ATOMIZATION OF SYNTHETIC AND REAL SAMPLES USING HEATED GRAPHITE ATOMIZERS FOR ATOMIC ABSORPTION SPECTROSCOPY.

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> "But, my son, be warned: there is no end of opinions ready to be expressed. Studying them can go on forever, and become very exhausting. Here is my final conclusion: fear God and obey His commandments, for this is the entire duty of man." (King Solomon 977 B.C.)

ABSTRACT.

The interference effects caused by a number of matrices including compounds such as NaCl, HCl, KBr, HNO_3, H_3PO_4, H_2SO_4 on Cu, Pb, Cd and Al atomic absorption signals when the elements are atomized from three non-flame graphite atomizers (furnace, cup and rod) are studied over several concentration ranges. Investigations show that most of the interferences found occur in the vapour phase. A comprehensive literature survey has been done and from this survey and the experimental work carried out, discussions are presented on the postulated mechanisms of interference. Two main theories are given for the vapour phase interference,

i) entrapment of the atom in the matrix particle forming in the vapour,

ii) rapid molecular condensation in the vapour phase.

Several degrees of interference (both enhancement and depression) were obtained for the different chemical and atomization systems used. Attempts were made at rationalizing the degree and type of interference in terms of the postulated models. Supporting evidence for the atom entrapment theory was gained from an investigation of the nature of the non-atomic absorption peak obtained mainly when alkali halides are present in the sample. Evidence is produced showing that the absorption spectra obtained from alkali halides here and by other workers are charge-transfer spectra.

An investigation into the use of a graphite atomizer for zinc analysis in bovine serum is presented and compared to determinations using flame atomic absorption on the same samples.

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CHAPTER I

I INTRODUCTION

1. General Introduction

a) Historical.

The use of atomic spectra for the detection and analysis of elements is not a 'modern technique'. In fact the first observation of atomic absorption lines was in 1802 by Woolaston [1] - these were the Fraunhofer lines in the solar spectrum. Kirchoff [2] together with Bunsen further investigated the phenomenon of atomic absorption in 1860 using atomic absorption lines to establish the presence of certain elements in the solar atmosphere. In subsequent papers they demonstrated the use of atomic spectra, emission and absorption, as a method for chemical analysis.

Briefly, "Atomic Absorption Spectrometry is a spectrochemical process whereby a free atom absorbs radiation of the same wavelength which it emits when it is in a state of excitation". Measurement of the radiation absorbed enables the concentration of the element to be determined. Although the physics of the atomic concentration and atomic absorption relationship were fully discussed by Mitchell and Zemansky [3] (1934) and Rosseland [4] (1956) analysis by atomic absorption was confined largely to astrophysical work and mercury vapour estimation [4a] until Walsh [5] published his first paper on the application of atomic absorption spectroscopy to chemical analysis in 1955.

Development and use of the technique increased slowly as more instruments were built, until in 1960 twentysix papers were published [7] increasing to over six hundred and sixty in 1970 while the number of instruments in use (1972) exceeded twenty thousand.[8]

b) Instrumentation.

Most texts on atomic absorption give descriptions of atomic absorption spectrophotometers. (e.g. 8, - 10). Essentially an atomic absorption spectrophotometer consists of :-

i) a stable radiation source emitting atomic spectra including resonance lines,

ii) an atomizing device producing an atomic vapour (usually a flame),

iii) a monochromator to isolate the resonance line,

iv) a radiation detector (usually a photomultiplier) coupled to amplification and readout facilities.

c) Theoretical.

The theoretical parameters of atomic absorption have been fairly rigorously presented by Walsh[5,6] and L'vov,[11] the latter showing that Walsh's treatment of atomic absorption theory is a special case of a more general theory. However, a brief summary will be applicable here.

An atom in the ground electronic state is capable of absorbing characteristic discrete energies. In practice absorption of radiation occurs over a very small frequency range resulting in an absorption profile which is determined by broadening parameters. Broadening of lines results from any factors influencing the energies of ground and excited electronic states. Major causes of broadening, in flames, in order of importance are:

i) Doppler broadening - due to different component velocities of the absorbing or emitting atoms caused by thermal agitation (along the line of observation)

ii) Collisional (pressure or Lorentz) broadening - due to the perturbation of the atomic energy levels of an atom close to foreign gas atoms

iii) natural width of the spectral line - due to the finite lifetime of the atom in the excited state (Heisenberg's Uncertainty Principle).

Broadening, mainly due to the first two effects, is in the range of .001 - .01 nm for the half width * of the spectral line in most flames. [12]

2. Development of Flameless Atomic Absorption Spectroscopy.

In the development of Atomic Absorption Spectroscopy most early investigators (13 - 18) used flames to produce the absorbing atomic vapour i.e. the test solution after being nebulised into very fine droplets is sprayed into a flame causing evaporation of the solvent and decomposition

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* Width of the spectral line at a point where the peak height is half the maximum value.

of the solution in the droplets. A column of vapour is thus produced in which the atom concentration of the element depends on its concentration in the original test solution. Flame cells are still more widely used to produce atomic vapours [19] than any other atomization process.

Since the sensitivity of atomic absorption spectroscopy depends directly on the vaporised atomic concentration, workers have endeavoured to increase the efficiency of the atom reservoir by using slotted burners [20] reducing high temperature flames, [21-24] and more efficient nebulizers.[25,26] These developments greatly improved the sensitivity and precision of the method but several disadvantages still exist with the use of flames:

a) only 15% (20% with the most efficient nebulizer) of the test solution reaches the flame using indirect nebulizers, "necessary for laminar pre-mixed flames," decreasing absolute sensitivity and necessitating a sample volume of at least 1 cm^3 for analysis of non-dilutable samples,

b) only rarely can solid samples be atomized,

c) dilution of the atoms occurs by a factor of approximately 10^4 when the sample is mixed with the flame gases; further dilution is caused by expansion of the flame gases to the flame temperature on combustion,

d) in some systems efficiency of free atom production is low.

The main advantages of flame cells are ease and rapidity of operation. However, early in the development of atomic absorption spectroscopy some workers began to look at non-flame cells in attempts to overcome some of the flame disadvantages, i.e. to increase the efficiency of atomization and to reduce the undesirable influence of variations of physico-chemical properties of solutions.* In an excellent review Kirkbright [27] has summarised most of the work in this field. For the sake of completeness a brief résumé will be given here.

In 1959 L'vov [28,29] adapted the King [30] furnace to study its potential as a source of atomic vapours for atomic absorption. He obtained reproducible results [31] for atomic absorption analysis using a graphite crucible for twelve elements. Some of the absolute sensitives he quoted have still not been bettered by any other workers. In a later paper [32] he discussed the potentialities of his crucible and extended by a further twenty-seven the list of elements analysed. The crucible consisted of a tube of graphite 5 cm long 0.25 to 0.5 cm i.d. being lined with tantalum foil placed in an inert atmosphere. Initially heating was effected by a spark between an auxiliary electrode and the furnace, but later work used simple resistive heating of the furnace by passing a current through it. Samples were micropipetted into a cavity on the end of a rod which was then placed through a hole into the furnace.

Vidale [33] in 1961 also followed King's work and constructed a sealed quartz cell within a quartz tube to atomize samples for atomic absorption.

Further work based on L'vov's graphite furnace was done by Massman [34] who used a small resistively-heated graphite tube furnace, and micro-pipetted

* See section I 3(a)

the sample directly into the furnace for a three-stage heating programme of drying, charring, and atomization. A furnace on a much larger scale (15 cm long x 0.7 cm i.d.) was built and used by Woodriff [35] et al. This system was also resistively-heated but the sample was placed into the tube by means of a small carbon cup.

In 1970 the performance of a commercially produced heated graphite atomizer manufactured by Perkin Elmer Corporation was published.[36] The furnace was a bulky graphite tube enclosed in a water-cooled metal jacket and to prevent oxidation the tube interior was continuously flushed with an inert gas (usually argon). Samples of 20 µl were introduced through a sample port directly into the furnace by a micropipette and the furnace was then heated through a three-stage heating programme. Twenty-six elements were analysed and their sensitivities reported, together with the determination of copper and strontium in milk.

West and Williams [37] atomized several elements using a heated carbon filament 5 cm long x 0.6 cm diameter with samples micropipetted into an indentation on the top of the rod. The mounts of the rod were water-cooled, the filament was heated through three heating stages and the entire system was encased in a pyrex chamber with quartz windows to enable the beam of light to pass unrestricted through the chamber at grazing incidence to the filament. The chamber was flushed with an inert gas to prevent oxidation of the filament.

Subsequently a Varian Techtron research group [38,39] designed an atomization system which consisted of an inductively heated rod which had a transverse hole bored in it to allow a beam of light to pass through and a vertical sampling port facilitating the placement of the sample droplet within the 'mini-furnace'. Sensitivity was greater than the open-rod system and the performance of the system resembled that of Massman's furnace - hence the connotation "mini-Massman furnace".

At the same time, work on non-flame cells using non-graphite supports was done by several workers. Brandenberger and Bader [40] used a platinum wire filament on which elements had been electrolytically deposited. The filament was heated to atomize the element. A Pt loop was used by Bratzel <u>et</u> <u>al</u>.[41] to atomize elements from a thin film obtained by immersion of the loop into the sample solution. Another non-graphite atomizer was Donega and Burgess's [42] tantalum boat which allowed larger volume samples to be used for direct drying, ashing and atomization.

The non-flame atomization methods mentioned thus far have been more widely used than any other non-flame method, as can be readily seen from the review paper on Flame Spectrometry by Wineforder and Vickers.[19] However other non-flame methods of atomization have been investigated including:-

cathodic sputtering - for direct atomization of solid samples [43]
- for solution analysis [44]

d c electric arc [45]

a c electric spark - sample sprayed into spark [46]

induction coupled plasma [47]

radio frequency plasma [48]

laser [49]

solid fuel pellet for field work [50]

various designs of furnaces using many different support materials (e.g. silica) [51] usually used for specific elements or matrices

flash-heated capacitor discharge lamp. [52]

Research is still continuing into the development of new methods and the performance of existing methods of non-flame atomization. The three most promising and widely used non-flame atomizers are variously designed graphite furnaces, cups and filaments, tantalum boats and filaments, and the cathodic sputtering atomizers.

3. Interferences in Atomic Absorption Spectrometry.

Walsh [5] predicted in his first paper on Atomic Absorption Spectrometry that the method compared with other spectral methods (e.g. emission) would be relatively free from interferences. Time has shown his prediction to be correct.

Generally "an interference in analytical chemistry can be any effect due to other constituents in the sample or its receptacle giving an erroneous result". Specifically in atomic absorption an interferent is normally classified as an 'enhancer' or a 'depressor' depending on whether the presence of the interferent respectively elevates or lowers the signal obtained compared to the 'true' result. However W .J. Price [8a] notes that all substances which produce an increased sensitivity for a given element actually do so by reducing an existing depressive interference as 100% efficiency of atomization can never occur in practice.

Because the success of atomic absorption as an analytical method depends on the production of uncombined (free), non-ionised, ground-state atoms in an atomic vapour for absorption of radiation at a unique and specific wavelength for a given element, any substance which hinders or masks the process will be an interferent in atomic absorption.

The history of an analyte in solution is vastly different in a flame atomizer compared with a non-flame atomizer and because more work has been done with flame atomizers than with flameless devices, mainly because of their early use and also their simplicity, a consideration of interferences in a nebulizer-flame atomization system will be presented first.

a) Interferences in Flame Absorption Cells.

For this discussion the history of the analyte will be followed through the atomization system using the following equation to help identify any interferences occurring. The concentration n, of analyte atoms in a flame (atoms cm $^{-3}$) is related to the concentration $\underset{\wedge}{c}$ of analyte (moles l $^{-1}$) in the solution aspirated into the flame by: (53)

$$n = 1 \times 10^{19} F\varepsilon\beta C / Q e_f \qquad 1.$$

where: F = solution transport flow rate cm^3 min^{-1}

ε = efficiency of aspiration (efficiency of producing a gas of the analyte)

β = efficiency of atomization (efficiency of producing atoms from gaseous analyte)

e_f = flame gas expansion factor due to increase in temperature of gases from room temperature and increase in number of moles of flame gas products.

In a pre-mixed flame using a nebulizer-burner system the mechanism for producing metal atoms is as follows (after Robinson) [54]: the solution is firstly converted to an aerosol by a nebulizer. This aerosol is then swept into the burner by the pre-mixed unburnt flame gases and thence into the flame where the droplets are dried, the residue (solid particles) melted and volatilized and compounds dissociated to produce free atoms enabling absorption to occur.

Solution Transport Flow Rate (F)

When a sample is aspirated into a flame system this parameter is the first affected by any interferent. Interference at this stage occurs where differences in the physical properties of analyte solutions exist. For example, when the physical properties differ between samples or between sample and standard a discrepancy in results occurs. Changing the acid concentration alters the viscosity of the solution, affecting the rate of uptake of the sample. The use of organic solvents compared with aqueous solutions also affects the uptake, owing to differences in viscosity, density, and surface tension. When a difference in solvent vapour pressure exists between samples, especially with low boiling point organic solvents, the rate of sample uptake is altered. The presence of dissolved solids in differing concentrations within the samples also affects the flow rate by increasing the viscosity of the solution.

Aspiration Efficiency (ε)

This can be loosely subdivided into three physical phenomena; nebulization (production of an aerosol or small droplets), solvent evaporation, and volatilisation (the elements are vaporized from the solid particle in the flame).

a) Nebulization.

Changes in the surface tension caused by altering any of the three effects mentioned above (acid concentration, solvent vapour pressure, dissolved solids concentration) affect the efficiency of the nebulizer and hence the parameter $\mathcal{E}$ by changing the size distribution of the droplets formed. Thus if the mean droplet size is decreased due to decreased surface tension (for example when organic solvent solutions are used in preference to aqueous solutions) more of the nebulized sample is swept into the flame for subsequent evaporation, disintegration, atomization and eventual absorption of radiation; in other words $\mathcal{E}$ is increased.

b) Solvent Evaporation.

Decreasing the mean droplet size of the sample introduced into the flame increases the efficiency with which the solvent is evaporated from the droplet. Also the lower the boiling point of the solvent the more efficient is the evaporation process. Both of these effects result in increased efficiency of evaporation.

All of the effects mentioned up to this point can be loosely defined as matrix interference effects, as the interference is related to bulk physical properties of the test solution.

c) Volatilization.

Another effect which alters the efficiency of producing a gas of the analyte in the flame (as defined by Winefordner) [53] is incomplete volatilization of the solid particles formed from the drying of droplets produced by the nebulizer in the base of the flames. This effect implies that the speed of the particles through the flame and/or their need for a high vaporization temperature does not allow complete conversion of the particles to the vapour phase at the flame temperature. Such an effect can be attributed to the formation of high boiling point metal/metal solutions as it is usually experienced in reducing flames.

An example of this type of interference is the depression of the chromium and molybdenum response by high concentrations of iron [55] which increases gradually as the iron concentration is increased until a plateau is reached in the presence of a large excess of iron. Hence the theory of the formation of a definite compound, e.g. a spinel, is not supported in this case; neither is the effect an example of mixed oxide formation, as the severity of this effect in different acid matrices decreases in the order $HCl > H_2SO_4 > H_3PO_4$. [56] If the presence of oxides was the controlling factor the reverse order would be expected.

Rhodium provides a similar example, its response in an air/acetylene flame being influenced by the presence of different acids and other metals. In rhodium solutions we assume because rhodium salts easily reduce to rhodium metal that the small solid particles left after solvent evaporation contain rhodium as the uncombined metal with a boiling point 2500°C causing incomplete volatilization. Thus when sodium sulphate, which appears to eliminate all the interferences, is present in the solution the formation of metallic 'clotlets' is prevented, allowing atomic rhodium to be released as evaporation occurs from the particle.

Atomization efficiency (β)

The factor β in equation 1 is described as that factor which "accounts for incomplete dissociation of the analyte compound volatilized into the flame, for formation of compounds resulting between the analyte and flame gas molecules and for ionization of the analyte atoms in the flame gases".[53] Such effects all result in decreased efficiency of atomization or decreased number of atoms present for absorption. Hence when interference occurs at this stage of the nebulization-atomization process it is due to the failure of the flame to break chemical bonds between the analyte and other materials in the sample matrix or in the flame.

i) Incomplete Dissociation and ii) Stable Compound Formation.

The separation of these two effects is of theoretical importance only. A distinction can be made because in i) the compound is formed from the matrix materials before the particle is partially broken up in the flame, ii) a stable compound is formed either from free matrix material or flame gases <u>after</u> the particle has disintegrated within the flame. However, because the effect of both forms of interference on the final result is very similar (the difference being in the 'formation' of the interfering compound) they will be treated together in the following discussion.

These two effects are the most commonly noted of all interferences in atomic absorption.

The lowering of alkaline earth metal absorbances in the presence of aluminate, silicate, phosphate, and other oxy-anions (especially when the anion is in stoichiometric excess over the metal) has been reported by several workers.[57-60,16] Price suggests [8a] that an equilibrium is set up between the species M-O, or M-X (in an X medium) and M-OX.

$$\text{as}\quad \underset{\substack{\text{metallic}\\ \text{oxy-anion}}}{M\text{-}O\text{-}X}\ \Big|\ \underset{\substack{\text{excess}\\ \text{oxy-acid}}}{\overset{\text{heat}}{\rightleftharpoons}}\ M\text{-}O\ \underset{\substack{\text{low-flame}\\ \text{temp.}}}{\overset{\text{heat}}{\rightleftharpoons}}\ M + O\ \overset{\text{C - reducing flame}}{\rightleftharpoons}\ M + CO \qquad 1.$$

Lower temperatures and/or excess of the oxy-anion favours the persistance of the stable oxy-salt.

However several workers have verified that the suppression of the alkaline earth absorption by oxy-anions can be minimised or overcome by adding excess releasing agents, e.g. lanthanum or strontium, to the sample and standard solutions.[16,61,62] The releasing agent affects the equilibrium (1) in the following way:

$$M - O - X + R \xrightleftharpoons{\text{excess R}} R - O - X + M \quad \ldots\ldots \quad 2.$$

A good releasing agent R, competes with Mfor OX to form a stable oxy-anion compound and since the law of chemical equilibrium dictates that reaction 2 must proceed to the right hand side a higher proportion of free M atoms is obtained.

For example Allan[19] noticed that magnesium absorption was depressed by the presence of aluminium in the sample solution. Elwell and Gidley[63] showed that the principal interferents in Mg determinations are those that form acidic stable oxides at high temperatures and postulated the formation of an Al-Mg mixed oxide in the case of aluminium suppression; x-ray work verified the formation of a spinel.[63a]

From the second and third stages of equation 1, Price argues that it is clear why metals forming refractory oxides give low sensitivity at low flame temperatures. The use of the high temperature nitrous oxide-acetylene flame increased atomization efficiency on two counts, a) by increased temperature, b) by removing more of the oxygen, thus moving the equilibrium in the third stage to the right hand side of the equation. However the low atomization efficiency in cases where the most stable refractory oxides are formed still continues to be a problem in flame atomization and research continues in this area.

iii) Ionization interference.

β is further affected when a significant proportion of atoms in the sample becomes ionized, the ions having a different absorption spectrum. When free electrons can be supplied from a second metal in the flame an enhancement is experienced in the absorption signal of the metal analysed. Although it appears as an enhancing interference effect it is really a decrease in an existing interference: ionization of the analyte, resulting in a reduction of the ground-state atom population. This effect is most often encountered in the easily ionized alkali metals. As the concentration of the wanted metal increases and/or a second ionizable metal is present in an unknown concentration the proportion of ionized atoms is decreased by an indeterminable amount.

Use of higher temperature flames such as the nitrous oxide-acetylene flame to 'crack' refractory oxides increases the proportion of ionized atoms. However addition to sample and standards of an excess amount of an ionization buffer (a second easily ionizable metal) alleviates this interference e.g. caesium can provide enough electrons to prevent the ionization of potassium:

$$\mathrm{Cs} \rightleftharpoons \mathrm{Cs} + e^-$$

$$\mathrm{K}^+ + e^- \rightleftharpoons \mathrm{K}$$

Interference in the Absorption of Light.

After the production of free ground-state atoms in the flame only spectral interference can occur. These interferences while not altering the actual number of atoms in the flame affect the specificity and the amount of radiation absorbed.

Spectral interferences can occur a) when radiation emitted from elements with spectral lines very close to the analyte resonance lines in the analysed solution is measured, b) when two elements in the analysed solution have resonance lines very close together (e.g. Gallium 403.298 nm interferes with Mn 403.307 nm [64] and Cobalt 253.647 nm interferes with Mercury 253.652). [65] Interference of type (a) can be corrected by using a detector tuned to a modulated light source.

A special type of spectral interference arises when volatilized molecules in the flame either (i) have absorption bands at the wavelength of the analyte resonance line or (ii) exist in particulate form of the necessary size to cause light scattering of the incident beam to occur. Both of these effects are included in the term "background absorption". These solid particles may be caused by the flame's inability to vaporize clotlets from a solution with a high content of dissolved solids or may be due to the formation of particles (e.g. of carbon) in the flame itself. Initially molecular absorption was ignored and all interference of this nature was labelled 'light scattering'. Willis [66] reported the 'scatter' caused by 5% solutions of NaCl, K_2SO_4 and a 2% solution of $CaCl_2$ aspirated into an air coal gas flame, and suggested using a non-absorbing line adjacent to the resonance line of the metal to determine overall background absorption. Earlier workers had also encountered 'higher apparent absorption' when metals were analysed in the presence of relatively large concentrations of other salts.[67,68]

In a group of three papers[69-71] Koirtyohann and Pickett discussed the contribution made by light scattering to background absorption using both theoretical considerations and experimental results from a method employing a hydrogen continuum lamp to measure background absorption. Using a long-path burner[72] they obtained molecular absorption spectra for several salts. The maxima and minima of the spectra are shown in Table I 1.

Table I 1.

SALT	CONCENTRATION ppm	MAXIMA nm	MINIMA nm
KI	2000	323 230	219 295 395
$NaNO_3$	10000	206 228 232	210 267 290
KCl	10000	248	220 292
KBr	2000	218 251 274	243 258 355
NaCl	10000	241	215 292

From these spectra they showed that the major component of background absorption was not scattering but molecular absorption due to molecular species not being dissociated in the flame. The spectra predicted by the Rayleigh scattering formulas increase steeply toward shorter wavelengths. This certainly was not the major effect observed in the spectra of Koirtyohann and Pickett. Calculations based on the Mie scattering theory (as the particle mean diameter was too large to utilise Rayleigh's formula) gave an expected light loss of 0.17% at all wavelengths due to scattering by particles and 4.6% light loss at all wavelengths due to scattering by water droplets. Reported losses were much higher, establishing the importance of molecular absorption in background interference compared to that of light scattering.

To overcome large background absorption from solutions of high solid content (e.g. brines and sea water) it may be necessary to remove the analytes by selective organic/aqueous extraction or, if the background absorption is not too severe, to ensure that the standards are similar in composition to the sample itself.

b) Interferences in Flameless Absorption Cells.

Early workers claimed two major advantages of these cells over flame cells.[31,34,35,37]

i) the sample did not require pre-treatment

ii) very few interferences occurred.

Work carried out at the time largely supported these claims but as more elements in increasingly variable matrices were analysed some limitations were discovered on the successful use of flameless devices.

Kirkbright[27] noted that more interference effects occur in the use of non-flame cells than in flame cells although refractory oxides are not as troublesome. Most interference work has been initiated by the unpredictability of some results obtained in the course of preliminary investigative work on non-flame cells using elements in various matrices. Of the four papers [83,95,76,103] in which interference is studied more exhaustively only limited theories have been advanced. In the main, however, the extent and mechanism of the interference experienced have been unpredictable.

A discussion along similar lines to 2 (a) will be presented here and all the reported interferences pertinent to each section will be briefly outlined. A brief summary of the authors' conclusions and theories will also be given. *

For the concentration of analyte atoms (atoms cm^{-3}) produced by a non-flame cell, n_1, Wineforder [53] gives the following equation

$$n_1 = N\beta \frac{CVs}{V} \times 10^{-3} \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where N = Avogadro's number

C = bulk concentration of the analyte (moles 1^{-1})

β = atomization efficiency

V_s = solution volume placed in the atomizer

V = volume in the vapour into which the atoms are vaporised

10^{-3} = conversion factor from moles 1^{-1} to atoms cm^{-3} (LHS)

i.e. $\frac{V_s}{V}$ = dilution of analyte in conversion from solution to atomic vapour.

In most flameless atomization cells the heating process is in three stages. After deposition of the sample on to the device the solvent is

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* work prior to January, 1973 (the date this work was commenced) will be presented here in the introduction in order to give the foundation of this work. Any relevant work reported after this date will be used in the Results and Discussion Section (III B) to compare with or support the present author's results and conclusions.

evaporated by gentle heating (over 20-30 s) at a temperature slightly above the boiling point of the solvent. Any residue (organic or salt) is removed in a second stage of heating at a higher temperature before a final burst of current is given to the device (2-10 s) to atomize any of the elements left from the sample. This system is simple compared with the flame because the sample is normally placed directly on to the atomizer as a solution or in solid form. Thus any term corresponding to aspiration efficiency (ε) and solution flow rate (F) in the flame is not required here. However, there is one factor which can affect the analyte concentration prior to atomization. A discrepancy may occur during transference of the very small sample (typically 5 μl of a 1 ppm solution) from the bulk solution to the atomizer, altering the effective concentration of the sample with respect to the bulk solution. Matousek and Stevens [75] gold plated the stainless steel components of the syringe to prevent the exchange of metals from the steel with the solution. Dipierro and Tessari[76] used a polyethylene capillary to prevent the detection of spurious signals in nickel analyses from the nickel in the needle. Both Bratzel _et al._[77] and Reeves _et al._[78] reported the loss of Ag by electro-deposition on to the needle. Kubasik _et al._[79] used teflon tips on a Hamilton syringe to avoid interference from any ionic exchange with the stainless steel needle. This interference can be overcome by allowing the solution to have contact during transfer only with inert substances (e.g. gold, teflon, polyethylene). Allowances for this factor could be made in equation (2) by substituting C_a [actual concentration of the sample in atomizer (moles l^{-1})] for C.

Atomic Vapour Volume (V)

A form of interference can occur here especially when standard solutions have viscosities and surface tensions differing from the sample solution. If the distribution of the atoms over the surface of the atomizer is altered the vapour volume into which the atoms are vaporised is also changed and consequently when the results are compared with analyses from different solutions a difference will be evident. Examples of this are quoted in the literature. Matousek and Stevens [75] applied xylene to the rod to prevent blood samples from soaking into the rod giving different results from an aqueous sample. L'vov [31] noted an improvement on using a tantalum metal liner with his furnace, and applied a 0.3% polystyrene solution to the sample electrode tip preventing the sample from spreading non-uniformly over the surface and hence V was similar for solutions of similar physical properties. Later pyrolytically-coated carbon was used both by L'vov [11] and Matousek [74] to give reproducible dispersion of the sample over the atomizer surface. However some workers [79-81] noted very little interference even when solvents of very different physical properties were used.

Atomization Efficiency (β).

This is the same parameter as that used in the flame. However, behaviour of the same analyte solution is very different in the two systems (flameless compared with flame).[27,31,32]

Flameless atomization is a much simpler process in one respect because the solvent and most, if not all, salts and organic matter have been removed before atomization occurs. Although the 'matrix' from which the sample is atomized in the atomizer is simpler than in the flame, interferences of varying degrees of severity have been noticed. A summary of most work is given below. Because of the transient nature of the signal there is an element of conjecture in most theories presented. Also, no 'concrete' evidence (in the form of stable compounds) can be collected in interference work as in the flame [63,82] owing to the very small amounts of sample used (10^{-9} - 10^{-12} g).

It should be pointed out that the atomization efficiency can be affected in two stages of the heating cycle. During ashing, compounds stable at elevated temperatures can form on the atomizer surface inhibiting the release of free analyte atoms in the atomization stage. Alternatively, stable compounds of low volatility may be formed which may be lost from the atomizer during the ashing stage. During atomization, stable compounds can again be formed at elevated temperatures on the atomizer surface or in the vapour phase before absorption of radiation occurs; spectral interference can also occur here. L'vov [11] recognised the limitation that ionization of the analyte imposes on the determination of some elements, especially the alkali metals. The discussion on ionization in section 3 applies in full to the flameless atomization system also.

Chemical Interferences.

