A STUDY OF SOME CHEMICAL INTERFERENCES

IN ATOMIC ABSORPTION SPECTROSCOPY

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

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ABSTRACT

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

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

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

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

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

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

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

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

identify the solid collected. Where calcium-containing solutions were aspirated, the solid products varied according to the nature and concentrations of various anions present in the solution. Calcium carbonate was the sole identifiable product when nitrate ions were present. The presence of both phosphate and chloride led to the formation of both chlorapatite, $3\ Ca_3(PO_4)_2$, $CaCl_2$, and α- calcium orthophosphate under some conditions; phosphate alone led to a solid which may be secondary calcium orthophosphate, $CaHPO_4$. Similar compounds were found with strontium and magnesium, although these did not correspond to any for which X-ray and infra-red data are recorded in the literature.

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

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I. INTRODUCTION AND REVIEW

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I. 1. GENERAL INTRODUCTION

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

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

In 1955, Walsh[1] published his first paper on the application of atomic absorption spectroscopy to chemical analysis, and outlined

the instrumental technique which would produce optimum results. Alkemade and Milaz[2] designed an atomic absorption spectrophotometer at about the same time. In 1958, Allan[3] and David[4] reported the application of the atomic absorption technique to the determination of magnesium and zinc in agricultural materials and plants. This analytical technique then grew rapidly and in 1968 over 10,000 atomic absorption instruments were in use throughout the world, and the literature on the subject had accumulated to over 1,200 papers, notes and reviews.

I. 2. INSTRUMENTATION

Kahn[5] has given an excellent review of instrumentation. In its simplest form, the essential components of an atomic absorption spectrophotometer are:

a) a primary source of radiation

b) a means of producing atomic vapour

c) a wavelength selector

d) a radiation detector and readout system

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

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

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

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

I. 3. ABSORPTION OF RADIATION

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

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

i) Doppler broadening -- due to thermal agitation of the absorbing and emiting atoms;

ii) Collisional broadening -- energy levels are perturbed when the atom is close to a foreign gas atom;

iii) The natural width of the spectral line -- due to the finite lifetime of the excited state;

iv) Stark and Zeeman broadening -- occurring in the presence of external electric and magnetic fields respectively.

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

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

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

state u for about 10^{-8} sec and then undergoes either non-radiational deactivation (from collisions with flame gas molecules, e.g., CO, CO_2, N_2, O_2, H_2O, etc.) or radiational deactivation called atomic fluorescence.

The intensity of the transmitted radiation, I_ν, is related to that of the incident radiation at frequency ν, I_ν°, by

$$\log_e \frac{I_\nu^\circ}{I_\nu} = K_\nu \ell$$

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

$$\log \frac{I_\nu^\circ}{I_\nu} = 0.4343\ k_\nu \ell.$$

The relationship between the atomic absorption coefficient, k_ν, and the number of atoms available to absorb can be shown to be of the form $k_\nu = \frac{\ln 2}{4\pi^2} \lambda_0^2 \frac{g_u}{g_l} N_\ell P_t\ f(\Delta\nu_c, \Delta\nu_D, \nu)$ where λ_0 is the wavelength at the centre of absorption line g_u, g_ℓ are the degeneracies of the upper and lower electronic states N_ℓ is the number of atoms per cm^3 in the lower electronic state P_t is the transition probability in sec^{-1} and $f(\Delta\nu_c, \Delta\nu_D, \nu)$ is a function of the collisional and Doppler half-widths and of the frequency, which defines the shape of the absorption profile. The way in which the total amount of light absorbed depends on N_ℓ is of particular interest. Two situations arise: (i) with a source emitting continuous radiation in the wavelength range of interest; (ii) with a source emitting a narrow line of appropriate wavelength. Most atomic absorption analysis methods utilise a narrow line source, especially hollow cathode lamps. In this case, radiation is absorbed over an interval determined by $\Delta\nu_s$, the source half-width. The total absorption is $\int k_\nu\, d\nu$ over the frequency range of the source and can be shown to be proportional to

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

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

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

TABLE I.1.

