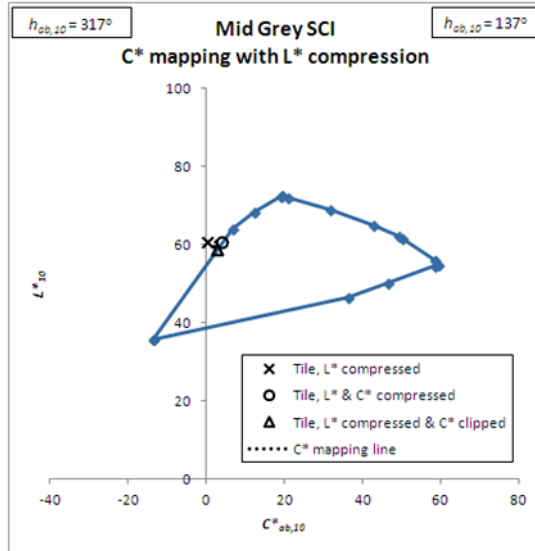
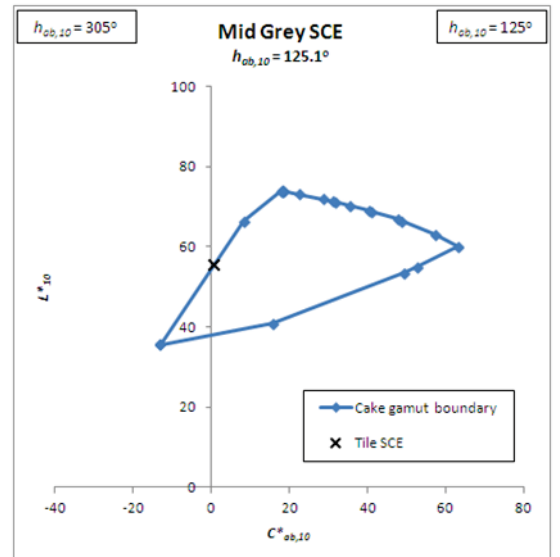
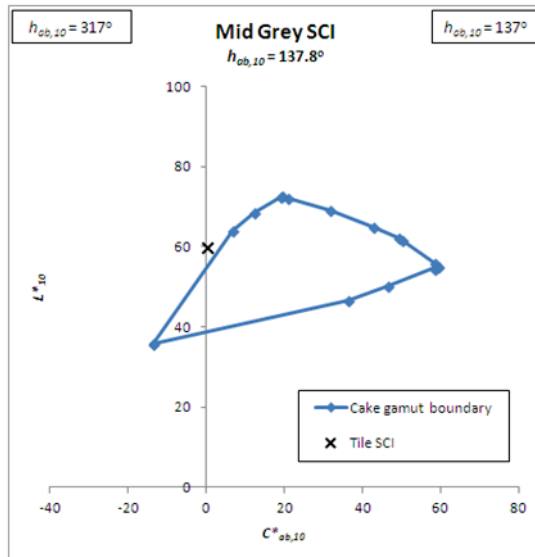


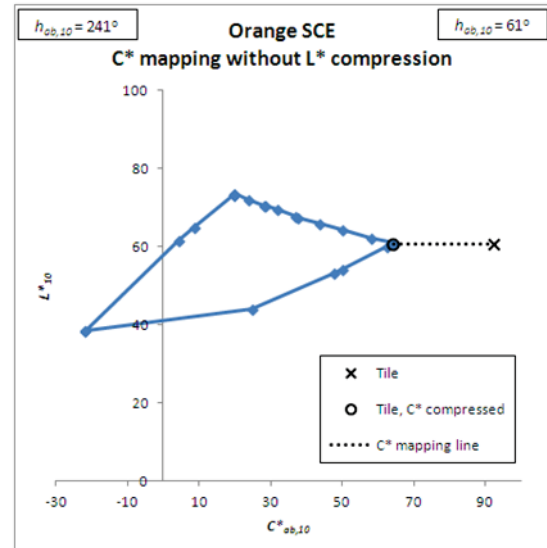
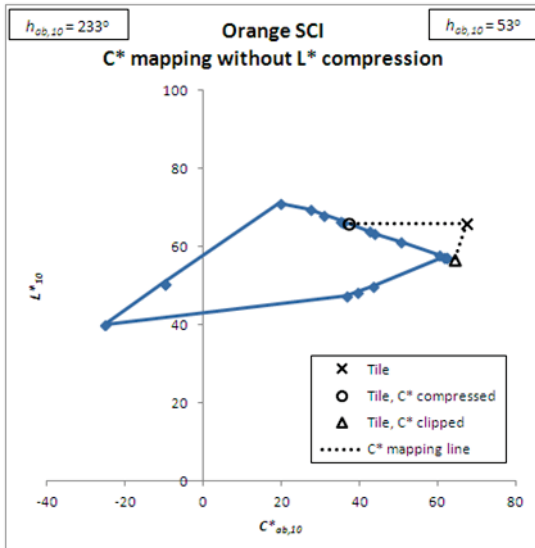
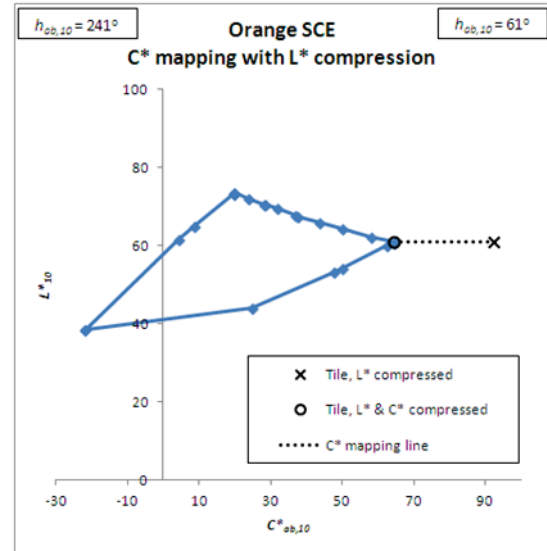
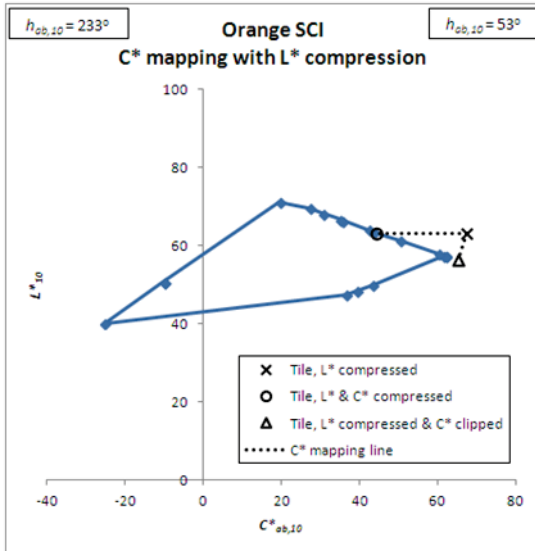
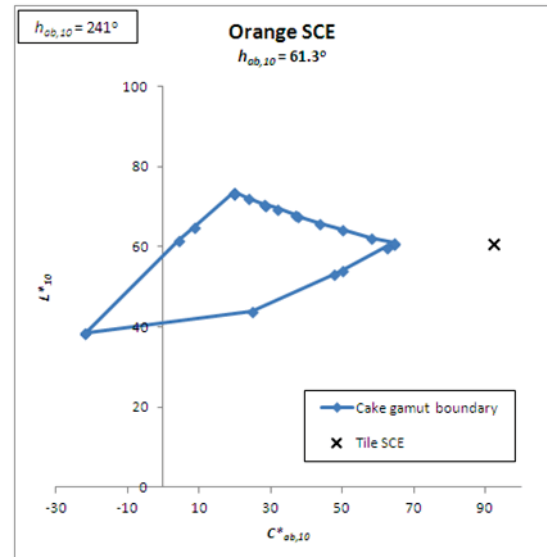
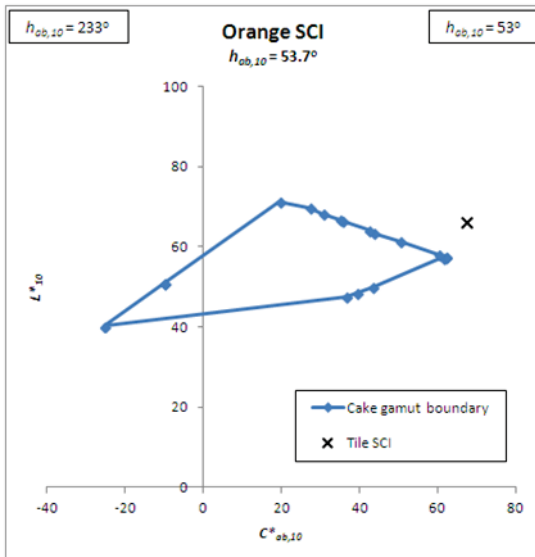


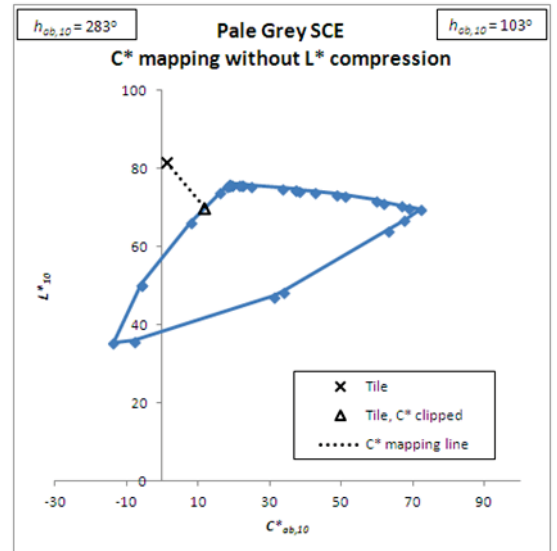
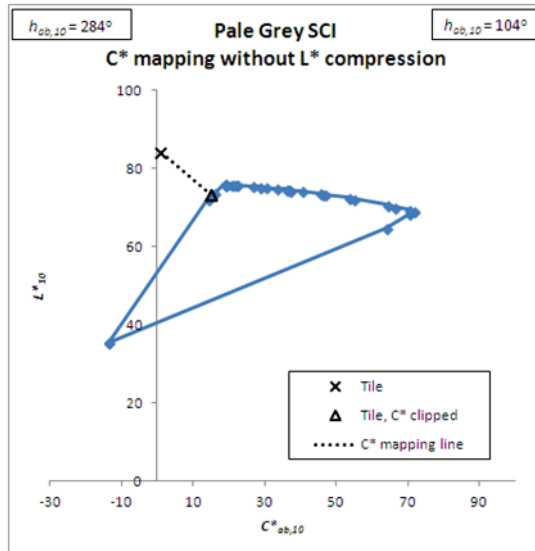
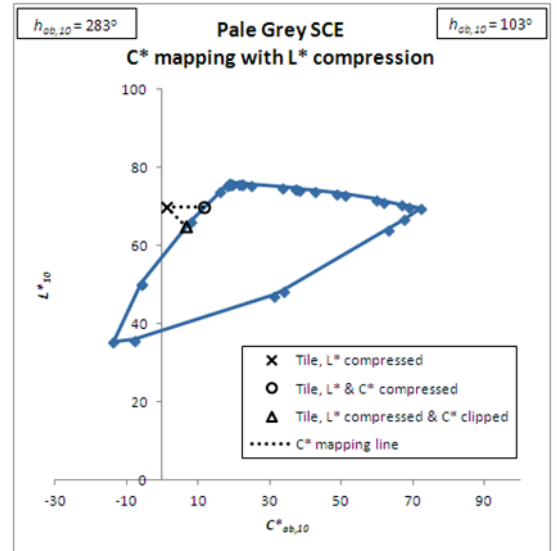
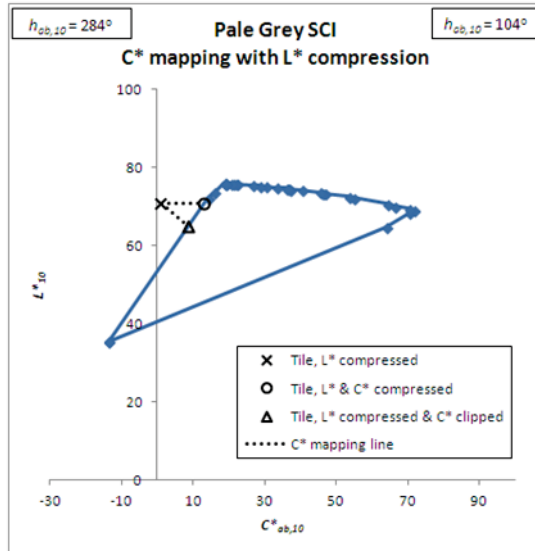
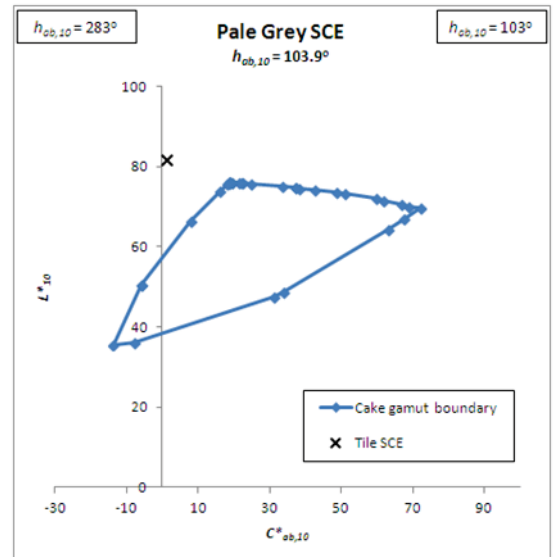
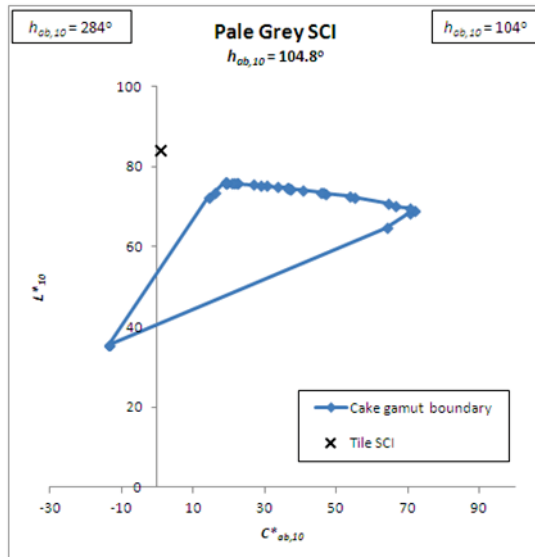