L'vov [31] looked at the standard curves of twelve elements using his crucible apparatus and noted that "because of the complete dissociation of the molecules .... the effect of the composition of the sample on the analytical results is eliminated as these effects are produced by changes in the degree of dissociation of certain compounds". He analysed manganese in the presence of NaCl, $Pb(NO_3)_2$. At Mn/X ratios of 1:10 to 1:10000 no interference was observed. Al(1000 ppm) did not affect the signal. However, G. Baudin et al.[83] using a King furnace (very similar to L'vov's crucible) obtained several types of interferences by atomizing Fe, Ag, Cr, Cu, from solutions containing various other chemical species including metallic cations. They listed four types of possible interferences:

a) physical effects (e.g. variation in the volatility of the elements)
b) absorption by molecular compounds (spectral interference)
c) formation of stable compounds in the solid phase (during ashing)
d) formation of compounds in the gaseous phase (during atomization)

From their results two main conclusions about interference were made when an element is atomized in the presence of a matrix (i.e. matrix interference),* The presence of a matrix containing the analyte

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* An unfortunate use of the term 'matrix interference' in flameless atomic absorption literature could lead to some confusion when compared with flame atomic absorption. In the former system 'matrix interference' is used when any component of the test solution (usually of a higher concentration than the analyte) interferes in any way with the analyte's absorption signal whereas in the latter system the term 'matrix interference' implies that the bulk properties of the solution (surface tension, viscosity etc.) alters the absorption signal.

in the atomizer interferes

i) by creating a fractionation in the volatility of the elements

ii) by forming volatizable compounds capable of molecular absorption.

Matousek, Amos, and Stevens et al. in a series of papers using a mini-Massman furnace noticed some interferences. Matousek [84] reported the effect on the absorption peak height obtained when analytes were atomized from several solutions of different matrices and mentioned the effect of some parameters (e.g. voltage/time settings) on the peak height. He concluded here that the peak height is proportional to the vaporization rate and the presence of any extraneous ions present in the sample decreased the peak height only by decreasing the vaporization rate of the analyte. He suggested the use of an integrated signal rather than the peak height to counteract the interference.

In a later paper Amos et al.[38] studied the absorption signals from lead in the presence of several coumpounds (H_3PO_4, $NaCl$, KCl, $MgCl_2$, $CaCl_2$) all being present in blood. Depressive interference occurred in varying degrees with all of the compounds, but was reduced by using an argon/hydrogen atmosphere and a limited field of view immediately above the rod. The hydrogen gas provided a reducing atmosphere by supporting a hydrogen diffusion flame. A thousand-fold excess of Al did not affect Mg determinations whereas the presence of H_3PO_4 did by 60% (depression). The authors proposed that the interference was caused by incomplete dissociation of molecules formed either in the solid state or vapour state in the presence of large numbers of extraneous ions, rather than by different vaporization rates. Later Brodie and Matousek [82] found that the volatility of compounds which could be formed was important in interference considerations e.g. lead analysed in the presence of free Cl^-. It was implied that some of the lead was vaporized as $PbCl_2$ before dissociation of the remaining lead compounds occurred on the rod. Although vapour phase decomposition of $PbCl_2$ occurs, the net effect is a reduction in the peak atom concentration. Because the area under the absorption-time curve was unaffected it was concluded that interference is a change in vaporization rate.

Further work [75] used a synthetic blood standard for analysis of Mg, Fe, Cu, Pb, Zn in blood without any direct interference studies being reported. Stevens [85] presented a graph showing the suppression produced on a copper signal by concentration of $0 - 10\ g\ l^{-1}$ of NaCl and KH_2PO_4, all ions being present in the blood. Standards were prepared with NaCl and KH_2PO_4 present, a 20% depression in the Cu signal being recorded for concentrations of NaCl and KH_2PO_4 $2\ g\ l^{-1}$. Na^+ and K^+ as nitrates also depressed the Cu signal. No theory was presented. Other interference effects from atomizers similar to that of L'vov include the following:

a) Lead signals in the presence of increasing sodium bicarbonate concentrations were depressed to a minimum of 40% of their original value. Sodium chloride enhanced Cu signals; the enhancement increasing as the concentration of NaCl increased. Cr,Pb,Sn, & As all gave depressed signals when atomized from river water matrices. The bulk of the interference was attributed to the presence of NaCl in the sample solution (since all natural waters contain NaCl). Hence the effect of NaCl on Cr and Pb absorption peaks were studied. The Pb signal was reduced by 30% at a NaCl concentration of 300 mg cm^{-3} while Cr was not affected at all. Thus compounds in the water other than NaCl must also be interfering. However no theory was presented and the authors stated that more extensive work was needed before generalizations could be made with respect to matrix interferences.[36]

b) Segar and Gonzalez made attempts to determine eleven elements atomized from sea water matrices.[87] Loss of even the involatile metals apparently occurred when removal of the salt matrix was attempted and consequently most elements could not be successfully analysed. The total salt content critically affected the recovery of most of the involatile elements, especially copper where a total salt concentration of 0.1 g l^{-1} reduced the response of a 100 mg l^{-1} Cu signal by 87% compared to a signal from Cu in distilled water. Mg salts interfered more than sodium salts and sulphates interfered more than chlorides. Mn, Co, and Ni also experienced signal reductions in sea water. A graph of absorbance <u>versus</u> percentage salinity was presented for a standard concentration of Cu - severe interference is shown.

c) An investigation of the effect of eleven cations on cadmium determinations gave no interference while 200 ppm KCl, 500 ppm NaCl severely depressed the signal and 1000 ppm KCl and 1000 ppm NaCl enhanced the signal. [88]

d) Several cations at 1000 x excess with Ag and Au gave < 10% change in absorption signal. [77]

e) Chromium was analysed in the presence of five sodium salts (Na_2HPO_4, Na_2SO_4, NaCl, $NaNO_3$, $NaClO_4$) but only Na_2HPO_4 interfered by depressing the Cr absorption signal. Of six cations investigated in a hundred-fold excess only cobalt and iron interfered, causing a 30% loss in the Cr signal. When attempts were made to analyse chromium in sea water the Cr signal was reduced by suspected loss of $CrCl_3$ during the ashing stage. Addition of ethylenediamine tetraacetic acid as the disodium salt.to the solution forming an EDTA-chromium complex alleviated the problem.[89]

f) An investigation was carried out on the effect of five acids, three cations as chlorides, and two cations as nitrates (0 - 500 ppm) on beryllium determinations. Phosphoric and sulphuric acids enhanced the signal, the enhancement increasing with concentration, while hydrochloric acid had no effect and nitric acid depressed the signal. Calcium (as nitrate) was the only cation to significantly affect the Be absorption signal (by depressing it) but the effect was removed by the addition of H_2SO_4 to the test solution. No coherent theory was presented although the author suggested that it was a chemical matrix effect.[90]

g) Investigations on the effects caused by high concentration of metal salts in solutions containing an analyte. Some interfered and the authors linked the amount of interference to mole concentration suggesting that the atoms under measurement were enveloped inside the salt particle preventing the absorption of any light.[91]

Meanwhile several other groups and individuals were investigating operation parameters and interference effects using atomization systems other than the ones mentioned above. Interferences experienced, the systems used and the literature references are tabled below.

TABLE I 3b 1. A tabulation of the effect of some interferences experienced with a given element using the systems noted, with the literature reference.

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions and remarks.
92	exposed carbon filament with Ar atmosphere	Cd	13 cations Al, Au, As, Bi, Ga, Hg, In, K, Mg, Na, Pb, Sn, Zn.	Depressive	Some severe others slightly	a) cold atmosphere above rod (no diffusion flame here) gives rapid condensation of atoms b) transient nature of signal and slow recorder response c) other atoms are more rapidly condensed than Cd.
93	same as in 92: two rods mounted one above the other	Au	Al, Ce, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pd, Pb, W.	Depressive	> 30% in some cases; all interfered	Most work was on fluorescence but showed that interference occurred in the absorption of radiation. Interference is in the vapour phase; as the observation height above the filament increases so does the interference; as vapour cools it reacts with gold, which i) may be occluded by interferent **or** ii) may react with interferent in vapour to give intermetallic compound. i) is supported as no chemical affinity exists among the interferents. limited field viewing decreases the interference.

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions and remarks
94	Same as above	Ag Bi Cd Cu Hg Mg Pb Tl Zn	62 cations and anions at 1000x excess. Tables in paper	Of those that interfered all depressed the signal	Some slight some very severe e.g. Mn on Cu	Suppression in gas phase due to interaction between the atomic species concerned and the cloud of condensing vapour. Elements forming refractory oxides did not produce many interferences. Elements most frequently interfering all had boiling points less than the maximum filament temperature ∴ atomised with analyte:- co-crystallization and rapid condensation occurs in vapour after atomization. ∴ view at grazing incidence to rod.
95	as in above with limited field of view at grazing incidence to filament.	Pb Al	Several compounds		decreased	none
96	as in 92	Mg	24 cations	depressive	14 interfered at 1000 x conc. 6 at 100x	degree of interference is related to amount of concomitant present rather than ratio to the analyte

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions and remarks
97	as in 92	Ag & Cu in lubricating oils	10 cations only Ba interfered seriously	Depressive		None
98	as above	Ni	Several cations	Depressive	Various	Supported earlier work i) interference occurs in vapour phase ii) interference is temperature independent Large interferences occur with metals of similar volatility to Ni.∴ variable atomization of compounds on the filament is not a factor influencing interferences. Mechanisms very complex.
99	as above	Fe	22 cations & anions in 10, 100, 1000 x excess.	9 metals depressed the signal at 1000x level only Cr & Co interfered at 10x level		
			ammonia & ammonium phosphate	enhanced Fe signal		proposed mechanism: formation of colloidal FeOH as OH can't penetrate into filament

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions and remarks
42	Ta W and graphite boats	Mo Al Si Na	Cl			Compounds resisting decompositon should be avoided - expected loss of Al in presence of chlorides as $AlCl_3$
76	Carbon rod	Ni	SO_4^{2-} NO_3^{2-} Cl from NaCl	Depressive giving greater curvature of analytical curve		Related interference to decomposition of Ni salts i.e. predicted results i) $NiCl_2$ - vaporizes at low temp. without decomposition ii) oxyanion salts - decompose to NiO as intermediate (the temp. was maintained at > 600°C for 1 min. before atomization to convert Ni salts to NiO and thus to free Ni.) iii) nickel oxylate decomposes directly to metallic metal which can be atomized In ii) recombination to NiO occurred in vapour phase.

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions and remarks
100	HGA70	Cu & Ni	NO_3^{2-}, HCl H_3PO_4 HNO_3, H_2SO_4	Depressive	50% signal reduction due to loss in drying stage	Cu - oxy-anion salts decompose to copper-oxide Copper (II) chloride decomposes to Cu (I) Cl. CuCl lower bp than CuO and different rate of evaporation. Explanation doesn't work for Ni, ∴ suggested reduction of CuO to Cu metal on the carbon different rates of reduction. NiO - Ni in presence of carbon sulphate and phosphate more difficult to reduce explains results.
101	Ta ribbon	37 different elements used. Pb most studied		Depressive	Varied	a) loss of sample through abrupt 'spurt' at high temp. prior to atomization b) density of atoms decreases due to thermal expansion at constant pressure c) line broadening, due to expansion and added turbulence of the inert gas at higher temps.

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions & remarks
102	Ta filament	Cu	a) HCl	a) depressive	moderate	i) Cl on Cu suggested loss of Cu as CuCl before atomization
			b) perchloric	b) none	-	
			c) HNO_3	c) enhancing	slight	ii) a) perchloric on Fe due to greater rate of oxide formation in the presence of perchloric
			d) H_3PO_4	d) enhancing	moderate	
		Fe		a) none	-	b) perchloric on Cr due to oxidation by perchloric to readily dissociated forms
				b) depressive	slight	
				c) none	-	iii) stable Cr oxides formed in presence of HNO_3
				d) depressive	marked	iv) a) phosphoric altered Cu rate of vaporization, increases Cu atom population in light path by the formation of phosphate which is less volatile than the chloride
		Cr		a) none	-	
				b) enhancing	marked	
				c) depressive	moderate	
				d) depressive	slight	b) Fe + phosphoric - formation of Fe (III) phosphate, more stable than Fe (III) chloride
						Nearly all interferences diminished by using higher atomization temperatures. Complex interferences are experienced with no coherent theory

Ref.	System used	Element	Interferent	Type of Interference	Degree of Interference	Authors' Conclusions and remarks
103	Ta strip	Al Cr Cu Fe Mg Mn				No coherent theory suggested; more work needed
		Mg	Al & PO_4	Depressive	marked	
		Cu	Mg			
41	Pt wire loop	Cd	Phosphoric	Enhanced	marked	reduced rate of vaporization in the presence of phosphate no mechanism proposed
104	carbon rod in Ar/H_2 atmos.	Cu	components of serum PO_4^{3-} Na^+ K^+ Mg^+ Cl^-	depressive	varied	no theory but combined effect in serum cancelled each other out. suggested change in vaporization rate as the cause
			Ca^+ Fe^{2+} Mn^{2+}	enhanced		
78	carbon rod	Ag Cr Cu Fe Mn Ni Pb Sn Zn	studied variations of response Vs height above rod			suggested gain in signal when used reducing H_2 flame as: $MO + H_2 \longrightarrow M + H_2O$ $MO + H \longrightarrow M + OH$

In summary, several conflicting theories in explanation of interferences using flameless atomization devices have been proposed.

It is:

a) a vapour recombination effect, occluding atoms of the analyte

b) a combination of components in the matrix resulting in rate-of-vaporization changes (analyte leaves device either too early or too slowly).

c) the formation of compounds volatilised concurrently with the element but not dissociating, preventing the occurrence of atomic absorption.

* Interferences in Light Absorption.

'Background' absorption occurs when flameless atomizers are used, as it may do in flames (section 3a). In nearly all work with flameless atomization, results have been reported on background absorption from the matrix used.

Light scattering from carbon particles released at high temperatures as 'soot' was an early problem [76,31] but was largely overcome by using pyrolytic graphite. [32,73] Molecular absorption has been

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* In flameless atomic absorption all peaks other than atomic absorption peaks are termed <u>non-specific absorption</u>; this includes <u>background absorption</u> (light scattering and molecular absorption).

reported by L'vov [32] and Takeuchi et al.[103] Absorption by vaporized potassium iodide in the 200 nm to 550 nm region corresponded to that reported by Koirtyohann and Pickett (section 3a). Very little other work has been done on distinguishing light scattering from molecular absorption in flameless cells by other workers and both are usually covered by the term background absorption in any results reported.

OBJECTS OF THE PRESENT WORK.

From the summary in the previous section on flameless atomic absorption interferences it is clear that further study needs to be undertaken to elucidate the extent and severity of some interference effects and their mechanisms. Few coherent theories have been presented and some of the experimental results have not been entirely conclusive. More exhaustive study on any given system needs to be undertaken to establish more rigorous models for each system.

In view of these points some carefully selected systems were studied here in more detail than any reported elsewhere. Elements of similar and very different atomization behaviour were atomized from solutions containing the same chemical species.

Studies on synthetic solutions containing inorganic salts together with the analyte were made on three electrode systems to evaluate the severity and type of interference experienced using each system.

Interferent/analyte concentration ratios were investigated in several systems at different instrumental settings to minimize the interference produced. Thus several systems were analysed to study the severity and type of interference produced, the chemical residues present after ashing,and to suggest the characteristics of the compounds affecting the analyte absorption signal.

An investigation into the nature of the non-specific absorption peak was undertaken to give a better indication of the chemical form in which the interferent was leaving the atomizer. It was felt that a better understanding of the source of this peak may clarify the interference mechanism.

CHAPTER II

EXPERIMENTAL PROCEDURE & APPARATUS.

1. Instrumentation.

a) Atomic Absorption.

A Varian Techtron (Melbourne, Australia) AA5 Atomic Absorption Spectrophotometer equipped with an HTV R196 photomultiplier operated in the high gain mode as recommended [73] was used throughout all experiments.

The AC amplifier operated in the transmission mode was coupled to a recorder balanced to give a full scale range of 0 - 100% transmission except in a few experiments (indicated) where scale expansion was used (50 - 100% T ≡ f.s.d.). The optical system was set up for optimum efficiency with the light beam at grazing incidence to the rod unless stated otherwise (section I 3b).

Lamps: All the lamps used were manufactured by Atomic Spectral Lamps Ltd. (Varian Subsidiary, Melbourne, Australia) except the cadmium lamp (Activion Glass Ltd., Special Products Div., Halstead England). The manufacturers' recommended operating current was used for every lamp. The aluminium lamp was a high intensity lamp operated without the secondary arc. Resonance lines used are given in the text in the appropriate places.

Atomizers:

A 10 cm laminar flame Varian AB 51 burner was used for air-acetylene flame work and a Varian AB 50 5 cm laminar burner for nitrous oxide-acetylene work. The burner was replaced by the workhead of the Model 63 CRA Carbon Rod Atomizer (Varian Techtron) for flameless atomization (Fig. II, 1). Power was supplied to the workhead by the CRA power pack at three different variable voltages; *dry 0 - 1.8 V, ash 0.4 - 4V atomizer 2 - 9V for varying lengths of time (5 - 60s, 5 - 60s, 0 - 10s respectively).

An inert atmosphere was provided for the rod by supplying Argon to the workhead via a gas flow meter. Argon was allowed to flow (3.8 1 min.$^{-1}$ for all experiments) throughout the entire cycle but hydrogen (supporting a hydrogen diffusion flame) was permitted to flow by means of a solenoid switch only during the ashing and atomization portions of the cycle (H_2 flow rate was 2.2 1 min.$^{-1}$). Water as a coolant flowed at a rate of 0.5 1 min.$^{-1}$.

From preliminary experiments in setting up the apparatus the masking plate provided on the workhead was removed as an arc between the steel plate and one of the support blocks could not be eliminated. This arc atomized some elements in the plate resulting in sporadic absorption peaks during the determination of any of the constituents of steel (e.g. Mo, Fe, Cr. etc.).

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* These voltages are actual voltages and <u>do not</u> correspond to the graduations on the voltage control knob which are linear 0 - 10.

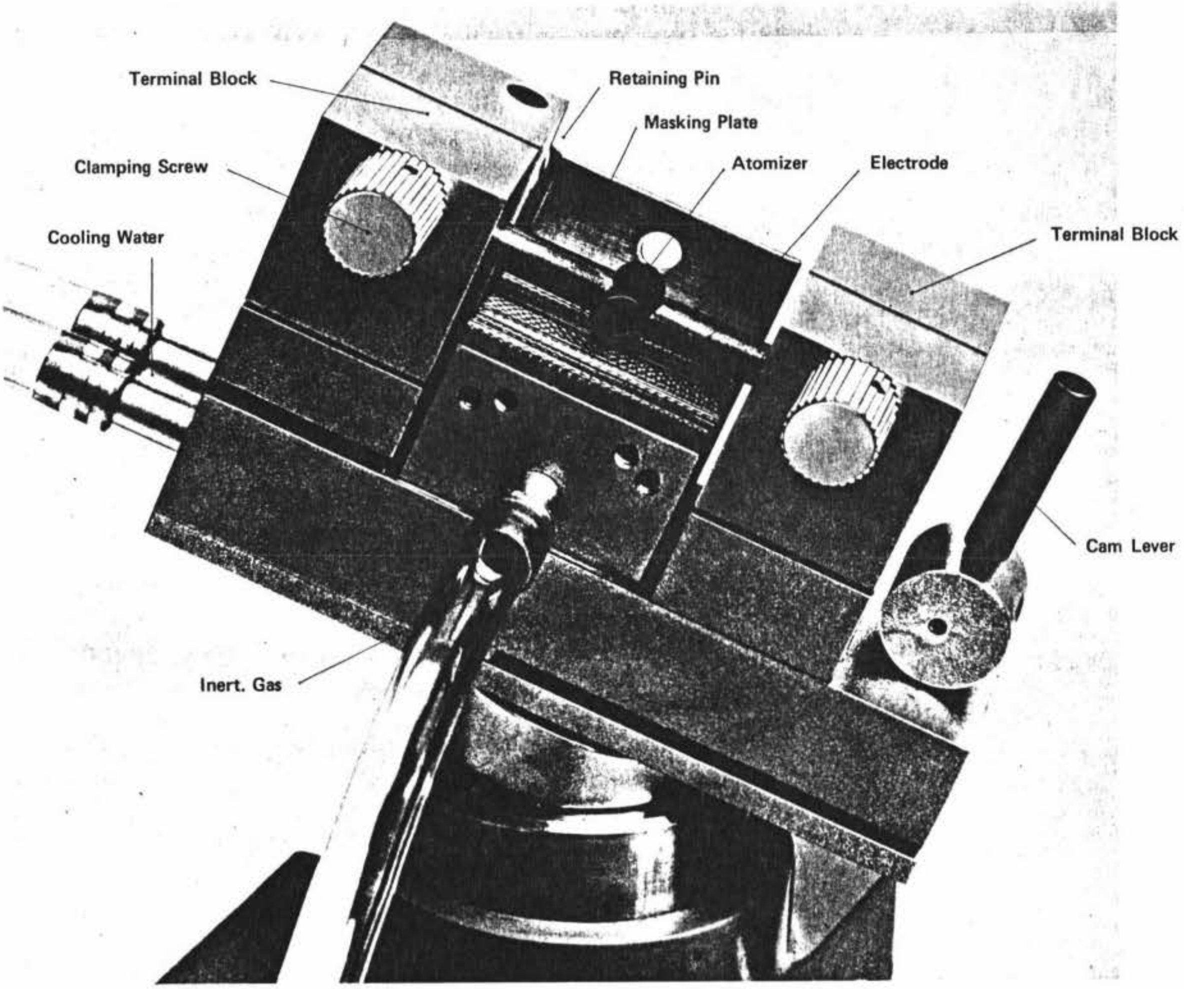


Fig. II 1.
A general view of the workhead of the Varian Techtron Carbon Rod Atomizer used in these studies. Notice the upright position of the cam lever in order to maintain tension on the electrode system.

Recorder:

The recorder used was a Rikadenki Kogyi fast response (0.35sf.s.d.) Model B161 recorder. This was coupled to the A.C. amplifier readout to give full scale deflection with a 10 m Vsignal. The attenuation was varied when amplification of the signal was required. The recorder was of the null-balance-point zero type which prevented base-line drift during continuous operation. Chart speeds used were between 15 inches h^{-1} to 30 inches $min.^{-1}$. The former speed setting was used most of the time.

b) Flame Photometry.

Sodium was determined using a Gallenkamp flame emission photometer.

c) Electrochemistry.

Chloride determinations (in solution) were carried out using an Electrical Instrument Laboratories' (EIL) chloride electrode system coupled to a Beckman Electroscan, (Fullerton, California, U.S.A.) as readout. The Hg/Hg_2SO_4 reference electrode was connected to the reference electrode terminal while the chloride electrode was connected to the glass electrode terminal.

2. Electrode Types.

a) Rod. Fig. II, 2a.

This electrode consisted of a 55 mm length of Poco FX9I (Poco Graphite Inc., Decatur, Texas, U.S.A.) 4.5 mm in diameter with a machined plateau 12-15 mm long in the centre of the rod reducing the thickness of the rod in this portion to approximately 2.2 mm in order to localize the heating. An indentation 1.5 mm deep and 3.5 mm in diameter drilled into the top of the plateau allows 5 μl of solution to be retained on the rod.

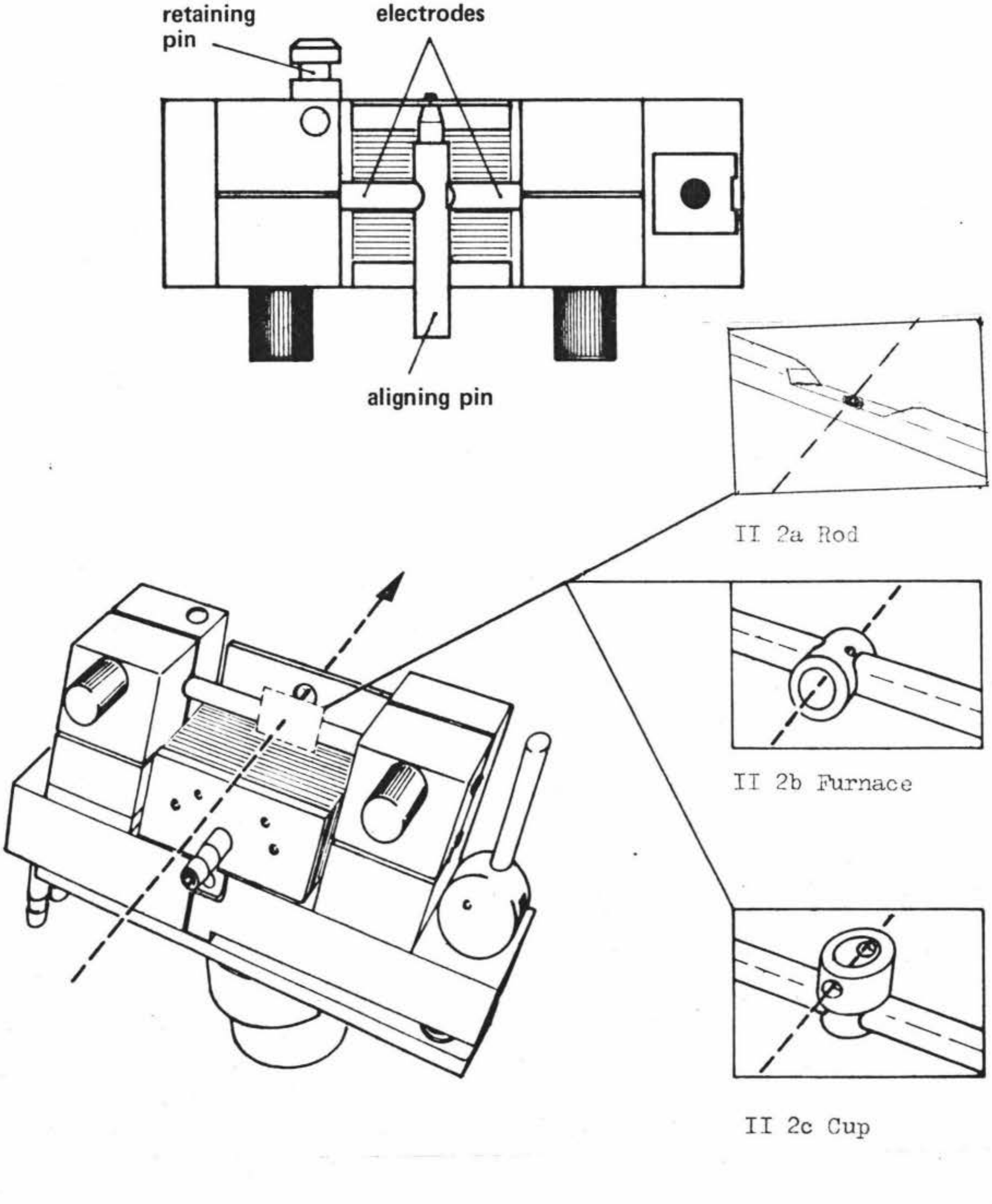
Double cavity rod: a second cavity of similar dimension was drilled in the rod adjacent to the first (4.5 mm apart centre to centre). This enabled a second 5 μl sample to be atomized from the rod under almost identical heating conditions.

A description of the following two electrodes (b, c) is given in the literature.[74]

b) Tube Furnace. Fig II, 2b.

A 9 mm length of pyrolytic graphite 3 mm i.d. is held in position by two support rods. Localized heating occurred at the rod-furnace interface resulting in the furnace being much hotter than the support rods. To facilitate sample injection a hole was drilled through the top wall of the furnace.[74]

A double cavity furnace was constructed by drilling two sampling ports 5 mm apart through the top of the furnace and down on



II 2a Rod

II 2b Furnace

II 2c Cup

Fig. II 2a, 2b, 2c.
Sketches of the atomizer workhead and the three electrode systems utilized in this work. The cup and the furnace are made from graphite and then pyrolytically coated whereas the rod is machined from very hard grahite without any surface hardening.

to the bottom inside wall to retain the samples within the furnace but allowing no mixing of the solution throughout the heating programme.

c) Cup. Fig. II, 2c.

A 9 mm length of graphite 3 mm i.d. was placed between the rods as shown.

The voltage/time settings for each stage of the cycle differed from electrode to electrode and in the case of the rod, from rod to rod due to differences in electrical conductance. Thus the temperature had to be obtained before any realistic comparisons could be made from one electrode to another.

During the use of the three piece electrode systems (tube furnace and cup) tension on the support electrodes was needed to maintain the electrical conductivity throughout the whole power cycle. As the electrodes heated up expansion of the graphite moved the electrodes apart. Tension was provided by means of the cam lever (Fig. II 2) and thus during heating expansion was allowed for by movement of the support blocks apart and then being forced together again by the cam lever system on cooling.

3. Analytical Reagents.

All the chemicals used were of analytical grade purity. Stock solutions were prepared by dissolving the appropriate amount of analyte (in the form of the compound containing the anion of interest) in distilled double deionized water to give a solution 1000 ppm with respect to the added ion. The more dilute solutions required were then obtained by successive dilutions with the purified water. The stock solutions were stored in polyethylene bottles while the weaker solutions were freshly prepared prior to analysis.