Relative Populations of Excited and Ground States at Several Temperatures

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

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

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

I. 4. ATOMIC VAPOUR PRODUCTION

Several methods of vapourising solid samples directly have been suggested. These include the sputtering chamber[6], L'vov furnace[7], flash lamp technique[8], and laser sampling[9]. Most investigators have vapourised the sample by spraying a solution of material into a flame. A nebuliser is used to produce very fine droplets of solution, and the flame causes evaporation of the solvent and decomposition of the solutes in the droplet. Atoms are thus produced in the light beam so that absorption may take place.

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

(a) the flow rate of the solution into the nebuliser;

(b) the efficiency of introduction of solution into flame, i.e., the aspiration efficiency of the nebuliser-burner-flame combination;

(c) the efficiency of converting the solid salt particle into ground state atoms in the flame gases, called the atomisation efficiency (β).

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

the sample. For example, if we have a solution of Ca Cl_2 aspirated into the flame, this efficiency is

$$\beta = \frac{(N_{Ca})_\ell}{(N_{Ca})_\ell + N_{CaCl_2} + N_{CaCl} + N_{CaO} + N_{CaOH} + N_{CaH} + N_{Ca^+} + \cdots + (N_{Ca})_u + (N_{Ca})_{u'} + \cdots etc}$$

where ℓ stands for the ground electronic state of Ca atoms, u, u'..... stand for the upper electronic states of Ca atoms.

β is a very complex function of flame temperature and composition, generally having a maximum value at a certain temperature and composition. The aspiration efficiency has been studied by Winefordner et al.[10], and the atomisation efficiency by de Galan and Winefordner[11], and by Willis[12]. The factors affecting the efficiency of atomic vapour production from the salt particles in flames are discussed below.

(a) Flame energy

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

air-coal gas	1800 K
air-propane	1925
air-H_2	2050
O_2 - H_2	2500
N_2O - H_2	2600
air-C_2H_2	2350
O_2 - C_2H_2	3100
N_2O - C_2H_2	2955

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

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

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

(b) Flame profile

The relationship between absorption signal and flame height is called the flame profile. It indicates the relative population of neutral atoms in the flame. For maximum sensitivity there is an optimum height in the flame at which observations should be made[13,14]. Rann and Hambly[15] examined the distribution of neutral atoms in absorption flames. They demonstrated that maximum absorption is a function of the light beam position in the flame, coupled with the fuel/air ratio of the flame. The elements investigated included Cu, Mo, Mg, Cr, Ca, Ag, Sr, Ba, Na and Se. The results suggested that atoms are released by pyrolysis of the salt in the hottest region of the flame, and then removed by secondary chemical reactions, in other parts, of the flame.

(c) Flame composition

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

Cowley et al.[16] studied the spatial distribution of various molecular species in a pre-mixed oxyacetylene flame by a combination of atomic absorption and atomic emission. They showed that the effectiveness of the air-acetylene flame results from the combination of a relatively high temperature with an environment which is relatively deficient of oxygen. A stoichiometric flame provides a higher temperature, but many metals suffer a loss of sensitivity relative to fuel-rich conditions. This results from an unfavourable environment which promotes chemical reactions that bind metal atoms. By contrast, the fuel-rich air-C_2H_2 flame provides an environment very effective for some metals but at a temperature which is too low for other metals. Turbulent flames from these mixtures provide a non-optimum environment because they do not form well-defined zones in the flame, and a chemically favourable environment does not prevail.

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

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

(d) Use of organic solvents

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

i) easier combustion of organic solvents than water, and

ii) easier chemical release of atoms from an organic addend than from an inorganic salt.

Robinson[14] studied the effect of chemical release of atoms in a flame, (i.e., from an organic addend) by using Sodium chromate, chromic nitrate and chromium naphthenate in water, ethanol, benzene and ethanol-benzene (50:50) mixtures. His results indicate that when organometallic solutions are used, a greater absorption signal is obtained. This supports the thesis that the population of metal atoms in a given flame is increased by using organic solvents and organometallic compounds. Organometallic compounds in organic solutions give the most absorption and inorganic aqueous solutions give the least sensitivity.

