

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

A STUDY OF SOME CHEMICAL INTERFERENCES

IN ATOMIC ABSORPTION SPECTROSCOPY

A thesis presented in partial fulfilment of
the requirements for the degree of

Master of Science

in Chemistry

at Massey University

HUANG YEH-WEN

1970

A C K N O W L E D G E M E N T S

The author would like to express sincere thanks to his supervisor, Dr R.D. Reeves, for his guidance and assistance throughout the work undertaken. He is indebted to Dr J. Kirkman for his assistance in the infra-red and X-ray diffraction studies. Thanks are also due to Miss J. Quigan for typing the thesis, Miss D. Scott for the photographic work, and Mr P. Herbert for printing the figures.

ABSTRACT

Atomic absorption spectroscopy is the study of the absorption of radiation by atoms. As an analytical process, it involves the conversion of compounds to atoms, and the absorption of energy by these atoms. A flame burning in air is the conventional means for converting the solution to be analysed into atomic vapour. The number of free atoms produced in the flame is reduced if chemical bonds between the analyte and its matrix fail to break readily at the flame temperature, i.e., chemical interference takes place under some conditions.

Chemical interference is a common occurrence in the determination of calcium, magnesium and strontium in low-temperature flames (below about 3000 K). As a general rule, the anions most likely to cause chemical interference are stable oxyanions. Studies have been made in this work of the interference of fluoride, molybdate, phosphate, sulphate and tungstate ions in the determination of the alkaline earth elements, chromium, molybdenum and nickel, using an air-acetylene flame.

Only in the case of calcium and strontium determinations were large interferences encountered. The magnitude of the interference was greatest with tungstate and phosphate, and least with fluoride.

Interferences in the determination of gallium and indium, which had not previously been studied in detail, were investigated. Twenty-eight cations, ten anions, three complexing agents and four acids were tested for potential interference. Several interferences

were found (calcium, strontium, borate and phosphoric acid with gallium, and iron (III), zinc, bromide and hydrochloric acid with indium), but none of the effects was as marked as the interferences with alkaline earths.

The inhibition by phosphate of the calcium signal is well known in both flame emission and atomic absorption. The variation of the magnitude of the interference with concentration of both calcium and phosphate was studied, and conditions are indicated under which phosphate might be determined quantitatively by means of the interference effect. A similar study was made for the tungstate ion. (Sulphate and molybdate at low concentrations do not interfere significantly with calcium absorption in the air-acetylene flame.).

In attempts to identify and/or separate the species responsible for chemical interference effects, the flame emission spectra were recorded when solutions containing calcium and phosphoric acid and a mixture of the two were aspirated into the flame. No new peaks or bands could be found which might be ascribed to electronic transitions of a new stable species containing both calcium and phosphate. However, the peaks and bands arising from the calcium and phosphate mixture were reduced in intensity. This indicates that the calcium is combined in one or more molecular species containing the calcium and the phosphate. Similar depression of emission peaks and bands was found with strontium and phosphate mixtures.

Solid material, entrained in the flame gases when solutions were aspirated, was collected from a region just above the top of the flame, and infra-red and X-ray diffraction studies were made to

identify the solid collected. Where calcium-containing solutions were aspirated, the solid products varied according to the nature and concentrations of various anions present in the solution. Calcium carbonate was the sole identifiable product when nitrate ions were present. The presence of both phosphate and chloride led to the formation of both chlorapatite, $3 \text{Ca}_3(\text{PO}_4)_2$, CaCl_2 , and α - calcium orthophosphate under some conditions; phosphate alone led to a solid which may be secondary calcium orthophosphate, CaHPO_4 . Similar compounds were found with strontium and magnesium, although these did not correspond to any for which X-ray and infra-red data are recorded in the literature.

The exact composition of the solid products of the flame reactions therefore varies with the nature and concentration of the anions, and is probably also sensitive to parameters such as the fuel-air ratio in the flame, and to changes in the location of the point of collection of the solids.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
ABSTRACT	ii
TABLE OF CONTENTS	v
LIST OF FIGURES	vii
LIST OF PLATES	vii
I. INTRODUCTION AND REVIEW				
1. General Introduction	1
2. Instrumentation	2
3. Absorption of Radiation	3
4. Atomic Vapour Production	7
5. Interference in Atomic Absorption	12
6. Chemical Interferences	15
II. OBJECTS OF THE PRESENT WORK				
1. Further Study of Chemical Interferences	23
2. Possibility of Quantitative Anion Determination	25
3. Attempts to Identify or Separate the Species Responsible for Chemical Interferences	25
III. APPARATUS AND EXPERIMENTAL PROCEDURE				
1. Atomic Absorption Apparatus	27
2. Preparation of Solutions	30
3. Experimental Procedure	31