4. Experimental Procedure.

The solutions required for each study containing the appropriate concentrations of ionic species were made up in 5 cm^3 polypropylene phials immediately prior to analysis.* In most cases a 5 μl sample of the solution was micropipetted on to the electrode by means of an Excalibur set volume pipette equipped with disposable Teflon tips. These tips were replaced when the volume dispensed was not reproducible as when the tips were damaged in any way. Occasionally where indicated Hamilton micropipettes (Models No. F101 NCH and No. 75 N/G) were used to dispense samples of up to 1 μl and 5 μl respectively. These syringes were used infrequently as care

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* Decontamination of the electrode was effected by heating it to a temperature above the optimum atomization temperature of the element involved and repeating the process until no more atomic vapour could be detected by the instrument.

had to be exercised to ensure that the analyte was unaffected by the stainless steel needle. Other workers have also experienced this type of problem, which decreases reproducibility and varies the amount of analyte dispensed by the pipette. [75-79]

A temperature voltage programme was then chosen which dried the sample without sputtering, ashed the sample without causing loss of the elements and then atomized the sample over 2.5 s. The atomizing temperature was chosen to be high enough that no memory effects occurred, yet not too excessive in order to prolong the life of the electrode.

After each sample the electrode was allowed to cool (~30s depending on atomization temperature) to ~30°C before placing another sample on to it.

5. Recording and Treatment of Data.

A fast response recorder was used to record all the absorption peaks. The % Transmission mode of the amplifier unit was utilised showing the absorption peaks to decrease from 100% T. In every case at least three peaks were used for any one result. If reproducibility was good (R.S.D. ~ 3%) then three peaks were used but usually five or more peaks were necessary to give a reasonable level of confidence to the results. From these peaks any peak (from a set of five or more) obviously outside a "reasonable" range was omitted before any further treatment of results occurred.[*] The absorption peaks were then read (to the nearest 0.1%) and averaged. The relative standard deviation (R.S.D.) was then calculated for each result according to the formula:

$$\text{R.S.D.} = \left(\frac{\sum x_i^2 - n\bar{x}^2}{n} \right)^{\frac{1}{2}}$$

The % Transmission values (mean and R.S.D.) were then converted to absorbance values by tables - all data is then represented as absorbance values ± R.S.D.

[*] From an experiment involving 45 atomization peaks on a 5 μl sample of 0.25 ppm Cu the mean was the same as for the first six peaks omitting one as being outside of the range. The only effect of increasing the number of repetitive samples appears to be an increase of the R.S.D.

CHAPTER III

RESULTS AND DISCUSSION.

1. Synthetic Solutions.

Four elements were analysed from solutions containing various chemical species at several different concentrations. Three different electrode systems were used and the effect of the interferent on the absorption signal at various instrumental settings was also investigated for each system.

Hydrogen was added to the argon atmosphere around the atomizers to support a diffusion flame providing a reducing atmosphere to minimise interference effects[38] and to decrease the atom population decay rate with respect to height above the rod.[78]

All results reported on interference effects have been corrected for background absorption.

i) COPPER.

A. Results

Instrumental parameters giving optimum conditions for Cu absorption signals were chosen (see section II - 4). Parameters used are given in Table III 1-1.

Table III 1-1. Parameters for Cu absorption signals using any of the three atomizers.

Wavelength (nm)	324.75	**Dry**	Voltage	4.0 to 4.8
Slit width (μ)	125		Time (s)	20 to 35
Slit height (nm)	5	Ash	Voltage	4.5 to 5.5
Lamp current (mA)	3		Time (s)	15
		Atomize	Voltage	5.5
			Time (s)	2.5
		Gas Flow Rate $1\ min^{-1}$	H_2	2.2
			Ar	3.8

The optimum ashing setting was obtained by atomizing a copper solution (2.5 ppm Cu as $CuSO_4$ in doubly deionised distilled water). An ashing temperature just below that at which copper was lost from the atomizer before atomization was then chosen. Fig. III 1-1.

The atomize settings were obtained by atomizing copper as $CuCl_2$ in solution. Analytical curves were produced for several atomization temperatures. When good sensitivity and reproducibility of signals was obtained, together with no memory effects due to incomplete atomization, then this setting was chosen as the optimum one. (Fig.III 1-2). At low atomization voltage settings it was necessary to heat the atomizer to a higher temperature after each firing to remove residual copper from the atomizer. This prevented accumulation of copper on the atomizer. Subsequent standard curves of copper as $CuCl_2$ and $CuSO_4$ in distilled water using these parameters were almost linear between 0 and 2.5 ppm (5 ppm for the rod). However slight deviation from linearity existed at higher concentrations. (This is to be expected and a theoretical explanation is presented in a paper by Zeegers et al.[114]).

a) Effect of some Alkali Halides on Copper.

To compare the effect produced on copper (as $CuSO_4$ in solution) by several alkali halides a series of solutions with increasing ratios of [interferent] / [copper] was prepared for each interferent. These solutions were then atomized using the settings in Table III 1-1 but with a longer ashing time of 35s. This allowed for the removal of as

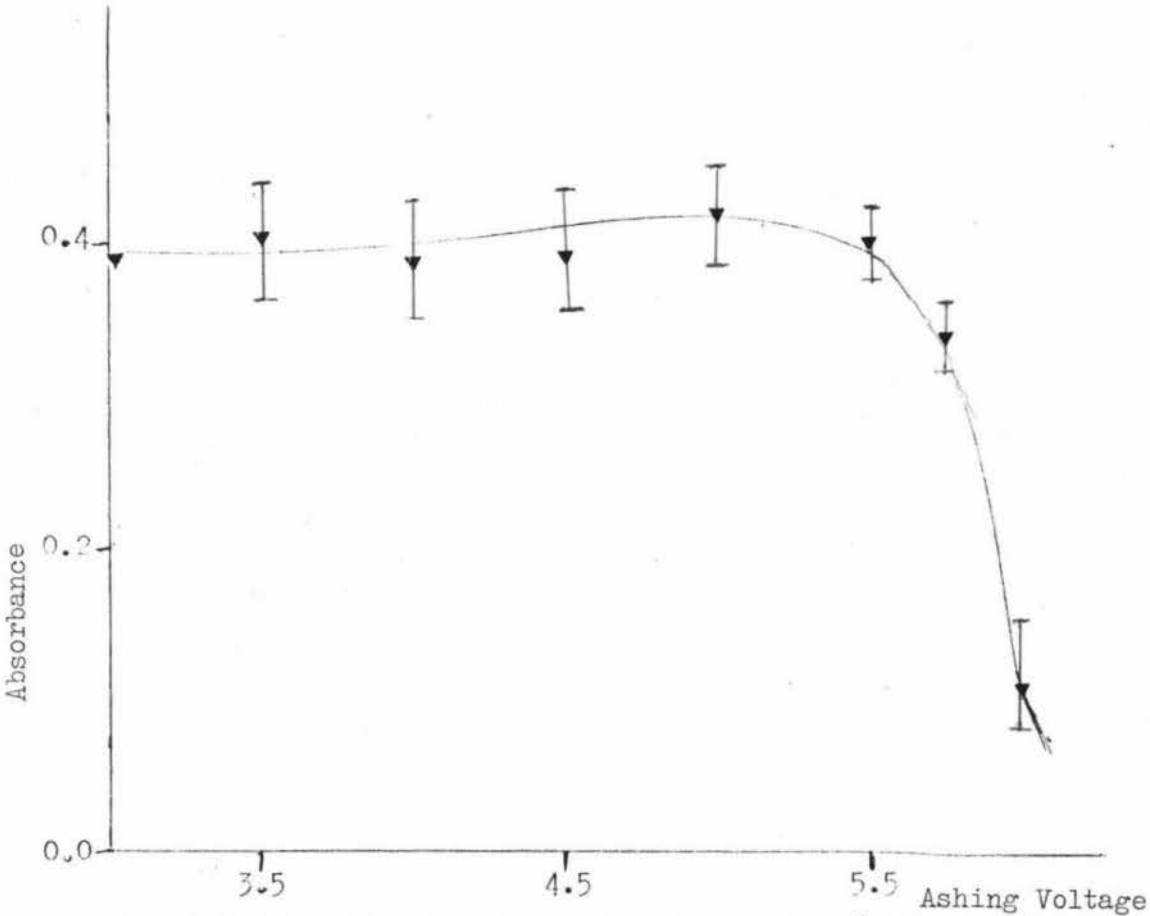


Fig. III 1-1. The absorbance from Cu samples (5μl of 2.5ppm $CuSO_4$ solution) atomized from the rod at several ashing voltages.

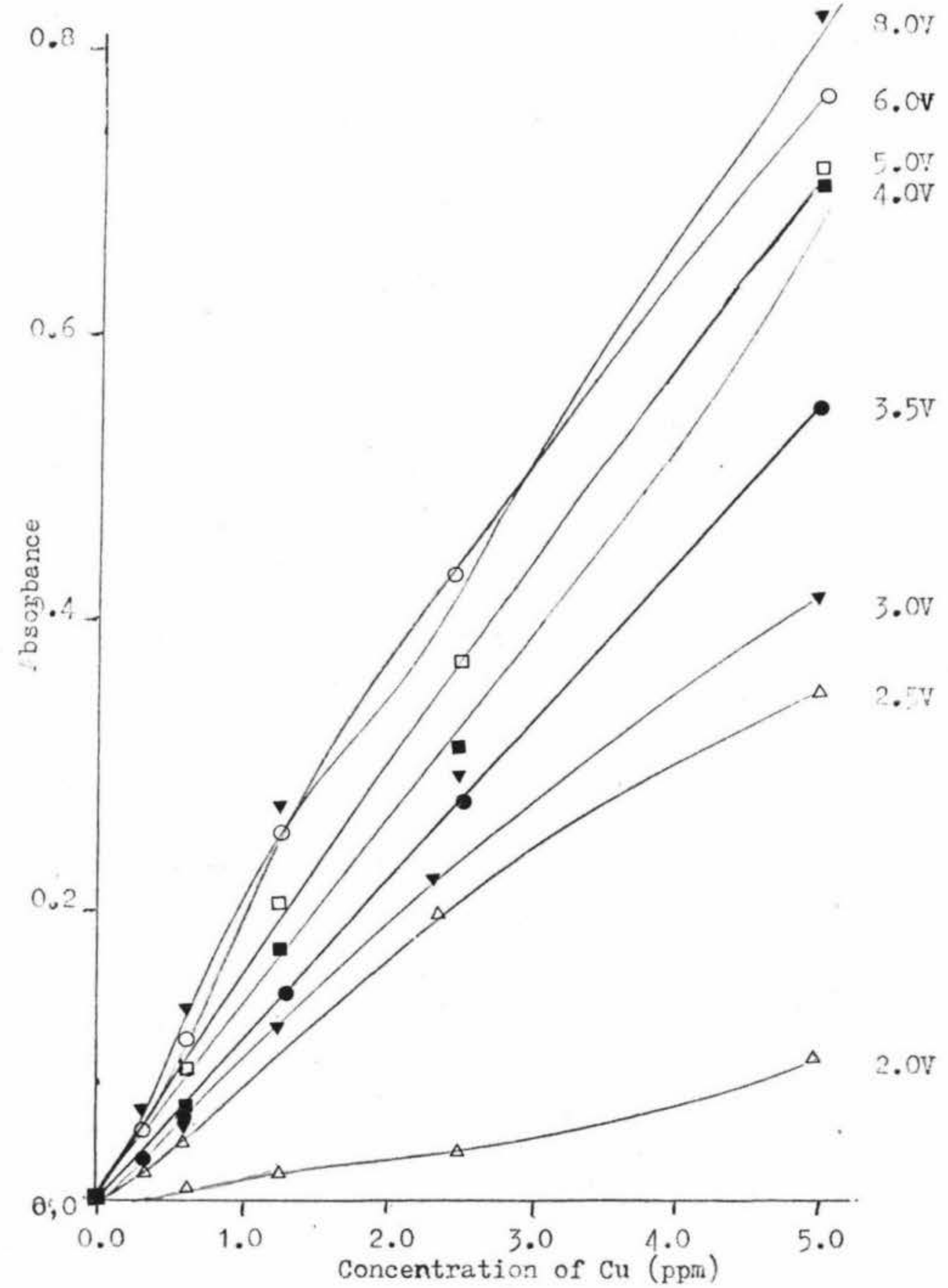


Fig. III 1-2. A series of analytical curves using 5µl samples of Cu solutions (as $CuCl_2$) atomized from the rod at different atomization voltages. The other instrumental conditions are given in Table III 1-1.

much salt as possible before the copper itself was atomized.* In order to verify that copper was not removed during ashing a solution containing copper only (as $CuCl_2$) was atomized at this and at lower settings. The signal obtained was constant. However at slightly higher settings the peak copper signal decreased as copper was lost during ashing.

The results of this experiment are shown in Figs. III 1-3 and III 1-4.

Serious interference occurred in all systems but one, even at such low [interferent] : [analyte] ratios as 1:1 and 2:1. Interference effects at such low stoichiometric ratios do not appear to have been reported previously. Anomalies in the NaCl-Cu system were also noticed (see Fig. III 1-4) in the region of 20:1 to 30:1 ([interferent] / [copper] ratio) which have been hitherto regarded as 'safe' levels of NaCl in copper analyses by most workers.

Background absorption was checked for each result and if any absorption was detected, the analyte absorption signal was corrected accordingly. In most of the systems background absorption during the atomization stage was low or non-existent.

Signal Profiles.

Diagrammatic representation of the type of signals obtained

* With some alkali halides a 'smoke' from the atomizer could be easily seen at concentration levels $>$100 ppm during the ashing stage owing to the vaporization of the alkali halide.

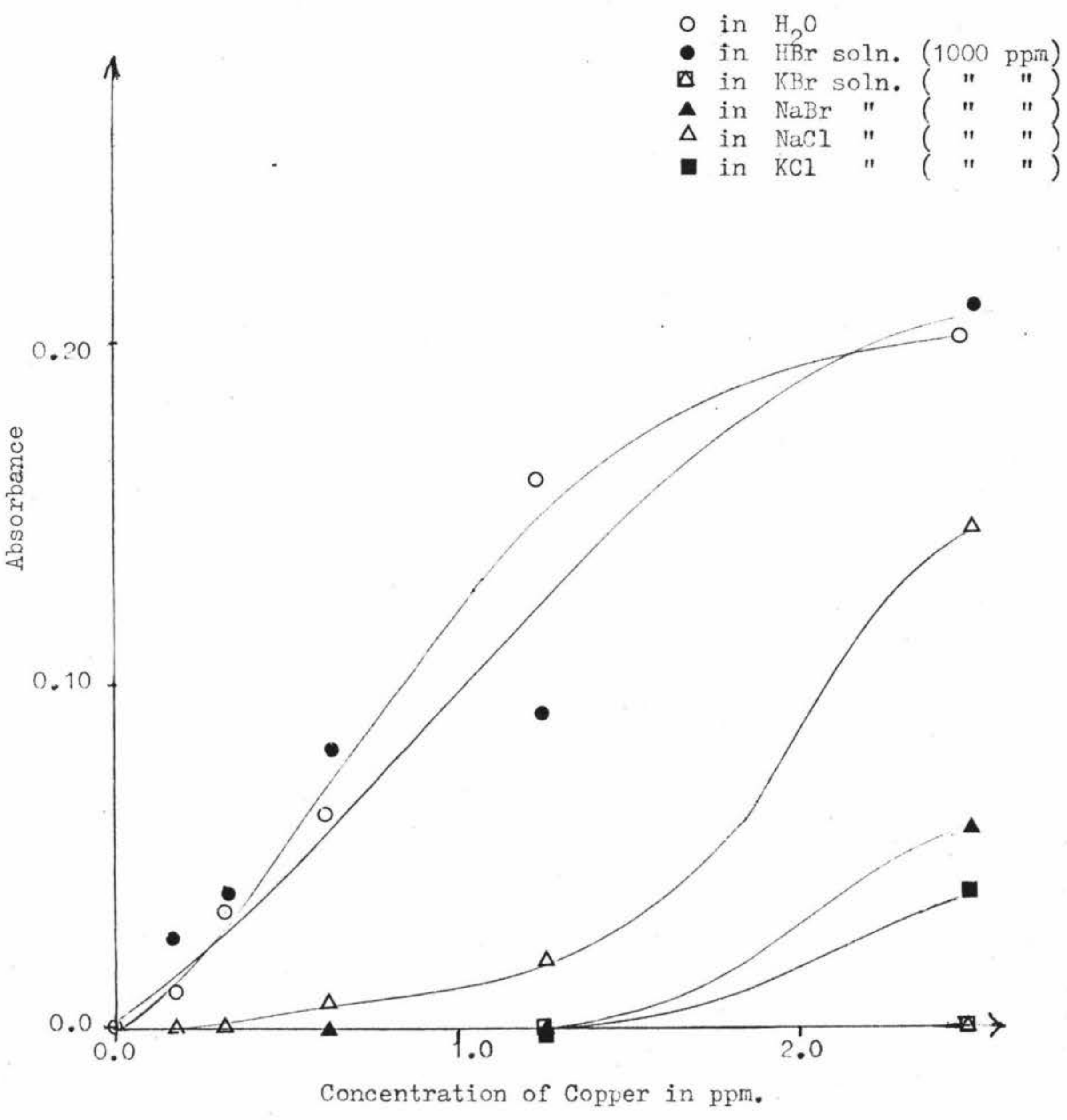


Fig III 1-3. The effect of various anions and their corresponding cations on Cu (as $CuCl_2$) analytical curves, using the Carbon Rod Atomizer optimised for copper analysis. The anion concentration is 1000 ppm.

Interferant:copper ratios are as follows;

Cu conc.	2.5	1.25	.625	.3125	.1563	ppm
x 10^{-3}	2.5	1.25	.625	.03125	.01563	

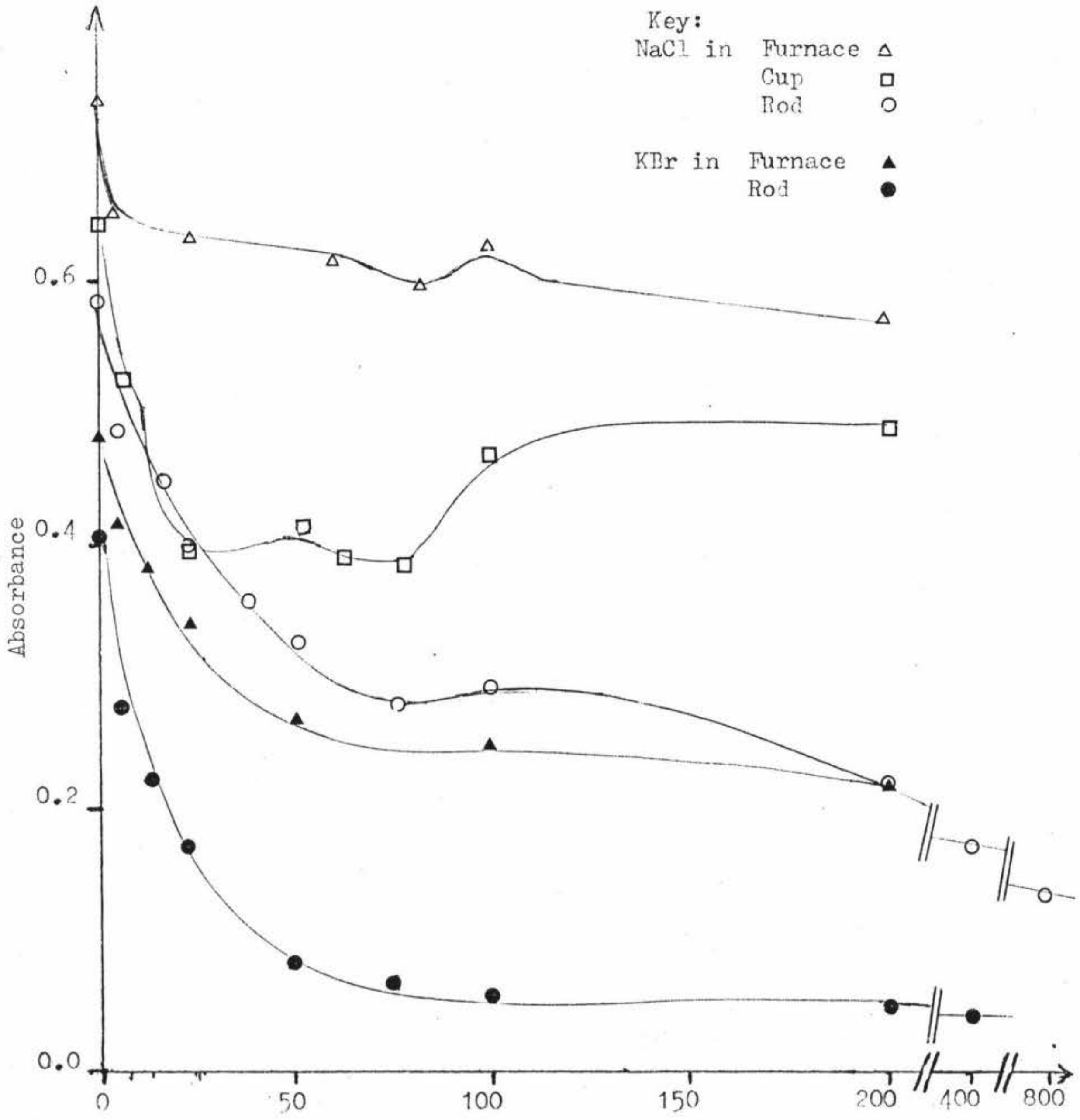


Fig. III 1-4. The effect on Cu absorbances (5µl samples of a 2.5 $CuSO_4$ solution) caused by varying the concentrations of NaCl and KBr within the same solution. Three atomizers are used under conditions given in Table III 1-1.

throughout these experiments and the condition associated with each type is given in Fig. III 1-5.

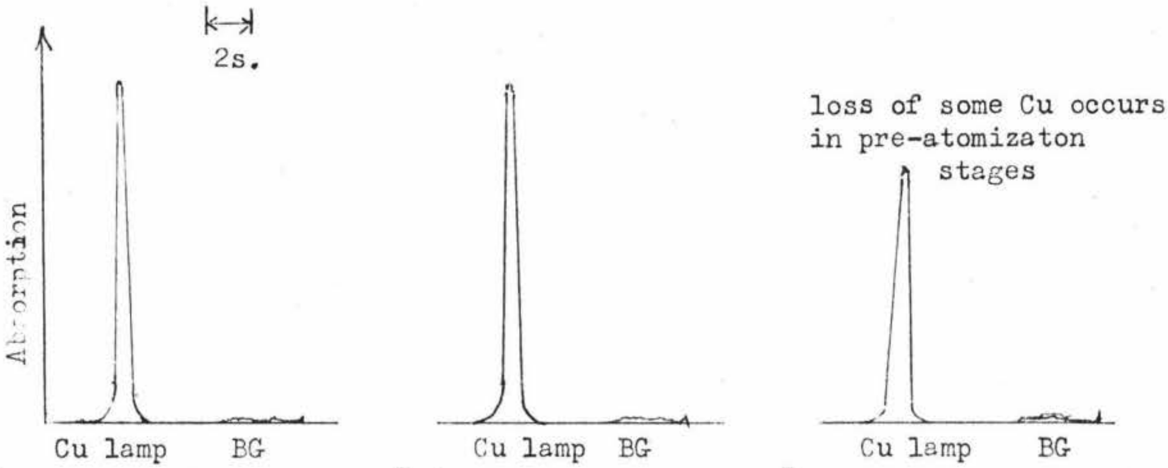
b) Effect of Added Anions on Copper.

Series of Cu standards were made up in concentrations from 0 to 0.5 ppm with Cu as $CuCl_2$, Cu $(NO_3)_2$, $CuSO_4$. The effect of additions of the same anion (in the form of corresponding acids) was investigated. Each series was analysed on a carbon rod using the following parameters at several different ashing voltages.

Table III 1-2. Instrumental settings for experiments investigating the effect of added anions on copper signals at various ashing voltage settings.

Wavelength (nm)	324.75	Dry	Voltage	4 to 4.8
Slit width (μ)	150		Time (s)	20s
Slit height (nm)	5	Ash	Voltage	x
Lamp current (mA)	3		Time (s)	20
		Atomize	Voltage	5.5
			Time (s)	2.5
		Gas Flow Rate $1\ min^{-1}$	Ar	3.8
			H_2	2.2

Where no additional quantity of the anion was present the curves were almost identical. In the case of each salt, loss of Cu at concentrations $>$ 1 ppm during the ashing stage occurred when ashing voltages $\geqslant$ 7.5v were used. Below this setting copper was presumably not lost during ashing, and the atomization process was uninfluenced by the anion present. This would indicate that Cu is not preferentially lost as $CuCl_2$ when Cl^- is present compared with the atomization of Cu in



1. Cu only in solution ashing temp.= 400°C

2. Only Cu in solution ashing temp.= 650°C

3. Only Cu in solution ashing temp.= 800°C

4. NaCl + Cu in soln. ashing temp= 400°C

5. NaCl + Cu in soln. ashing temp.= 650°C

6. NaCl + Cu in soln. ashing temp.= 800°C

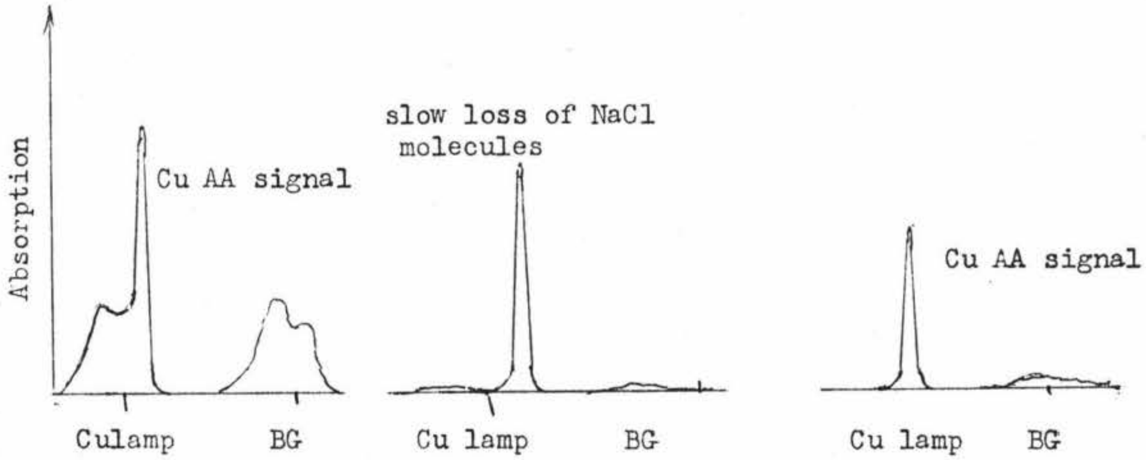


Fig. III 1-5. Peak profiles obtained from Cu atomization in the abscence and in the presence of NaCl. (BG = background absorption obtained when using an H_2 continuum lamp).

the presence of two very different anions NO_3 and SO_4^{2-}. Hence the rate of vaporization theory is not supported by these results.

Solutions containing 2.5 ppm Cu (as nitrate, sulphate, chloride) were investigated with varying amounts of the corresponding anion added (as HNO_3, H_2SO_4, HCl, respectively), using the same conditions as above, with a range of ashing voltages. Table III 1-3 gives the results of these experiments. As was the case with added alkali halides, a small excess of the anion (e.g. 4:1) was enough to provide a suppressive interference. Over a range of ashing voltages 10-500 ppm of the added anion caused a suppression of the Cu atomic absorption by 20-30%. The suppression is generally not significantly worse at 500 ppm than at the 10 ppm level, nor is the effect strongly modified by changing the ashing voltage.

In the light of these observations it is evident that care still needs to be exercised when solutions obtained by acid dissolution of solids are analysed. Even at low concentration levels of the acids it is evident that both standards and sample solutions need to be very similar in acid concentration. Thus standards made up in constant concentrations of acid would obviously be preferred in Cu determinations in acid media compared with standards made by simply dissolving 'pure' salts in distilled water.

Table III 1-3.

Absorbances obtained from a 2.5 ppm Cu solution atomized from the rod in the presence of increasing concentrations of added anions (HCl, HNO_3, H_2SO_4) at various ashing voltage settings. Atomization conditions are given in Table III 1-2.

ANION	Added Anion CONCENTRATION (ppm)	ABSORBANCES		
		4.0	5.0	6.5 Ashing Voltage Setting
NO_3^-	0	.735	.680	.714
	10	.567	.581	.582
	50	.523	.572	.567
	100	.524	.590	.571
	200	.510	.567	.557
	500	.535	.562	.560
SO_4^{2-}	0	.661	.689	.649
	10	.521	.525	.530
	50	.483	.532	.512
	100	.480	.497	.514
	200	.465	.508	.494
	500	.468	.502	.509
Cl^-	0	.635	.646	.690
	10	.458	.493	.493
	50	.473	.482	.490
	100	.480	.500	.501
	200	.472	.476	.512
	500	.500	.526	.533

R S D = ± 0.020 for most results.