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

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

I. 5. INTERFERENCE IN ATOMIC ABSORPTION

Interferences are those effects, due to the presence of other constituents in the sample, which cause an analysis to be in error. Interferences in emission methods are well known; atomic absorption, however, is subject to fewer interferences, as predicted by Walsh[1]. The following interferences will be discussed:

(a) Spectral interference

(b) Excitation interference

(c) Ionisation interference

(d) Bulk or Matrix interference

(e) Chemical interference

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

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

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

i) The cobalt 2536.49 Å line arising from a metastable state interferes with the determination of mercury (at 2536.52 Å)[22].

ii) Mutual interference between gallium (4032.982 Å) and manganese (4033.073 Å)[23].

Another type of interference arises when molecules formed in the flame have absorption bands at the analytical wavelengths of a particular element. This molcular absorption occurs most when low temperature flames are used. For example, when barium is determined in the presence of large amounts of calcium in the air - C_2H_2 flame, the calcium oxide formed will absorb strongly at the barium wavelength (5536 Å)[24]. This interference, however, vanishes in the high temperature generated by the nitrous oxide-acetylene flame[25].

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

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

Baker and Gordon[26] studied the determination of potassium by both emission and absorption in an oxy-acetylene flame, and have shown that the presence of lithium, sodium or cesium increases the apparent concentration. The enchancement is in the same order as the increasing ionisation potential of the interfering elements. Trent and Slavin[27] investigated the determination of strontium, and observed that there is an increase in absorption after an alkali metal has been added to the solution. As the concentration of the interfering element is increased, the enhancement rises to a plateau value. The enhancement is accompanied by a decrease in absorption if the ionic ground state line is used. The percent of metal ionised is related largely to the temperature of the flame. Alkali metals ionise to an appreciable extent in cool flames like air-propane, while alkaline earths ionise slightly in the air-acetylene flame and to a great extent in the nitrous oxide-acetylene flame.

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

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

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

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

I. 6. CHEMICAL INTERFERENCES

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

Cationic Interferences

Allan[3] in the first paper to describe the analysis of plant materials by AAS, found that aluminium depressed the absorption signal of magnesium. Elwell and Gidley[28] showed that the principal interfering elements in the determination of magnesium are those that form acidic oxides that are stable at high temperature, e.g., Al, Ti, Zr and Hf. Allan also observed that K, Na, and Ca do not interfere in the magnesium determination.

David[29] studied the analysis of calcium in plant materials and found that ions such as aluminium and zirconium suppress the calcium absorption. He observed that Ca absorption is dependent on the ratio of fuel to air in the flame, and that the absorption signal varies along the height of the flame, being greatest close to the base of the flame.

The determination of strontium is similar to that of calcium. David[30] found that aluminium and silica supress the Sr signal whereas calcium does not. Trent and Slavin[27] gave a detailed account of the interence effects, including the enhancement of Sr absorption produced by the presence of other alkali metals.

Anionic Interferences

The interference of sulphate, phosphate and silicate on the determination of calcium have been reported by a number of authors. Rochiccioli and Townshend[31] examined the effects of various ions and complexing agents on Ca absorption in the air-propane flame. They confirmed the previous observations that relative magnitudes of depression effects of sulphate and phosphate decrease higher in the

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

$$SiO_4^{4-} > PO_4^{3-} > SO_4^{2-} > EDTA > NO_3^- > CH_3COO^- = \text{8-hydroxyquinoline} > Cl^-$$

Hall & Townshend[32] also investigated the effects of a number of ions and complexing agents on the absorbance of magnesium in the air-propane flame. They found that sulphate and phosphate (as reported by Allan[3]) and oxalate decrease the signal, whereas chloride, nitrate, EDTA and 8-hydroxyquinoline enhance the absorption. Trent and Slavin[27] reported that HCl, HNO_3 and glycerine depress the strontium signal at high concentration (a few %).

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

Suppression of Interference

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

i) addition of other salts which suppress the interference;

ii) removing the interference by ion exchange or selective extraction;

iii) using a standard similar in composition to the sample.