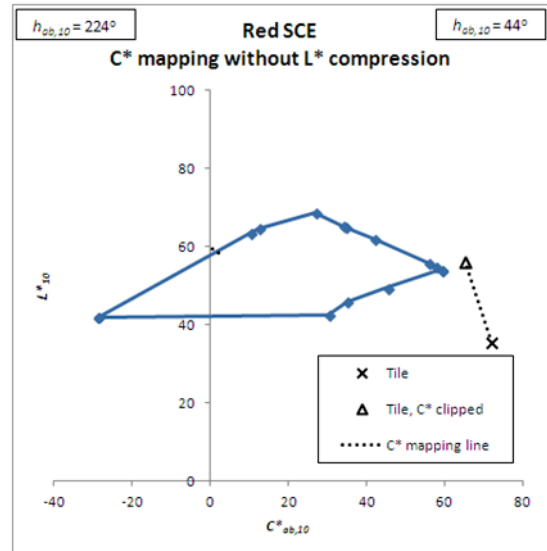
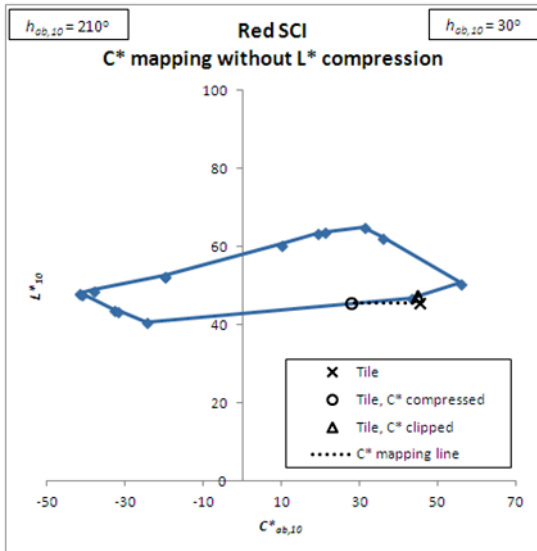
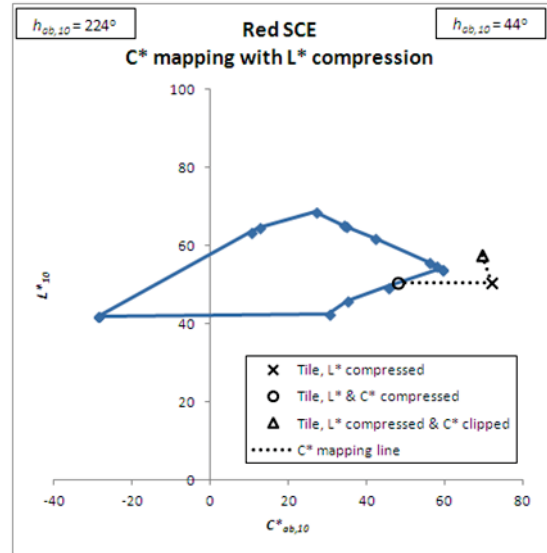
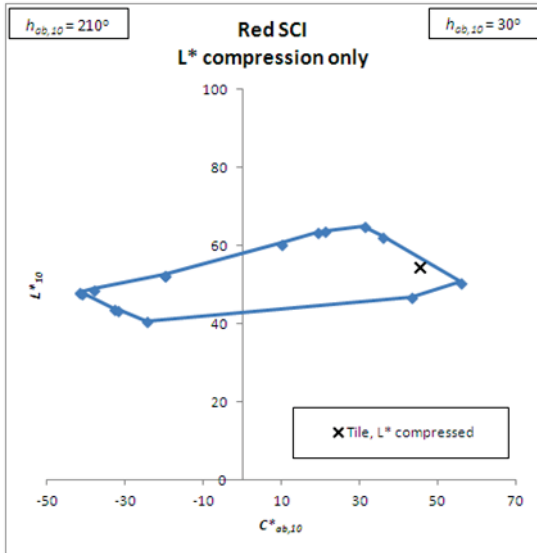
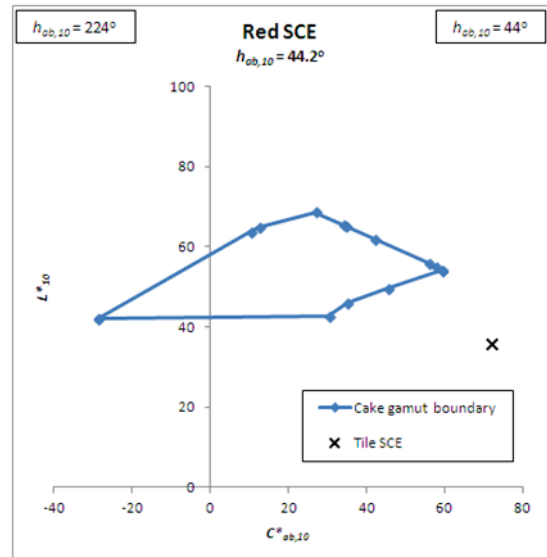
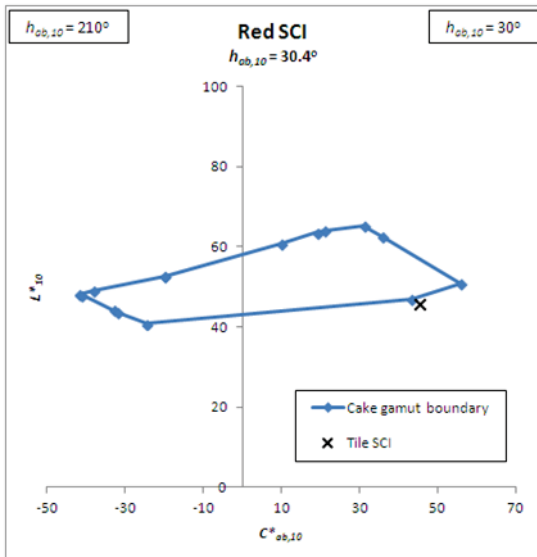


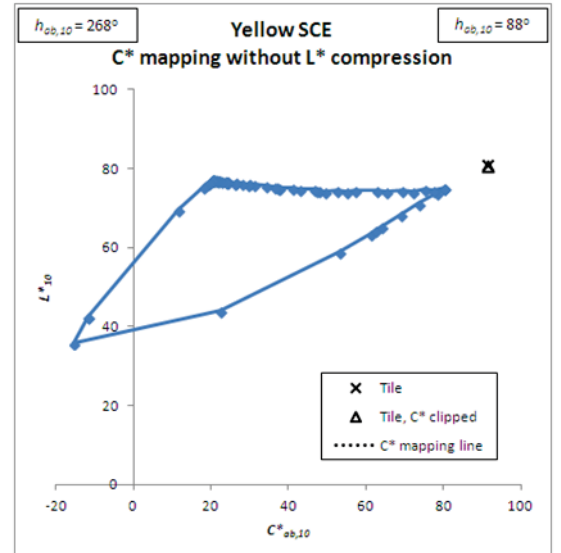
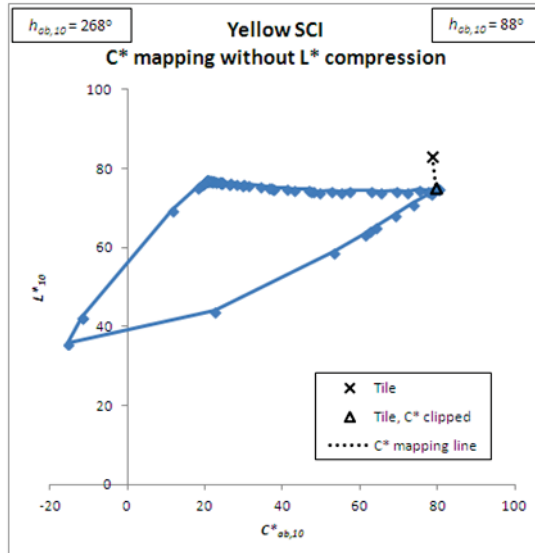
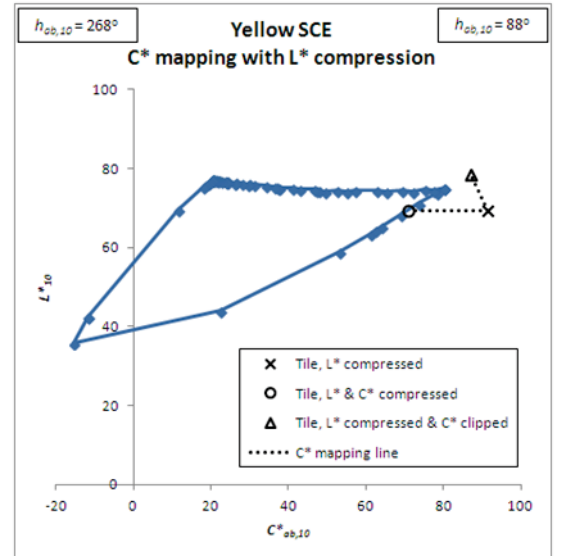
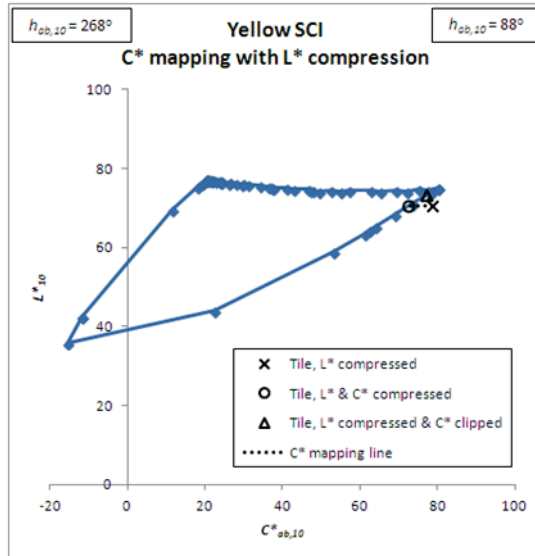
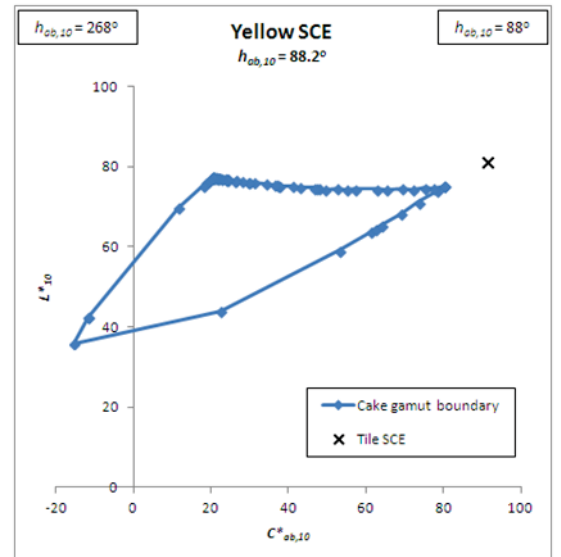
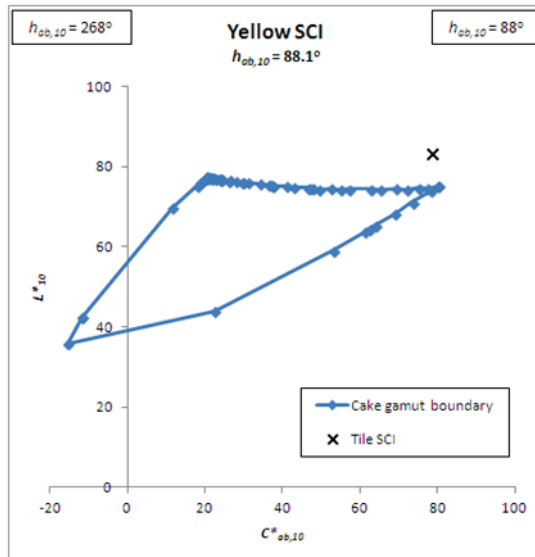












Chapter Eight: Overall Discussion

8.1. Recap: The background to the thesis

The research in this thesis contributes to the development of a novel 3D colour food printer in the Riddet CoRE Technofoods programme. To recap, the printer is being designed to produce fully customised, on-demand, food outputs that meet user specifications not only for nutritional and sensory characteristics, but also for visual appearance, having the capability to render any chosen complex image or design in 3D colour *within* the food matrix. The specific type of printing technology that is being developed is one in which three or four primary-coloured liquid dyes are each contained in separate ‘cartridges’ and are blended in the correct quantities and delivered at the correct time, for each voxel, to an uncoloured raw substrate paste as it is being extruded from a separate vessel. The dyes are blended with the substrate immediately prior to the point of extrusion resulting in a continuous stream of coloured raw voxels, which is built layer by layer into a desired 3D shape, in the style of fused deposition modelling (see Chapter Three, Literature Review, Part 2). The final step is rapid cooking which develops and sets the structure, resulting in a food object containing a multitude of colour voxels to match the original design.