IV.	RESULTS AND DISCUSSION	
1.	Further Study of Chemical Interferences	32
	(i) Calcium, Magnesium, Strontium	32
	(ii) Chromium, Molybdenum, Nickel	40
	(iii) Gallium, Indium	45
2.	The Possibility of Anion Determination by Atomic Absorption Spectrometry ...	52
3.	Attempts to Identify the Species Causing Interference	56
	(i) Investigation of Flame Emission Spectra	56
	(ii) Investigation of Solids in the Flame Gases	59
4.	General Conclusions and Suggestions for Further Work	68
	REFERENCES	70

LIST OF FIGURES

FIG. IV.1.	Flame Profiles of Ca in Fuel-Rich Air-Acetylene Flame	p.p. 33/34
FIG. IV.2.	Flame Profiles of Ca in Stoichiometric Air-Acetylene Flame	p.p. 33/34
FIG. IV.3.	Effect of Foreign Anions on Ca Absorption				p.p. 34/35
FIG. IV.4.	Flame Profiles of Sr in Fuel-Rich Air-Acetylene Flame	p.p. 35/36
FIG. IV.5.	Flame Profiles of Sr in Stoichiometric Air-Acetylene Flame	p.p. 35/36
FIG. IV.6.	Effect of Foreign Anions on Sr Absorption				p.p. 36/37
FIG. IV.7.	Effect of Foreign Anions on Ca Absorption in 50 % v/v Isopropanol	p.p. 38/39
FIG. IV.8.	Effect of Foreign Anions on Ca Absorption in 50 % v/v Acetone	p.p. 38/39
FIG. IV.9.	Effect of Foreign Anions on Ca Absorption in 50 % v/v Ethanol	p.p. 38/39
FIGS.IV.10 and 10(a)	Effect of Phosphate on Ca Absorption	...			p.p. 52/53
FIG. IV.11.	Calcium Recovery Curve	p.p. 52/53
FIGS.IV.12 and 12(a)	Effect of Tungstate on Ca Absorption	...			p.p. 54/55
FIG. IV.13.	Infra-red Spectra of Solids from Flame Gases				p.p. 61/62
FIG. IV.14.	Infra-red Spectra of Solids from Flame Gases				p.p. 65/66

LIST OF PLATES

Plate 1.	Techtron AA3 Atomic Absorption Spectrophotometer	73
Plate 2.	Optical System of Techtron AA3 Atomic Absorption Spectrophotometer	74
Plate 3.	X-Ray Powder Diffraction Photographs of Solids from Flame Gases	75

I. INTRODUCTION AND REVIEW

C H A P T E R I

I. 1. GENERAL INTRODUCTION

Atomic absorption spectrometry is a spectrochemical process in which an atom absorbs radiation of the same wavelength which it emits when it is in a state of excitation. By measuring the absorption of radiation in atomic vapour produced from a sample the concentration of the element can be determined. The principles underlying atomic absorption were established about 1860 by Kirchoff, who used atomic absorption lines in the Fraunhofer spectrum to deduce the presence of certain elements in the solar atmosphere. Together with Bunsen, he demonstrated shortly afterwards that atomic spectra, both emission and absorption, could be the basis of a useful method for qualitative chemical analysis.

From that time onwards emission methods of spectrochemical analysis have been widely developed and have culminated in direct reading spectrographs which provide multielement analysis of high speed and accuracy. However, atomic absorption was neglected as a possible analytical approach. Analysis was confined to astrophysical work on the determination of the composition of solar and stellar atmospheres, and the estimation of the contamination of laboratory atmospheres by mercury vapour.

In 1955, Walsh¹ published his first paper on the application of atomic absorption spectroscopy to chemical analysis, and outlined

the instrumental technique which would produce optimum results. Alkemade and Milaz² designed an atomic absorption spectrophotometer at about the same time. In 1958, Allan³ and David⁴ reported the application of the atomic absorption technique to the determination of magnesium and zinc in agricultural materials and plants. This analytical technique then grew rapidly and in 1968 over 10,000 atomic absorption instruments were in use throughout the world, and the literature on the subject had accumulated to over 1,200 papers, notes and reviews.