Many of the common ions, e.g., sulphate, silicate, aluminium and zirconium, which suppress the alkaline earth absorption, can be minimised or almost overcome by adding excess of lanthanum or strontium chloride to both sample and standard solutions[3,28,36,37,38]. David[30] examined the determination of Sr in biological and soil materials. He chose to remove the phosphate interference by ion-exchange. The small amounts of sodium and potassium, which enhance the calcium absorption, can be tolerated if Na or K is added to the standard solutions. The

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

Explanation of Chemical Interference

A prerequisite for the understanding of the occurrence of chemical interference is the understanding of the mechanism by which metal atoms are produced. Robinson[14] suggested the following mechanism, shown in Table I.2.

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

Cowley[41] studies the molecular and atomic emission from portions of the fuel-rich oxy-acetylene flame fed with a soultion of refractory metals. He found that atomic emission is intense in the base of the flame and falls off at higher levels. Molecular band emission of the metal oxide is weak at the flame base but increases in strength at

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

TABLE I.2

Mechanism of Atom Production

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

Slavin, Sprague and Manning[13] examined various flame parameters in the determination of calcium. They found that although Ca may be determined at about equal sensitivity in the air-acetylene flame or the air-hydrogen flame, the effect of anionic interferences is much less in the acetylene flame. The use of a fuel-rich flame moves the absorption peak higher in the flame. The effect of phosphate depression is somewhat reduced in a rich flame, particularly higher in the flame. Mavrodineanu[42] reported a similar effect on the emission of calcium in a fuel rich oxy-acetylene flame. The use of a low

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

Yofe, Avni and Stiller[43] showed that orthophosphates of Ca, Sr and Ba are converted at 1000 C into corresponding pyrophosphates which are partially decomposed in the flame. If La is added to the solution of alkaline earth metal and the phosphate, interference disappears. They found that lanthanum phosphate precipates before the alkaline earth phosphate as water is evaporated at 140C from a solution containing both. Thus in the presence of lanthanum, the Ca, Sr or Ba reaches the flame free from phosphate, a condition suitable for complete vaporisation.

Elwell and Gidley[28] postulated the formation of an Al-Mg mixed oxide to account for the suppression by Al of the Mg signal. To confirm that the effect is due to the chemistry of the aspirated droplets they aspirated separate solutions of Al and Mg into the same spraying chamber, where they were mixed before entering the flame. No depressing effect of Al was observed. Rubeska and Moldan[44] obtained X-ray diffraction patterns of the unevaporated particles leaving the flame after spraying Al and Mg. The X-ray Debye-Scherrer diffractograms revealed that spinel ($MgO.\ Al_2O_3$) is formed.

Mansell[45] used thermodynamic data (Table I.3) for the formation of spinels to account for the releasing action of La, Ba or Sr salts. The thermodynamic data for an oxygen-deficient system revealed magnesium aluminate $Mg\ Al_2\ O_4$ as being more stable than the constituents MgO, Al_2O_3 and $MgCl_2$. Al_2O_3 is more stable than MgO;

MgO is the least stable of the alkaline oxides and tends to lose oxygen in the presence of Ba, Sr or La. The free energy of formation of alkaline earth aluminates at 2000 K (Table I.4) has been approximated by Sinke (quoted by Mansell[45]). $MgAl_2O_4$ is the least stable of the series at temperatures approaching that of the C_2H_2 - air flame. The greater stability of Ca, Sr or Ba aluminates would therefore cause their preferential formation or precipitation, leaving Mg atoms free for absorption. The releasing action of La is presumably caused by the same mechanism.