While other PhD and Masters thesis research in the Technofoods programme has been focussed on developing printer hardware and software, on the mixing of liquid dyes with model food materials, and on controlling the rheology, and structure formation, of the food printing substrate, this thesis was concerned with developing algorithms to compute dye recipes, as needed, for each voxel coloured. The biggest challenge to developing such an algorithm is presented by the combination of the large number of colours needed within a short time frame, the printing substrate being a food matrix; and printing being in 3D. Even before any colorants are added, customisation of the printed food substrate itself means that printed outputs will vary in their physical and chemical characteristics. These, along with processing conditions, will all impact final colour rendition and, together with restrictions on dye levels in food, the range of

colours that can be achieved. Examples of such characteristics are: the chemical and thermal environment of the substrate prior to and during cooking; the native colour of the substrate (post cooking); the degree of viewed surface texture (affecting the degree of light scattering); volume expansion, which will have a diluting effect on the colour from the dyes relative to the colour from the dyed, raw substrate. The printer will need the capability to render (as closely as possible) the same colours across different customised food outputs, and to do this by correcting quickly and on-demand, the dye recipes for each colour according to the type of food substrate requested.

A review of the literature (Chapter Two) concluded that non-food methods of computer colour matching (computer recipe prediction) and colour gamut mapping, rather than methods usually applied to food would best suit the needs of the printer. These methods offer between them speed, and can be applied to colorants that are mixed into a substrate matrix. These techniques have not been applied to foods, which are more diverse and more complex, particularly as 3D colour reproduction substrates. This thesis therefore sought to investigate whether computer colour matching and colour gamut mapping could be applied to the controlled coloration of food substrates, and how these techniques might be modified to account for the effects of different food characteristics. In the following sections the main findings from the thesis are revisited, and the extent to which these meet the original research objectives (listed at the end of Chapter Three) is discussed. Then, to properly consolidate the work of the thesis, and to fulfil its main aim, consideration is given to how the findings could be integrated into an overall colour image reproduction process for the 3D colour food printer.

8.2. Research objectives and summary of main findings

To develop model food substrates appropriate to 3D colour food printing, and to the application of the coloration methods being tested

To simplify the experimental approach, two model food systems were used as the colour reproduction substrates, which shared some characteristics with the types of food outputs that

the printer might produce. A microwave-baked cake was used in both colorimetric matching (Chapter Four) and colour gamut mapping (Chapter Seven). The cake was regarded as an appropriate model substrate in that it already had many of the properties suitable for a printed food. Variants of a wheat starch gel which differed in their levels of artificial browning were used to investigate the impact of browning (in isolation from other food properties) on the outputs from colour gamut mapping (Chapter Six). The maximum level of gel browning resulted in the gel and cake being similar in lightness and chroma (Chapter Five).

In hindsight, the gel would have sufficed as the single model system throughout the thesis. It was a simpler system which already shared (measurement) surface characteristics with the tile colours, and could have been built gradually to a more complex system by adding more features, beyond browning. This would have allowed the impact of several food properties (individually and together) to be investigated, on both colour gamut mapping and colorimetric matching outcomes.

To determine the absorption behaviour of each primary dye in each substrate, leading to the development and validation of models of dye blending for each substrate

One of the key findings from this thesis research is that, by using the single-constant form of the Kubelka-Munk (K-M) colorant additive blending model (which forms the basis of controlled coloration in various non-food industries), it was possible to predict the colour of the food substrates containing added primary-dye blends, from the spectral contributions of the substrate itself, and the unit spectral contributions of the dyes scaled by the (known) quantities of dyes in the blends (Chapters Four and Five). This then enabled:

- colorimetric matching to compute the (unknown) quantities of the dyes that were needed in a food substrate (the microwave-baked cake), for the substrate to match the colours of non-food materials (the standard tiles) (Chapter Four);

- computation of detailed colour gamut boundaries for food substrates containing primary dye blends, specific to the D65 standard illuminant and 10 degree standard observer conditions used in this thesis (Chapters Five and Seven);
- iterative recipe correction to compute dye recipes for colours that were mapped (by colour gamut mapping) to fit within the achievable range of colours in the food substrates (Chapters Six and Seven).

Further:

- It was shown that the magnitude of the absorption spectra for unit concentration of each primary dye did not appear to change significantly in substrates (model starch gels) which differed only in their intensity of a single characteristic, i.e. in their level of artificial browning (Chapter Five), and therefore:
- by capping the total quantity of dye in a blend at the legal limit for each individual gel, it was possible to:
 - compute the colour gamut boundary for each of the related (brown) gel substrates by substituting the same dye blends and the unit absorption spectra for the dyes into the K-M blending equation, changing only the spectral contribution of the substrate, and
 - observe the changes in the colour gamut with increased artificial browning of the gel substrate, which were a decrease in its size, and a shift in its lightness and chroma ranges.

Although the blends used to validate the dye blending models represented a range of dye combinations, the number of blends was small compared to the vast number of combinations possible. Based on a single criterion, a $\Delta E^*_{ab,10}$ difference of three units or less between computed and measured colours, there were indications that the models might not apply with

equal measure to all blends within a single substrate (Chapter Fours and Five) or across the variants of a substrate (Chapter Five), or to low-chroma blends (Chapter Five).

In reality the contribution of scatter should be more significant in food systems than is allowed for by the single-constant K-M equation, for example in foods such as gels which can vary in their translucency. The extension of colour prediction models for coloured foods to include two-constant blending should be investigated in future.

To use colorimetric matching to compute dye recipes for each target colour

Colorimetric matching was applied to finding matches for the tile colour targets using the cake-dye system only (Chapter Four). The technique gave good first (computed) solutions for all colours. In practice, colorimetric matching can be applied successfully to targets that are within the gamut of a food coloration system. Out-of-gamut targets require extra computation, without the guarantee of a good visual match for some colours.

To use colour gamut mapping to find the best equivalent of each target colour and its corresponding dye recipe in each model substrate, including those which differ only in their level of a single food characteristic, to measure the impact of this characteristic on the solutions possible

The original positions of the tile colours relative to the position of the reproduction gamut boundary colours determined the extent to which colour gamut mapping was possible using the algorithms that were applied. In the vast majority of cases, tile colours were able to be mapped to a reproduction colour gamut, whether this was the gamut of cake colours (Chapter Seven) or the gamut of colours for a given gel variant (Chapter Six). The exceptions were the compressed Cyan and Deep Pink colours for which solutions were not available at the higher levels of browning tested (Chapter Six). However, finding the ‘true’ best equivalent of certain colours (for example, Cyan and Deep Blue in Chapter Six) in each model substrate was limited by not having full colour gamut information for the tile colours. On the other hand, a lack of colour gamut information (i.e. computed colours) for the reproduction gamut (Chapter Five) limited

the ability to find dye recipes corresponding to some of the mapped colours (Deep Grey, Chapter Six). Computed gamut colours were a source of starting recipes for the iterative correction technique used to find recipes for the mapped colours.

Using the variants of the wheat starch gel, dye recipes were computed to provide the best equivalent of each tile colour for each level of gel browning (Chapter Six). The results were intended to provide examples of the effects on dye quantities and on colour outcomes of changing the intensity of a single characteristic. The changes in dye recipes for mapped colours with increasing levels of substrate browning were measured against substrate lightness as an indicator of browning (Chapter Six). These changes appeared to be a function of whether a clipping or compression algorithm was used, and also of tile colour. The dye recipes computed usually reflected the changes observed in the lightness and chroma of the mapped colours.

To make appropriate assessments of the closeness of matching between target colours and the solutions provided by colorimetric matching and by colour gamut mapping

The conclusions drawn about the closeness of the matches can be constrained by applying the criterion of a maximum three-unit $\Delta E^*_{ab,10}$ difference to all matches. This criterion might be too strict for situations where non-food colours are matched with coloured foods, as indicated by the visual inspection of the tiles with their prepared cake matches (Chapter Four). For colorimetric matching, examining lightness, hue and chroma differences individually may prove more informative than relying on a total colour difference.

Target colours are not expected to differ in hue to computed matches from colour gamut mapping if the mapping algorithms used are hue-preserving. These matches need to be inspected for differences in lightness and in chroma, given the different ways in which compression and clipping algorithms impact these dimensions. In this thesis these assessments were made on the basis of computed outcomes only.

To compare colorimetric matching and colour gamut mapping for the closeness of their solutions to the target colours, and in the dye quantities computed

The cake was a substrate for both methods, which allowed them to be compared on the basis of the overall differences, and differences in lightness and chroma, between the original or target colour and the reproduction obtained using the computed dye recipe (Chapters Four and Seven).

Table 8.1 lists the features and relative merits of colorimetric matching and colour gamut mapping, which are based on the findings of this thesis.

Table 8.1 Features and relative merits of colorimetric matching and colour gamut mapping as applied to the problem of computing microwave-baked cake colours (and their corresponding primary-dye recipes) which best match the standard tile colours.

Colorimetric matching	Colour gamut mapping	
	Clipping	Compression
• Least computational load • Hue of original colour not necessarily preserved • Applied to all colours • Can produce similar ΔE result to clipping (satisfactory results if used in place of clipping for out-of-gamut colours that are close to reproduction gamut) • Does not necessarily use more or less dye than is needed for mapped colours	• Heavier computational load • Hue preserved if hue-preserving mapping algorithm applied	
	• Applied to out-of-gamut colours only • Resulting colours closer than compressed counterparts to original colours • Clipped colours more chromatic than compressed colours • Might use more dye than compressed colours, depending on the colour being mapped	• Applied to all colours • Needs to be preceded by lightness compression in order to return a solution • Resulting colours further away (i.e. larger ΔE) than clipped counterparts from original colours • Less chromatic than clipped colours • Might use less dye than clipped counterparts for some colours

Comparisons were made on the basis of *computed* colours and dye recipes. There was enough detail in the results from colorimetric matching and colour gamut mapping to allow discussion of their relative merits as methods for reproducing target colours in food substrates. Dye recipes were not used to prepare samples for a visual assessment of the solutions from the different methods, but it would have been very useful to have done so for at least two or three representative tile colours.

8.3. Translation to 3D colour food printing

This thesis research has shown that colorimetric matching and colour gamut mapping, which until now have not been used for the controlled 3D coloration of foods, can be applied to the problem of matching the colours of non-food materials with a food substrate containing added

primary dye blends. Furthermore, colour gamuts are able to be computed rapidly to accommodate changes in the characteristics of the coloration substrate itself, allowing dye recipes to be computed to give the best equivalent of a given original (i.e. target) colour with each change. Between them colorimetric matching and colour gamut mapping offer choices in the desired levels of computational load, colour accuracy, and dye usage.

With the colours of standardised non-food materials (the tiles) having stood in for screen or image colours, and model foods standing in for printed food substrates, this discussion now naturally turns to how the findings and methodologies developed in this thesis translate to the 3D colour food printer. What is needed for the 3D colour food printer is an algorithm, or set of *'transformations'* or calculations to process a colour image data file (containing RGB values for each pixel) to a dye recipe file, and which accounts for the complexity of the printed food matrix by correcting for the effects of different food substrate characteristics.