I. 2. INSTRUMENTATION

Kahn⁵ has given an excellent review of instrumentation. In its simplest form, the essential components of an atomic absorption spectrophotometer are:

- a) a primary source of radiation
- b) a means of producing atomic vapour
- c) a wavelength selector
- d) a radiation detector and readout system

Requirements for the light source are that it should emit radiation of the required wavelength at a constant intensity and with a minimum of unwanted radiation. For volatile elements such as thallium, mercury and most of the alkali metals, the usual source is a vapour discharge lamp. However, the most commonly used source is a hollow cathode lamp, and when it is powered by a stabilised supply it is often possible to maintain an emission stability of +0.5%.

The energy required to atomise the sample can theoretically be supplied in a number of ways: plasma jet, electric discharge, and burner. The conventional means of producing atomic vapour is to spray

the sample solution into a flame. A nebuliser sprays the solution into the gas stream of the flame and a spray chamber allows the separation of the coarse and fine droplets of solution and a thorough mixing of the flame gases. The fine droplets pass with the gases into the flame and usually become vapourised. Two types of burner have been used: total consumption burners and pre-mixed burners.

A wavelength selector basically should be able to separate the required spectral line from all others and to keep any background intensity to a minimum. For spectra containing little but the resonance lines, e.g., the alkali spectra, a simple selector such as a filter suffices. For most ultraviolet spectra and particularly for complex spectra, the most useful selector is a monochromator which can be set to pass any wavelength between ca. 1930 and 9000 Å. Among elements whose resonance lines are closely surrounded by other lines are iron, nickel and cobalt, and these require a monochromator of about 2 Å resolution. Coupled with the need for a narrow band-pass is the ability to detect low intensities. This necessitates the use of a photomultiplier with its stabilised power supply and measuring system. Two types of photomultipliers have been used: Bi-O-Ag and Cs-Sb types of cathodes. A galvanometer is used in the readout system. A recorder or a digital readout may be used.

I. 3. ABSORPTION OF RADIATION

When an atom is in the ground electronic state, it is capable of absorbing radiation of characteristic discrete energies. In practice, the absorption of radiation occurs over a very narrow frequency interval, i.e., absorption is not confined to one exact

frequency, but there is instead, an absorption profile, the shape of which is determined by several broadening parameters. Broadening of spectral lines results from any factor which influences the energy of the ground and excited states, when an electronic transition takes place. Major causes of broadening of atomic spectral lines in hot flame gases include:

- i) Doppler broadening -- due to thermal agitation of the absorbing and emitting atoms;
- ii) Collisional broadening -- energy levels are perturbed when the atom is close to a foreign gas atom;
- iii) The natural width of the spectral line -- due to the finite lifetime of the excited state;
- iv) Stark and Zeeman broadening -- occurring in the presence of external electric and magnetic fields respectively.

Stark broadening may be important in arcs and sparks where the charge density is high, but is unimportant in flames.

The natural width of atomic spectral lines (of the order of 10^{-4} Å) may be neglected as compared to Doppler and collisional broadenings. For flame spectroscopy, for most lines in most flames at temperatures of 1500 - 3000 K, the broadening effect of each of these two factors is in the range 0.01 - 0.1 Å, as measured at the point where the peak height is half the maximum value. This is the so-called half-width of the spectral line.

Absorption results in an electronic transition from an electronic state l to state u . The excited atom remains in the excited

state u for about 10^{-8} sec and then undergoes either non-radiational deactivation (from collisions with flame gas molecules, e.g., CO, CO₂, N₂, O₂, H₂O, etc.) or radiational deactivation called atomic fluorescence.

The intensity of the transmitted radiation, I_y , is related to that of the incident radiation at frequency ν , I_y^0 , by

$$\log_{10} \frac{I_y^0}{I_y} = k_y \ell$$

where ℓ is the path length and k_y the atomic absorption coefficient, with units of cm^{-1} . The absorbance, or optical density, is

$$\log \frac{I_y^0}{I_y} = 0.4343 k_y \ell.$$

The relationship between the atomic absorption coefficient, k_y , and the number of atoms available to absorb can be shown to be of the form $k_y = \frac{\ln 2}{4\pi^2} \frac{\lambda_c^2}{\lambda_c} \frac{g_u}{g_l} N_l P_{ul} f(\Delta\nu_c, \Delta\nu_D, \nu)$ where λ_c is the wavelength at the centre of absorption line g_u, g_l are the degeneracies of the upper and lower electronic states N_l is the number of atoms per cm^3 in the lower electronic state P_{ul} is the transition probability in sec^{-1} and $f(\Delta\nu_c, \Delta\nu_D, \nu)$ is a function of the collisional and Doppler half-widths and of the frequency, which defines the shape of the absorption profile. The way in which the total amount of light absorbed depends on N_l is of particular interest. Two situations arise: (i) with a source emitting continuous radiation in the wavelength range of interest; (ii) with a source emitting a narrow line of appropriate wavelength. Most atomic absorption analysis methods utilise a narrow line source, especially hollow cathode lamps. In this case, radiation is absorbed over an interval determined by $\Delta\nu_s$, the source half-width. The total absorption is $\int k_y d\nu$ over the frequency range of the source and can be shown to be proportional to

N_l , where N_l is small, but when N_l is large the total absorption reaches a limiting value and becomes independent of N_l .