The effect of H_3PO_4 on Cu (as $CuCl_2$ at 0.625 ppm) was also examined over an interferent/analyte concentration ratio of 0 to 2240. Some unusual features were revealed in the graphical representation of the results (Fig. III 1-6a). With increasing amounts of phosphate (from about 2:1 to 60:1 phosphate:copper ratios) there was an enhancement of the Cu absorption signal, the enhancement increasing steadily from about 10% to 50% over the above ratio range. Further addition of phosphate gave an additional but less marked enhancement.

c) Combined effect of NaCl and H_3PO_4 on Cu absorption signals using the three electrodes.

Instrumental parameters (see Table III 1-1) except for the voltage/time settings which are listed in Table III 1-4 below.

Dry Voltage	4.0	Atomize	Voltage	6.5
Time (s)	14.0		Time	2.5
Ash Voltage	6.0			
Time (s)	18.0			

Previously copper had successfully been analysed in blood or serum matrices by flameless atomizers.[104,85,76] However, Stevens[85] showed that slight depression of the signal occurred while Glenn <u>et al</u>.[105] showed that no interference by the serum matrix was evident. In view of the high NaCl content in blood (1-3.5g lit.$^{-1}$)[85] it is rather surprising that any copper absorption signals are obtained at all. Here and elsewhere[88] severe depression of the Cu signal is experienced at concentrations well below this level. However because of the presence

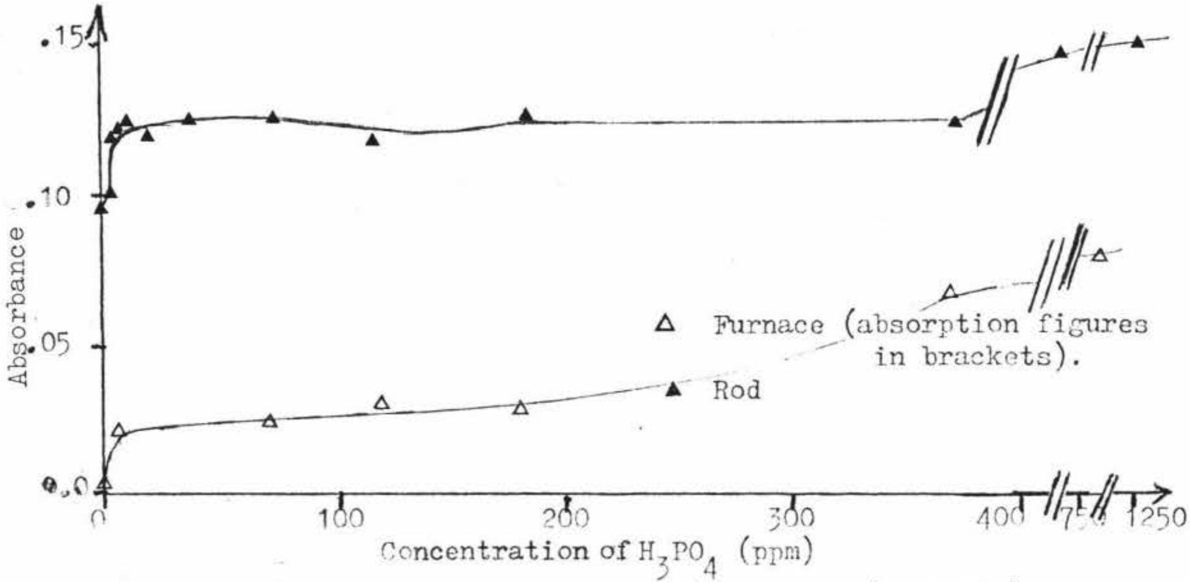


Fig. III 1-6a. The absorbance of a .625 ppm Cu (as $CuCl_2$) atomised from the rod in the presence of increasing concentrations of H_3PO_4 in the same solution. A similar curve is shown using the furnace.

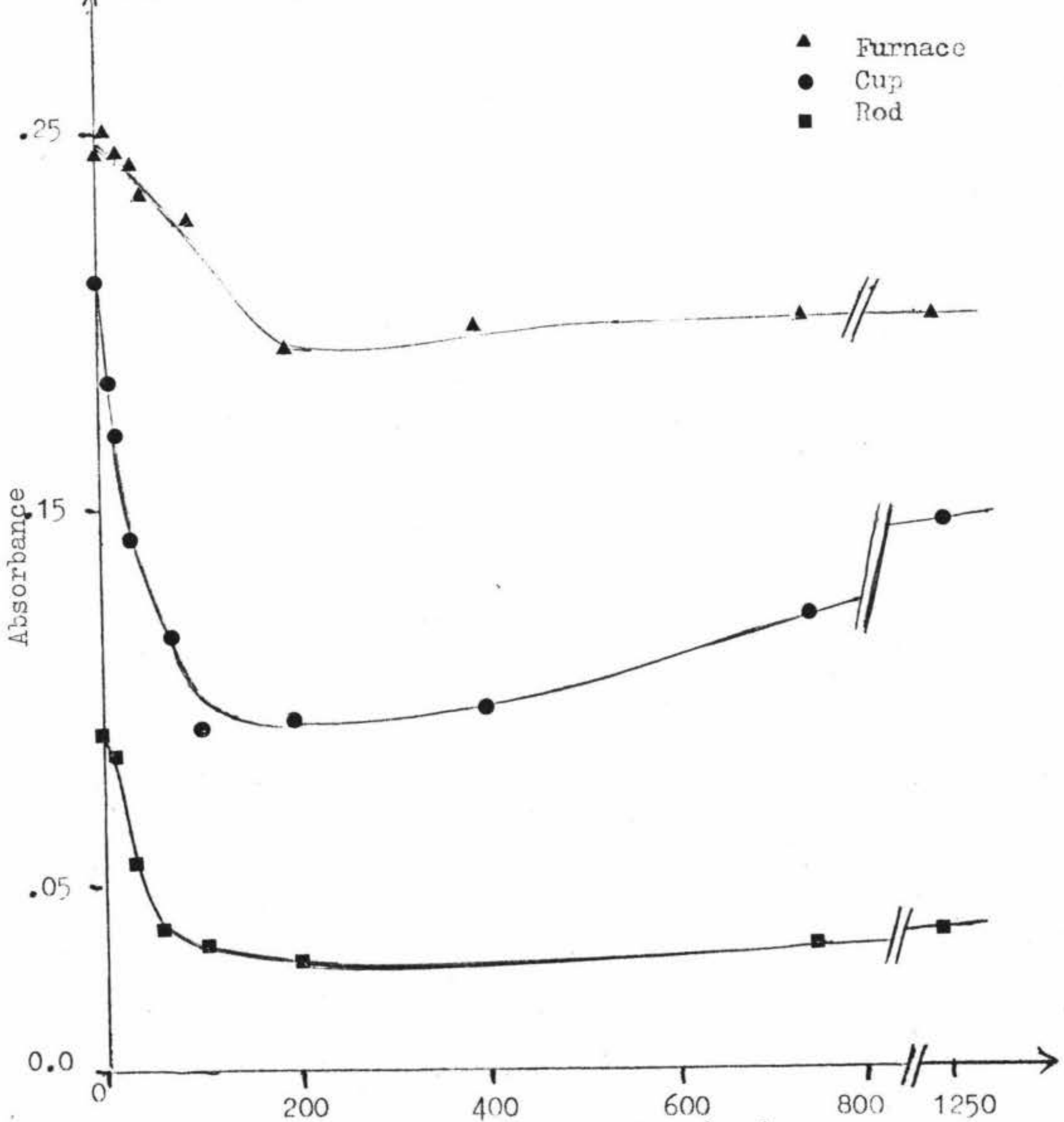


Fig. 1-6b. A graph showing the combined effect of NaCl & H_3PO_4 on 5µl samples of a 1.25ppm solution of Cu(as $CuCl_2$). Atomization conditions used in both experiments are given in Table III 1-1.

of PO_4^{3-} in blood (equivalent to 1.4-6.3 g l^{-1} of KH_2PO_4) and also due to the reported enhancement it produced on the Cu signal, an investigation into the combined effect of PO_4^{3-} and NaCl on Cu determinations was considered to be worthwhile. It was thought that the enhancing effect of PO_4^{3-} balanced against the depressive effect of NaCl might account for the lack of any appreciable interference experienced in blood Cu determinations.

Solutions containing increasing but equal amounts of NaCl and H_3PO_4 (former compound concentration is expressed as ppm of Na and the latter as ppm of PO_4) and 1.25 ppm Cu as $CuCl_2$, were prepared and analysed using the conditions mentioned above on each atomizer. Results of the experiment are represented in Fig. III 1-6 (b). Low concentrations of the interferents gave a suppression of the Cu signal which was however less serious than that with NaCl alone. After reaching a minimum Cu signal at a ratio interferent:analyte of 160:1 the signal increased slightly, but even at a 1000:1 ratio it was still less than the signal from the pure $CuCl_2$ solution. The loss of signal (as a % of the signal obtained from the solution containing no interferents) at the minimum and at the 1000:1 ratio for each curve is given below.

Atomizer	Minimum signal			
	Interferent: Analyte Ratio	% Signal Loss.	Interferent: Analyte Ratio	% Signal Loss
Rod	160	66	1000	60
Furnace	160	25	1000	19
Cup	80	55	1000	30

Clearly interference from the combination NaCl and H_3PO_4 is less in the furnace than in the cup or the rod. However the ensuing restoration after the initial minima is most marked in the case of the cup.

d). Double Cavity Interference Experiments.

Aggett and West [80] used a double rod system to determine whether or not the interferences observed occurred in the vapour phase. In the double rod system differences in atomization conditions between the two rods could exist, e.g. because of slight differences in the resistivity of the two rods. Consequently different results would be obtained from the actual situation where the analyte and interferent are volatilized from the same environment. A better alternative would be experiments with a rod having two identical cavities as close as possible to each other and of equal distance from the rod centre. Thus the temperature of these two cavities should be much closer than the temperature of the cavities in two different rods. Furthermore where rods are mounted one above the other the turbulence pattern in the gas flow around the upper rod would be considerably altered by the presence of the lower rod. Hence the mixing of the two vapours could not be expected to simulate the actual situation very closely. The conditions for operation were then optimised with the light path focussed above one particular cavity into which the Cu solution (1.25 ppm as $CuCl_2$) was placed. Into the second cavity the interferent (NaCl, H_3PO_4 or HCl) or, in the case of the blank, water was placed. Several different concentrations of the interferent were used. Similar experiments were carried out using a double cavity furnace.

A lower ashing voltage setting (4.5v) was used to ensure that some of the interferent remained on the atomizer until atomization. The results are presented in Figs. III 1-7 (a) and III 1-7 (c).

On the rod, severe depression of the signal occurred in the presence of even low concentrations of NaCl (10 ppm reduced the Cu signal by ~53%). HCl also slightly depressed the Cu absorption signal whereas H_3PO_4 barely changed the signal from that when H_2O was added to the second cavity. The degree of interference was very similar to that reported in the earlier experiment. Suppression of the signal also occurred in the furnace when NaCl was used. Suppression increased with increasing NaCl concentration. HCl also suppressed the signal but the degree of suppression was less when the HCl concentration was increased. H_3PO_4 suppressed the signal at low concentrations but doubled the signal at a higher concentration (5000ppm).

For comparison two samples of the same solutions were mixed in the <u>same</u> cavity on the rod and subsequently atomized. These results are presented in Fig. III 1-7 (c).

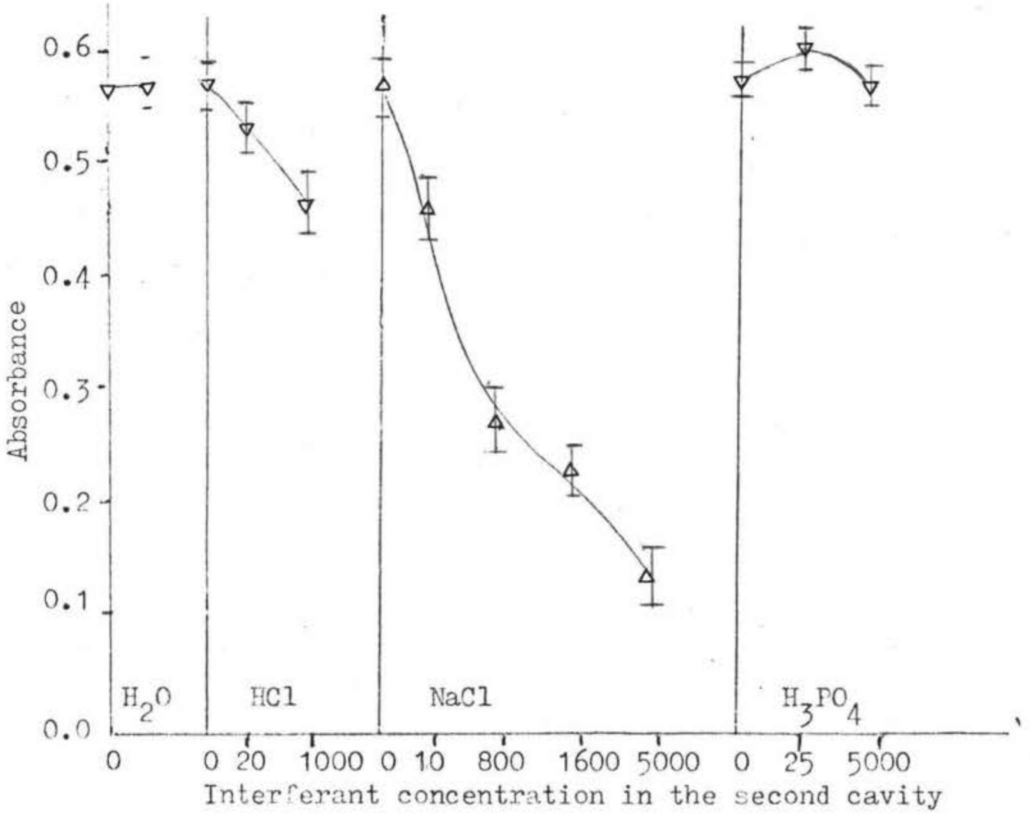


Fig. III 1-7a. Absorbances from 5µl samples atomized from the rod together with the given concentration of interferant in the second cavity. The Cu soln. used was 2.5ppm (as $CuCl_2$). Except for an ashing voltage of 4.5V the instrumental parameters used here and in Fig.III 1-7b are contained in Table III 1-1.

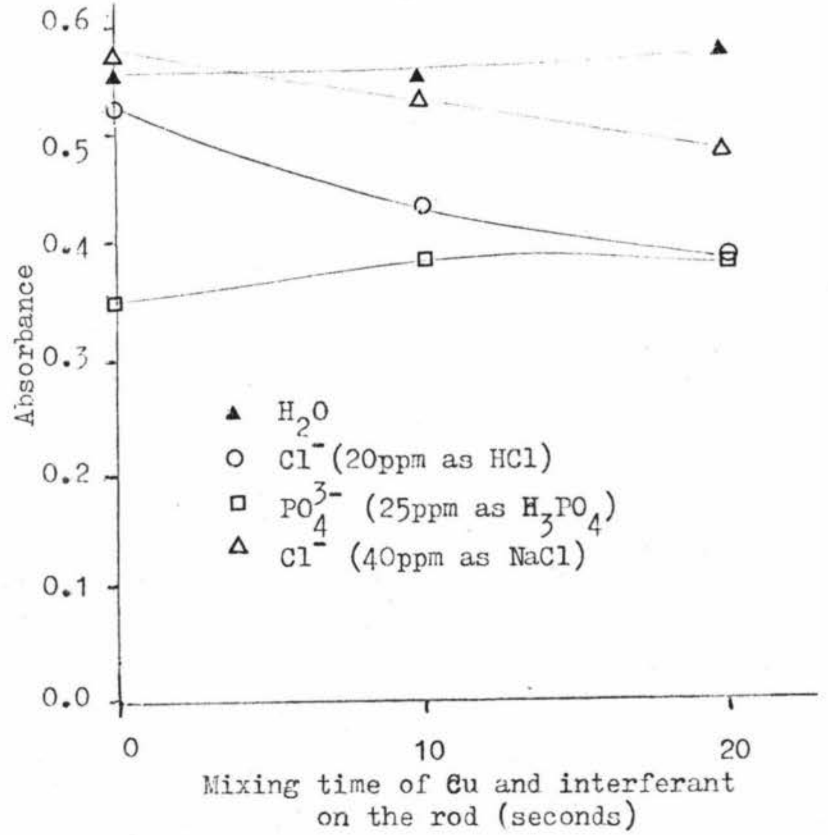


Fig. III 1-7b. Absorbances produced from atomization of Cu samples (5µl of a 2.5ppm Cu soln. as $CuCl_2$) from the rod after mixing with an interferant for the relevant time period.

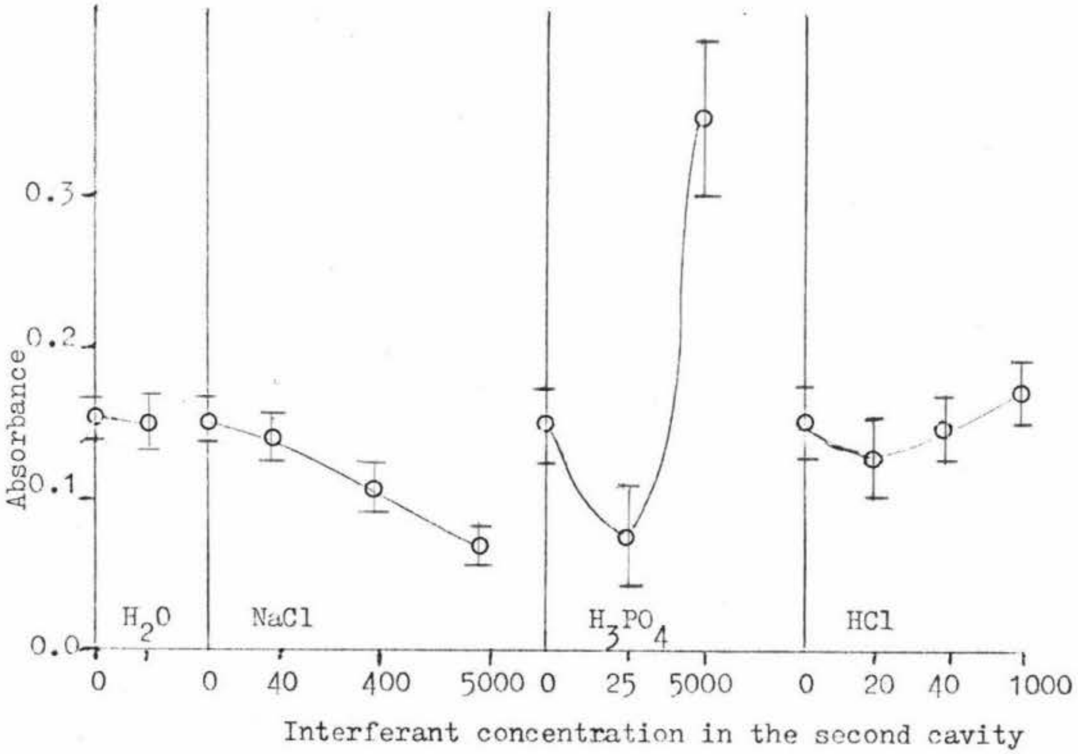


Fig. III 1-7c. The absorbances obtained when 5µl samples of a 0.5ppm Cu solution (as $CuCl_2$) are atomized from the furnace together with the given concentration of interferant in a second cavity. Atomization parameters are given in Table III 1-1; except that the ashing voltage used was 4.5V.

In these experiments[*] the signal is reduced by HCl and H_3PO_4 more than in the double cavity experiments. This is easily explained by the closer proximity of the interferent to the analyte in the single cavity compared with the double cavity rod. Thus the atomic vapour produced during the atomization stage would be more homogeneous and more of the analyte atoms are rendered less efficient in their light absorption properties in the former experiment compared with the latter. The difference between the two situations is slight compared with the overall suppression of the signal which indicates that the interference mechanism is the same in both cases.

D. Discussion.

In work reported after 1972 the three main conflicting theories on the mechanism of interference listed in an earlier section (page 36) have all received support in one or more papers. Although very little work has yet been carried out in depth, several interesting hypotheses have been supported.

Work on Cr determinations in the presence of 20 cations

[*] In the first case of 0s mixing time the Cu solution (as $CuCl_2$) was placed in the cavity first and during the drying stage the second sample was added - keeping the surface of the cavity just moist at all times. For the other points the copper solution was completely dried before adding the interferent for mixing times of 10 and 20s. (See Fig. III 1-7c).

as chlorides,[105] in analyses in the presence of 15 cations and anions,[106] and determinations of soluble Cd, Pb, Ag, In, in natural waters[107] all showed interferences of varying amounts. In all cases the authors suggested that the interferences were caused by the occlusion of the analyte atoms within condensed matrix particles after volatilization. Jackson et al.[103] consequently suggested that elements of similar volatility to chromium would interfere the most while Rattonetti[107] showed that the suppression of Pb signals from natural waters did not result from loss of volatile Pb compounds during drying/ashing as this temperature was varied from 50 - 300°C without altering the Pb signal. Clark et al.[106] found that with most elements interference occurred only when the interferent was present in relatively high concentrations.

Other workers[108-113] supported the hypothesis that the ease with which the analyte was vaporized was altered by the thermal stability of the salt matrix which in turn affected the rate of production of atoms decreasing the peak height. A paper presenting particularly good arguments is one by Lundgren et al.[112] Several workers[115-118] suggested an interference mechanism involving loss of the analyte by volatilization of undissociating compounds. (See Appendix I for additional interferences reported between 1972 - 1974).

Clearly, from the results in the double cavity experiments all the interactions investigated, except possibly for the H_3PO_4-Cu interaction, depress the Cu signal by decreasing the efficiency with which Cu atoms are produced in the vapour phase. These experiments indicate that the presence of any of the interferents studied in the matrix has little effect on the initial atomization efficiency of Cu, i.e. free Cu atoms are formed at the same vaporization rate irrespective of the presence of an interferent. However once free Cu atoms have been formed the suppression of the signal can be considered to occur in two different ways.

i) molecular recombination of the Cu atoms with other atomic and molecular species in the matrix volatilized by the atomizer.

ii) conglomerate formation of matrix components entrapping the Cu atoms.

With the help of these two models an explanation for the different suppressions experienced when Cu is atomized in the presence of HCl and NaCl can be offered. Because HCl volatilizes at a relatively low temperature little interference would be expected when HCl was atomized from the second cavity. However some HCl must still be present at atomization as the Cu signal is suppressed and since HCl crystal formation is unlikely under the experimental conditions used, the condensation of cuprous chloride in the cooler vapour region above the atomizer could effectively reduce the free Cu atom population.

In the case of NaCl it is possible for a regular crystal or conglomerate of molecules to condense rapidly, entrapping a Cu atom in the conglomerate or replacing one or more sodium ions with copper ions.

Capture of the copper atom within the crystal can be considered as occurring in two ways. The atom is physically entrapped within the 'spaces' in the crystal distorting the crystal but not breaking any bonds. Cu replaces one or more of the cations in the crystal, which is feasible because of the similar ionic radii ($Cu^+ = 0.96$Å, $Na^+ = 0.97$Å, $K^+ = 1.33$Å) and the similar electronic configuration ($\frac{1}{2}$ full 's' orbital with a full 'p' orbital).[120] The particles thus formed would be too small to cause any detectable light scattering with the apparatus used.* Consequently the entrapped atom would be unable to absorb any radiation. Some of the chloride present from dissociated NaCl molecules (see Discussion on Non Atomic Absorption Peak page 86) could combine with the Cu atoms in the vapour.

* Calculations based on the Mie Scattering Formulae given by Kerker[119] showed that for an absorbance of .06 to be obtained at 200 nm, using a viewing rectangle of width 10^{-4}m and height 5×10^{-3}m from a 5 µl sample of a 1000 ppm NaCl solution, spherical particles with an average radius of 9 nm would need to be formed. This much larger than the particle size considered as beihg formed here and hence no detectable light scattering would be expected.

The relative importance of each mechanism is difficult to ascertain. The mixing experiments on the rod indicate that although mixing of the analyte and interferent seriously affects the HCl-Cu mechanism (supposed Cu_xCl_y formation[*]) the NaCl-Cu suppression of the Cu signal is the same regardless of the time allowed for mixing. If chloride formation was the most important factor the length of mixing time on the atomizer would be expected to alter the degree of suppression experienced.

The furnace is more effective at reducing the interference because the vapour has a greater residence time in a high temperature zone. The conglomerate may still form, but at a reduced rate, or to a reduced extent.

In the case of HCl in the double cavity furnace the decrease in suppression experienced as the concentration of HCl increases could be explained by considering the time lapse needed for the same number of Cu_xCl_y molecules to form. At the higher HCl concentration a much greater Cl to Cu ratio would exist after a given time than at the lower HCl concentrations. More Cu_xCl_y molecules would be formed initially at the higher concentration but because of the longer residence time in the furnace proportionally more of them would be dissociated, than at the lower HCl concentrations.

[*] In the vapour phase the principal species appears to be a trimer with alternating Cu and Cl atoms.[120]

high concentrations of HCl vapour present.

$$XCu + YCl^- \rightleftharpoons Cu_xCl_y \qquad t = t_1$$

due to greater mixing

$$xCu + YCl^- \rightleftharpoons Cu_xCl_y \qquad t = t_2$$

low concentrations of HCl vapour present.

$$\left\{\begin{array}{ll} \text{Very little } Cu_xCl_y \text{ is formed due to very little mixing} & t = t_1 \\ xCu + YCl^- \rightleftharpoons Cu_xCl_y & t = t_2 \end{array}\right.$$

Similar arguments can be presented for KCl, HBr, NaBr, and KBr. The molecular condensation mechanism is favoured for the very slight interference caused by HBr and a combination of this mechanism and the entrapment mechanism for the alkali halides.

The entrapment mechanism of interference would account for the kinetic-effect-like curves obtained as the interferent concentration is increased because only a limited number of Cu atoms can be entrapped before the atomic cloud enters the light path.

Interference at low stoichiometric interferent/analyte ratios experienced in this work can still be explained in terms of the entrapment theory. The proportion of Cu atoms removed when the interferent is present at its lowest concentration together with <u>half</u> the number of interferent molecules available for each Cu atom removed are listed below. These results are calculated from the graphs in Figs. III 1-3 and III 1-4.

Interferent.	Percentage of Cu atoms removed (from signal decrease).	No. of interferent molecules / Cu atom. 2
NaCl	17	6
	19	5
KBr	13	4
	34	7.5

Interferences by such volatile acids as HNO_3, HCl, H_2SO_4 are unexpected in that all of the acid should have been removed. However because of the remarkable uniformity in signal suppression regardless of the acid anion present a similar mechanism must be operating in all of the investigations. If a molecular vapour condensation is considered to occur then it must occur very rapidly in that additional acid cannot effectively reduce the free Cu atom population in the vapour.

In the discussion on the enhancement by H_3PO_4 of Cu absorption, Price's definition of an enhancement in atomic absorption will be accepted, viz. "an enhancement is a decrease in or a suppressive effect already present in the system". The question as to whether or not the interference occurs in the vapour phase is not conclusively answered in the double cavity work. Only slight differences in the absorption occur in the situation where H_3PO_4 is atomized from a separate cavity with one exception. Marked enhancement is experienced when 5000 ppm H_3PO_4 is atomized from the second cavity in the furnace and the $CuCl_2$ solution is atomized from the first cavity.

The formation of molecular compounds between metal chlorides and graphite at elevated temperatures has been reported (e.g. $C_{13}CuCl_2$ at 600°C).[121a] The formation of this and associated compounds could effectively alter the rate of vaporization of Cu atoms from the atomizer. Because the enhancement at low phosphoric acid concentrations does not appear to occur in the vapour phase the formation of Cu phosphate compounds such as $Cu_2P_2O_7$ and Cu HPO_3 xH_2O (these are readily formed under the experimental conditions),[121b] would alter the vaporization behaviour before or during atomization. The formation of these compounds would prevent any of the graphite-copper chloride compound forming and because the former compounds are more easily dissociated than the latter the population of free Cu atoms is consequently increased.

Much greater enhancement is experienced when a <u>higher</u> concentration of H_3PO_4 is present in the atomic vapour cloud. Evidently, the H_3PO_4 vapour decreases a form depressive interference normally present when Cu solutions are atomized (after Price's definition of enhancement[9a]). A fairly comprehensive literature search failed to illuminate the mechanism of the enhancement. More extensive experimental study is needed before a mechanism could be postulated.

ii) LEAD.

A. Results.

In order to optimize operating parameters, experiments similar to those used for copper were carried out with Pb (as Pb $(NO_3)_2$) in solution.