8.3.1. Transformations models for use with colour gamut mapping

8.3.1.1. Transformations for single, individual substrate characteristics

Colour gamut mapping already forms the pivotal step in existing processes for cross-media colour reproduction, for example, those which transcribe colours from screen to print. Cross-media colour reproduction is described in (Morovic, 2003) and Fairchild (2005), and illustrated in Figure 8.1 (which is the same as Figure 2.9 from the Literature Review). On the other hand it has been shown in this thesis that it might be possible to compute rapidly colour gamuts on the basis of substrate characteristics alone, because the absorption properties of the dyes do not appear to change across a set of substrates that differ only in the level of a single characteristic. This raises the possibility of incorporating a set of substrate-driven transformations into the main colour reproduction workflow, feeding in at the point of gamut mapping, resulting in a process which is compatible with the aims and customised nature of 3D colour food printing.

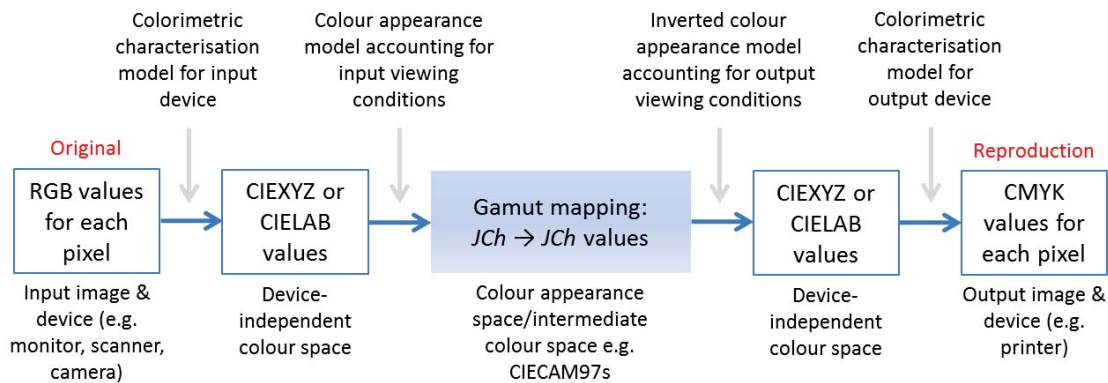


Figure 8.1 Flowchart illustrating the general process of cross-media colour reproduction, using the example of device-independent colour imaging from screen to print. Adapted from Fairchild (2005) and (Morovic, 2003).

In this new scenario (Figure 8.2), the substrate-driven transformations take the form of stepwise changes to the colour gamut (size and shape) with each individual characteristic (type or level) that is ‘read’ by the printer as being a part of the food that is requested, or ‘keyed in’ by the user. The transformations process begins with a ‘standard’ colour gamut (i.e. the colour gamut for a smooth-surfaced, colour-neutral food substrate containing primary dye blends) and ends with a single reproduction colour gamut representing the combined effects of the individual substrate characteristics, and which is used in the gamut mapping step in the main colour reproduction process. The change in the substrate gamut with each additional characteristic is computed by an as yet unknown function, $f(x)$, and the changes in gamut that occur collectively during the transformations process are based on, but are different to, the changes that occur with each characteristic separately. By using dyed samples displaying multiple as well as single characteristics, the transformations functions could be determined and validated.

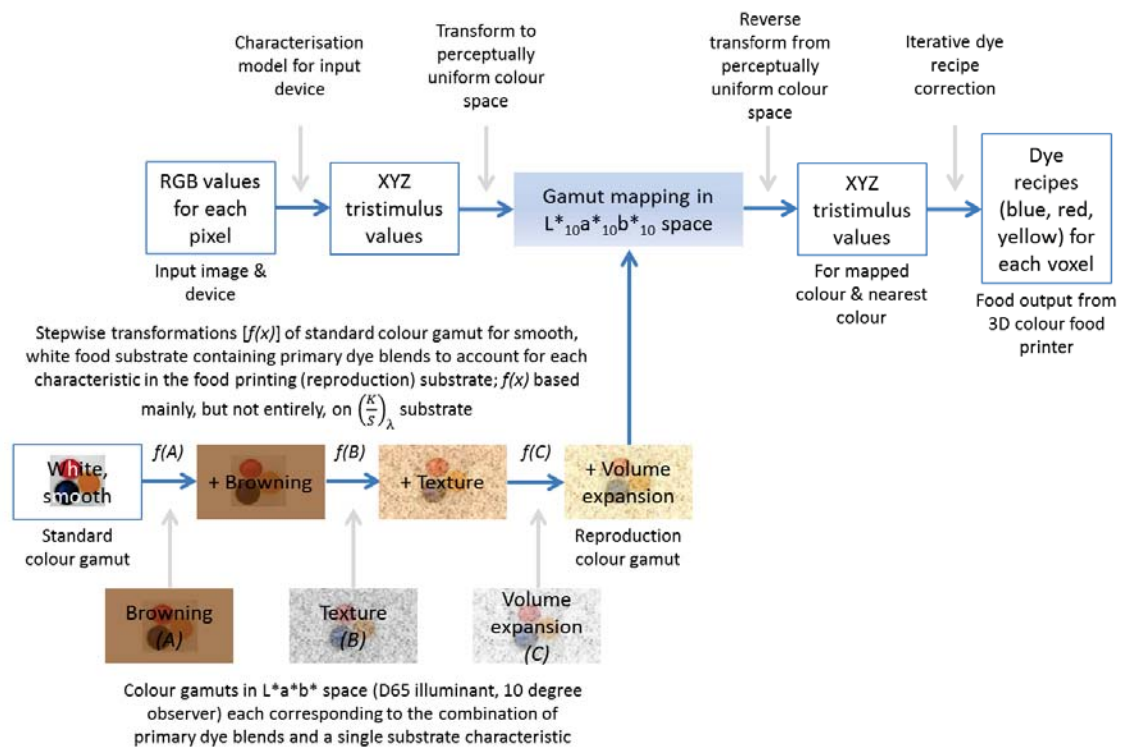


Figure 8.2 Generalised algorithm proposed for the 3D colour food printer, modelled largely on device-independent colour imaging (Figure 8.1), for rendering 3D colour images within food matrices, with provision for accounting for the effects of each individual food characteristic on the reproduction colour gamut via an additional series of transformations.

The process to transform the colour gamut of the dyed substrate will begin, and end, with a gamut of colours in the $L^*_{10}a^*_{10}b^*_{10}$ colour space, the last of which is available for use as the reproduction colour gamut in the mapping stage of the main colour reproduction process. Conventionally however, colour gamut mapping as part of cross-media colour reproduction is done in a colour appearance space (such as CIECAM97s, with coordinates J, a, b or J, C, h), in which viewing conditions have been accounted for by using a colour appearance model. For convenience, the uniform $L^*_{10}a^*_{10}b^*_{10}$ colour space is used here in place of a colour appearance space (or intermediate colour space). The limitations of using the CIELAB space should be kept in mind, which include it applying strictly to colours of identical size, shape and viewing conditions for specifying the differences between them, and its inability to predict luminance-dependency (such as the increase in *colourfulness* and *contrast* with luminance), or the effects of background and surround (Fairchild, 2005).

8.3.1.2. How the transformations might take shape (an example)

8.3.1.2.1. Other characteristics in addition to browning

While it is only the effects of browning that were investigated in this thesis, examples of other substrate effects that could be modelled include volume expansion and surface texture. Expansion upon cooking and the setting to a foam structure are processes that would result in desirable textures and eating qualities in a printed food. Using again the example of the model starch gel, increasing the volume alone of the standard White gel containing primary dye blends would be expected to increase the lightness, and decrease the chroma of the achievable colours due to a dilution effect. Increasing the degree of surface texture (i.e. surface roughness) alone might be expected to increase lightness, this time due to the increase in scattered light relative to specularly reflected light. In future work, surface texture of the gels could be modified by moulding the gels over sandpaper of different grit sizes to create surface textures of different roughness, as has been done for chocolate (Briones *et al.*, 2006).

Other processes requiring transformations to account for might include axial dispersion of dye material through contiguous voxels, chemical changes in dye material during cooking, partitioning of dye between different phases of a food material, and others.

8.3.1.2.2. Transformations process

In a transformations process that accounts for browning, surface texture and volume - in that order - the progressive changes that might be seen in the standard colour gamut of the substrate, are as follows:

- with browning, a decrease in the lightness and chroma ranges, with a shift towards redder and darker colours, followed by
- a shift in the lightness range, back towards lighter colours with the addition of surface texture, followed by

- another shift in the lightness range, with the addition of volume, with the direction of the shift depending on the relative effects of volume and surface texture on lightness, but remaining in the region of lighter colours, together with
- a possible shift in the chroma range away from redder colours by virtue of the effective dilution of the volume concentration of the dyes; the size of the chroma range itself could also change (i.e. decrease) as the effective volume concentration of dye decreases, but this will depend on the relative effects of browning and volume.

An example of what might occur (in part) to the colour gamut, as a result of the cumulative effect of transformations, is depicted in Figure 7.1 (Chapter Seven). Although the gel and cake differ in their formulation, preparation, and measured sample size, the colour gamut for cake – a complex substrate having background colour, surface texture and volume - is shifted towards redder, more yellow, and darker colours, relative to the standard colour gamut based on the dyed, white gel, when both contain the same primary-dye blends.

8.3.1.2.3. Added complexities

In practice the transformations might embody more complexity than simply accounting for the spectral contribution of the un-dyed substrate (Chapter Five). The transformations will need to factor in any changes in the (magnitude of the) unit spectral contribution from each dye that might occur with changes in substrate characteristics. In this study slight changes in unit absorption spectra for the dyes in the starch gel were seen with an increase in the level of artificial gel browning (Chapter Five); because absorption is inversely related to reflectance, small differences in dye absorption spectra will translate to large differences in colour values (here $L^*_{10}a^*_{10}b^*_{10}$). Therefore, computed gamut $L^*_{10}a^*_{10}b^*_{10}$ values from the substitution of the substrate absorption spectral values *only* in the K-M equation when moving from one level of artificial substrate browning to the next (Chapter Five) will differ from those computed when substitutions are made for *both* the substrate and primary dye absorption values. In turn, the colour gamuts resulting from the two different sets of $L^*_{10}a^*_{10}b^*_{10}$ values are likely to differ in size and shape.

Transformations will be made to the colour gamut for a reproduction substrate which is comprised of *computed* colours. Therefore a computed gamut will need to be a good representation of the colours that can actually be achieved in the reproduction substrate. The work of Chapter Five showed that discrepancies between computed colours and measured colours of a starch gel containing primary dye blends meant that the actual size of a colour gamut is likely to be smaller than the one computed. Accordingly, transformations might need to correct for these discrepancies by shrinking the reproduction substrate colour gamut at each step.

Weight loss and final weight of a food substrate after processing also need to be taken into account, in order to not breach the legal limit of dye (of 290 mg/kg) in the finished food, assuming that dye has remained stable during processing. In turn, final sample weight sets the maximum concentration of dye that can be added to the food in its raw form, prior to processing, for the computation of gamuts. For example, in this study, mean weight loss of the gel material after cooking was 5%, meaning a final dye concentration of 29.0 mg/100 g cooked gel was achieved by adding 27.5 mg of dye to 100 g of raw gel; if weight loss were 10%, the maximum level of dye addition allowed would have been 26.1 mg/100 g raw gel (Figure 8.3). The plot of the relationship between dye concentrations before and after cooking in Figure 8.3 resemble plots used in textile dyeing, where a distinction is made between the concentration of dye in the dye bath (the ‘theoretical concentration’) and the dye that is taken up from the bath by the fabric (the ‘effective concentration’) (Berns, 2000).

Note that for this research we *elected* to apply a rule that dye substance must not exceed the legal concentration in each and every component voxel of a food object, rather than over the entire food object. This was primarily for reasons of conservation and partly for simplicity of calculation.

Weight needs to be accounted for because, while colour might be perceived visually more on the basis of volume rather than on the basis of weight of the food, restrictions on dye addition

are applied on a weight basis. In transformations accounting for single substrate characteristics the substrate weight will be that of the ‘standard’ or ‘starting’ substrate, and remain unchanged throughout the transformations.