It is worth emphasising that all flame spectrometric methods depend ultimately on N_l . In flame emission N_u is related to N_l via a Boltzmann expression

$N_u = N_l (g_u/g_l) \exp(-E/KT)$. Walsh¹ has calculated the ratio of N_u/N_l for the most populated states of several elements as a function of temperature. The data are shown in Table I.1.

TABLE I.1.

Relative Populations of Excited and Ground States at Several Temperatures

Resonance Line (Å)	G_u/G_l	N_u/N_l		
		2000 K	3000 K	4000 K
Cs 8521	2	4×10^{-4}	7×10^{-3}	3×10^{-2}
Na 5890	2	1×10^{-5}	6×10^{-4}	4×10^{-3}
Ca 4227	3	1×10^{-7}	4×10^{-5}	6×10^{-4}
Zn 2139	3	7×10^{-15}	6×10^{-10}	1×10^{-7}

It is apparent that the fraction of the total available atoms which exist in the excited state becomes appreciable only for atoms with low ionisation potentials and at high temperatures. Most elements have their strongest resonance lines at wavelengths below 6000 Å, and since atomic absorption measurements are made at flame temperatures below 3500 K, the number of atoms in the ground state can generally be assumed to be equal to the total number of atoms, i.e., $N_l = N$. Since changes in temperature produce an exponential change in the number of

atoms in the excited state while having an insignificant effect on the number of atoms in the ground state, it follows that emission methods are very sensitive to changes in temperature, while absorption methods are relatively independent of such changes.

I. 4. ATOMIC VAPOUR PRODUCTION

Several methods of vapourising solid samples directly have been suggested. These include the sputtering chamber⁶, L'vov furnace⁷, flash lamp technique⁸, and laser sampling⁹. Most investigators have vapourised the sample by spraying a solution of material into a flame. A nebuliser is used to produce very fine droplets of solution, and the flame causes evaporation of the solvent and decomposition of the solutes in the droplet. Atoms are thus produced in the light beam so that absorption may take place.

The number of free atoms produced in the flame per unit time is governed by three main factors:

- (a) the flow rate of the solution into the nebuliser;
- (b) the efficiency of introduction of solution into flame, i.e., the aspiration efficiency of the nebuliser-burner-flame combination;
- (c) the efficiency of converting the solid salt particle into ground state atoms in the flame gases, called the atomisation efficiency (β).

β is influenced by ionisation, incomplete dissociation of the salt introduced, and compound formation by the atom of interest with flame gas products or with other atoms or molecules also present in

the sample. For example, if we have a solution of CaCl_2 aspirated into the flame, this efficiency is

$$\beta = \frac{(N_{\text{Ca}})_\lambda}{(N_{\text{Ca}})_\lambda + N_{\text{CaCl}_2} + N_{\text{CaCl}} + N_{\text{CaO}} + N_{\text{CaOH}} + N_{\text{CaH}} + N_{\text{Ca}} + \dots + (N_{\text{Ca}})_\mu + (N_{\text{Ca}})_{\mu'} + \dots \text{etc}}$$

where λ stands for the ground electronic state of Ca atoms,

stand for the upper electronic states of Ca atoms. μ, μ', \dots

β is a very complex function of flame temperature and composition, generally having a maximum value at a certain temperature and composition. The aspiration efficiency has been studied by Winefordner *et al.*¹⁰, and the atomisation efficiency by de Galan and Winefordner¹¹, and by Willis¹². The factors affecting the efficiency of atomic vapour production from the salt particles in flames are discussed below.