A set of standard curves was obtained (Fig. III 1-8) for the analysis of Pb (as $Pb(NO_3)_2$) in water and in HNO_3 using several different atomization voltages. The optimum ashing voltage was determined as in Section III A (i). Similar graphs to the ones using Cu were obtained when Pb was atomized.

Because of the low volatility of lead a preliminary check was carried out on each atomizer in order to establish the optimum parameters before each individual experiment.

The instrumental parameters used throughout the lead analyses are shown in Table III 1-4.

Table III 1-4. Instrumental Parameters for lead analyses.

Wavelength (nm)	217.0	Dry	Voltage	4.8
Slit width (μ)	150		Time (s)	25
Slit height (nm)	4	Ash	Voltage	3.0
Lamp current (mA)	6		Time (s)	14
		Atomize	Voltage	3.1
			Time (s)	2.5
		Gas Flow Rate $1\ \text{min}^{-1}$	Ar	3.8
			H_2	2.2

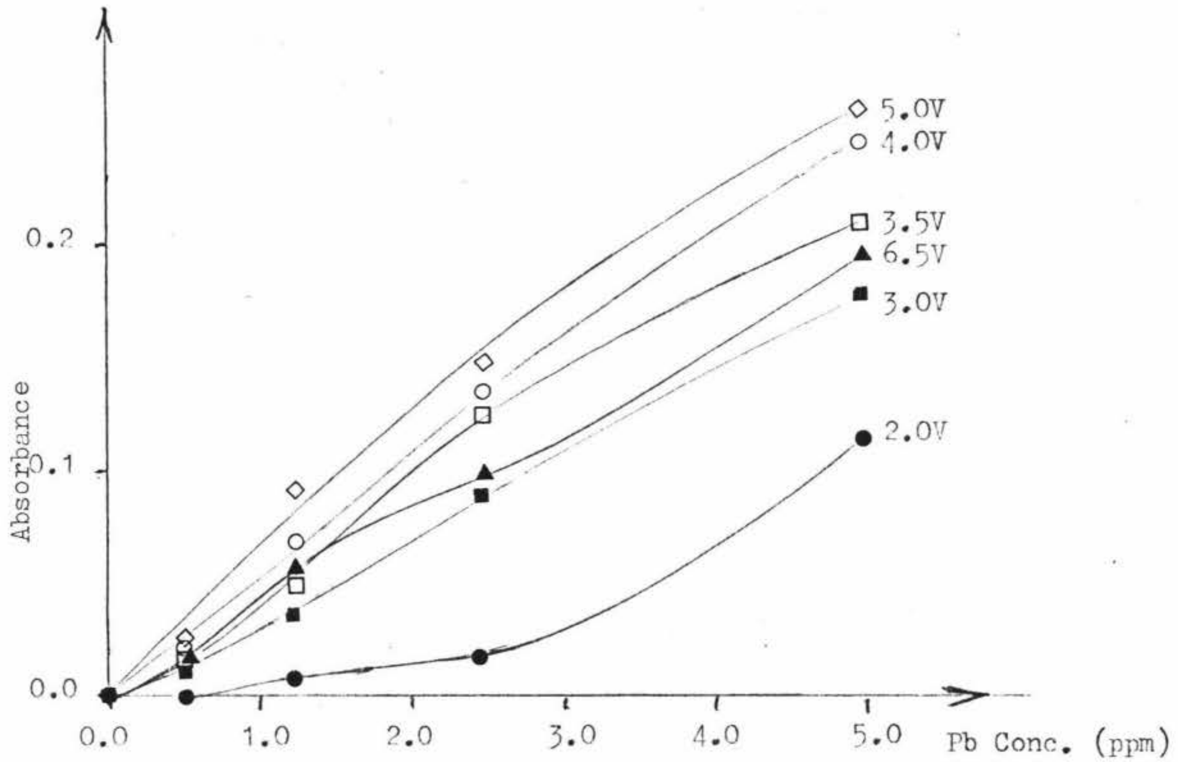


Fig. III 1-8a. Analytical curves obtained from 5μl samples of lead (as $Pb(NO_3)_2$) atomized from the rod using several different atomize voltages. The standards were prepared in distilled water.

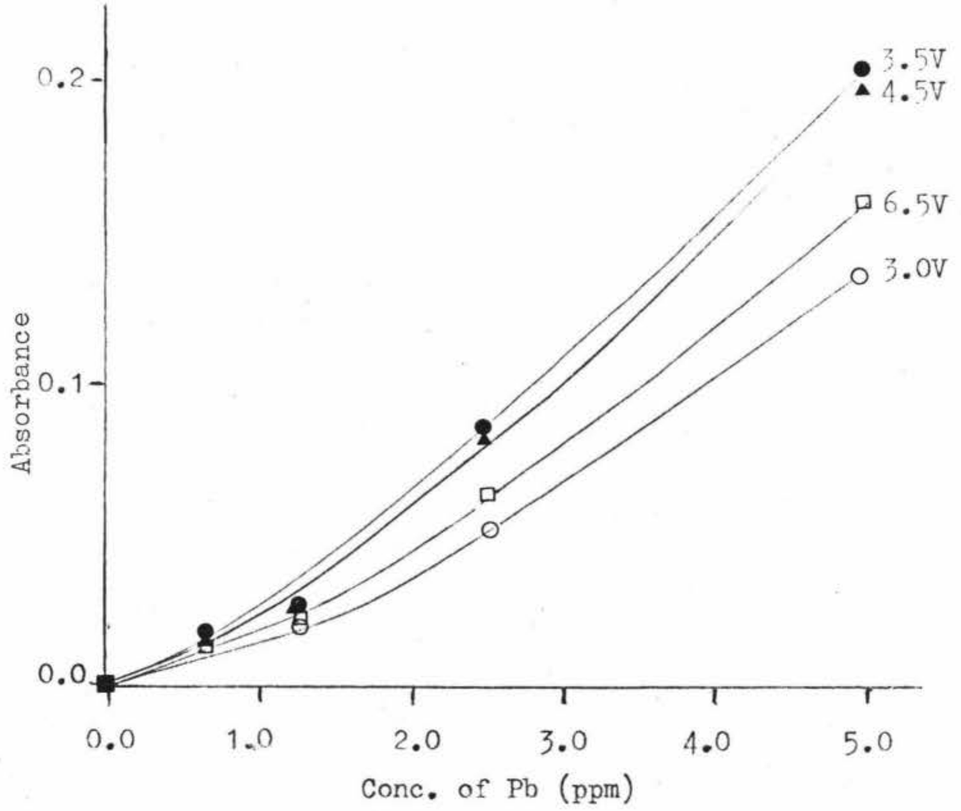


Fig. III 1-8b. Analytical curves of 5μl samples of lead (as $Pb(NO_3)_2$) dissolved in 2M HNO_3 atomized from the rod at four different atomizesettings. The instrumental settings utilized are given in Table III 1-4.

a) Effect of added acids (2M) on Pb signals.

Standard curves of Pb (as $PbNO_3)_2$) in hydrochloric and nitric acids (both 2 M) using the tube furnace as shown in Fig. III 1-9. A peculiar form of interference occurred at low lead concentrations (< .05 ppm). This is at a concentration lower than most other workers have shown on Pb standard curves and consequently this effect has not been reported before. This experiment was repeated using different solutions and the same effect was obtained.

b) Effect of NaCl and H_3PO_4. A series of solutions containing 2.5 ppm lead (as Pb $(NO_3)_2$) and increasing amounts of NaCl (0 to 5000 ppm Cl^-) were atomized from the rod. A similar set of solutions was prepared containing H_3PO_4 at concentrations between 0 and 2500 ppm PO_4^{3-}. These were also atomized from the rod. Both sets of results are presented in Table III 1-5.

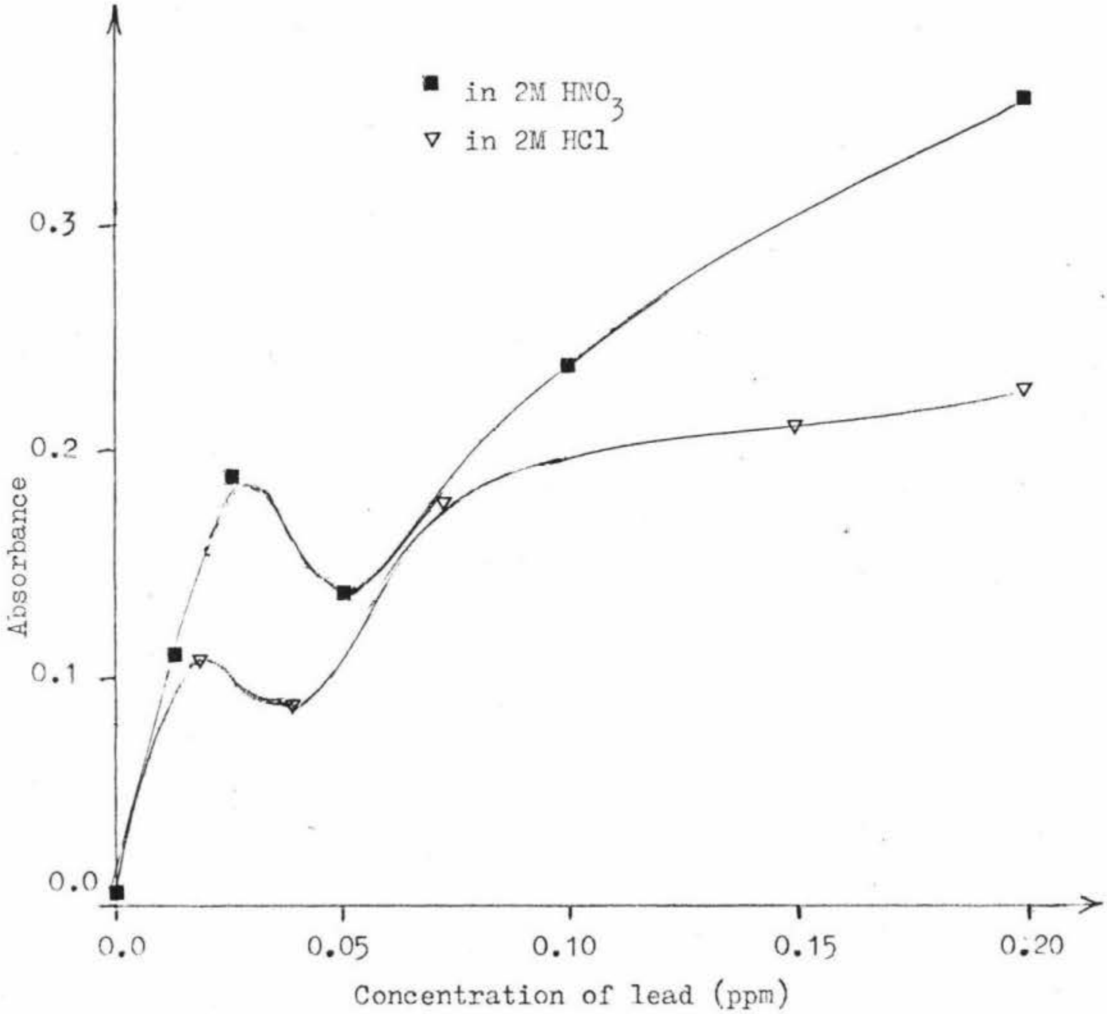


Fig. III 1-9. Analytical curves of lead obtained by atomizing 5µl samples of **lead** solutions (as $Pb(NO_3)_2$) in 2M HNO_3 and 2M HCl. The furnace atomizer was used with the instrumental settings given in Table III 1-4.

Table III 1-5. Effect of various concentrations of NaCl and H_3PO_4 on a 2.5 ppm Pb absorption signal atomized from a carbon rod atomizer. Atomization conditions are given in Table III 1-4.

Interferent.	Concentration (ppm)	Absorbance.	% change of signal
NaCl	0	.506	0
	5	.179	- 65
	20	.110	- 78
	50	.099	- 81
	100	.068	- 86
	200	.094	- 82
	400	.160	- 68
	800	.091	- 82
	5000	.078	- 85
H_3PO_4	0	.500	0
	1.25	.498	0
	2.5	.509	+ 2
	6	.453	- 9
	9	.413	- 17
	18	.508	+ 2
	75	.544	+ 9
	187	.500	0
	375	.504	+ 1
	750	.505	+ 1
	1250	.527	+ 5
	2500	.344	- 31

Because of the low ashing voltage used, to avoid the loss of any lead prior to atomization, a good proportion of the interferent was still on the rod for atomization.

Consequently a severe signal suppression is evident in the case of NacL even at low interferent concentrations of 5 ppm ([interferent] / [analyte] weight ratio = 2:1. At a concentration of 100 ppm NaCl the signal is suppressed to a minimum and the suppression decreases until 800 ppm after which a 'plateau' exists in the curve. Although the suppression of the signal occurs at very low interferent concentrations the suppression is altered by the amount of interferent present.

After the concentration of PO_4^{3-} has reached 200 ppm very little interference occurs until much higher concentrations are encountered (~2500 ppm). However variable differences in the lead absorption signal are shown for PO_4^{3-} concentrations of 0 - 200 ppm.

c) Double Cavity Interference Experiments.

The same atomizers used in Section III A 1 (a) were utilised here to investigate the vapour-phase effect of NaCl, HCl, H_3PO_4, H_2SO_4, HNO_3 on lead absorption signals. (See Fig. III 1-10 for results).

Two 5 µl samples were micropipetted on to the atomizer surface and then dried, ashed and atomized using the parameters listed in Table III 1-4, A 2.5 ppm Pb (as $Pb(NO_3)_2$) was used. Slight depression of the peak lead signal on the rod was caused by the addition of 'pure' water to the second cavity. Probably more of the

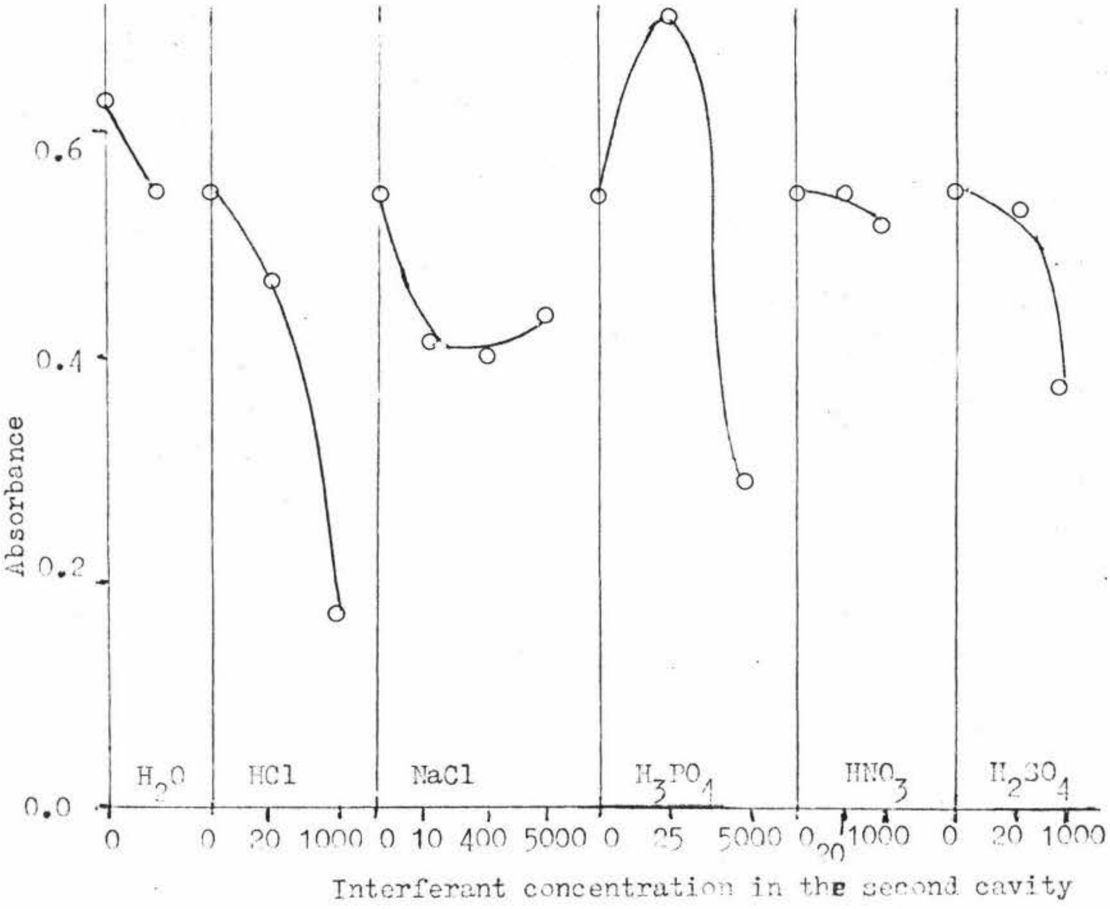


Fig. III 1-10a. Absorbances from 5μl lead (as $Pb(NO_3)_2$ in a 2.5ppm solution) atomized from the rod together with a 5μl sample of an interferant placed in the second cavity. Atomization conditions are given in the text (p. 69).

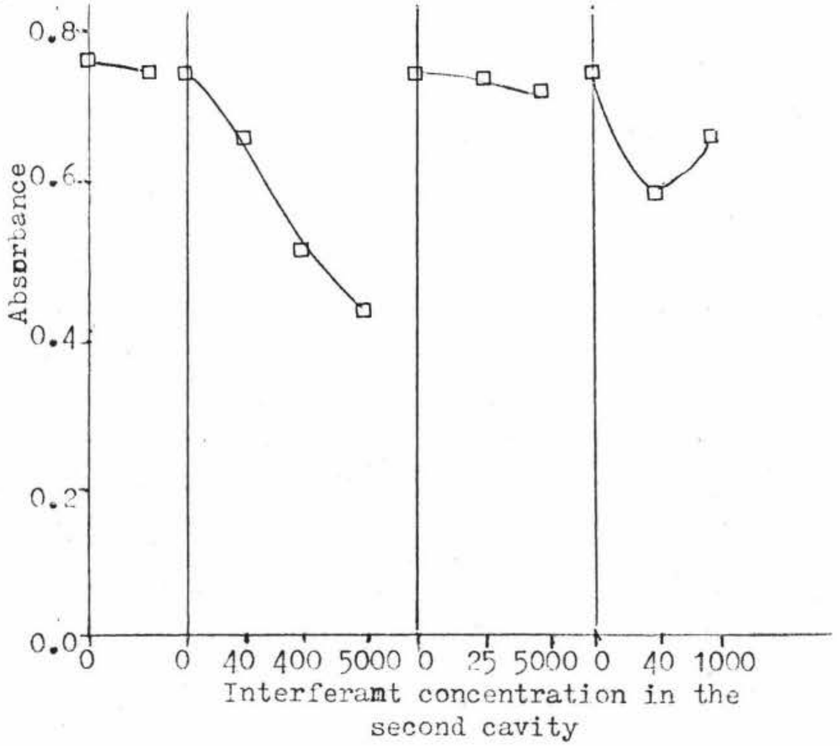


Fig. III 1-10b. A similar experiment to that above(III 1-10a) was carried out using a 0.5ppm lead solution, on the double cavity furnace.

analyte was absorbed into the top layer of graphite because of the slightly longer residence time on the rod compared with the atomization where only Pb solution present. An integrated signal would be expected to correct this difference.

1. H_3PO_4 Rod. Interference by H_3PO_4 on the Pb absorption followed the trend in the earlier experiment Table III 1-5. The degree of interference was of the same magnitude as that in the earlier experiment.

   Furnace. H_3PO_4 had very little effect on the Pb signal.

2. NaCl Rod. Fairly uniform interference occurred at the three concentrations used and is only different from the earlier experiment (where the two species were in the same solution) at the 400 ppm concentration. However overall the signal suppression is less than in the earlier experiment (Table III 1-5).

   Furnace. Interference was less than that experienced on the rod with the interferent in vapour form. Here again the effect of the interferent concentration differed from the experiment in Table III 1-5. Less interference was produced by low concentration levels of NaCl in these experiments than was produced using the same concentration in the single cavity.

3. HCl Rod. Depressive interference was more severe than that caused by NaCl and the interference increased with increasing interferent concentration.

Furnace. Slight suppression of the signal occurred but was less severe at the higher concentrations.

4. HNO_3 and H_2SO_4

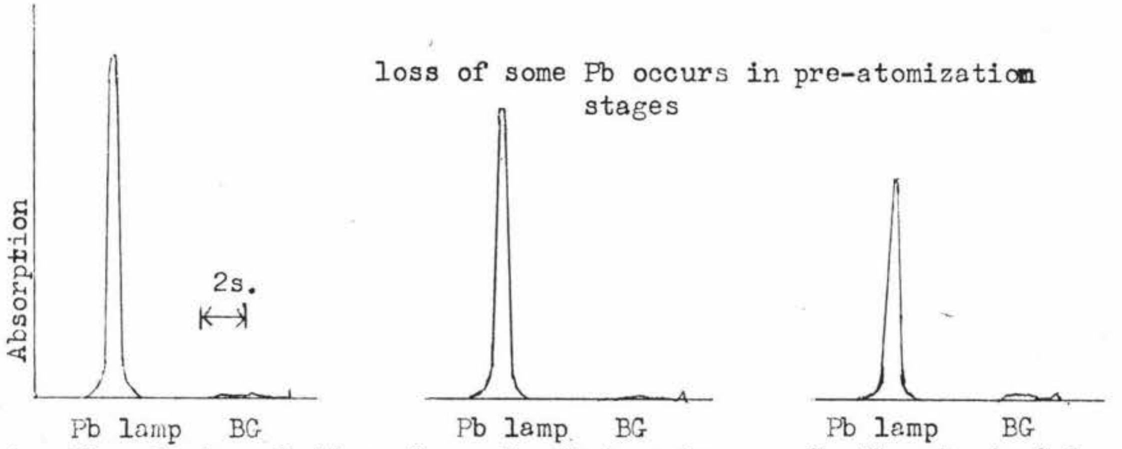
Both of these acids suppressed the lead signal using the rod atomizer. The suppression increased as the concentration of the interferent increased.

Peak Profiles - these are shown in Fig. III 1-11.

B. Discussion.

Although the double cavity experiments show that vapour phase interferences occur by co-crystallization or condensation of the analyte with interferent components, there is some evidence that compounds (which are not readily dissociated in the vapour) are formed on the atomizer surface. This is particularly true of the situation when NaCl was the interferent. Lundgren et al.[112] give some evidence that this interference is effected by a change in the rate of vaporization of the Pb. They suppose that premature loss from the atomizer of some Pb as $PbCl_2$ occurs in the early atomization stage, owing to the lower volatilization temperature of the $PbCl_2$ formed on the rod during the earlier heating stages. However, contrary to their conclusions, a considerable amount of vapour phase interference occurs with all the interferents investigated (NaCl, HCl, H_2SO_4, HNO_3, and H_3PO_4).

When the same concentrations of sodium chloride and hydrochloric acid are present, the lead signal is depressed by an almost identical amount. Thus the interference appears to be primarily a condensation effect rather than an entrapment of analyte atoms in



1. Pb only in solution ashing temp.= 350°C
2. only Pb in soln. ashing temp= 550°C
3. Pb only in Soln. ashing temp.= 750°C

4. NaCl + Pb ashing temp.= 350°C
5. NaCl + Pb ashing temp.= 550°C
6. NaCl + Pb ashing temp.= 750°C

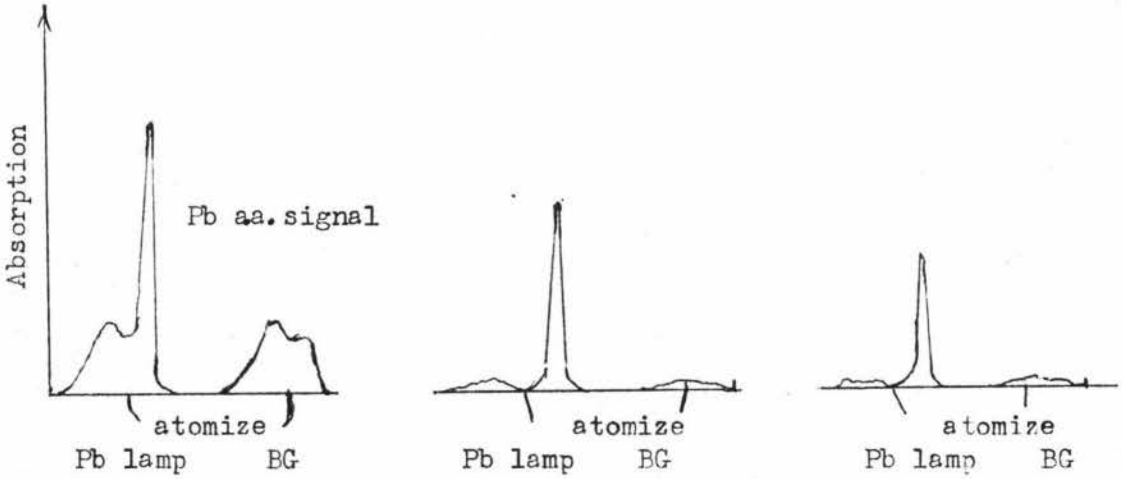


Fig. III 1-11. Absorption peaks profiles obtained from Pb atomization both in the presence and in the abscence of NaCl. (The BG signal is the signal obtained when using an H_2 continuum lamp).

crystals. Hydrochloric acid does not form crystals at these temperatures and the formation of mixed chlorides (as Pb_xCl_y) in the vapour is considered to be the most likely method of decreasing the yield of free Pb atoms.

A similar system is proposed for the vapour phase interference of nitric and sulphuric acids. The rate of the formation of $Pb_p(NO_3)_q$ and $Pb_r(SO_4)_s$ respectively would account for the different degrees of interference obtained.

In all the interferences discussed thus far (Pb in the presence of NaCl, HCl, HNO_3, H_2SO_4) a plateau is reached in the depression caused by the interferents in the Pb signal. This could be explained in terms of the time available for condensation to occur in the vapour phase before the atom cloud passes through the optical path. The extent to which the condensation of Pb atoms occurs may be limited by the time elapsed before leaving the light beam.

Changes in Pb absorption signal caused by the presence of H_3PO_4 occur almost exclusively in the vapour phase. An accurate explanation of this complicated interference behaviour could not be found in recorded work and more practical research is necessary to clarify the situation.

At higher H_3PO_4 concentrations the formation of a conglomerate containing Pb and PO_4^{3-} in the vapour phase would effectively reduce the population of free lead atoms. Compounds such as dimorphic $Pb_3(PO_4)_2$ (melting pt = 1104°C) or $3\left[Pb_3(PO_4)_2\right]$. $Pb\ X_2$ where X = F, Cl, Br, I or OH could form under the experimental conditions. These compounds form quite readily at elevated temperatures from lead or lead halide in the presence of orthophosphate.[121c]

iii) CADMIUM

A. Results

Effect of H_3PO_4 and NaCl on cadmium.

Cadmium was chosen as an analyte because its chemical and physical properties differed substantially from the previous two elements. However, like lead, it is an element of low volatility. Operational procedure was optimised for the element and the parameters used are listed in Table III 1-6.

Table III 1-6. Parameters used for cadmium analyses.

The absorption signal was amplified 5x for the rod experimen

Wavelength (nm)	222.88	Dry	Voltage	5.0
Slit width (μ)	150		Time (s)	25
Slit height (nm)	5	Ash	Voltage	4.4
Lamp current (mA)	3		Time (s)	15
		Ramp atomize	Voltage	4.6
			Rate (s)	10.0
		Gas Flow Rate $1\ min^{-1}$	H_2	2.2
			Ar	3.8

Difficulty was encountered in separating the cadmium atomic absorption peak from the non-atomic absorption component (Fig. III 1-13). To overcome this difficulty the ramp atomize mode was utilized whereby the applied voltage was increased at a constant rate. Thus the Cd atomic absorption signal was obtained first, completely separated from the non-atomic absorption signal following shortly afterwards ($\sim$0.5s). Clearly, the ashing voltage* used did not remove any Cd or very much NaCl either. A curve showing the optimum ashing voltage is shown in Fig. III 1-12a.

The results of the effect of concentration of H_3PO_4 and NaCl on Cd signals (.025 ppm Cd as cadmium acetate) using the rod and furnace atomizers are shown in Fig. III 1-12b.

Phosphoric acid on the rod and NaCl on both atomizers enhanced the Cd signal by a maximum of 30%. Interferent concentrations above 200 ppm caused little variation in the Cd signal regardless of the compound present. The furnace experiments showed less interference than the rod experiments with H_3PO_4 - in fact after a small initial depression of the signal at concentrations below 200 ppm H_3PO_4, no interference was experienced. Sodium chloride did not affect the absorption of Cd atomized from the rod as much as it did in the furnace. An enhancement of the Cd signal was caused by the addition of NaCl atomized in the furnace.