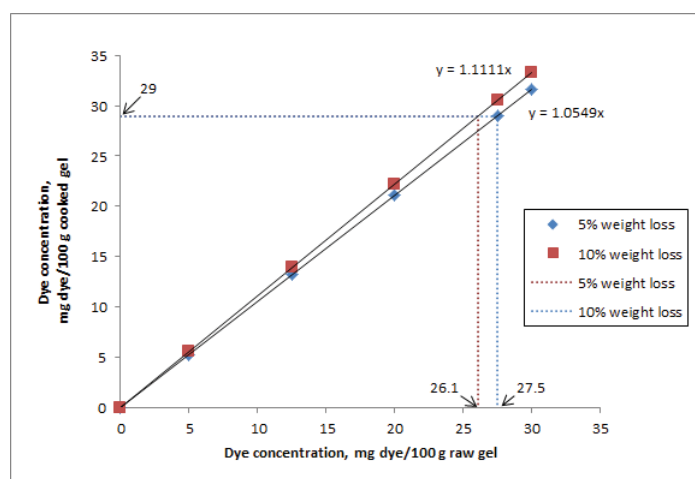


Figure 8.3 The relationship between the concentration of added dye in a model starch gel before cooking (mg dye/100g raw gel), and the concentration after cooking. Weight loss of 5% after cooking was a measured loss, whereas the weight loss of 10% is a theoretical loss.

8.3.1.3. Alternative approach: transformations for different sets of mixed substrate characteristics

In reality, a substrate-driven transformations approach based on one transformation per characteristic will be difficult to translate to the food printer; the approach was developed using a simple model system not necessarily representative of all foods that the 3D colour food printer might produce, and changes in each characteristic of a printed food are unlikely to occur in isolation from one another. A better approach might be to have the printer set up to print foods of a single type (referencing the POSIFoods™ approach), such as a cake-type formulation, or alternatively, a small, well-defined range of foods. Instead of storing colour gamut information for individual characteristics, gamut information is stored for a range of (whole) outputs, or variants, of the food (such as a cake) which meet different sensory and nutritional specifications - for example, for cakes with lighter ‘sponge-type’ or dense ‘fudge-type’ textures, and for cakes that are ‘low in sugar’, ‘low in fat’, and ‘gluten free’. Each variant will have associated with it a unique *mix* of characteristics (including background colour and texture), each with its own

effect on the possible range of colours that can be achieved, relative to a standard cake formulation, for the same set of primary dyes. For an emulsion-based product such as a dairy dessert, the colour outputs from high-fat and low-fat variants may differ due to the relative partitioning of dyes between the different phases of the emulsion. The user would be presented with a number of options for sensory and nutritional outputs, and the option to combine outputs if these are compatible with one another. The printer would then combine or process the colour gamut information for the constituent outputs from each variant, to arrive at a final, single colour gamut which is used in the gamut mapping stage of the main cross-media colour reproduction process. This alternative approach is illustrated in Figure 8.4.

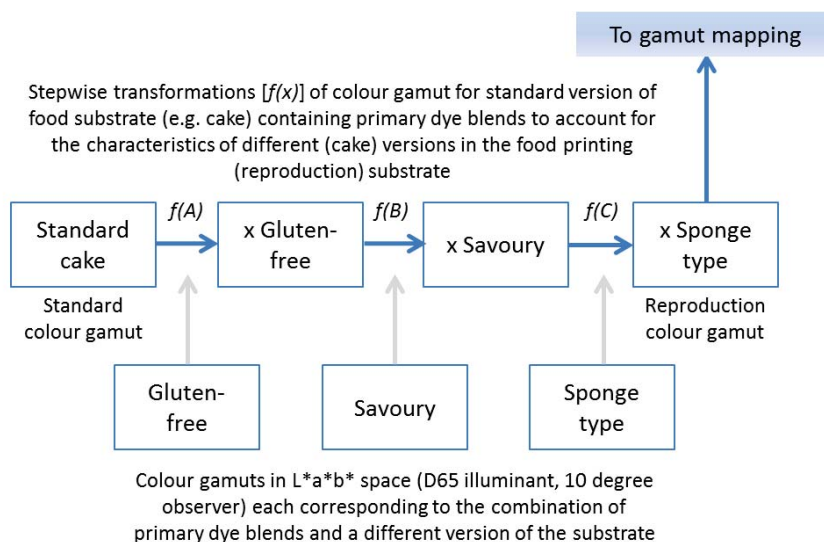


Figure 8.4 An alternative approach to substrate-based gamut transformations based on the effects of different variants of a standard substrate (i.e. different sets of mixed characteristics) rather than of individual characteristics.

Developing this alternative approach would require unit absorption spectra for the primary dyes to be derived in a ‘standard’ cake formulation (meaning one made with wheat flour), and again for the cake variants, and the colour gamuts to be computed for each variant containing the same primary dye blends (with the maximum quantity capped at the legal limit). Again, methods to compute the final colour gamut for a given combination of sensory and nutritional outputs from the gamuts of the individual variants would need to be developed and validated,

taking into account any changes in the unit absorption spectra of the dyes that might occur across different cake variants, any adjustments that are needed in gamut size and shape, and the final weight of the substrate. As final substrate weight is likely to vary with each new version of the cake, these alternative transformations would need to make an allowance for this at each step.

Any changes that are made to the standard substrate (e.g. cake) formulation to meet individual nutritional or sensory specifications that involve major ingredients are likely to have the biggest impact on background colour and surface texture, and therefore the biggest impact on the range of colours that can be achieved from the addition of primary dye blends. For example, when the rice flour in a standard, microwave-baked idli (Indian savoury cake) recipe is replaced with other types of gluten-free flour, each flour produces a finished idli with a different colour (as indicated by their measured L^* values) and foam structure to the idli made with the other flours, even though there is no change in final idli volume (Teresa Wegrzyn, personal communication).

8.3.1.4. Computation of dye recipes for the reproduction

In the latter phase of the cross-media colour reproduction workflow, recipes for the colorant primaries are computed to produce the reproduction. Here, recipes will be computed which will specify the quantities of primary-coloured Brilliant Blue, Ponceau 4R (red) and Tartrazine (yellow) food dyes that are needed for each voxel in the cake, with each voxel corresponding to a pixel in the original image. The reproduction medium characterisation model to convert the X,Y and Z tristimulus values for each colour in the reproduction to primary dye quantities will in this case be the process that was used to compute dye quantities for the mapped colours – iterative recipe correction - in Chapter Six.

The results of Chapter Six indicated that a more appropriate number and distribution of computed gamut colours was needed, to fill the inside of the gamut as well as the boundary itself. This feature should be applied to the colour gamut computed for the standard substrate at the start of the transformations to ensure that the gamut for the final reproduction substrate has

enough starting colours (and therefore corresponding dye recipes) for iterative dye recipe correction to arrive at a recipe for each voxel. This is particularly important because the colours that will be reproduced - image colours - are those for which full gamut information should be available; this will enable colours mapped by compression algorithms to be mapped to inside the reproduction gamut rather than to as far as the gamut boundary (as was the case for some of the tile colours). The validation of the Kubelka-Munk dye blending model for food coloration becomes useful again here, because unit absorption spectra for the dyes are used in the recipe correction equations (Chapter Six).

8.3.2. Transformations models for use with colorimetric matching

The method other than colour gamut mapping that was used to compute dye recipes for the tile colours – colorimetric matching – did so for a single, complex reproduction substrate (the microwave-baked cake) and was not applied to other substrates, or to different substrate characteristics. However this does not preclude colorimetric matching as an alternative basis for a substrate-driven transformations model. Substitutions could be made for the substrate term in the matching equations, producing dye recipes for potentially less computational load than is involved in gamut computations and gamut mapping, if highly accurate colour rendition (specifically, the preservation of hue) is not desired.

A transformations model for use with colorimetric matching that accounts for substrate properties (Figure 8.5) resembles the colorimetric matching workflow shown in Figure 4.6 of Chapter Four, and in Figure 2.8 of the Literature Review, rather than the cross-media colour reproduction process that involves gamut mapping. In the cross-media process image RGB data is converted into device-independent tristimulus values (X , Y and Z), using the characterisation model for the imaging device, whereas colorimetric matching requires the pseudo-tristimulus values (X^p , Y^p and Z^p), and therefore the measured spectra of the original colours, or alternatively, an arbitrary starting recipe (McDonald, 1987) or recipe for a colour close to the original, as the starting point to obtaining the dye recipe (Chapter Six).

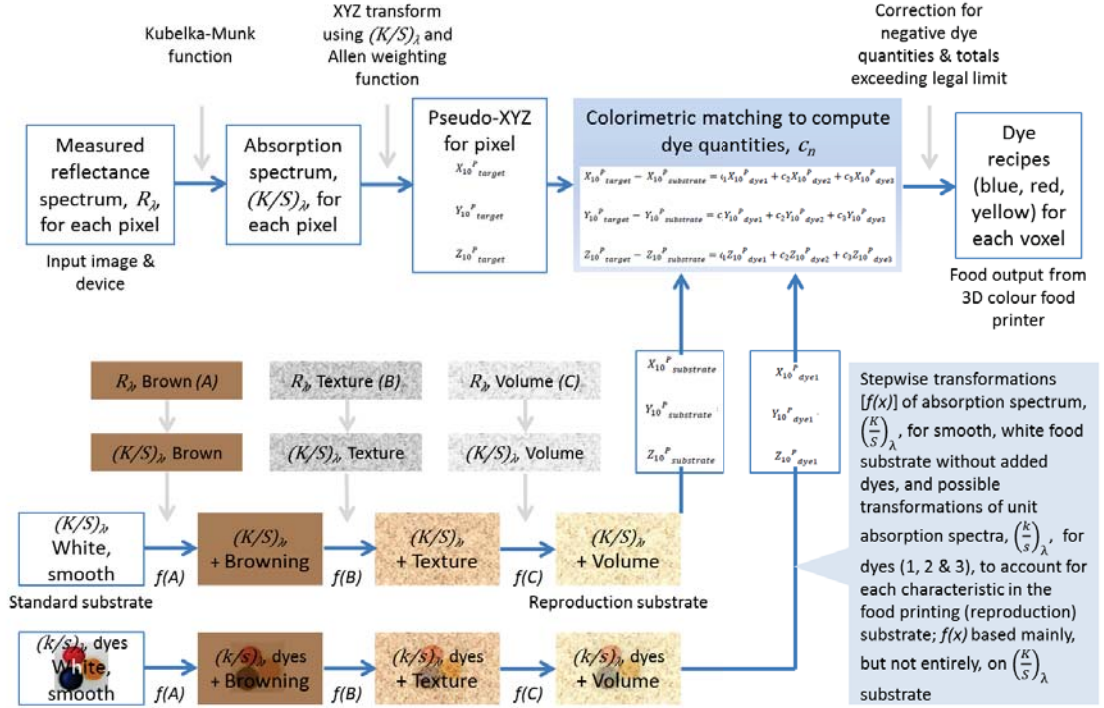


Figure 8.5 A second generalised algorithm proposed for the 3D colour food printer for rendering 3D colour images within food matrices, this time is modelled on a colorimetric matching algorithm (Chapter Four), with a second series of transformations accounting for the effects of individual food characteristics on the absorption spectra of the un-dyed substrate itself and (possibly) of the dyes.

The transformations model for use with colorimetric matching accounts for substrate properties in a similar way to the gamut-based process. The former will still need to account for any changes in the unit absorption spectra of the dyes, and in substrate weight and volume that occur with changes in the substrate, as well as for any discrepancy between computed colours and measured colours. As with the gamut-based approach, transformations can be applied to specific substrate characteristics, or to different variants of the (whole) substrate. But instead of transformations taking the form of stepwise changes in the colour gamut of the substrate, it is the absorption spectrum of the substrate that changes. Also, while changes in the colour gamut indicate changes in the substrate and primary dye spectra occurring together, here the two feed separately into the dye recipe computation step (Figure 8.5).

Once the spectra for the substrate and primary dyes have been finalised, the colorimetric matching equations (Equations 4.14, Chapter Four) can be used to compute the dye recipes

which are needed to match the original or target colour, when the dyes are mixed with the substrate in the specified quantities. Individual negative dye quantities and recipe totals exceeding the legal maximum indicate the resulting colour will be outside the range achievable in the substrate, and should be scaled back accordingly, maintaining the proportions of the non-zero quantity dyes.

8.3.3. Summary: transformations models

For each colour voxel in a 3D colour printed food, computation of its dye recipe will be a '*once only*' step in the colour image reproduction process. However different food characteristics will have different effects on the colour output(s), in turn impacting the quantities of dyes that are needed. In order to compute *single* dye recipes on the basis of a *single* collection of food characteristics (that belong to the final printed food substrate), the effects of individual substrate characteristics, or subsets of characteristics, on colour outputs first need to be accounted for; this takes place in a separate series of transformations which are added to the main set which transcribes colour image data to dye recipe data.

Embedded in the substrate-driven transformations, $f(x)$, are:

- the spectral contribution of the un-dyed substrate;
- any changes in the magnitude of the unit absorption spectra (Chapter Five), should these occur with changes in individual substrate characteristics (type or level), or with changes in different sets of mixed characteristics;
- any necessary adjustments to gamut shape, to correct for any discrepancies between measured colours and computed colours (Chapter Five), for colour gamut-based transformations only;
- weight loss and final weight of the substrate after cooking - this will remain the same for transformations based on individual characteristics, but will be different for each transformation as the result of changes to sets of mixed characteristics.