(a) Flame energy

The energy of the flame is used to produce neutral atoms from droplets coming out from the aspirator-burner. The thermal energy liberated from a flame is best represented by the theoretical flame temperature. The approximate range of temperatures available from commercial burners is:

air-coal gas	1800 K
air-propane	1925
air- H_2	2050
$\text{O}_2 - \text{H}_2$	2500
$\text{N}_2\text{O} - \text{H}_2$	2600
air- C_2H_2	2350
$\text{O}_2 - \text{C}_2\text{H}_2$	3100
$\text{N}_2\text{O} - \text{C}_2\text{H}_2$	2955

For elements which are easily converted into atomic vapour like Zn, Cu, Cd and Pb, the most sensitive results are obtained by using low temperature flames such as those produced from air-propane or air-coal

gas mixtures. In the case of elements that form refractory oxides, such as the alkaline earths, a hot flame like air-acetylene is essential. A further range of elements, including Al, Be, Ti, V and the rare earths, require an acetylene flame supported by oxygen or nitrous oxide to obtain sufficient atomic vapour to make useful and sensitive measurements.

It is to be noted that as the temperature of the flame increases, the proportion of atoms ionised also increases. The alkali metals and the alkaline earths ionise to a significant extent in the hottest flames listed above, and the nitrous oxide flames produce considerable ionisation even for an element like aluminium. The ionised atoms absorb at a different wavelength and are thus lost to the determination.

(b) Flame profile

The relationship between absorption signal and flame height is called the flame profile. It indicates the relative population of neutral atoms in the flame. For maximum sensitivity there is an optimum height in the flame at which observations should be made^{13,14}. Rann and Hambly¹⁵ examined the distribution of neutral atoms in absorption flames. They demonstrated that maximum absorption is a function of the light beam position in the flame, coupled with the fuel/air ratio of the flame. The elements investigated included Cu, Mo, Mg, Cr, Ca, Ag, Sr, Ba, Na and Se. The results suggested that atoms are released by pyrolysis of the salt in the hottest region of the flame, and then removed by secondary chemical reactions, in other parts, of the flame.

(c) Flame composition

It is found with metals that form refractory oxides that a fuel-rich flame is required for maximum sensitivity. In an oxidising flame there is an excess of oxygen present, and oxidation of metal atoms is promoted. In a fuel-rich flame there is an excess of fuel and presumably only reduced amounts of oxygen. This would prolong the life of neutral atoms and hence provide better sensitivity.

Cowley et al.¹⁶ studied the spatial distribution of various molecular species in a pre-mixed oxyacetylene flame by a combination of atomic absorption and atomic emission. They showed that the effectiveness of the air-acetylene flame results from the combination of a relatively high temperature with an environment which is relatively deficient of oxygen. A stoichiometric flame provides a higher temperature, but many metals suffer a loss of sensitivity relative to fuel-rich conditions. This results from an unfavourable environment which promotes chemical reactions that bind metal atoms. By contrast, the fuel-rich air-C₂H₂ flame provides an environment very effective for some metals but at a temperature which is too low for other metals. Turbulent flames from these mixtures provide a non-optimum environment because they do not form well-defined zones in the flame, and a chemically favourable environment does not prevail.

The nitrous oxide-acetylene flame provides a high temperature without very rapid burning velocity, so that a favourable chemical and thermal environment is provided. This arrangement made it possible to determine almost all metals by atomic absorption spectroscopy. It further permitted the determination of metals such as Ca, Sr, Ba and

and Mo, which are only partially atomised in cooler flames, with higher sensitivity and greater freedom from chemical interference.

(d) Use of organic solvents

It has been observed on numerous occasions^{18,19,20}, that enhancement of absorption takes place if an organic solvent is used instead of water. This enhancement has been attributed to a more efficient production of atoms from organic solutions and to the increased temperature. The increase in efficiency of atom production may be divided into two aspects:

- i) easier combustion of organic solvents than water, and
- ii) easier chemical release of atoms from an organic addend than from an inorganic salt.

Robinson¹⁴ studied the effect of chemical release of atoms in a flame, (i.e., from an organic addend) by using Sodium chromate, chromic nitrate and chromium naphthenate in water, ethanol, benzene and ethanol-benzene (50:50) mixtures. His results indicate that when organometallic solutions are used, a greater absorption signal is obtained. This supports the thesis that the population of metal atoms in a given flame is increased by using organic solvents and organometallic compounds. Organometallic compounds in organic solutions give the most absorption and inorganic aqueous solutions give the least sensitivity.

Strong supporting evidence was found by Sastri et al.²¹. Their studies on sensitivity in atomic absorption of Ni, Sn, Zr, Hf, Nb, Ta, as metallocenes and as simple salts or oxy-salts, have shown that metal-oxygen bonded species in solution contribute to the total amount

of metal oxide in the flame, with a depopulation of the neutral atoms. In the case of metals which form oxides of high dissociation energy, sensitivity is enhanced if the metal in solution is not bonded to oxygen, as in metallocenes or fluoro-complexes.