* An earlier comment is pertinent here. In order to obtain the same temperature with all the electrodes, unique voltage settings are required for each electrode.

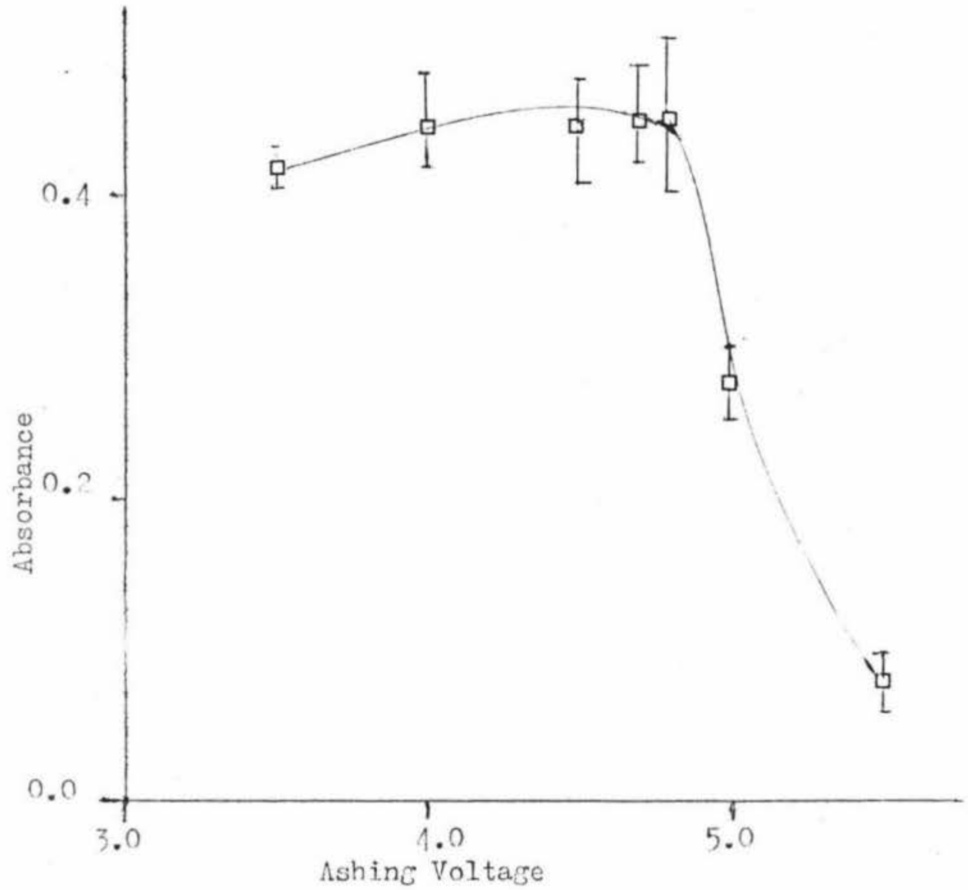


Fig. III 1-12a. Absorbances obtained upon atomization of .025 ppm Cd samples (5µl) after ashing for 15s at various voltages.

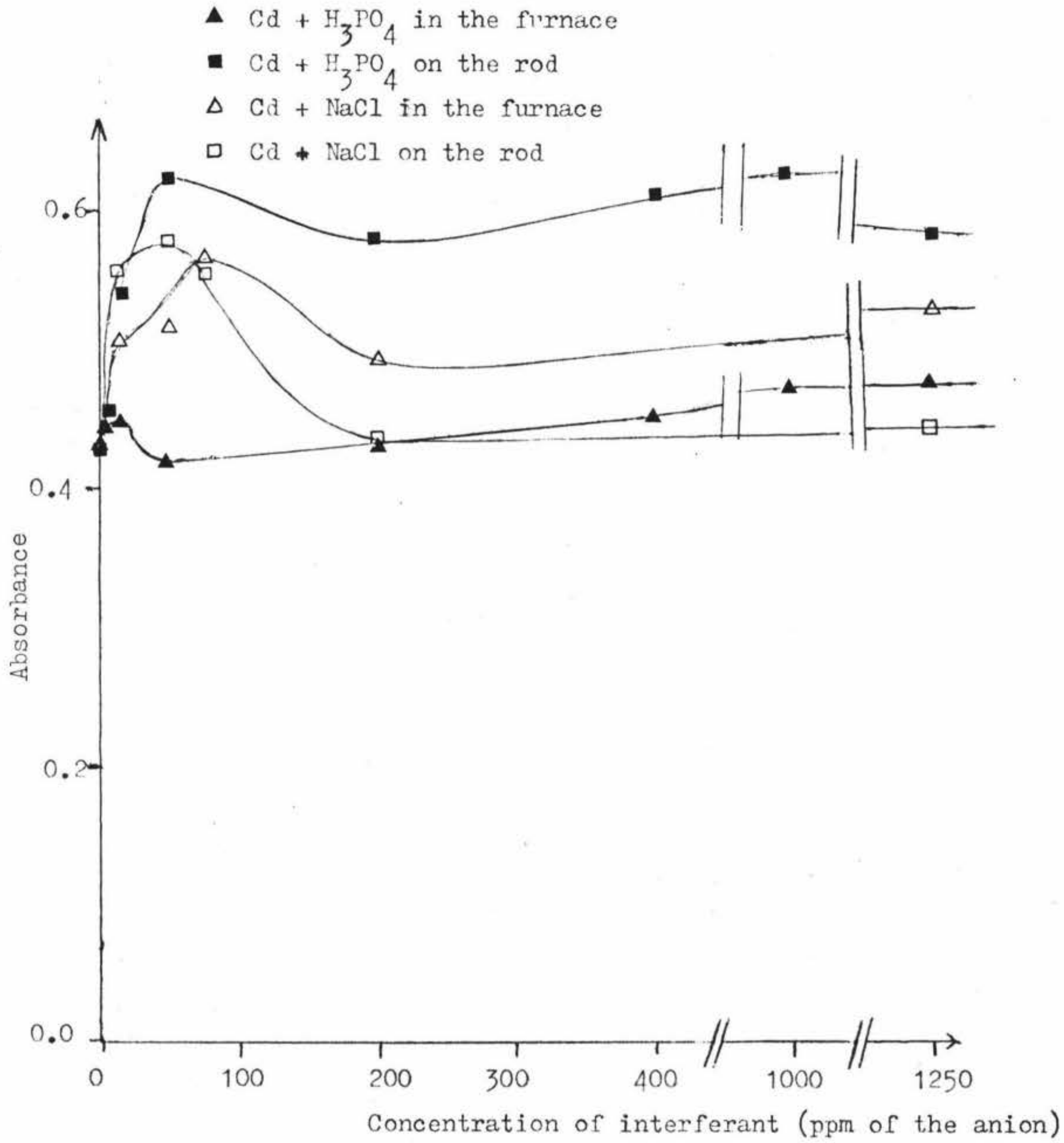


Fig.III 1-12b.Absorbances obtained from 5µl samples containing .025ppm Cd (as cadium acetate) and the relevant interferant at several concentrations. Both the rod and the furnace atomizers are used. Operational parameters are given in Table III 1-6. The absorption signals from the rod have been amplified by a factor of five.

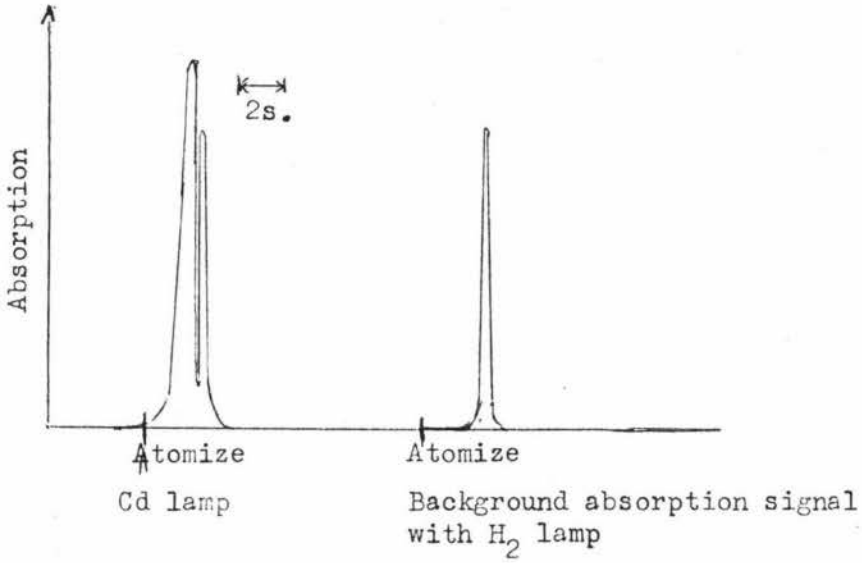
In all experiments corrections were made for background absorption.

Peak Profile: A non-specific absorption peak (especially from NaCl) appeared after the cadmium absorption peak (see Fig. III 1-13). This was due to the difference in volatilization temperature of the two substances and the separation of the two peaks was accentuated by the use of the ramp atomization mode.

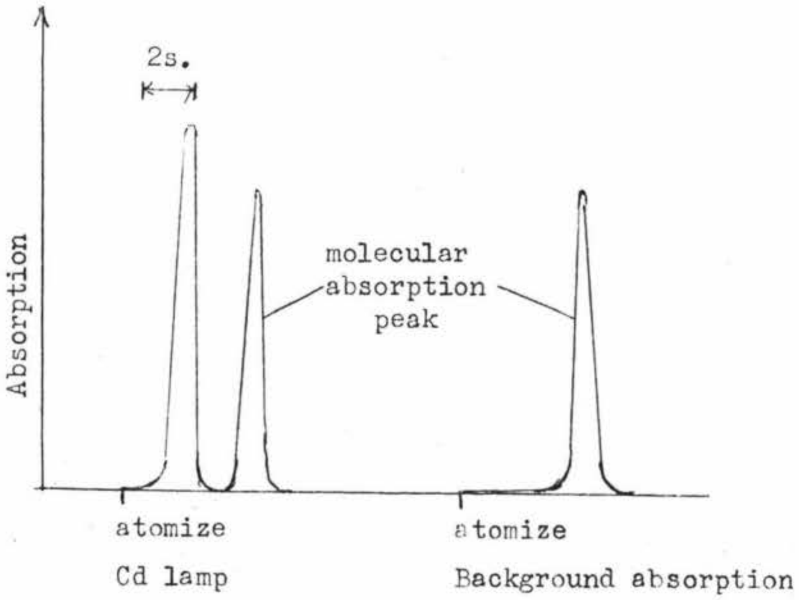
B. Discussion.

Lundgren et al.[112] favoured a rate-of-vaporization mechanism for NaCl interference of Cd signals. They maintained that because of the low atomization temperature of Cd, the signal would be dependent on the final temperature and its time of attainment. They eliminated practically all NaCl interference by rapidly raising the atomizer temperature to 820°C and maintaining this temperature ± 10°C for a few seconds. However all their work involved NaCl concentrations greater than 5,000 ppm.

From the results reported in this work, variations in the degree of interference caused by changing the interferent concentration are slight (over the concentrations used). Contrary to the results Lundgren et al.[112] found, only enhancement was found in these experiments. If the enhancement is caused by a change in the vaporization rate all the interferents must narrow the volatization



Cadium absorption peak profiles obtained when the step atomization mode is used for atomizing Cd solutions in the presence of NaCl. The first peak is the Cd atomic absorption peak, and the second is the interferant's molecular absorption peak.



Cd signals obtained by atomizing Cd solutions using the ramp atomization mode in the presence of NaCl.

Fig. III 1-13. Atomic absorption peak profiles from cadium solution analysis in the presence of NaCl.

temperature range and consequently decrease the time period over which the analyte is being vaporized. No evidence has been found here or in the literature indicating whether or not the interference occurs entirely in the vapour phase.

The presence of graphite may affect the type of interference (enhancement or depression) experienced by Cd atomized in the presence of H_3PO_4. Bratzel <u>et</u> <u>al.</u>[41] using a <u>platinum</u> atomizer found that H_3PO_4 depressed the Cd absorption signal. The overall effect would be an enhancement of the cadmium absorption signal obtained.

iv) ALUMINIUM.

A. Results.

Effect of NaCl and H_3PO_4.

Solutions containing 1.25 ppm of Al (as $AlCl_3$) were prepared with varying amounts of NaCl and H_3PO_4 present (0 - 2500 ppm as Cl^- and as PO_4^{3-} respectively). These were analysed under the following conditions on the rod and the furnace. (Ashing and atomization voltage/time settings were obtained in the manner previously described).

Table III 1-7. Parameters used for Aluminium analyses.

Wavelength (nm)	309.3	Dry	Voltage	5.2
Slit width (μ)	150		Time (s)	23
Slit height (nm)	5	Ash	Voltage	8.0
Lamp current (mA)	7		Time (s)	14
		Atomize	Voltage	6.2
			Time (s)	3.0
		Gas Flow Rate 1 min^{-1}	Ar	3.8
			H_2	2.2

Aluminium was chosen mainly because of its higher volatility compared with Cu, Pb or Cd and because it is normally not very sensitive to analysis by atomic absorption. The rod atomizer was not sensitive enough to give reproducible readings even when using 20x scale expansion. Step atomization was used in these experiments. A curve similar to that in Fig. III 1-12awas obtained for the determination of the ashing setting.

Using the settings in the table above ensured that in the case of NaCl as interferent all of the interferent was removed during ashing without removing any of the Al (checked out with Al solutions and Al in the presence of NaCl). Results are presented in Table III 1-8.

Table III 1-8. Absorbance signal of 1.25 ppm Al in the presence of different concentrations of NaCl and H_3PO_4. The difference in each signal compared with that of a solution free from NaCl and H_3PO_4 is expressed as a % enhancement (+) or % suppression (-).

Interferent.		Interferent Concentration. (ppm)	Absorbance* from 1.25 ppm Al in presence of interferent.	% change in signal
NaCl		0.0	.298	0
		.025	.275	- 7
		1.0	.282	- 5
		5.0	.285	- 4
		10.0	.304	+ 3
	visible smoke appeared during ashing but was not detected by the apparatus	50	.328	+ 10
		75	.232	- 22
		200	.218	- 26
		800	.188	- 37
		2500	.177	- 60
H_3PO_4		0.0	.298	0
		.025	.342	+ 15
		1.0	.309	+ 4
		2.0	.352	+ 18
		12.5	.365	+ 22
		50	.394	+ 32
		200	.410	+ 37
		400	.370	+ 24
		1000	.402	+ 35
		2500	.439	+ 47

* all absorbances have r.s.d. ± 5%

All the results were corrected for any background absorption (very little appeared).

It is evident that, in the furnace, suppressive interference by NaCl and enhancement by H_3PO_4 is quite severe even when it is suspected that all of the interferent has been removed from the atomizer during the ashing stage.

Peak Profiles: No non-specific absorption of any consequence (i.e. other than electronic 'noise') occurred and the peaks produced during atomization were from Al absorption only. During the ashing stage no peak appeared even though NaCl and H_3PO_4 were probably being removed. The evidence for this removal was

a) the absence of any non-atomic absorption peak during atomization

b) the appearance of smoke during the ashing stage when the higher concentrations of NaCl were used.

B. Discussion.

The presence of comparatively volatile compounds causes considerable interference. Two opposing competitive effects seem to be operating when NaCl is in the solution along with Al. Entrapment of Al atoms within NaCl particles could account for the more severe suppression ($Al^{3+} = 0.54\mathring{A}$ radius)[120] appearing above 75 ppm NaCl. The formation of mixed chlorides could account for the removal of some of the atoms.

Formation of Al_4C_3 at high temperatures [121f] (~2000°C) may partially account for the relatively low sensitivity of Al determinations from graphite atomizers.* The presence of phosphate which forms a compound with Al stable up to 1200°C ($AlPO_4 . x H_2O$) could reduce the formation of Al_4C_3 thereby enhancing the Al absorption signal.

v) ANALYSIS OF RESIDUAL ELEMENTS ON THE ROD AFTER ASHING.

A. Results

To obtain an even better understanding of the interference mechanism an investigation was undertaken to ascertain the ratio of the species (analyte and interferents) present on the atomizer at atomization (i.e. after ashing).

An experiment was devised whereby the element from the solution placed on the rod remaining after ashing at various voltages

* It is well known that Al is not very sensitive in atomic absorption. However graphite atomizers are less sensitive for some elements (including Al) than are non-graphite flameless atomizers.

for 10 seconds was determined. The systems used were Na, Cu, Pb and Al in the presence of Cl^- in amounts corresponding to their compound ratios from NaCl, $CuCl_2$, $PbCl_2$, $AlCl_3$. These compounds were dissolved in distilled, double-deionized water to give concentrations of 1600 ppm for Na (as NaCl) and 1000 ppm for Cu, Pb and Al.

The sample (5 µl of a 1000 ppm solution except for NaCl) was then placed on the rod, dried, and then ashed at a set voltage. At this point the power pack was switched off. The rod was then carefully removed from the workhead by tweezers and placed into a stoppered poly-ethylene phial containing 3 cm^3 of doubly-deionized, distilled water. After 3 minutes of shaking the rod was taken out of the phial by tweezers, allowed to drain for a few seconds and then placed back into the work-head ready for the next sample. Care was taken to clean the work-head initially and to avoid touching the rod at any time to prevent contamination.

Dilution of 5 µl (sample size) of 1000 ppm to 3 cm^3 gives a final concentration in the phial of 2.67 ppm with respect to Na and Cl from NaCl, 1.67 ppm for Cu, Pb and Al, 3.34 ppm for Cl^- from Pb and Cu, and 5.00 ppm for the Cl^- from Al.

Chloride as interferent was chosen because;

i) it is relatively easy to analyse by using a chloride-ion specific electrode,

ii) these elements have been previously studied in this work for chloride interferences,

iii) the last three cations showed interferences from even low concentrations of added chlorides.

The temperature at which the elements were lost was determined by the method used by Hwang *et al.*[101] This entailed constructing a curve of voltage setting *versus* temperature (for a particular rod) by observing the voltage applied needed to just melt a series of metals whose melting points were known.

The standard curves for the cation analyses Na (flame photometer) Cu and Pb (air-acetylene flame A.A.), Al (nitrous-oxide acetylene flame A.A.) were all straight curves over the range needed. (Refer to Table III 1-9 for analyses parameters).

Table III 1-9. Parameters used for the analysis by flame a.a. of the residual cations left on the rod after ashing

Wavelength nm	Slit Width. (μ)	Gas Flow Rate (Gas Flow Meter) units			Element
		air	acetylene	nitrous-oxide	
	150	8.0	4.0	-	Cu
	150	8.0	4.0	-	Pb
	150	10.0		6.0	Al

The results of all these experiments including the standard curve for chloride ion determinations are shown in Fig. III 1-14 (a) to (c).

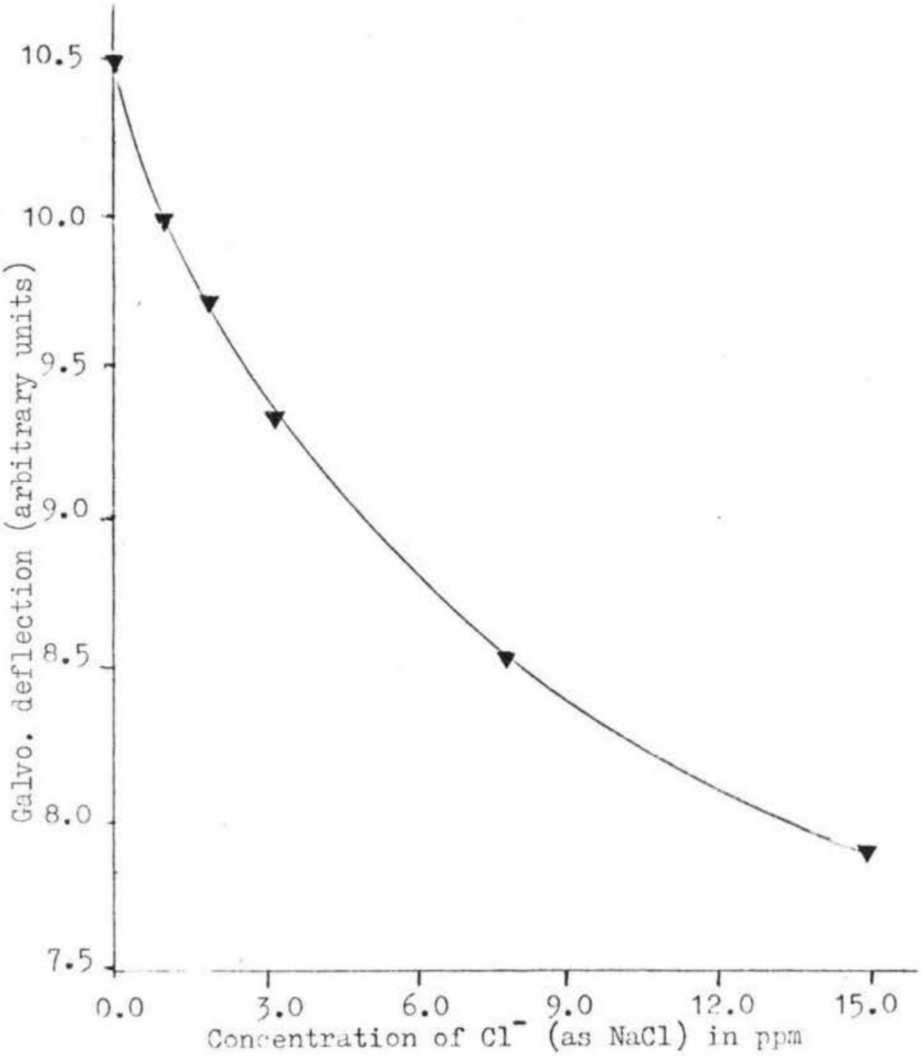


Fig. III 1-14a. The standard curve obtained with the Chloride Electrode for use in the determination of Cl$^-$ in the residual experiments.

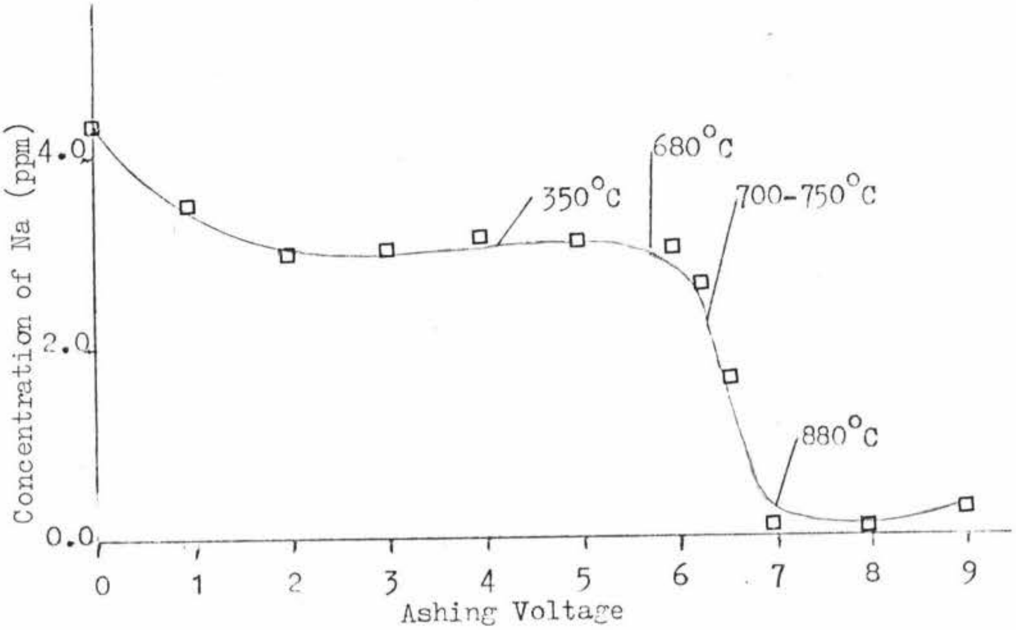


Fig. III 1-14b(i). The concentration of sodium (analysed by flame photometry) in 3cm^3 of NaCl from residue experiment. Five µl of a 1600ppm NaCl solution was ashed at various voltages for 10s and then shaken with 3cm^3 distilled water for 3 min. The concentration of this solution is shown above.

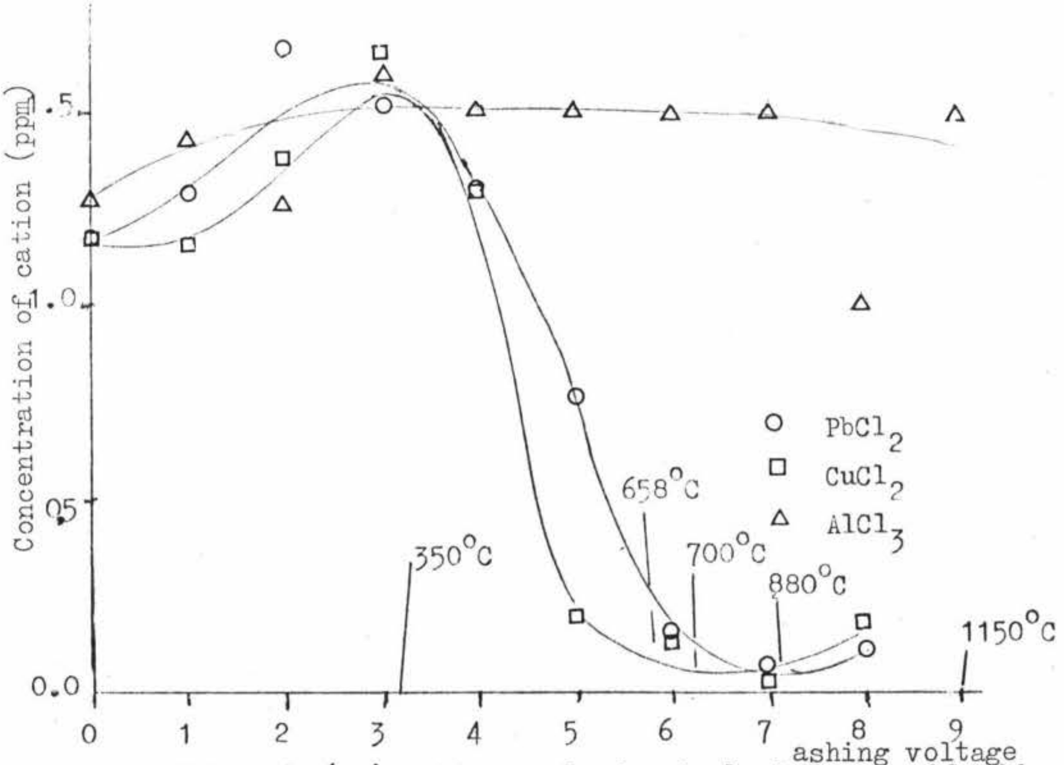


Fig. III 1-14b(ii). Copper, lead and aluminium as chlorides left on the rod after ashing at stated setting for 15s. The metal remaining was extracted into distilled H_2O (as in the above expt.), and analysed by flame a.a.

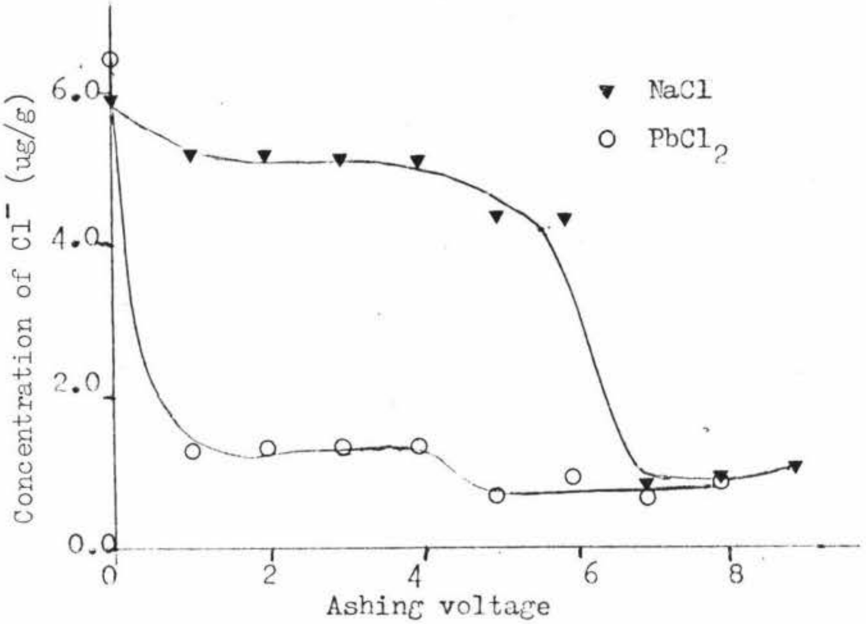


Fig. III 1-14c(i). The water soluble Cl residue on the rod after ashing 5µl samples of 1000ppm and 1600ppm $PbCl_2$ & NaCl solutions respectively. The samples were ashed at various voltages.