Substrate transformations compatible with gamut mapping might be preferred over those for use with colorimetric matching. The former transforms the colour gamut of the substrate which contains primary dye blends, with changes in the gamut occurring with changes in substrate characteristics (individual or mixed sets). At each stage, the colour gamut can be seen as embodying *all* the changes that occur together: in the substrate and dye spectral contributions, and in substrate weight. The colour gamut is also the outcome of the physical and chemical interactions between substrate and dyes that occur during processing. For transformations compatible with colorimetric matching, changes in substrate and dyes are treated somewhat separately before the dye recipe computation stage.

It should be possible for the printer to have stored in its memory dye recipes computed for foods printed previously. In this way, if a food is selected again as the substrate in which to render colour images, the substrate transformations process can be bypassed, and coloration can proceed straight away.

8.3.4. Alternative printing technologies

The type of 3D colour food printing technology that has been the subject of this thesis research is a set-up that works largely on the subtractive blending of the primary dye colours, and on the liquid dyes and raw substrate having compatible rheology to allow for the mixing of dyes into the substrate without any diffusion of dyes between voxels being allowed to take place. Alternative printing technologies and alternative dyes could be considered. One alternative is to use primary-coloured raw pastes, which are blended selectively to create each voxel prior to the point of extrusion, which has the advantage of blending materials which (should) have the same rheological properties. Voxels can be extruded either in a continuous stream (using a single nozzle arrangement) or several voxels at a time (for example, voxels of a single colour) using multiple nozzles, with the voxels positioned selectively to create each layer before the next layer is built up. For the mixing of pre-coloured batters, the laws of subtractive mixing, and therefore the predictive coloration algorithms developed in this thesis, would still apply.

For 3D colour food printing using liquid primary dyes, diffusion of liquid dyes into neighbouring voxels could be minimised by using insoluble, particulate dyes, known as lakes. Lakes have the added advantage of imparting high opacity which potentially could help to mask the background colour of the substrate. The use of lakes would require substantial expansion of the algorithms developed, to include the scattering effects of the particles, which can be modelled using the two-constant Kubelka-Munk approach, rather than the single-constant approach which is used for dyes. However the potential drawback of using lakes is that their colouring strength is not necessarily proportional to their dye content; it is very dependent on the physical properties of the lakes, which in turn will vary according to their manufacturing conditions (Francis, 1999).

8.3.5. Single-coloured model substrates vs. multi-coloured printed foods

When attempting to apply the findings and methodologies from this thesis to the 3D colour food printer, some important differences between a multi-coloured printed food item, and the single-coloured model substrates that were used in this study for practical reasons, need to be considered. In the printed food the proposed colour voxel size is 0.5 cm x 0.5 cm x 0.5 cm (0.125 cm³), corresponding to an area of 0.25 cm² when viewed in two dimensions, and each voxel will be surrounded by voxels of other colours. This voxel area will be smaller than the smallest substrate surface area measured in this study (the cast surface of the gels, at eight cm²) and therefore will occupy a smaller field of view. The eye might be less sensitive to colours when the angle of view is smaller, as ‘large field colour matching has higher precision’ (Berns, 2000). The perception of each colour voxel might also be subject to the contrast effects of the surrounding colours. *Simultaneous contrast* usually refers to the perception of two identical samples of colour as being different when each is placed against a different background to the other, and viewed side-by-side. While the definition of simultaneous contrast might not strictly apply to the printed food, it is conceivable that a single voxel surrounded by one set of voxels might be perceived as being of a different colour when surrounded by a different set of voxels.

The combined effects of voxel size and surrounding voxels potentially mean that the dye recipe computed for a voxel to be perceived as a given colour might be different to that computed for a larger field equivalent in a model substrate. Also, with a voxel being at a smaller scale, any dye that is needed for a recipe in very small quantities for the larger scale equivalent could be discarded for the voxel; the effects of such dyes might not be easily seen, and it might not be practical to physically deliver the correspondingly very small quantities of dye.

8.3.6. Quality of reproduction

Ultimately though, the colours inside a printed food will not be evaluated individually by the consumer, but as a whole, against the entire original colour image or design. In conventional cross-media colour reproduction of images, either an accurate, or a pleasant, reproduction is desired, yet no established model exists for quantifying the difference between original and reproduction (Kang, 2006). In this thesis gamut mapping algorithms for accurate, rather than pleasant, reproduction were used because they are the more extensively studied (Morovic, 2003). However, for 3D colour food printing it might make more sense to aim for pleasant reproduction (bearing in mind notions of ‘pleasantness’ can differ between individuals and between populations) for a number of reasons:

- it would be very difficult to achieve the same resolution in the reproduction as in the original, when both are at their original scale, given the relatively large voxel size relative to image pixel size;
- original and reproduction may not necessarily be viewed side-by-side (as they would need to be for the evaluation of accuracy); a potentially appealing aspect of the 3D colour food printer would be the ability to print the food locally from an image file sent remotely from another location;
- users of the 3D colour food printer may not have a high expectation of accuracy of reproduction, knowing that food is obviously different to the usual substrates for the reproduction of colour images and patterns, such as paper and plastics;

- users may want to add special effects to the rendered image at the point of printing, such as those available in cameras and in photo editing software (e.g. sepia toning, which gives warm, reddish-brown hues), thus removing expectations of colour accuracy.

Therefore it can be concluded that the main benefit of adapting and applying non-food coloration algorithms to 3D colour food printing will lie in their speed of computation, while getting the results to within acceptable reach of the original colours. Performance of these algorithms will ultimately rely on feedback from users, as food printing as a technology and as an element of popular culture matures over time.

References

- 3D Systems. 2014. *ProJet® 660Pro Professional 3D Printer: Full color 3D printing like no other*. Available: <http://www.3dsystems.com/3d-printers/professional/projet-660pro>.
- [CIE] International Commission on Illumination 1987. *International Lighting Vocabulary*, 4th edition. Vienna, Austria: CIE Central Bureau.
- [CIE] International Commission on Illumination 2001. *Improvement to industrial colour-difference evaluation*. Vienna, Austria: CIE Central Bureau.
- Airbus Group Inc. 2011. *The future of manufacturing...on two wheels*. Available: http://northamerica.airbus-group.com/north-america/usa/en/news/press.20110307_eads_airbike.html.
- All American Manufacturing and Supply Co. 2010. *Neoflex Edible Ink Option [Video file]*. Available: <http://www.neoflexprinter.com/videos>.
- Allen, E. 1966. Basic equations used in computer color matching. *Journal of the Optical Society of America*, 56, 1256-59.
- American Association of Cereal Chemists & American Association of Cereal Chemists. Approved Methods Committee 1995. *Approved methods of the American Association of Cereal Chemists*. St. Paul, Minn., Aacc.
- Ariño, I., Kleist, U. & Rigdahl, M. 2005. Effect of gloss and texture on the color of injection-molded pigmented plastics. *Polymer Engineering and Science*, 45, 733-744. Available: <http://www.scopus.com/inward/record.url?eid=2-s2.0-19844374842&partnerID=40&md5=e5e676ceee4f7bd7b3348227603607>.
- ASTM International 2008. ASTM E0308-06: Practice for computing the colors of objects by using the CIE system. West Conshohocken, PA.
- ASTM International 2013. ASTM E284-13b: Standard Terminology of Appearance. West Conshohocken, PA.
- Attractions Blackpool. 2014. *How is Rock Candy Made?* Available: http://www.attractionsblackpool.co.uk/Blackpool_Rock.htm.
- Australia New Zealand Food Authority. 2000. *Australia New Zealand Food Standards Code: Standard 1.3.1 - Food Additives - F2008B00614*. Canberra: ComLaw, Australian Government. Available: <http://www.comlaw.gov.au/Details/F2008B00614/>.
- Badaruddin, M., Abdullah, S. U., Sayeed, S. A., Ali, R. & Riaz, M. N. 2007. Sunset yellow: A food color for protein staining with SDS-PAGE. *Cereal foods world*, 52, 12.
- Baixaui, R., Salvador, A. & Fiszman, S. M. 2008. Textural and colour changes during storage and sensory shelf life of muffins containing resistant starch. *European Food Research and Technology*, 226, 523-30.
- Balaban, M., Aparicio, J., Zotarelli, M. & Sims, C. 2008. Quantifying nonhomogeneous colors in agricultural materials. Part II: comparison of machine vision and sensory panel evaluations. *Journal of food science*, 73, S438-S442.
- Baydo, R. A., Fabian, B. D., Fathollahi, Z. S., Graff, D. V., Lee, C. L. & Martin, P. F. 2008. *Food grade ink jet inks for printing on edible substrates*.
- BBC News 2013. Nokia backs 3D printing for mobile phone cases. *BBC News Technology*.
- Beatriz, M. & Gloria, A. 2005. Synthetic Colorants. In: Hui, Y. (ed.) *Handbook of Food Science, Technology and Engineering*. CRC Press.
- Bechtold, T., Mahmud-Ali, A. & Mussak, R. 2007. Anthocyanin dyes extracted from grape pomace for the purpose of textile dyeing. *Journal of the Science of Food and Agriculture*, 87, 2589-2595.
- Bee, S. C. & Honeywood, M. J. 2002. Colour sorting for the bulk food industry. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.

- Benjakul, S., Visessanguan, W. & Kwalumtharn, Y. 2004. The effect of whitening agents on the gel-forming ability and whiteness of surimi. *International journal of food science & technology*, 39, 773-781.
- Berns, R. S. 2000. *Billmeyer and Saltzman's Principles of color technology*. New York, John Wiley and Sons, Inc.
- Berset, C., Clermont, H. & Cheval, S. 1995. Natural Red Colorant Effectiveness as Influenced by Absorptive Supports. *Journal of Food Science*, 60, 858-861. Available: DOI 10.1111/j.1365-2621.1995.tb06247.x.
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S. & Escaleira, L. A. 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, 76, 965-977.
- Blackburn, R. S. 2004. Natural polysaccharides and their interactions with dye molecules: Applications in effluent treatment. *Environmental Science and Technology*, 38, 4905-4909. Available: <http://www.scopus.com/inward/record.url?eid=2-s2.0-4544346060&partnerID=40&md5=29b479f70e2bad78a7dce87432868b2f>.
- Boland, M. 2006. Mass customisation of food. *Journal of the Science of Food and Agriculture*, 86, 7-9.
- Boland, M. J., Haylock, S. J., Munro, P. A., Alexander, D. L. J., Thompson, A. K. & Archer, R. 2010. *Customised nutritional food and beverage dispensing system*.
- Bolcheriet. 2014. *Everyone has a favourite. What is yours?* Available: <http://www.bolcheriet.dk/logo-sweets.aspx>.
- Braun, K. M., Balasubramanian, R. & Eschbach, R. Development and evaluation of six gamut-mapping algorithms for pictorial images. Color and Imaging Conference, 1999. Society for Imaging Science and Technology, 144-148.
- Bridgeman, I. 1987. The nature of light and its interaction with matter. In: McDonald, R. (ed.) *Colour physics for industry*. Bradford, England: Society of Dyers and Colourists.
- Briones, V., Aguilera, J. M. & Brown, C. 2006. Effect of surface topography on color and gloss of chocolate samples. *Journal of food engineering*, 77, 776-783.
- Broyart, B., Trystram, G. & Duquenoy, A. 1998. Predicting colour kinetics during cracker baking. *Journal of food engineering*, 35, 351-368.
- Butts, K. 2010. *Database preparation for successful computer color matching*. Cary, NC: [TC]2. Available: www.techexchange.com [Accessed 16 August 2010].
- Chantrapornchai, W., Clydesdale, F. & McClements, D. J. 1998. Influence of droplet size and concentration on the color of oil-in-water emulsions. *Journal of Agricultural and Food Chemistry*, 46, 2914-2920.
- Cimbria. 2014. *Sea Chrome Electronic Sorting*. Available: http://www.cimbriakaack.com/SEA_Chrome_GB.pdf.
- Clydesdale, F. M. 1993. Color as a factor in food choice. *Critical Reviews in Food Science & Nutrition*, 33, 83-101.
- Coelho, M. 2010. *Cornucopia: Prototypes and concept designs for a digital gastronomy*. Available: <http://web.media.mit.edu/~marcelo/cornucopia/> [Accessed 17 September 2010].
- Cohen, D. L., Lipton, J. I., Cutler, M., Coulter, D., Vesco, A. & Lipson, H. Hydrocolloid printing: a novel platform for customized food production. 20th Solid Freeform Fabrication Symposium (SFF'09), 2009 Austin, Texas, USA.
- Cook, S. 2014. *Battenberg cake*. Available: <http://www.bbcgoodfood.com/recipes/1120657/battenberg-cake>.
- CSIRO Australia. 2013. *3D printed horseshoe to improve racing performance*. Available: <http://www.csiro.au/Portals/Media/3D-printed-horseshoe-to-improve-racing-performance.aspx>.