I. 5. INTERFERENCE IN ATOMIC ABSORPTION

Interferences are those effects, due to the presence of other constituents in the sample, which cause an analysis to be in error. Interferences in emission methods are well known; atomic absorption, however, is subject to fewer interferences, as predicted by Walsh¹. The following interferences will be discussed:

- (a) Spectral interference
- (b) Excitation interference
- (c) Ionisation interference
- (d) Bulk or Matrix interference
- (e) Chemical interference

(a) Spectral interferences occur in emission when radiation from the sample is surrounded by an unwanted output of radiation from another element at a similar wavelength. The resultant reading depends on the concentration of more than one element. For instance in the determination of magnesium in the presence of sodium, by flame emission, the 2583.2 \AA line of sodium will make some contribution to the measured intensity of the magnesium line 2582.1 \AA , since most monochromators are unable to separate these lines completely.

However in atomic absorption, the only absorption measured is that of the resonance line, with a half-width of ca. 0.01 \AA . Thus the

resolution is far better than that of most of the emission methods, resulting in correspondingly increased freedom from spectral interference. Diligent searches recently, however, have turned up a few interferences:

- i) The cobalt 2536.49 \AA line arising from a metastable state interferes with the determination of mercury (at 2536.52 \AA)²².
- ii) Mutual interference between gallium (4032.982 \AA) and manganese (4033.073 \AA)²³.

Another type of interference arises when molecules formed in the flame have absorption bands at the analytical wavelengths of a particular element. This molecular absorption occurs most when low temperature flames are used. For example, when barium is determined in the presence of large amounts of calcium in the air - C_2H_2 flame, the calcium oxide formed will absorb strongly at the barium wavelength (5536 \AA)²⁴. This interference, however, vanishes in the high temperature generated by the nitrous oxide-acetylene flame²⁵.

(b) Excitation interference is due to the change in the number of excited atoms when the introduction of another species produces a change in the effective temperature of the radiating vapour. This type of interference is often encountered in arc and spark emission, but it also exists in flame emission. Since the total number of excited atoms is negligibly small, the number of unexcited atoms can generally be regarded as constant and equal to the total number of atoms, so that no counterpart to excitation interference is found in atomic absorption.

(c) Ionisation interference takes place when a substantial proportion of atoms in the sample become ionised, causing them to absorb at different wavelengths. If another element is present which can supply free electrons, there is an increase in the number of ions which return to the form of ground state atoms. This results in a positive interference or enhancement of absorption. The various alkalis enhance the absorption of each other. Sodium and potassium enhance the absorption of calcium in the air - C_2H_2 flame. This effect is less pronounced in atomic absorption than in flame emission.

Baker and Gordon²⁶ studied the determination of potassium by both emission and absorption in an oxy-acetylene flame, and have shown that the presence of lithium, sodium or cesium increases the apparent concentration. The enhancement is in the same order as the increasing ionisation potential of the interfering elements. Trent and Slavin²⁷ investigated the determination of strontium, and observed that there is an increase in absorption after an alkali metal has been added to the solution. As the concentration of the interfering element is increased, the enhancement rises to a plateau value. The enhancement is accompanied by a decrease in absorption if the ionic ground state line is used. The percent of metal ionised is related largely to the temperature of the flame. Alkali metals ionise to an appreciable extent in cool flames like air-propane, while alkaline earths ionise slightly in the air-acetylene flame and to a great extent in the nitrous oxide-acetylene flame.

(d) Bulk or matrix interferences are changes in the analytical results caused by variations of the viscosity or other physical properties of

the sample solutions. One common matrix effect is the enhancement caused by an organic solvent. (see also Section I.4(d)). The improvement of sensitivity by the use of an organic solvent is partly the result of an increased amount of sample carried to the flame, because of lower viscosity and the improved vapourisation (due to the small droplet size resulting from the lower surface tension of the organic solvent).

Another matrix effect is caused by different concentrations of dissolved solids in the sample solutions. As the solution becomes more concentrated, it flows more slowly through the burner and absorption therefore decreases. Such an interference can be distinguished from chemical interference in that its slope is much more gradual and that it does not reach an asymptote.

(e) Chemical interference is due to the failure to break chemical bonds between the analyte and other materials in the matrix, when the solvent is evaporated out of the aerosol in the flame. The effect is similar in emission and absorption since the effect is to limit the atomisation of the analyte. Two well-known examples are the combination of calcium with phosphate, and the combination of magnesium with aluminium. Chemical interference is discussed in more detail in the next section.