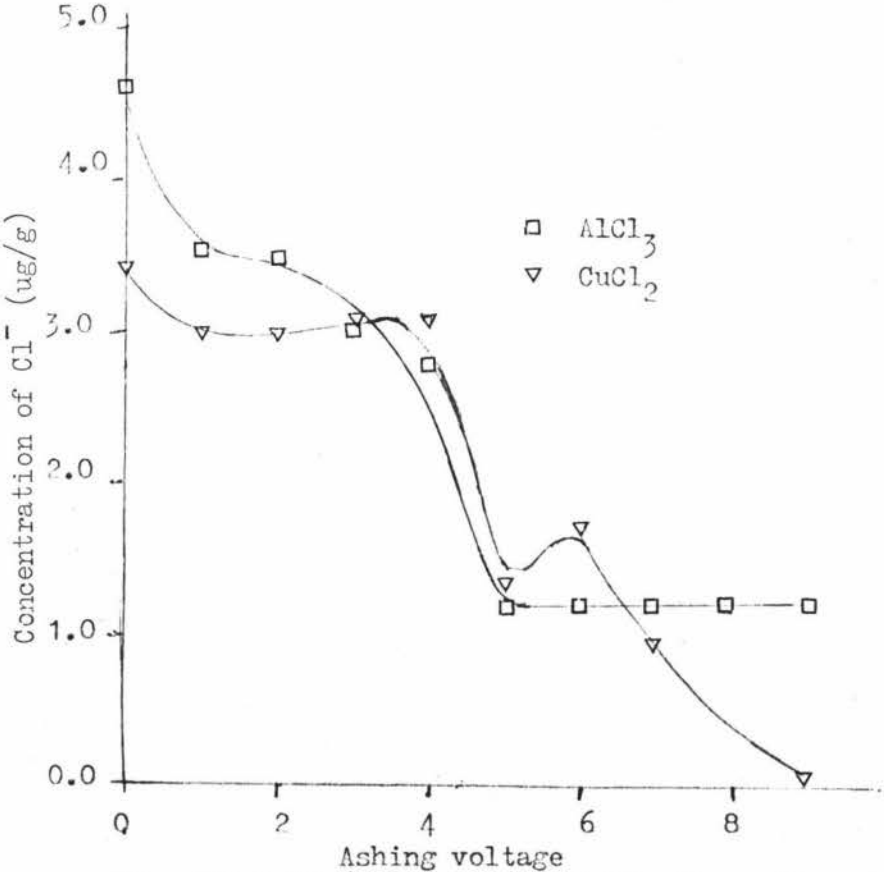


Fig. III 1-14c(ii). Water soluble Cl residues left on the rod after ashing at various voltages 5µl samples of $AlCl_3$ & $CuCl_2$ (1000ppm) solutions.

NaCl. From the NaCl set of curves the loss of Na is paralleled by the loss of Cl^- at all temperatures. However after an initial loss of both species nothing more is lost until a temperature of ~ 720°C is reached. At this temperature both species begin to be volatilized. At 860°C very little of either species remain on the rod in a water extractable form.

$CuCl_2$. The $CuCl_2$ results are similar in that the loss of Cu and Cl parallel each other almost exactly. However initial loss of both elements occurs at a relatively low temperature (~400°C). Most of the Cu is lost by 700°C but at this temperature the decrease in Cl^- concentration is equivalent to the loss of only one Cl^-. The second Cl^- is volatilized slowly as the temperature increases.

$PbCl_2$. Although the loss of Pb from the rod occurs over the same temperature range as does the loss of Cu,the loss of the Cl^- does not correspond with the loss of Cl^- from Cu. In fact the Cl^- loss from Pb is seemingly independent of the final Pb concentration. At a temperature of ~250°C the (Cl^-) is equivalent to about 0.4 of the expected theoretical concentration and does not correspond to the retention of 1 Cl^- per Pb atom (actual ratio is 0.8:1),

$\underline{AlCl_3}$. In general, aluminium is not lost from the rod at any temperature $< 1200^{\circ}C$. The loss of the equivalent of 1 Cl^- in every $3Cl^-$ occurs by $\sim 230^{\circ}C$ and this level is maintained to $\sim 350^{\circ}C$ when the equivalent of one more Cl^- is removed from the rod. The final plateau concentration is of similar concentration as that obtained in the $PbCl_2$ experiment.

In all these experiments a background level of Cl^- is reached, possibly due to slight contamination from the rod support blocks.

B. Discussion.

The loss of chloride from the rod closely follows the atomization of copper and sodium from the rod. However loss of Cl^- is independent of the atomization of Al and Pb. Conclusive discussion can not be given due to lack of knowledge of the nature of the compound on the surface of the rod prior to dissolution in the solution analysed. Also the concentration of the elements on the rod are much greater than in the analytical situation. Nevertheless some limited explanations will be advanced.

Donega and Burgess[42] expected the loss of aluminium to occur as $AlCl_3$ from flameless atomizers. These experiments indicate that although two thirds of the chlorine atoms have been lost at a temperature of 350-400°C no aluminium is lost even at temperatures exceeding 1100°C. Thus premature loss of aluminium as $AlCl_3$ would not be expected to be the cause of any suppression in the aluminium absorption signal in the presence of chloride.

The equivalent of 1 in every 3, and 1 in every 2 chlorine atoms from $AlCl_3$ and $PbCl_2$ respectively are lost at a very low temperature, ~ 200°C. This could be due to hydrolysis and the loss of Cl as HCl, the remaining Cl atoms still being bound to the respective cation.

Sodium chloride molecules or conglomerates of sodium chloride molecules appear to be volatilized, rather than dissociated sodium and chlorine atoms.* This is very important in the consideration of the analyte-atom entrapment theory. It should be noticed that the temperature at which these molecules are lost is very close to that at which the Cu and Pb are atomized. (NaCl causes severe suppression of the Cu and Pb absorption signals).

These experiments indicate that aluminium and lead are not lost from the rod as $Al\,Cl_3$ or $PbCl_2$ molecules but sodium is lost as NaCl molecules.

The copper experiment does not give any clear indication as to whether or not individual atoms of copper and chlorine are lost or if $CuCl_2$ molecules are volatilized from the rod surfaces. If $CuCl_2$ molecules were volatilized rapid dissociation must occur before atomic absorption could occur.

* Support for this is given in the following section (III 1 - vi).

vi) INVESTIGATION OF THE NATURE OF THE NON-ATOMIC ABSORPTION PEAKS.

Non-atomic absorption peaks were noticed in earlier experiments when analytes were atomized in the presence of some interfering compounds. The compounds giving the strongest non-atomic absorption peaks were the alkali halides. These compounds also affect the analyte atomic absorption signal more than any other compounds investigated here and elsewhere.[36,32,85,17] However other compounds used also gave some very small non-atomic absorption peaks e.g. H_3PO_4.

In view of the differences in the severity of interferences claimed by authors using different atomizers, the comparison between the three atomizers was continued into this investigation.

A Potassium iodide wavelength dependance curve has been reported by L'vov.[32] Little other work on the nature and characteristic features of non-atomic absorption peaks has been reported. It was hoped that any link which might exist between the presence and character of the non-atomic absorption peak and the loss of analyte would help in the elucidation of the nature of the interference.

Throughout all the experiments Ar and H_2 gas were supplied to the workhead at flow-rates of 3.8 $l\ min^{-1}$ and 2.2 $l\ min^{-1}$ respectively. This was done in order to increase the signal as much as possible i.e. conditions were optimised for good atomic absorption and minimal interference.

The concentration of the solutions are expressed as parts per million of the anion (Cl^- or Br^-).

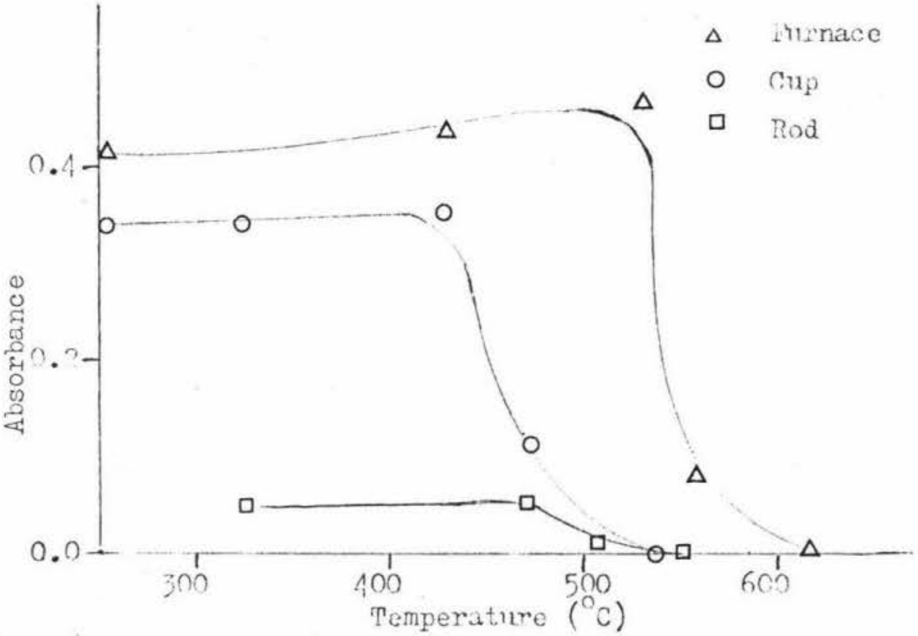
Volatilization conditions for NaCl and KBr.

To investigate volatilization conditions for NaCl and KBr in each of the atomizers an 800 ppm solution was placed on to the atomizer in 5 µl portions, dried at 4.0v for 20s and then ashed at different voltage settings for varying lengths of time. The non-atomic absorption signal was then obtained by atomizing the sample at 1800°C. The signal was measured at 250 nm using a hydrogen continuum lamp operated at 25 mA. The slit width and height were those normally used (150 µ and 5 mm). The results for NaCl are shown in Fig. III 1-15.

Potassium bromide was lost from the atomizers between ashing temperatures of 470°C to 530°C using an ashing time of 25 s. The temperatures were obtained by the method mentioned previously (section III 1-V).

The atomization temperature utilized (1800°C) was the optimum temperature for Cu atomization. This temperature was chosen because of the earlier experiments on copper in the presence of alkali halides in which serious interference occurred.

The NaCl was more readily lost than KBr from the atomization systems. The sensitivity of the system in detecting non-atomic absorption was in the following order: furnace > cup > rod. (see Fig. III 1-16).



Fig, III 1-15a. Absorbance signal on atomizing at 1800°C after ashing under given conditions on the three atomizing devices. An 800ppm NaCl solution was used for an ashing time of 25s. The lamp was an H_2 continuum lamp operated at 25mA.

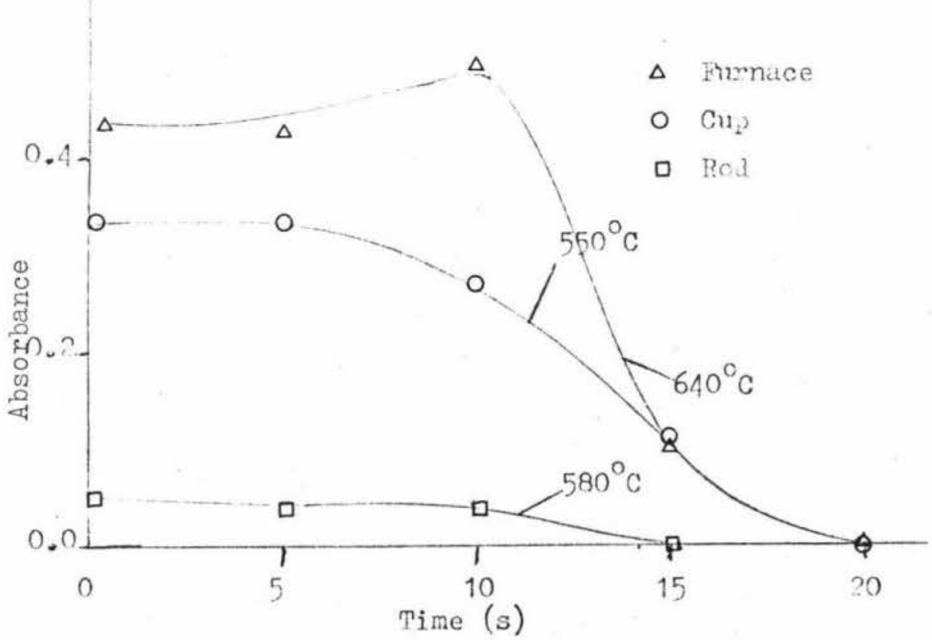


Fig. III 1-15b. Absorbances obtained from 800ppm NaCl (5µl samples) upon atomization at 1800°C after ashing at 6.0V for the times given.

Concentration-dependence of the non-atomic absorption peak.

Two series of solutions with increasing concentrations of NaCl and KBr were analysed on all the atomizers. An ashing temperature was chosen to ensure that the alkali halide was retained for atomization (i.e. ashing temp. $< 460^{\circ}C$) and the atomization temp. was $\sim 1800^{\circ}C$. The concentration at which each alkali halide could first be detected leaving the atomizer is listed in Table III 1-10.

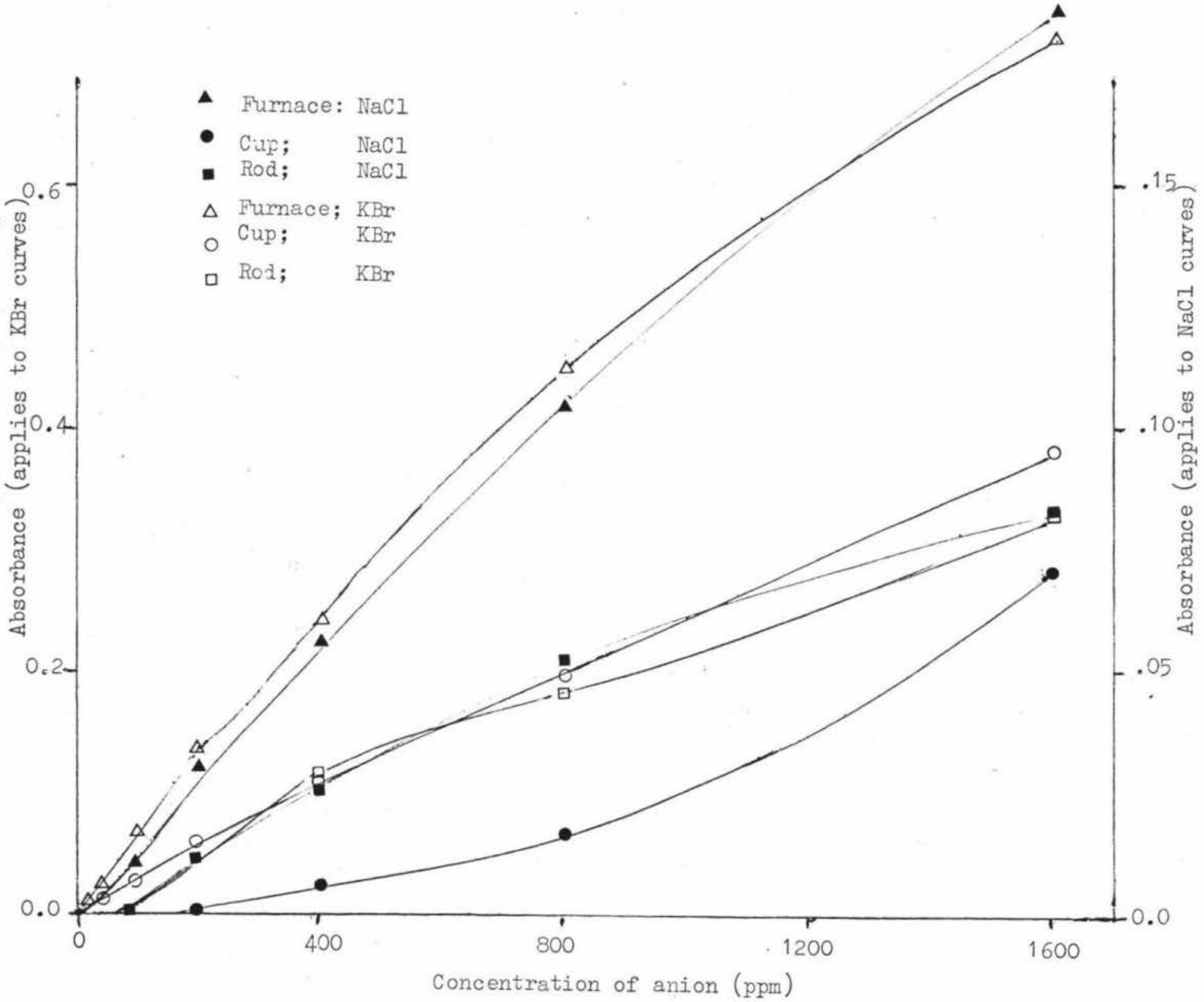
Table III 1-10. Concentrations of the alkali halide at which it could first be detected as being lost from the atomizer using a H_2 continuum lamp at 250 nm. Smoke from the atomizer was also noticed at these concentrations.

	atomizer		
alkali halide	rod	cup	furnace
KBr	100 ppm	20 ppm	25 ppm
NaCl	100 ppm	200 ppm	30 ppm

Wavelength dependence of non-atomic absorption peak.

As mentioned earlier (Chap. II) little distinction has been made between the contributions of light scattering and molecular absorption. To help establish the nature of the non-atomic absorption peak, the wavelength dependence of the non-atomic absorption

Fig. III 1-16.
NaCl and KBr non-atomic absorption peak absorbances at several concentrations from the furnace, cup and rod atomizers. An 1800°C atomize temp. was used in all curves with an ashing temp. of 450°C. The observation wavelength was 250nm with an H_2 lamp.



signal was plotted using various concentrations and different atomization temperatures. The effect of the three different atomizers on the curves obtained were compared together with the relative sensitivity of each atomizer with respect to the signal.

Figs. III 1-17 (a) and III 1-17 (b) show the absorption spectra of NaCl and KBr (between wavelengths of 190 and 330 nm) using the three atomizers. The absorption spectrum is clearest when the furnace is used, because of the high residence time of the vapour in the absorption path. The spectrum produced by the rod atomizer is noticeably lacking in detail but contains a minimum comparable with the cup and furnace although the maxima are very broad bands and are barely distinguishable from the general trend of decreasing absorption with increasing wavelength.

A solution containing 800 ppm NaCl gave almost the same spectra on all atomizers as the spectra shown in Figs. III 1-17a and III 1- 17b although a slight loss of detail was evident. A 100 ppm solution gave very little absorption at all (as is indicated by Fig. III 1-16).

A comparison was made of the spectra obtained from 100 ppm, 800 ppm and 5000 ppm NaCl solutions on the rod using the H_2 continuum lamp and the lamps listed utilized at the wavelengths indicated. The lamps were all operated at the manufacturers' recommended current settings.

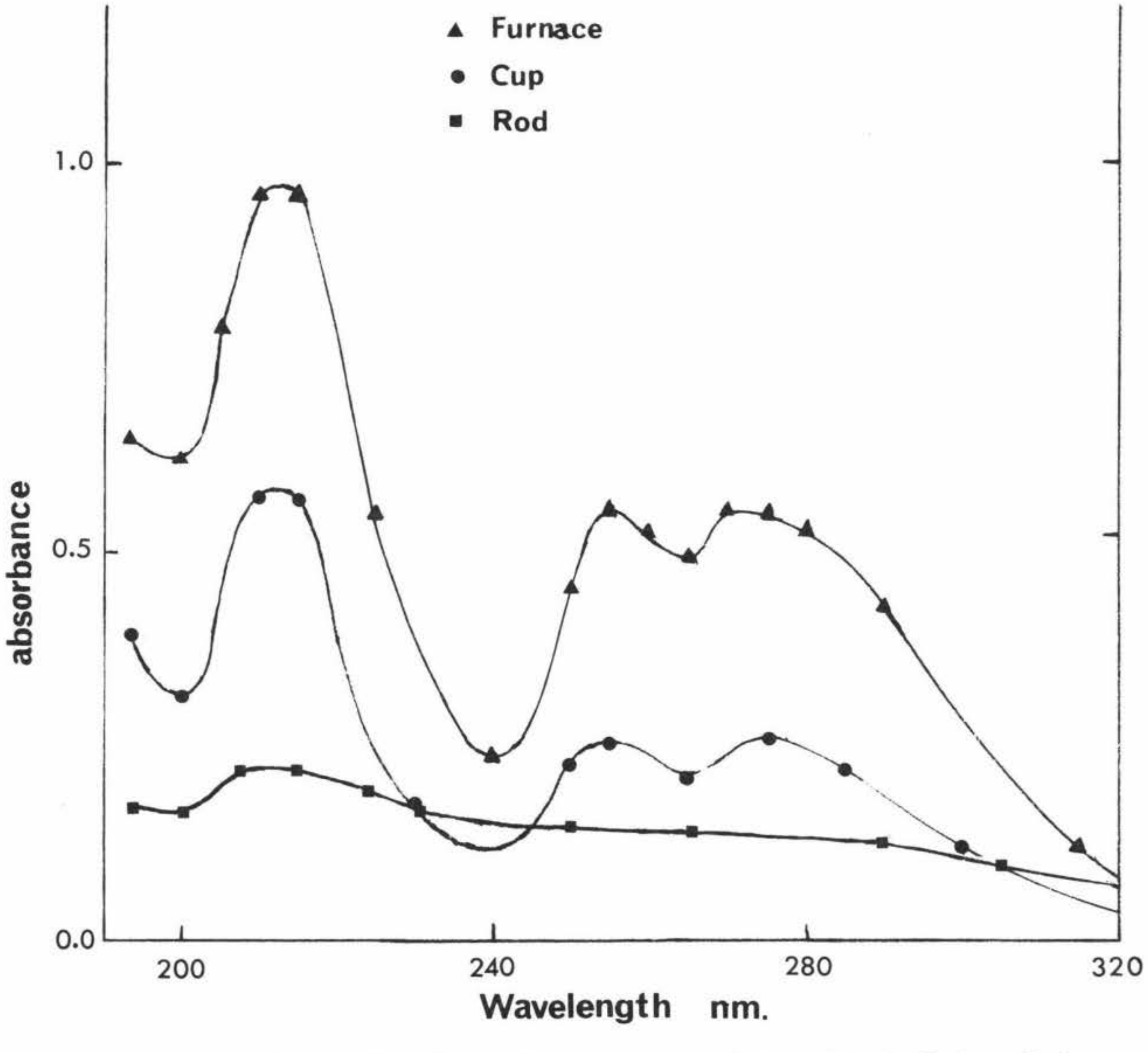


Fig. III 1-17a. The absorption spectrum of KBr obtained from 5 µl samples of an 800 ppm solution using the furnace, cup and rod atomizers under the conditions given in the text (p. 87 ff).

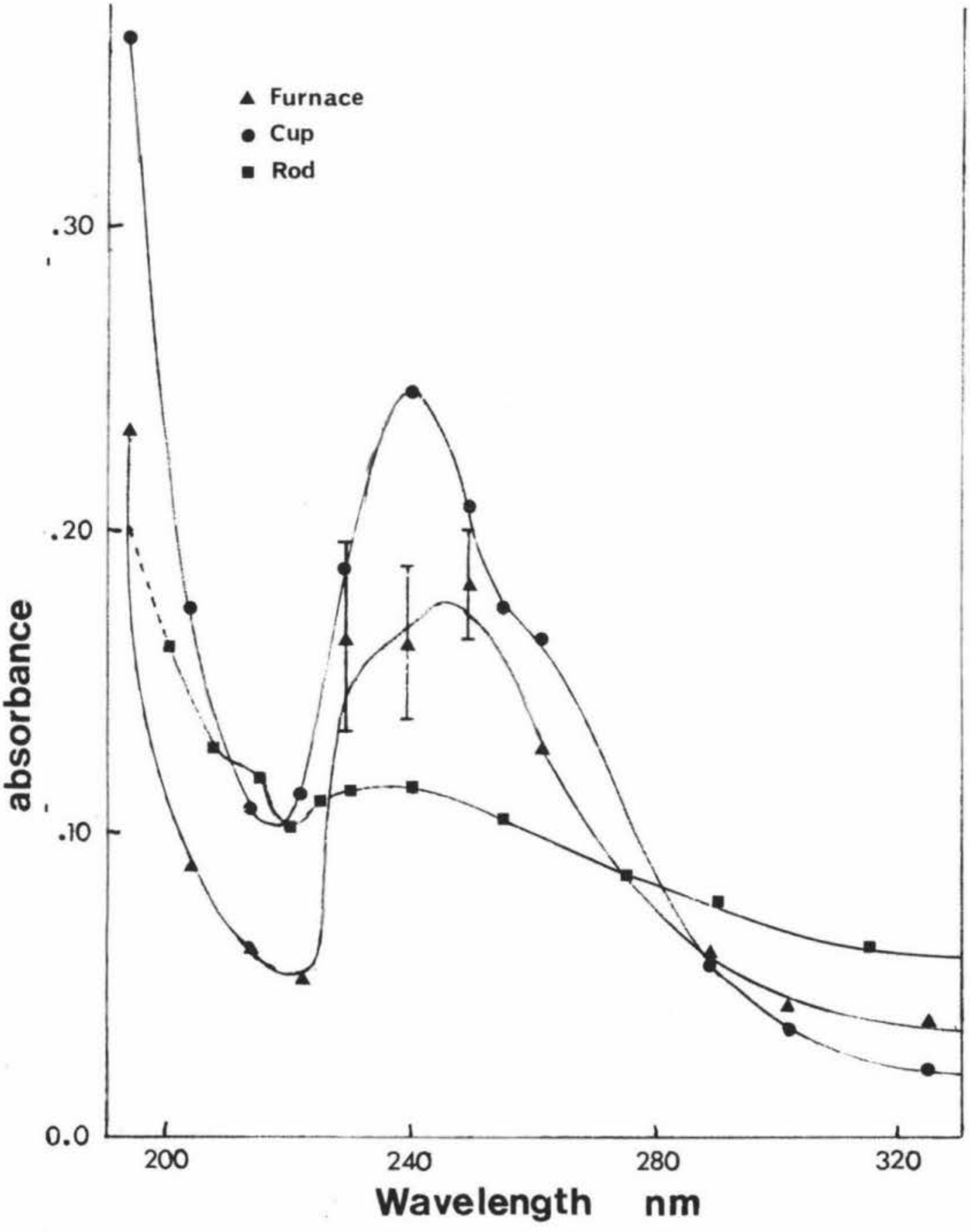


Fig. III 1-17b. NaCl absorption spectra produced from the furnace, cup and rod atomizers. A 5 µl solution sample containing 800 ppm NaCl was atomized under the conditions given in the text (p. 87 ff).

Lamp	As	Zn	Cd	Cu	Pb	Cr	Ce	Cu	Cr
Wavelength (nm)	193.7	213.9	228.8	249.2	261.4	288.9	302.1	324.7	357.9

Absorption signals from all the solutions atomized at ~ 1800°C using the atomic spectral lamps were the same (within the r.s.d.) as the absorption obtained from the H_2 lamp at the corresponding wavelength. However the use of the Zn lamp resulted in a larger signal at the 213.9 nm wavelength than did the H_2 lamp revealing the presence of Zn in all solutions. Zinc is a ubiquitous laboratory contaminant and as the concentration was the same in all the solutions it was assumed that the water was contaminated. A check on the water supply verified this assumption. When solutions containing 400 ppm and 800 ppm NaCl were atomized at two different temperatures (1800 and 1450) in the furnace, slight variations in the spectra were obtained. Although the different concentrations atomized at the same temperatures resulted in almost identical curves (except for slight loss of detail at the lower concentrations), the use of the lower temperatures gave a slightly different response compared with the higher atomization temperature. (see Table III 1-11).

Table III 1-11. Ratio of absorbances from an 800 ppm NaCl solution at given wavelengths from 5 µl samples atomized at two different temperatures (1450°C and 1800°C) in the furnace.

Wavelength nm	194	210	230	254	290	310
Ratio of Absorbances Abs 1450°C/Abs 1800°C.	8	15	8	5	3	1

At lower wavelengths the difference in the two curves is more noticeable.

Similar results were obtained when some of the experiments mentioned above were repeated using KBr. Lower concentrations of KBr (400 ppm) gave lower absorbances and curves with less detail than the results from 800 ppm and 5000 ppm solutions. The same trend in the atomizer's sensitivity, as shown in Fig. III 1-17b, remained throughout all of the experiments, in that the rod gave less detail than the furnace or the cup.

Identification of Spectra.

The spectra shown by all these experiments are molecular absorption spectra of NaCl and KBr. These spectra have been looked at by two different workers using two different types of atomizers. Müller (1929) used a graphite furnace heated to 1100°C to observe the absorption spectra of NaCl, KBr and several other alkali halides. Koirtyohann and Pickett, using a long path burner, also obtained spectra of this kind which they showed to be molecular absorption spectra with very little light scattering present.