TABLE I.3

Free Energy of Formation at 2400 C and 2000 C[45]

Compounds	2400 C ΔG_f (kcal mol^{-1})	Compounds	2000 C ΔG_f (kcal mol^{-1})
MgO	-57	BeO	-96
Al_2O_3	-216	MgO	-77
Al O	-18	CaO	-96
Al_2O	-67	SrO	-89
Al_2O_2	-78	BaO	-91
$AlCl_3$	-104	Al_2O_3	-248
$MgAl_2O_4$	-284	La_2O_3	-293
MgCl	-29		
$MgCl_2$	-73		
La_2O_3	-266		

TABLE I.4

Free Energy of Formation of Aluminates at 2000 C [45]

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

II. OBJECTS OF THE PRESENT WORK

C H A P T E R I I

OBJECTS OF THE PRESENT WORK

II. 1. FURTHER STUDY OF CHEMICAL INTERFERENCES

Many studies of chemical interferences in AAS have been limited to observing the effect of a specific concentration of an added cation or anion on the absorption signal produced by a specific concentration of the element being analysed. In a few cases (e.g., AAS of calcium[31] and AAS of magnesium[32]), the work has covered a wider range of concentrations of both the analytical element and the potential interfering substances.

In other cases, the testing for interferences has been confined to the ions most likely to be present in the particular type of sample being analysed. Chemical interferences in the determination of chromium, and nickel, for example have been studied mainly in the connection with the analysis of steel and other alloys[46,47], and in the measurement of metal ion concentrations in natural waters[48]. Mostyn and Cunningham[49] and David[50] investigated the likely interferences in the determination of molybdenum in ferrous alloys and in fertilisers. The interferences reported were mainly cationic.

For some elements, the development of AAS techniques has been only recently carried out, and no detailed information on chemical interferences has been reported. The AA determination of gallium and indium, for example, was reported by Mulford[51], with little attention

being paid to the study of interferences. (A few interferences in the determination of gallium and indium by flame emission have been found[52].)

The enhancement of the absorption signal in organic solvents[14,21] has been referred to in the previous section. Interference effects in such media do not appear to have been investigated.

In the light of the foregoing comments, the following additional work on the existence of chemical interferences appear to be of value.

i) A study of potential interferences in magnesium, calcium and strontium determination with some anions not previously studied in detail. In the case of calcium, studies of interference in aqueous-organic mixtures were also carried out.

ii) A search for anionic interferences in the determination of chromium, nickel and molybdenum.

iii) A study of possible interferences in the determination of gallium and indium.

In most cases it was considered essential to look at a range of concentrations of both the analytical element and the potential interfering agent. In the case of anionic interferences it was possible to use the theoretical approach already outlined (section I.6) to restrict the scope of the investigation to those anions most likely to have any effect.

II. 2. POSSIBILITY OF QUANTITATIVE ANION DETERMINATION

The inhibition of the flame emission signal from calcium caused by the addition of phosphate is well known, and has been used to determine phosphate indirectly[53]. A close study was made in the present work of the feasibility of using AAS for a similar type of determination.

The results of the work described in II.1 above were also examined to see if there is any possibility of using interference effects for the determination of any other anions. The conditions and limitations of this type of determination will be discussed.

II. 3. ATTEMPTS TO IDENTIFY OR SEPARATE THE SPECIES RESPONSIBLE FOR CHEMICAL INTERFERENCES

Several possible approaches to this problem were studied.

i) With increasing amounts of an interfering ion in the solution, the extent of interference tends towards a limiting value. In the case of calcium-phosphate interference, studies have been made, using the calcium emission spectrum, of the ratio of calcium to phosphate at the point where the limiting interference was reached. The results of different workers on this problem have been in disagreement.
This approach was examined using AAS, and the results compared with those of the previous investigations on flame emission.

ii) In view of the likelihood of chemical interferences being due essentially to the formation of stable molecules in the flame, there is the possibility that flame emission spectra in the presence of interfering agents will show bands characteristic

of such stable molecules which are not present in the absence of interfering agents. Accordingly, the emission spectra of a number of solutions were recorded in an attempt to find evidence for the appearance of simple stable species.

iii) The most direct evidence of the formation of stable compounds in the flame would be provided by the successful separation and identification of such compounds from the burning gases. Only the most technically easy experiments along these lines were carried out, involving the accumulation of solid materials from a region just above the top of the flame. Infra-red spectra and X-ray crystallographic powder diagrams were used in the attempts at identification of the powders obtained.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

C H A P T E R I I I

APPARATUS AND EXPERIMENTAL PROCEDURE

III. 1. ATOMIC ABSORPTION APPARATUS

Most experiments in this work were carried out with a Techtron AA 3 Atomic Absorption Spectrophotometer. A Techtron AA 5 Atomic Absorption Spectrophotometer was available in the later part of this work. The work to be described was carried out with the AA 3 Atomic Absorption Spectrophotometer, unless otherwise stated.