I. 6. CHEMICAL INTERFERENCES

Chemical interferences are a common occurrence in both emission and atomic absorption analysis. In the case of atomic absorption spectrometry, interferences resulting from the presence of both added cations and of added anions have been reported.

Cationic Interferences

Allan³ in the first paper to describe the analysis of plant materials by AAS, found that aluminium depressed the absorption signal of magnesium. Elwell and Gidley²⁸ showed that the principal interfering elements in the determination of magnesium are those that form acidic oxides that are stable at high temperature, e.g., Al, Ti, Zr and Hf. Allan also observed that K, Na, and Ca do not interfere in the magnesium determination.

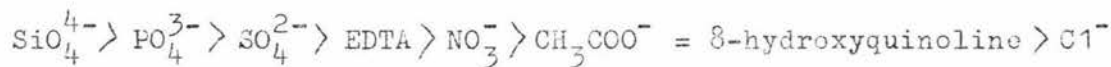
David²⁹ studied the analysis of calcium in plant materials and found that ions such as aluminium and zirconium suppress the calcium absorption. He observed that Ca absorption is dependent on the ratio of fuel to air in the flame, and that the absorption signal varies along the height of the flame, being greatest close to the base of the flame.

The determination of strontium is similar to that of calcium. David³⁰ found that aluminium and silica suppress the Sr signal whereas calcium does not. Trent and Slavin²⁷ gave a detailed account of the interference effects, including the enhancement of Sr absorption produced by the presence of other alkali metals.

Anionic Interferences

The interference of sulphate, phosphate and silicate on the determination of calcium have been reported by a number of authors. Rochiccioli and Townshend³¹ examined the effects of various ions and complexing agents on Ca absorption in the air-propane flame. They confirmed the previous observations that relative magnitudes of depression effects of sulphate and phosphate decrease higher in the

flame, although the absorbance also decreases. The relative magnitudes of depressive effects decrease in the order



Hall & Townshend³² also investigated the effects of a number of ions and complexing agents on the absorbance of magnesium in the air-propane flame. They found that sulphate and phosphate (as reported by Allan³) and oxalate decrease the signal, whereas chloride, nitrate, EDTA and 8-hydroxyquinoline enhance the absorption. Trent and Slavin²⁷ reported that HCl, HNO₃ and glycerine depress the strontium signal at high concentration (a few %).

Other work on the determination of alkaline earth metals and their interferences has also been reported^{33,34,35}.

Suppression of Interference

There are three ways to overcome the chemical interference effects. These involve:

- i) addition of other salts which suppress the interference;
- ii) removing the interference by ion exchange or selective extraction;
- iii) using a standard similar in composition to the sample.

Many of the common ions, e.g., sulphate, silicate, aluminium and zirconium, which suppress the alkaline earth absorption, can be minimised or almost overcome by adding excess of lanthanum or strontium chloride to both sample and standard solutions^{3,28,36,37,38}. David³⁰ examined the determination of Sr in biological and soil materials. He chose to remove the phosphate interference by ion-exchange. The small amounts of sodium and potassium, which enhance the calcium absorption, can be tolerated if Na or K is added to the standard solutions. The

use of ammonium pyrrolidine dithiocarbamate (APDC), extracted into methyl isobutyl ketone (MIBK), or other organic solvents, as an effective concentration elimination of interference has been well established^{39,40}.

Explanation of Chemical Interference

A prerequisite for the understanding of the occurrence of chemical interference is the understanding of the mechanism by which metal atoms are produced. Robinson¹⁴ suggested the following mechanism, shown in Table I.2.

A sample solution is introduced through the nebuliser-burner system into the flame. When a pre-mixed burner is used, the nebuliser first converts the solution to an aerosol. This aerosol is then swept into the burner and thence into the flame. In the flame, the droplets are dried, the residue melted and vapourised, and any compound dissociated to free atoms, so that absorption may take place. If the dried salt happens to be a compound that does not dissociate readily at the flame temperature, the proportion of ground-state metal atoms will be small. Thus the presence of phosphate in a solution of calcium results in the formation of a refractory calcium salt and results in a negative interference. In the determination of magnesium in the presence of aluminium an intermetallic compound is believed to be formed that does not dissociate at the flame temperature.

Cowley⁴¹ studies the molecular and atomic emission from portions of the fuel-rich oxy-acetylene flame fed with a solution of refractory metals. He found that atomic emission is intense in the base of the flame and falls off at higher levels. Molecular band emission of the metal oxide is weak at the flame base but increases in strength at

higher elevations. This supports the theory that dried salt is converted into atomic vapour and is eventually oxidised as it rises in the flame.