The spectra obtained by Müller and by Koirtyohann and Pickett, together with that from the furnace* in this work, are presented in Fig. III 1-18 for NaCl and Fig. III 1-19 for KBr. It is evident

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* The spectrum from the furnace is used for comparison because of all the atomizers it is closest to the apparatus used by the other two groups of workers.

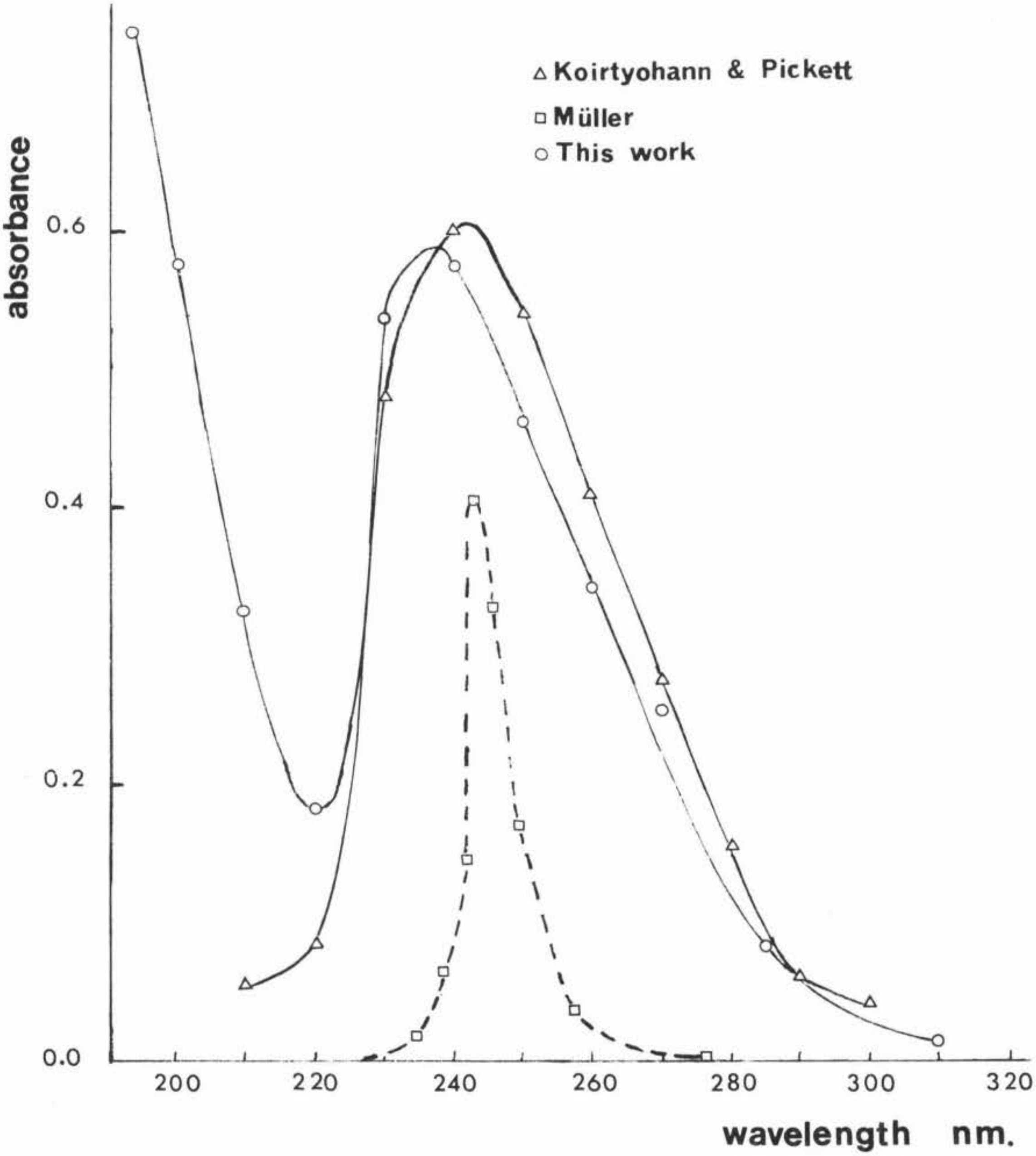

Fig. III 1-18. The absorption spectra of sodium chloride: obtained in this work (using the furnace with conditions given in the text), given by Koirtyohann & Pickett, and separately by Müller. Müller's spectrum has been

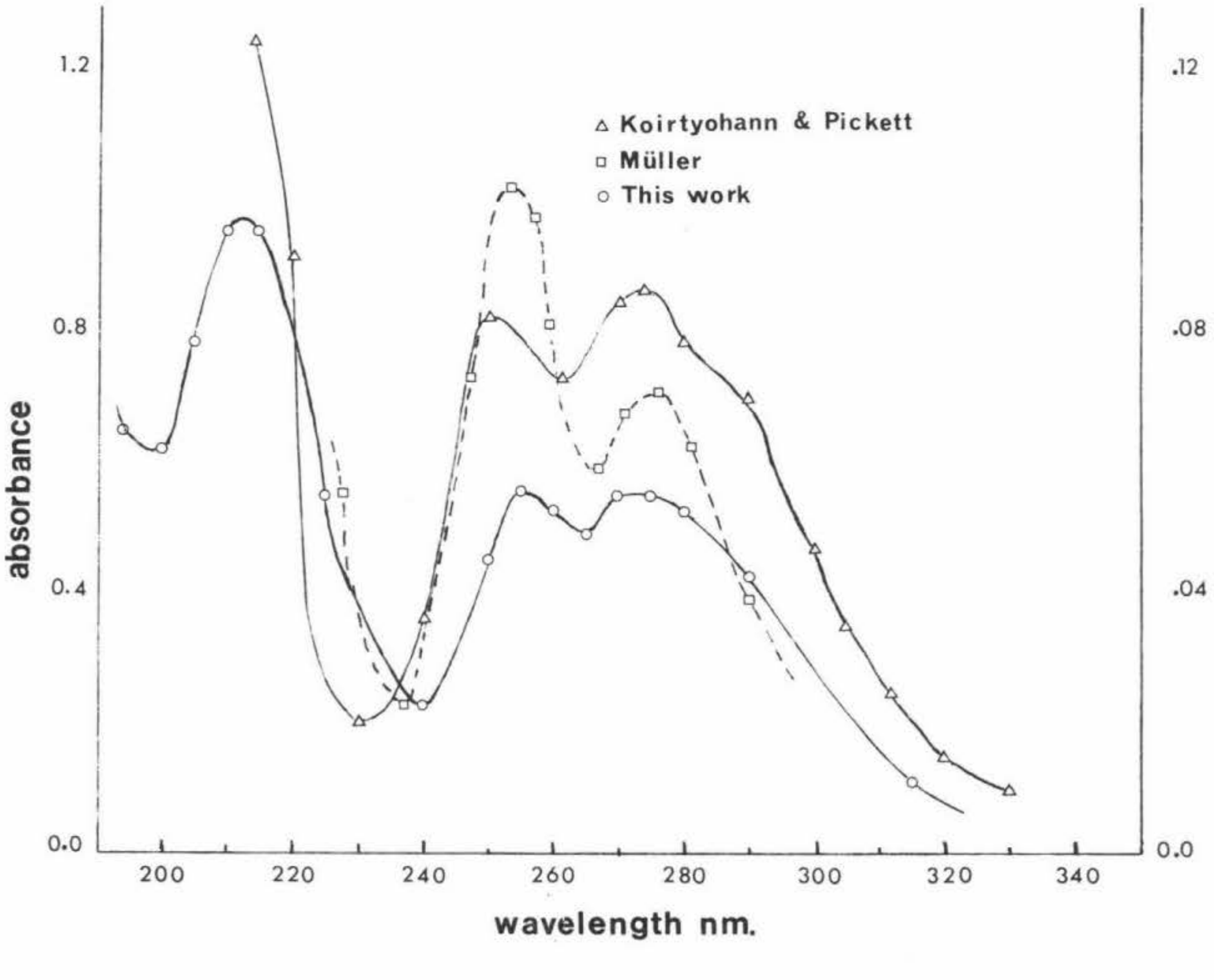

Fig. III 1-19. The absorption spectra of potassium bromide obtained by three different groups of workers using similar vaporization chambers. The left abscissa scale applies to the curves of Müller and this work.

that in each case the same absorption spectrum is being viewed i.e. the molecular absorption spectrum of the particular alkali halide present.

Several unsuccessful attempts were also made to determine the wavelength dependence of $CuCl_2$ vapour absorption. If a molecular absorption curve could have been produced a better appreciation of the mechanism for the reduction of Cu signals in the presence of chlorine-containing compounds could be postulated.

Investigation of the scattered light intensity.

Several authors (see p.16-18) of flameless atomic absorption work have attributed almost all of the non-atomic absorption signal to light scattering when an alkali halide or similar salt is present in the matrix. Therefore an estimation of the proportion of the absorption signal caused by light scattering would be advantageous in assessing the relative importance of the molecular absorption spectrum in the present work. As stated earlier (section II p 18) Koirtyohann and Pickett showed that using their apparatus light scattering was of little consequence.

Five µl samples of a 10,000 ppm solution were placed on the rod, dried, ashed at a low temperature and then atomized at 1800°C. An H_2 lamp was operated at 30 mA and placed at a 110° angle to the monochromator. The amplifier gain was switched to maximum and operated in the transmission mode. The output signal was measured at several wavelengths over a range of 190 - 360 nm. The curve obtained is represented in Fig. III 1-20. This signal could conceivably include a contribution from molecular fluorescence as well as light scatter.

The signal follows very closely that of the lamp output itself. Thus the 'scattered' radiation intensity is an almost constant proportion of the lamp output except at lower wavelengths (< 210 nm).

The Non-Atomic Absorption Signal.

DISCUSSION:

With flameless atomizers the loss of material other than the analyte from the atomizer can generally be monitored by this peak. From the results presented earlier it can be clearly seen that in the systems studied* the signal is mainly due to molecular absorption and very little if any is caused by light scattering.

A very high gain and a large concentration of NaCl on the rod was necessary to enable the light scattering signal to be measured (Fig. III 1-21) indicating that the scattering of light was very small at an angle of 110°.

Omenetto **et al.** [122] studied light scattering in fluorescence systems. The maximum scattering experienced was not at 90° to the source as expected but at 120°. Thus the measurement of the scattered intensity at 110° was near the maximum scatter (assuming that the same

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* KBr and NaCl molecular absorption curves are the only ones presented although H_3PO_4, HCl, HNO_3, H_2SO_4 and KH_2PO_4 were all checked to see if a large enough non-atomic absorption (using H_2 lamp) peak could be obtained.

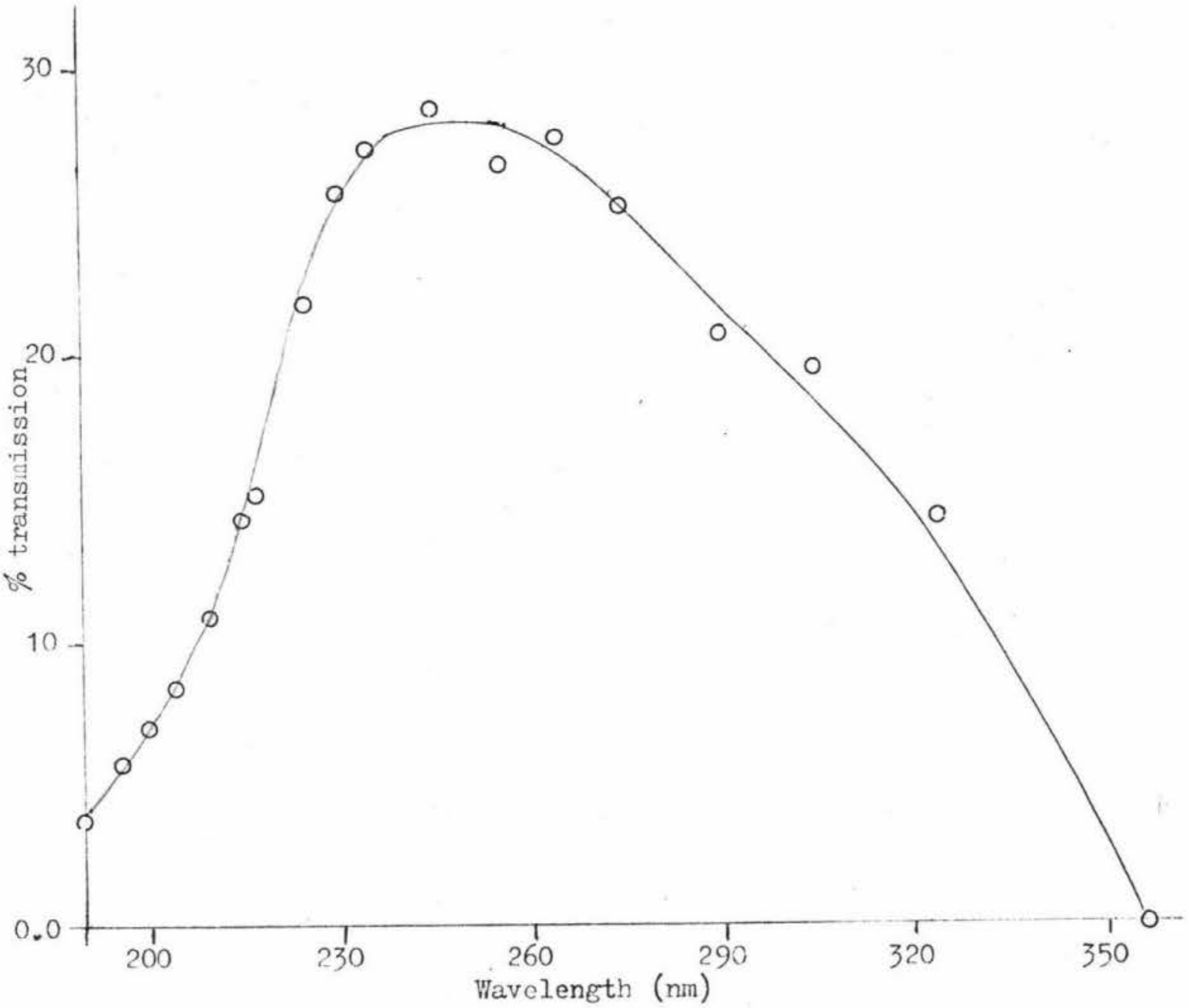

Fig. III 1-20. Output signal from **rod** atomizer when 10,000 ppm NaCl samples (5µl) were atomized under the following conditions; dry, 4.5V for 25s, ash 450°C for 15s, atomize 1800°C for 2.5s. The signal was observed at ~110° to the source (an H_2 continuum lamp operated at 25mA).

KBr has a minimum at $\sim$240 nm whereas NaCl and the 'scattering' curve both have maxima here. The light scattering obtained was clearly not Rayleigh scattering, as the relationship of the intensity of the scattered light to the wavelength ($I_S \propto \frac{1}{\lambda^4}$) did not exist.* Therefore if the very small amount of light measured at 110° is the result of scattering - the type of scattering is not Rayleigh. Omenetto <u>et al.</u>[122] also experienced non-Rayleigh scattering.

In addition to Koirtyohann and Pickett's work and that of L'vov (see Section I 3 p 8) ultraviolet absorption spectra of alkali halide vapours producedfrom furnaces maintained at 800 - 1100°C were reported.[123,124]

The similarity of all these spectra indicates that the rapid vaporization of sodium chloride from the atomizers under the conditions specified leads to a high vapour phase concentration of undissociated NaCl molecules. The observed spectrum can be identified as the charge transfer spectrum of these species.[125] ** The spectrum of potassium bromide shows a pair of peaks at 254 nm and 274 nm, the separation corresponding to that between the

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* Although this is accepted as the main criterion for testing for the presence of Rayleigh scattering it is not the only one.[122]

** These transitions can be represented as

$$\mathrm{K{+}Br^- \xrightarrow{h\nu} K{:}Br} \qquad \text{and} \qquad \mathrm{Na^+Cl^- \xrightarrow{h\nu} Na{:}Cl}$$

$$\text{or} \ \xrightarrow{h\nu} \mathrm{K^{\cdot}Br^{\cdot}} \qquad\qquad \text{or} \ \xrightarrow{h\nu} \mathrm{Na^{\cdot}Cl^{\cdot}}$$

$^2P_{3/2}$ and $^2P_{\frac{1}{2}}$ electronic state of the bromine atom. A further peak at higher energy (212 nm) indicates the formation of some potassium atoms in an excited state. Similar main features can be seen in the spectrum of potassium iodide vapour obtained by various means.[124,69,32.]

The higher absorbances obtained with the furnace and cup are probably a result of the greater effective path length and greater residence there of the vapour in the optical path when these atomizers are used. Loss of detail on the rod is mainly a result of the decreased sensitivity.

At temperatures much lower than the boiling point of the alkali halide all atomizers volatilize the compound.

Compound	Melting Point (1 atm) (121g)	Boiling Point (1 atm.) (121g)	Volatilization Temp. *
KBr	748°C	1383°C	520°C
NaCl	772°C	1407°C	550°C

* from experiment.

L'vov[4] has discussed this phenomenon in terms of the vapour pressure required to volatilize the actual amount of sample present in the atomizer. A vapour pressure of about 4 mm of Hg is sufficient to completely volatilize the sample present (5 µl of 10 ppm). Hence a temperature of 968°C and 982°C for NaCl and KBr respectively is sufficient to produce the required vapour pressure to remove all of the compound. This argument also applies to metallic analytes and pre-atomization loss of analyte which has been reported by other workers.[100]

When single beam atomic absorption instruments are used successive determinations are needed in order to separate the non-atomic absorption peak from the absorption peak by using a hydrogen continuum lamp and an atomic spectral lamp respectively. This procedure is not as successful with flameless atomizers as with the flame as conditions in the former atomization system are not easily reproduced from atomization to atomization. Therefore double beam instruments where the determination of the non-atomic absorption component in the absorption peak is simultaneously determined with the atomic absorption peak would be preferred.

The application of the information gained in this section is readily apparent. The loss of NaCl molecules does occur. Conglomeration of these molecules in the vapour phase could entrap an analyte atom (entrapment theory). The presence of the high energy peak in the KBr spectrum indicating the presence of free K^+ ions gives a strong indication that free Cl^- ions are present in the vapour phase. These are free to combine with the analyte. Hence vapour phase interference by alkali halides is feasible when the chemical state of the interferent in the vapour phase is considered.

2. Real Solution Analysis.

Application of the carbon rod atomizer to zinc analysis in bovine serum.

A. Results.

The instrument was set up for optimum Zn analysis.

Table III 2-1. Parameters for zinc analysis in bovine serum on the carbon rod atomizer.

Wavelength (nm)	213.9	Dry	Voltage	4.10
Slit width (μ)	150		Time (s)	22
Slit height (nm)	5	Ash	Voltage	38
Lamp current (mA)	4		Time (s)	12
		Atomize	Voltage	3.5
			Time (s)	2.7
		Gas Flow Rate $1\ \mathrm{min}^{-1}$	Ar	3.8
			H_2	2.2

After considerable difficulty aliquots of water sufficiently free from zinc for use in these analyses were obtained.

The serum samples were diluted 40x and analysed using a set of standards containing Zn (as ZnO) dissolved in the purified water to give the appropriate concentration (a 1000 ppm stock solution of Zn was utilized).

The results were then compared with the same serum samples (diluted 5x) analysed by flame A.A. using a set ofaqueous zinc standards. The standard curves are shown in Fig. III 2-1(a) and (b) while Table III 2-2 gives the results.

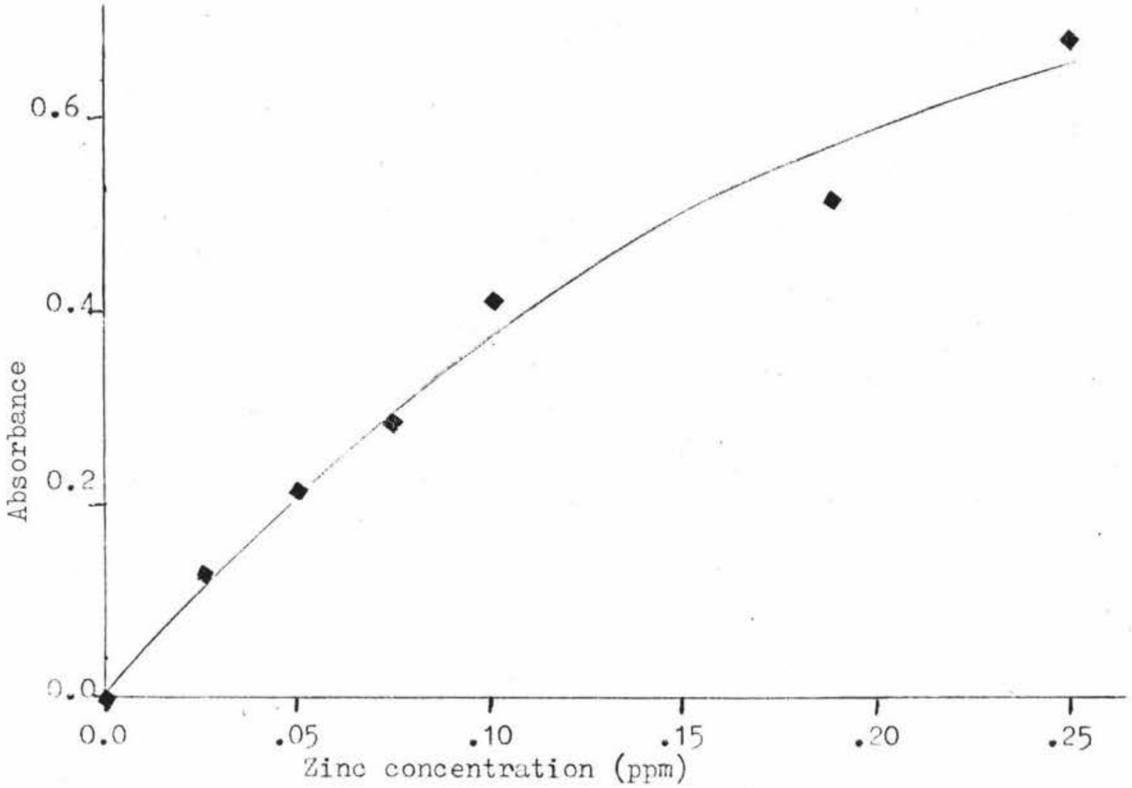

Fig. III 2-1a. The zinc standard curve obtained from aqueous standards volatilized from the rod atomizer. This curve was used for a series of zinc determinations in bovine serum.

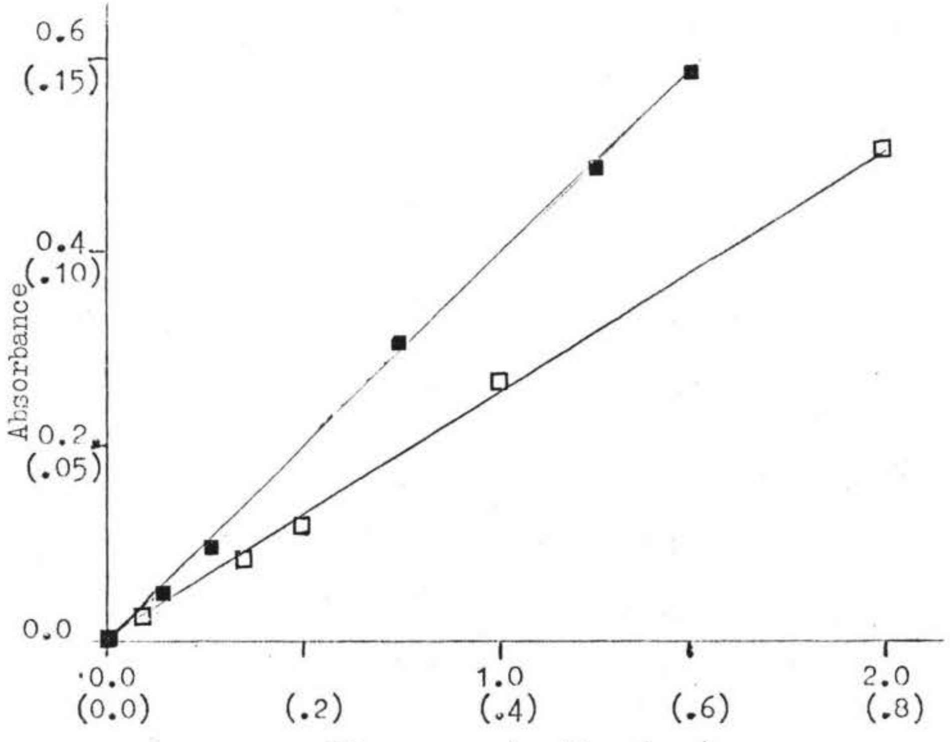

Fig. III 2-1b. Two concentration ranges of zinc analytical curves are shown for zinc analyses using flame a. a. (The bracketed figures apply to the lower concentration range indicated thus ■).

Table III 2-2. Results of two sets of analyses on fourteen bovine serum samples from four separate farms by flameless A.A. and flame A.A. All results are corrected for any background absorption and the error is expressed as ± r.s.d.

	Concentration of Zn in serum (ppm)		
Sample* No.	Rod.Aqueous Standards	Flame.Aqueous Standards	CRA result - Flame result.
A1	3.41 ± .30	2.88 ± .20	+ 0.53
A3	8.92 ± .69	8.75 ± .61	+ 0.17
A5	2.88 ± .24	2.45 ± .17	+ 0.43
A8	2.74 ± .34	2.50 ± .18	+ 0.24
B1	2.40 ± .28	1.79 ± .13	+ 0.61
B3	3.14 ± .17	3.00 ± .21	+ 0.14
B5	1.80 ± .37	1.12 ± .08	+ 0.68
C1	5.27 ± .12	5.60 ± .39	- 0.33
C2	2.59 ± .32	2.38 ± .16	+ 0.21
C5	2.25 ± .21	2.12 ± .15	+ 0.13
D1	2.68 ± .52	1.71 ± .12	+ 0.97
D3	2.84 ± .16	2.76 ± .19	+ 0.08
D4	2.85 ± .36	2.03 ± .14	+ 0.82
D7	2.59 ± .16	1.80 ± .13	+ 0.79

average + ve error by rod = 20%

* Samples supplied by J.E. Oldfield.

B. Discussion.

Good standard curves are obtained. A positive difference exists when the aqueous standard rod results are compared with flame A.A. results. Hence the flame results would appear to have a consistent negative bias probably due to the decreased rate of sample uptake due to the increased viscosity of the sample (the serum is only diluted 5x) compared with the standard aqueous solutions. It has already been noted that the solution viscosity has little effect on the final result when a rod atomizer is used.

CHAPTER IV

CONCLUSION.

Although many elements in several different matrices such as blood, serum, biological tissues and lubricating oils have been successfully analysed by atomic absorption using flameless graphite atomizers, it is clear, from this work and other works, that the analysis of the same elements from some aqueous matrices is not so successful. Even if good results are obtained when a given element is atomized from a particular matrix (e.g. blood) it does not necessarily follow that solutions containing any of the constituents of the matrix (e.g. NaCl, K_2HPO_4) in synthetic solutions, or natural waters will not interfere with the same element. Consequently care needs to be exercised when an element is atomized from any new matrix.

Due to the fact that some, if not all interferences occur in the vapour phase, it may be very difficult to eliminate interferences such as those caused by the alkali halides involving the entrapment of the analyte atom. Although Lundgren et al.[112] have increased the response of lead determinations in the presence of NaCl by obtaining better separation, on a time scale, of the volatilized substances it will not be so easy to separate the volatilization of compounds or elements having similar vapour pressures at the same temperatures.

At low interferent concentration levels the effect on the analyte absorption signal is generally more unpredictable than at higher concentrations. The analysis of most elements in concentrated matrices such as sea water is documented as being virtually impossible. However, analyses at lower interferent concentrations (e.g. river water has a NaCl concentration of $\sim$50 ppm[121g]) would also give difficulties owing to the large effect on the absorption signal caused by a small variation in the interferent concentrations at these levels.

The dilution in water of solid samples dissolved in acids is common pre-treatment for the analysis of solid samples. This should be avoided where possible as greater variability in the suppression caused by the acid is evident at lower concentration levels.

An area needing more research is the mechanism of enhancement on the analyte absorption signal caused by some matrices especially in the vapour phase. Although some intensive work has been carried out on the systems studied it is by no means exhaustive. More extensive work would enable generalizations to be made. However it would appear that each individual matrix has a unique effect on different analytes. From this work it becomes apparent that the successful application of the flameless atomization technique for atomic absorption may only be extended to new matrices by separation techniques such as that used by Fairless and Baird.[126]

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APPENDIX I.

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