- Dalal, E. N. & Natale–Hoffman, K. M. 1999. The effect of gloss on color. *Color Research & Application*, 24, 369-376.
- Damodaran, S., Parkin, K. L. & Fennema, O. R. (eds.) 2008. *Fennema's food chemistry*. Boca Raton: Taylor & Francis.
- Day, P. 2011. Will 3D printing revolutionise manufacturing? *BBC News Business*.
- de Ancos, B., Cano, M. P., Hernandez, A. & Monreal, M. 1999. Effects of microwave heating on pigment composition and colour of fruit purees. *Journal of the Science of Food and Agriculture*, 79, 663-670.
- De Cindio, B. & Correria, S. 1995. Mathematical modelling of leavened cereal goods. *Journal of Food Engineering*, 24, 379-403.
- Dean, R. & Ball, C. 1960. Analysis of the myoglobin fractions on the surfaces of beef cuts. *Food Technology*, 14, 271-286.
- DuBose, C. N., Cardello, A. V. & Maller, O. 1980. Effects of Colorants and Flavorants on Identification, Perceived Flavor Intensity, and Hedonic Quality of Fruit-Flavored Beverages and Cake. *Journal of Food Science*, 45, 1393-1399.
- European Food Safety Authority. 2008. *EFSA evaluates Southampton study on food additives and child behaviour*. Available: <http://www.efsa.europa.eu/en/press/news/ans080314.htm>.
- fab@home Project. 2011. *fab@home: The open-source personal fabrication project*. New York: Cornell University Computational Synthesis Laboratory. Available: <http://www.fabathome.org/>.
- Fairchild, M. D. 2005. *Color appearance models*. Chichester, West Sussex, England ; Hoboken, NJ, J. Wiley. Available: <http://www.loc.gov/catdir/toc/wiley051/2004043111.html>.
- Figoni, P. 2008. *How baking works : exploring the fundamentals of baking science*. Hoboken, N.J., Wiley. Available: <http://www.loc.gov/catdir/toc/ecip077/2006103521.html>.
- Food Standards Agency UK. 2007. *Chronic and acute effects of artificial colourings and preservatives on children's behaviour*. Available: <http://tna.europarchive.org/20120620180604/http://www.food.gov.uk/science/research/foodcomponentsresearch/additives/a01programme/a01projlist/t07040/>.
- Food Standards Agency UK. 2014. *Additives or E numbers*. Available: <http://www.food.gov.uk/science/additives>.
- Francis, F. J. 1999. *Colorants*. St Paul, American Association of Cereal Chemists.
- Francis, F. J. & Clydesdale, F. M. 1975. *Food colorimetry: theory and applications*. Westport, The AVI Publishing Company, Inc.
- Garber Jr, L. L., Hyatt, E. M. & Starr Jr, R. G. 2001. Placing food color experimentation into a valid consumer context. *Journal of Food Products Marketing*, 7, 3-24.
- Gay, J. & Hirschler, R. Determination of industrial color tolerance limits: case studies in the textile industry. 9th Congress of the International Color Association, 2002. International Society for Optics and Photonics, 646-649.
- Gibbs, P. 1997. *Why is the sky blue?* Available: http://math.ucr.edu/home/baez/physics/General/BlueSky/blue_sky.html.
- Gomez, M. 2008. Low-Sugar and Low-Fat Sweet Goods. In: Sumnu, S. G. & Sahin, S. (eds.) *Food Engineering Aspects of Baking Sweet Goods*. Boca Raton, FL: CRC Press.
- Gorji Kandi, S., Amani Tehran, M. & Rahmati, M. 2008. Colour dependency of textile samples on the surface texture. *Coloration Technology*, 124, 348-354. Available: <http://www.scopus.com/inward/record.url?eid=2-s2.0-58149197752&partnerID=40&md5=46229c19edf87cc7e29056cc9725d6b3>.
- Grey, T. 2004. *Color Confidence: The Digital Photographer's Guide to Color Management*. San Francisco, CA, Sybex.
- Hadhazy, A. 2013. Will 3D Printers Manufacture Your Meals? *Popular Mechanics*.

- Han, J. H. & Floros, J. D. 1998. Modelling the change in colour of potassium sorbate powder during heating. *International journal of food science & technology*, 33, 199-203.
- Handmade Charlotte & Denneker, S. 2013. *How to Make a Tie-Dye Cake*. Available: <http://www.handmadecharlotte.com/diy-colorful-peace-cake/>.
- Hao, L., Mellor, S., Seaman, O., Henderson, J., N., S. & Sloan, M. 2010. Material characterisation and process development for chocolate additive layer manufacturing. *Virtual and Physical Prototyping*, 5, 57-64.
- Harkness, N., Leedham, D. & Butterworth, M. 2010. Application of non-contact digital imaging for “measuring the un-measurable”. In: Caivano, J. L. & Lopez, M. A. (eds.) *AIC 2010 Color and Food: From the Farm to the Table, Proceedings of the Interim Meeting of the International Color Association*. Buenos Aires, Argentina: Grupo Argentino del Color and Nobuko.
- Hawkins Watts Limited. 2014. *Colours*. Available: http://www.hawkinswatts.com/prod_cols.htm.
- Hicsasmaz, Z., Yazgan, Y., Bozoglu, F. & Katnas, Z. 2003. Effect of polydextrose-substitution on the cell structure of the high-ratio cake system. *LWT-Food Science and Technology*, 36, 441-450.
- Hofmann, T. 2001. Structure, Color and Formation of Low- and High-Molecular Weight Products Formed by Food-Related Maillard-Type Reactions. In: Ames, J. M. & Hofmann, T. (eds.) *Chemistry and Physiology of Selected Food Colorants*. Washington, DC: American Chemical Society.
- Hsu, C. K. & Chiang, B. H. 2002. Effects of water, oil, starch, calcium carbonate and titanium dioxide on the colour and texture of threadfin and hairtail surimi gels. *International journal of food science & technology*, 37, 387-393.
- Huang, I. L., Francis, F. & Clydesdale, F. 1970a. COLORIMETRY OF FOODS. 2. Color Measurement of Squash Puree Using the Kubelka-Munk Concept. *Journal of Food Science*, 35, 315-317.
- Huang, I. L., Francis, F. & Clydesdale, F. 1970b. Colorimetry of foods. 3. Carrot puree. *Journal of Food Science*, 35, 771-773.
- Huang, Z., Xu, H., Luo, M. R., Cui, G. & Feng, H. 2010. Assessing total differences for effective samples having variations in color, coarseness, and glint. *Chinese Optics Letters*, 8, 717-720.
- Hungry Happenings & Klosterboer, B. J. 2014. *Rainbow Tie-Dye Surprise Cake*. Available: <http://www.tablespoon.com/recipes/rainbow-tie-dye-surprise-cake/15086094-ad54-4d4f-82b3-68bffd7a0c9a>.
- Hutchings, J. 2002. The perception and sensory assessment of colour. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.
- Hutchings, J. 2010. Food, expectations, colour and appearance. In: Caivano, J. L. & Lopez, M. A. (eds.) *AIC 2010 Color and Food: From the Farm to the Table, Proceedings of the Interim Meeting of the International Color Association*. Buenos Aires, Argentina: Grupo Argentino del Color and Nobuko.
- Hutchings, J., Luo, R. & Ji, W. 2002. Calibrated colour imaging analysis of food. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.
- Hutchings, J. B. 1999. *Food color and appearance*. Gaithersburg, Aspen Publishers.
- Hutchings, J. B. 2003. *Expectations and the food industry: The impact of color and appearance*. Kluwer Academic/Plenum Publishers New York, NY.
- Inspix. 2014. *Chef Jet 3D Food Printer*. Available: <http://inspix.net/chef-jet-3d-food-printer/>.

- Institute of Food Technologists. 2011a. *Artificial dyes pose no risk, says FDA expert panel*. Available: <http://www.ift.org/food-technology/daily-news/2011/april/04/artificial-dyes-pose-no-risk.aspx>.
- Institute of Food Technologists. 2011b. *FDA to investigate food dyes' effect on youth*. Available: <http://www.ift.org/public-policy-and-regulations/recent-news/2011/january/06.aspx>.
- Johnson, J. & Clydesdale, F. 1982. Perceived sweetness and redness in colored sucrose solutions. *Journal of Food Science*, 47, 747-752.
- Joshi, P. & Brimelow, C. J. B. 2002. Colour measurement of foods by colour reflectance. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.
- Kang, H. R. 2006. *Computational Color Technology*. Bellingham, Washington, USA, SPIE Press.
- Kim, S., Golding, M. & Archer, R. H. 2012. The Application of Computer Color Matching Techniques to the Matching of Target Colors in a Food Substrate: A First Step in the Development of Foods with Customized Appearance. *Journal of Food Science*, 77, S216-S225. Available: <http://www.scopus.com/inward/record.url?eid=2-s2.0-84861987266&partnerID=40&md5=c935b5c49b28aed7f717f733be5ddc7f>.
- Kocer, D., Hicsasmaz, Z., Bayindirli, A. & Katnas, S. 2007. Bubble and pore formation of the high-ratio cake formulation with polydextrose as a sugar-and fat-replacer. *Journal of Food Engineering*, 78, 953-964.
- Kocer, D., Karwe, M. V. & Sumnu, S. G. 2008. Alternative Baking Technologies. In: Sumnu, S. G. & Sahin, S. (eds.) *Food Engineering Aspects of Baking Sweet Goods*. Boca Raton, FL: CRC Press.
- Koksel, H. & Gokmen, V. 2008. Chemical Reactions in the Processing of Soft Wheat Products. In: Sumnu, S. G. & Sahin, S. (eds.) *Food Engineering Aspects of Baking Sweet Goods*. Boca Raton, FL: CRC Press.
- Lakshminarayan, S. M., Rathinam, V. & KrishnaRau, L. 2006. Effect of maltodextrin and emulsifiers on the viscosity of cake batter and on the quality of cakes. *Journal of the Science of Food and Agriculture*, 86, 706-712.
- Lana, M. M., Hogenkamp, M. & Koehorst, R. B. M. 2006. Application of Kubelka-Munk analysis to the study of translucency in fresh-cut tomato. *Innovative Food Science and Emerging Technologies*, 7, 302-308. Available: <http://www.scopus.com/inward/record.url?eid=2-s2.0-33750982103&partnerID=40&md5=66e6ee41844995ed4a040a6bb5ea3305>.
- Leatherhead Food International 2008. *Essential guide to food additives*. Leatherhead, Surrey, U.K., Leatherhead Food International & Royal Society of Chemistry.
- Lee, K. Y., Park, S. Y. & Lee, H. G. 2011. Effect of oat β -glucan and its oxidised derivative on the quality characteristics of sponge cake. *International Journal of Food Science & Technology*, 46, 2663-2668.
- Leedham, D. & Boulter, G. 2007. *DigiEye - Case Study*. VeriVide Limited. Available: <http://www.verivide.com/assets/files/datasheets/01%20-%20Food%20-%20CCFRA.pdf>.
- Li, S., Shamey, R. & Xu, C. 2009. Prediction of depth of shade of a dyed polyester fabric based on fibre fineness and fabric structure. *Coloration Technology*, 125, 296-303.
- Lindley, D. & Scott, W. 1984. *New Cambridge Elementary Statistical Tables*. Cambridge University Press.
- Lipton, J., Arnold, D., Nigl, F., Lopez, N., Cohen, D., Norén, N. & Lipson, H. Multi-material food printing with complex internal structure suitable for conventional post-processing. 21st Solid Freeform Fabrication Symposium (SFF'10), 2010 Austin, Texas, USA.
- Loh, J., Ku, S., Lugay, J. C., McArdle, R. N. & Soedjak, H. S. 1998. *Process for making low-fat, cake donuts*.