TABLE I.2

Mechanism of Atom Production

Physical form of sample in flame	Reaction	Factors controlling Reaction	Part of flame
Droplets	Evaporation	Droplet size, flame temp., feed rate, combustibility	Base ↓
Solid particles	Disintegration	Stability of compound, anions, flame temperature ultra-violet light emitted from flame	Inner cone ↓
Atoms	Accumulation or oxidation	Flame composition, stability of atoms	Reaction zone ↓
Oxide	No reaction or reduction	Stability of metal oxide flame composition	Outer mantle

Slavin, Sprague and Manning¹³ examined various flame parameters in the determination of calcium. They found that although Ca may be determined at about equal sensitivity in the air-acetylene flame or the air-hydrogen flame, the effect of anionic interferences is much less in the acetylene flame. The use of a fuel-rich flame moves the absorption peak higher in the flame. The effect of phosphate depression is somewhat reduced in a rich flame, particularly higher in the flame. Mavrodineanu⁴² reported a similar effect on the emission of calcium in a fuel rich oxy-acetylene flame. The use of a low

temperature flame reduces the Ca sensitivity and greatly increases the interference effect. The use of an organic solvent enhances the signal and shifts the absorption higher in the flame profile.

Yofe, Avni and Stiller⁴³ showed that orthophosphates of Ca, Sr and Ba are converted at 1000 C into corresponding pyrophosphates which are partially decomposed in the flame. If La is added to the solution of alkaline earth metal and the phosphate, interference disappears. They found that lanthanum phosphate precipitates before the alkaline earth phosphate as water is evaporated at 140C from a solution containing both. Thus in the presence of lanthanum, the Ca, Sr or Ba reaches the flame free from phosphate, a condition suitable for complete vaporisation.

Elwell and Gidley²⁸ postulated the formation of an Al-Mg mixed oxide to account for the suppression by Al of the Mg signal. To confirm that the effect is due to the chemistry of the aspirated droplets they aspirated separate solutions of Al and Mg into the same spraying chamber, where they were mixed before entering the flame. No depressing effect of Al was observed. Rubeska and Moldan⁴⁴ obtained X-ray diffraction patterns of the unevaporated particles leaving the flame after spraying Al and Mg. The X-ray Debye-Scherrer diffractograms revealed that spinel ($MgO \cdot Al_2O_3$) is formed.

Mansell⁴⁵ used thermodynamic data (Table I.3) for the formation of spinels to account for the releasing action of La, Ba or Sr salts. The thermodynamic data for an oxygen-deficient system revealed magnesium aluminate $Mg \cdot Al_2O_4$ as being more stable than the constituents MgO , Al_2O_3 and $MgCl_2$. Al_2O_3 is more stable than MgO ;

MgO is the least stable of the alkaline oxides and tends to lose oxygen in the presence of Ba, Sr or La. The free energy of formation of alkaline earth aluminates at 2000 K (Table I.4) has been approximated by Sinke (quoted by Mansell⁴⁵). MgAl₂O₄ is the least stable of the series at temperatures approaching that of the C₂H₂ - air flame. The greater stability of Ca, Sr or Ba aluminates would therefore cause their preferential formation or precipitation, leaving Mg atoms free for absorption. The releasing action of La is presumably caused by the same mechanism.

TABLE I.3

Free Energy of Formation at 2400 C and 2000 C⁴⁵

Compounds	2400 C ΔG_f (kcal mol ⁻¹)	Compounds	2000 C ΔG_f (kcal mol ⁻¹)
MgO	-57	BaO	-96
Al ₂ O ₃	-216	MgO	-77
Al O	-18	CaO	-96
Al ₂ O	-67	SrO	-89
Al ₂ O ₂	-78	BaO	-91
AlCl ₃	-104	Al ₂ O ₃	-248
MgAl ₂ O ₄	-284	La ₂ O ₃	-293
MgCl	-29		
MgCl ₂	-73		
La ₂ O ₃	-266		

TABLE I.4

Free Energy of Formation of Aluminates at 2000 C⁴⁵

ΔG_f (aluminnte) \doteq ΔG_f (MO) + ΔG_f (Al_2O_3) + Heat of formation of aluminate at 298 C	
Compounds	ΔG_f (kcal mol ⁻¹)
Be Al_2O_4	-345
Mg Al_2O_4	-333
Ca Al_2O_4	-348
Sr Al_2O_4	-339
Ba Al_2O_4	-340
$4/3La$ $Al O_3$	-360