Photographs of the AA 3 Atomic Absorption Spectrophotometer and its optical system are shown as Plates 1 and 2.

The essential components of the AA 3 Atomic Absorption Spectrophotometer include: lamp power supply, hollow cathode lamp, burner, monochromator, photomultiplier, W.M.A. indicator and gas control unit.

Hollow cathode lamp - The hollow cathode lamps used were manufactured by Atomic Spectral Lamp Pty. Ltd, Melbourne. A high-intensity hollow cathode lamp, made by the same company was used for nickel.

Hollow cathode power supply - This unit provides current stabilisation for operating the lamp with partial stabilisation for warm-up operation of other lamps.

Burner - A Techtron AB 41 burner was used. It is a 10 cm

stainless steel burner with a slit 0.012 - 0.020 inches wide, and is suitable for both air-coal gas and air-acetylene mixtures.

Gas control unit - This unit serves to control and meter the supply of compressed air and combustible gas. On the panel there are control valves for air, coal-gas (propane) and acetylene, a pressure gauge for the air flow and gauge for coal-gas and acetylene. A calibration curve is available for the conversion of the meter reading of combustible gas into flow-rate. For example the meter reading 4 for acetylene is equivalent to 4.0 1/min and meter reading 5 is equivalent to 6.6 1/min. Air was supplied at 15 p.s.i. from a compressor.

Monochromator - The monochromator, which serves to isolate a narrow spectral region from the spectrum of the light source is of the Ebert type. It employs a two inch square grating ruled with 16,200 lines / inch and giving a linear dispersion at the exit slit of 33Å/mm in the first order. The focal length is twenty inches so that the aperture of the instrument is F/ 10.

Photomultiplier - A R.C.A. type 1 P28 photomultiplier was used. It is sensitive throughout the ultraviolet and visable, the useful range being about 1950-6000 Å.

W.M.A. Indicator Unit - This unit contains both a stabilised E.H.T. supply for the photomultiplier and an A.C. amplifier for amplification of the modulated signal from the photomultiplier. The transmission readings are read on the 0-100% numerical scale on the meter. A scale expansion unit may be attached, providing a means of expanding the upper 50% or the upper 20% of the ordinary 0-100% scale, thus increasing the reading accuracy for small absorption values.

The essential components of the Techtron AA 5 Atomic Absorption Spectrophotometer are the same as those of the AA 3 counterpart. Some modifications occur in the read-out unit, lamp power supply and gas control unit, as follows.

A.C. Amplifier and Read-out

In the normal mode, the six inch meter scale represents a linear absorbance range of 0-1.00 or a transmission range of 0-100%. The absorbance can be continuously varied by a factor of ten. An automatic baseline corrector reestablishes the baseline between readings.

Lamp power supply

Operating current for each of the four hollow cathode lamps is independently controlled and metered out with all channels modulated and regulated. The unit is synchronously modulated with the amplifier to assume 'lock in' amplification and a drift-free operation. A turret is fitted to hold four hollow cathode lamps.

Gas control unit

Two separate two-way valves permit rapid selection of fuel-oxidant mixture. Thus one can use nitrous oxide without having to change gases after lighting. An auxiliary support-gas control is convenient for stiffening the flame or for working with organic solvents. The flame conditions can be precisely adjusted by the fuel and support gas flow meters.

III. 2. PREPARATION OF SOLUTIONS

Stock solutions of metallic ions being studied were prepared at a concentration of 1000 ppm by dissolving 1 g of metal in conc. hydrochloric acid and diluting with distilled water to 1 litre. In some cases the metallic ions were prepared by dissolving the appropriate chlorides. The interfering substances were prepared in 2000 ppm concentration by dissolving 2 g of the substance in 1 litre of solution. The interfering cations were present in solution as chlorides, and in some cases as nitrates or sulphates, and the interfering anions as sodium salts. Other solutions were prepared from the stock solutions by appropriate dilutions. All concentrations quoted later in this work refer to the final mixed solution.