- Lucideon. 2014. *Ceramic Colour Standards - Product Specifications*. Available: <http://www.ceram.com/materials-development/colour-standards/product-specifications>.
- Luiggi, C. 2013. Color from Structure. *The Scientist*.
- Luo, M. R., Cui, G. & Rigg, B. 2001a. The development of the CIE 2000 colour-difference formula: CIEDE2000. *Color Research and Application*, 26, 340-50.
- Luo, M. R., Cui, G. H. & Li, C. 2001b. *Apparatus and method for measuring colour (DigiEye system)*.
- Luzuriaga, D. A., BALABAN, M. O. & YERALAN, S. 1997. Analysis of visual quality attributes of white shrimp by machine vision. *Journal of Food Science*, 62, 113-118.
- MacDougall, D. B. 2002a. Colour measurement of food: principles and practice. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.
- MacDougall, D. B. 2002b. Discontinuity, bubbles and translucence: major error factors in food colour measurement. In: Chung, R. & Rodrigues, A. (eds.) *The 9th Congress of the International Colour Association*. Rochester, New York: SPIE.
- Maga, J. 1974. Influence of color on taste thresholds. *Chemical Senses*, 1, 115-119.
- Maga, J. & Kim, C. 1990. Stability of natural colourants (annatto, beet, paprika, turmeric) during extrusion cooking. *Lebensmittel-Wissenschaft+ Technologie*, 23, 427-432.
- Martínez, J., Melgosa, M., Pérez, M., Hita, E. & Negueruela, A. 2001. Note. Visual and instrumental color evaluation in red wines. *Food Science and Technology International*, 7, 439-444.
- McCann, D., Barrett, A., Cooper, A., Crumpler, D., Dalen, L., Grimshaw, K., Kitchin, E., Lok, K., Porteous, L., Prince, E., Sonuga-Barke, E., Warner, J. O. & Stevenson, J. 2007. Food additives and hyperactive behaviour in 3-year-old and 8/9-year-old children in the community: a randomised, double-blinded, placebo-controlled trial. *Lancet*, 370, 1560-1567. Available: <http://www.scopus.com/inward/record.url?eid=2-s2.0-35548943929&partnerID=40&md5=b4ce62eaeae503ed3b0a67f5d249c095>.
- McClements, D., Chantrapornchai, W. & Clydesdale, F. 1998. Prediction of food emulsion color using light scattering theory. *Journal of Food Science*, 63, 935-39.
- McClements, D. J. 2005. *Food emulsions : principles, practices, and techniques*. Boca Raton, FL, CRC Press.
- McDonald, R. 1987. Computer match prediction - dyes. In: McDonald, R. (ed.) *Colour physics for industry*. Bradford, England: Society of Dyers and Colourists.
- Mcor Technologies Ltd. 2013. *3D Printing and Rapid Prototyping: Mcor Technologies*. Available: <http://mcor technologies.com/>.
- Melgosa, M. 2013. CIE/ISO New Standard: CIEDE2000. University of Leeds, UK.
- Melgosa, M., Hita, E., Romero, J. & del Barco, L. J. 1992. Some classical color differences calculated with new formulas. *JOSA A*, 9, 1247-1254.
- Minolta Camera Co. Ltd. 1993. *Precise Color Communication: Color Control from Feeling to Instrumentation*. Osaka, Japan, Author.
- Mitchell, H. L. 1996. The Role of the Bulking Agent Polydextrose in Fat Replacement. In: Roller, S. & Jones, S. A. (eds.) *Handbook of Fat Replacers*. Boca Raton: CRC Press.
- Mohammed, I., Ahmed, A. R. & Senge, B. 2012. Dough rheology and bread quality of wheat–chickpea flour blends. *Industrial Crops and Products*, 36, 196-202.
- Morovic, J. 2003. Gamut mapping. In: Sharma, G. (ed.) *Digital color imaging handbook*. Boca Raton, FL: CRC Press.
- Morovic, J. 2008. *Color Gamut Mapping*. Chichester, West Sussex, England, John Wiley & Sons Ltd.
- Morovic, J. & Luo, M. R. 2000. Calculating medium and image gamut boundaries for gamut mapping. *Color research and application*, 25, 394-401.

- Moskvitch, K. 2011. *Printer produces personalised 3D chocolate*. Available: <http://www.bbc.co.uk/news/technology-14030720> [Accessed August 1 2011].
- Moskvitch, K. 2013. Modern Meadow aims to print raw meat using bioprinter. *BBC News Technology*.
- Moss, B. W. 2002. The chemistry of food colour. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.
- Mundt, S. & Wedzicha, B. L. 2007. A kinetic model for browning in the baking of biscuits: Effects of water activity and temperature. *LWT-Food Science and Technology*, 40, 1078-1082.
- NASA. 2014. *3D Printing In Zero-G Technology Demonstration (3D Printing In Zero-G) - 09.17.14*. Available: http://www.nasa.gov/mission_pages/station/research/experiments/1115.html#results.
- Nate, J. 2004. Understanding rendering intents: Which one and why? *Newspapers and Technology*.
- Natural Machines. 2014. *Natural Machines: The Makers of Foodini - a 3D food printer making all types of fresh, nutritious foods*. Available: <http://www.naturalmachines.com/>.
- NCS Colour AB. 2014. *NCS - Natural Colour System: Logic Behind the System*. Available: <http://www.ncscolour.com/en/ncs/how-ncs-works/logic-behind-the-system/>.
- Negueruela, A. I. 2010. Is the colour measured in food the colour that we see? In: Caivano, J. L. & Lopez, M. A. (eds.) *AIC 2010 Color and Food: From the Farm to the Table, Proceedings of the Interim Meeting of the International Color Association*. Buenos Aires, Argentina: Grupo Argentino del Color and Nobuko.
- New Zealand Food Safety Authority (NZFSA). 2008. *Synthetic colours in highly coloured foods*. Available: <http://www.nzfsa.govt.nz/consumers/chemicals-nutrients-additives-and-toxins/food-colourings/foodcolouring.htm>. [Accessed June 2009].
- Palmer, J. & Danzico, M. 2011. 'Printing out' new ears and skin. *BBC News Science and Environment*.
- PhotovoltaicLightingGroup 2013. The Electromagnetic Spectrum.
- Prabhakara Rao, P., Jyothirmayi, T., Balaswamy, K., Satyanarayana, A. & Rao, D. 2005. Effect of processing conditions on the stability of annatto (<i>Bixa orellana</i> L.) dye incorporated into some foods. *LWT-Food Science and Technology*, 38, 779-784.
- R&D Mag 2013. Nanostructures filter light to order. *R&D Mag*.
- RIT Munsell Color Science Laboratory. 2010. *Useful Color Data*. Available: <http://www.cis.rit.edu/research/mcsl2/online/cie.php>.
- Rodríguez-García, J., Puig, A., Salvador, A. & Hernando, I. 2012. Optimization of a sponge cake formulation with inulin as fat replacer: structure, physicochemical, and sensory properties. *Journal of food science*, 77, C189-C197.
- Roenfeldt Nielsen, S. & Holst, S. 2002. Developments in natural colourings. In: MacDougall, D. B. (ed.) *Colour in food: Improving quality*. Cambridge, England: Woodhead Publishing Limited.
- Ronda, F., Gómez, M., Blanco, C. A. & Caballero, P. A. 2005. Effects of polyols and nondigestible oligosaccharides on the quality of sugar-free sponge cakes. *Food Chemistry*, 90, 549-555.
- Sahi, S. S. 2008. Cake Emulsions. In: Sumnu, S. G. & Sahin, S. (eds.) *Food Engineering Aspects of Baking Sweet Goods*. Boca Raton, FL: CRC Press.
- Sahin, S. 2008. Cake Batter Rheology. In: Sumnu, G. & Sahin, S. (eds.) *Food Engineering Aspects of Baking Sweet Goods*. Boca Raton, FL: CRC Press.
- Sakiyan, O., Sumnu, G., Sahin, S. & Meda, V. 2007. Investigation of dielectric properties of different cake formulations during microwave and infrared-microwave combination baking. *Journal of Food Science*, 72, E205-13. Available:

<http://onlinelibrary.wiley.com/store/10.1111/j.1750-3841.2007.00325.x/asset/j.1750-3841.2007.00325.x.pdf?v=1&t=grr4ece5&s=0aaa14420391109d4e3a2dfe2fa9ad40a031805a>.

- Satake Europe Ltd. 2014. *Colour Sorting Machines*. Available: http://www.satake.co.uk/colour_sorting/ColourSort_Range.html.
- Schabbach, L., Bondioli, F., Ferrari, A., Petter, C. & Fredel, M. 2009. Colour in ceramic glazes: efficiency of the Kubelka–Munk model in glazes with a black pigment and opacifier. *Journal of the European Ceramic Society*, 29, 2685-2690.
- Scotter, M. & Castle, L. 2004. Chemical interactions between additives in foodstuffs: a review. *Food additives and contaminants*, 21, 93-124.
- Sensient Colors Inc. 2005. *Certified Food Colors*. St. Louis, Missouri, Author.
- Sensient Colors Inc. 2008. *Specification for No. 03970 Kowet Titanium dioxide*. St. Louis, Missouri.
- Sensient Colors LLC. 2014a. *Products*. Available: <http://www.sensientfoodcolors.com/Products/>.
- Sensient Colors LLC. 2014b. *Resources*. Available: <http://www.sensientfoodcolors.com/Resources/>.
- Seth, R. 2009. *Surreal food is real and printed*. Available: <http://www.yankodesign.com/2009/08/26/surreal-food-is-real-and-printed/> [Accessed 17 September 2010].
- Sharma, A. 2003. *Understanding Color Management*. Clifton Park, NY, Thomson/Delmar Learning.
- Sharma, A. 2007. ICC Color Management: Architecture and Implementation. In: Lukac, R. & Plataniotis, K. (eds.) *Color Image Processing: Methods and Applications*. Boca Raton, FL: CRC Press.
- Shaw, M., Sharma, G., Bala, R. & Dalal, E. N. 2003. Color printer characterization adjustment for different substrates. *Color Research & Application*, 28, 454-467.
- Sleeuwen, R. M., Gosse, A. J. & Normand, V. 2013. Indirect Color Prediction of Amorphous Carbohydrate Melts as a Function of Thermal History. *Journal of food science*, 78, E1022-E1028.
- Souppouris, A. 2013. NASA is funding a 3D food printer, and it'll start with pizza. *The Verge*.
- Stratasys Ltd. 2014. *Objet500 Connex3: Vivid color and multi-material 3D printing*. Available: <http://www.stratasys.com/3d-printers/design-series/precision/objet500-connex3#content-slider-1>.
- Sumnu, G. 2001. A review on microwave baking of foods. *International journal of food science & technology*, 36, 117-127.
- The CandyFab Project. 2014. *CandyFab: A DIY 3D Sugar Printer*. Available: <http://candyfab.org/>.
- Thomas, D. J. & Atwell, W. A. 1999. *Starches*. Minnesota, American Association of Cereal Chemists, Inc.
- Turkmen, N., Poyrazoglu, E. S., Sari, F. & Sedat Velioglu, Y. 2006. Effects of cooking methods on chlorophylls, pheophytins and colour of selected green vegetables. *International journal of food science & technology*, 41, 281-288.
- Umer Abdullah, S., Badaruddin, M., Asad Sayeed, S., Ali, R. & Riaz, M. N. 2008. Binding ability of Allura Red with food proteins and its impact on protein digestibility. *Food chemistry*, 110, 605-610.
- Vance, A. 2012. Turn Your Baby's Cry Into an iPhone Case. *Bloomberg Businessweek*.
- Vukusic, P., Sambles, J. & Lawrence, C. 2000. Structural colour: Colour mixing in wing scales of a butterfly. *Nature*, 404, 457-457.
- Wainwright, O. 2013. Faces to order: how 3D-printing is revolutionising prosthetics. *The Guardian*.

- Wei, S.-T., Ou, L.-C., Luo, M. R. & Hutchings, J. B. 2012. Optimisation of food expectations using product colour and appearance. *Food Quality and Preference*, 23, 49-62.
- Weinstein, J. N. & Tolson, S. A. 1997. *Apparatus for making a complexly patterned extrudate*.
- White, J. 2014. Zebra cake. Available: http://www.bbc.co.uk/food/recipes/zebra_cake_76226.
- Wikipedia. 2011. *3D printing*. Available: http://en.wikipedia.org/wiki/3-D_printer [Accessed 17 March 2011].
- Wikipedia. 2014a. *Fused deposition modeling*. Available: http://en.wikipedia.org/wiki/Fused_deposition_modeling.
- Wikipedia. 2014b. *Selective laser sintering*. Available: http://en.wikipedia.org/wiki/Selective_laser_sintering.
- Wilton Industries. 2014a. *Checkerboard Cake Set*. Available: <http://www.wilton.com/store/site/product.cfm?sku=2105-9961>.
- Wilton Industries. 2014b. *Violet Icing Color*. Available: <http://www.wilton.com/store/site/product.cfm?id=3E30B51B-475A-BAC0-5C43337CEC4AD93D&killnav=1>.
- Woodside Electronics Corporation. 2013. *Revolutionary Technology*. Available: http://www.wecotek.com/html/weco_tech.html.
- X-Rite Incorporated. 2014. *Munsell Products/Color Communication Products*. Available: http://www.xrite.com/top_munsell.aspx?action=products&CategoryID=22.
- Xu, T., Shi, H., Wu, Y. K., Kaplan, A. F., Ok, J. G. & Guo, L. J. 2011. Structural colors: from plasmonic to carbon nanostructures. *Small*, 7, 3128-3136.
- Yang, J., Wu, L. W. & Liu, J. 2001. *Rapid prototyping and fabrication method for 3-D food objects*.
- Zanoni, B., Peri, C. & Bruno, D. 1995. Modelling of browning kinetics of bread crust during baking. *LWT-Food Science and Technology*, 28, 604-609.
- Zhou, W. & Therdthai, N. 2008. Heat and Mass Transfer during Baking of Sweet Goods. In: Sumnu, S. G. & Sahin, S. (eds.) *Food Engineering Aspects of Baking Sweet Goods*. Boca Raton, FL: CRC Press.