Reagent or 'Analar' grade chemicals were used throughout. The limits of impurities, generally not more than 0.5%, are satisfactory because

i) accuracy of absorption measurement is not better than 1%

ii) solutions were used at very low concentrations (e.g., 20 ppm Ca solution would not contain more than 0.1 ppm of other alkaline earth elements). Interference effects are usually only measurable at these low concentrations when the ratio of interferent : analyte exceeds 5 - 10%.

The distilled water supplied to the laboratory was found to contain 0.2 ppm Mg. Although this amount of Mg does not significantly affect the determination of metals other than Mg, double-distilled water was used throughout. In preparing solutions beakers were found more suitable than test tubes as proper mixing is more readily achieved in the former.

III. 3. EXPERIMENTAL PROCEDURE

The hollow cathode lamp, amplifier and readout system (W.M.A. indicator unit) were allowed to warm up for 30 - 45 minutes. Distilled water was sprayed before each determination.

A serious drift of signal occured in the case of indium. The % transmission increased with time after lighting the burner. The following table shows the change of transmission readings with time in the case of a 20 ppm indium solution.

Time(min)	0	5	10	15	20	25	30	35	40
% T	41.5	42	42.5	43.5	45	46	45.5	46	45.5

A similar occurrence was noted by Chakrabarti[54] in the case of selenium. No explanation of this behaviour was suggested. The phenomenom is not simply a case of insufficient warming up of the lamp, as the lamp can be warmed up to the point where a steady signal is obtained. The drifting then starts from the time of lighting the burner. This was probably due to slight heating of grating adjustments in the monochromator. This effect can be checked by lighting the burner for about 20 - 30 min. after the warming up of the lamp and the instrument. In some cases where the flame has been used for about one hour or more, some drifting of signal from a standard solution occurs, giving gradually decreased absorption. The danger of this affecting results can be avoided by frequent checks on the absorption of a standard solution.

IV. RESULTS AND DISCUSSION

C H A P T E R I V

RESULTS AND DISCUSSION

IV. 1. FURTHER STUDY OF CHEMICAL INTERFERENCES

i) A study of chemical interferences in calcium, magnesium and strontium with anions not previously studied, or not studied in detail.

Several instrumental parameters in the absorption of these three elements were examined, as detailed below for calcium.

a) Wavelength : The 4227 Å line, the most sensitive line, was used.

b) Effect of lamp current on Ca absorption:

No appreciable change of % transmission with a 5 ppm Ca solution was observed when the current was increased.

Current (mA)	5	10	15
% T	77.5	77.5	77

c) Effect of slit width on Ca absorption:

The % transmission with a 5 ppm Ca solution increased as the slit opening was widened. Therefore a small slit width was favoured. However, too small a slit width requires greater amplification. As a compromise, the slit opening chosen was 100μ.

Slit width (μ)	50	100	150
% T	76.5	77.5	78.5

d) Flame profile:

This was obtained by measuring the absorption with the light beam traversing different regions of the flame. In the case of calcium, maximum absorption occurs within 2 mm of the base of the flame, and there is a continuous decrease in the absorption as the flame is lowered (allowing the beam to traverse the upper part of the flame).

e) Flame composition:

A fuel-rich acetylene flame gave better sensitivity than a stoichiometric flame.

Similar preliminary investigations were carried out for magnesium and strontium. The final operating conditions for the three elements are tabulated below.

TABLE IV.1.

Experimental conditions for calcium, magnesium and strontium			
	Ca	Mg	Sr
Wavelength(Å)	4227	2852	4607
Current (mA)	10	5	10
Slit width (μ)	100	50	100
Height above burner-top traversed by light beam (mm)	1.0	1.0	1.0
Air pressure (p.s.i.)	15	15	15
Acetylene flow rate (meter reading)	5	5	5

FIG.IV.1

FLAME PROFILES FOR CALCIUM IN A FUEL-RICH AIR-ACETYLENE FLAME

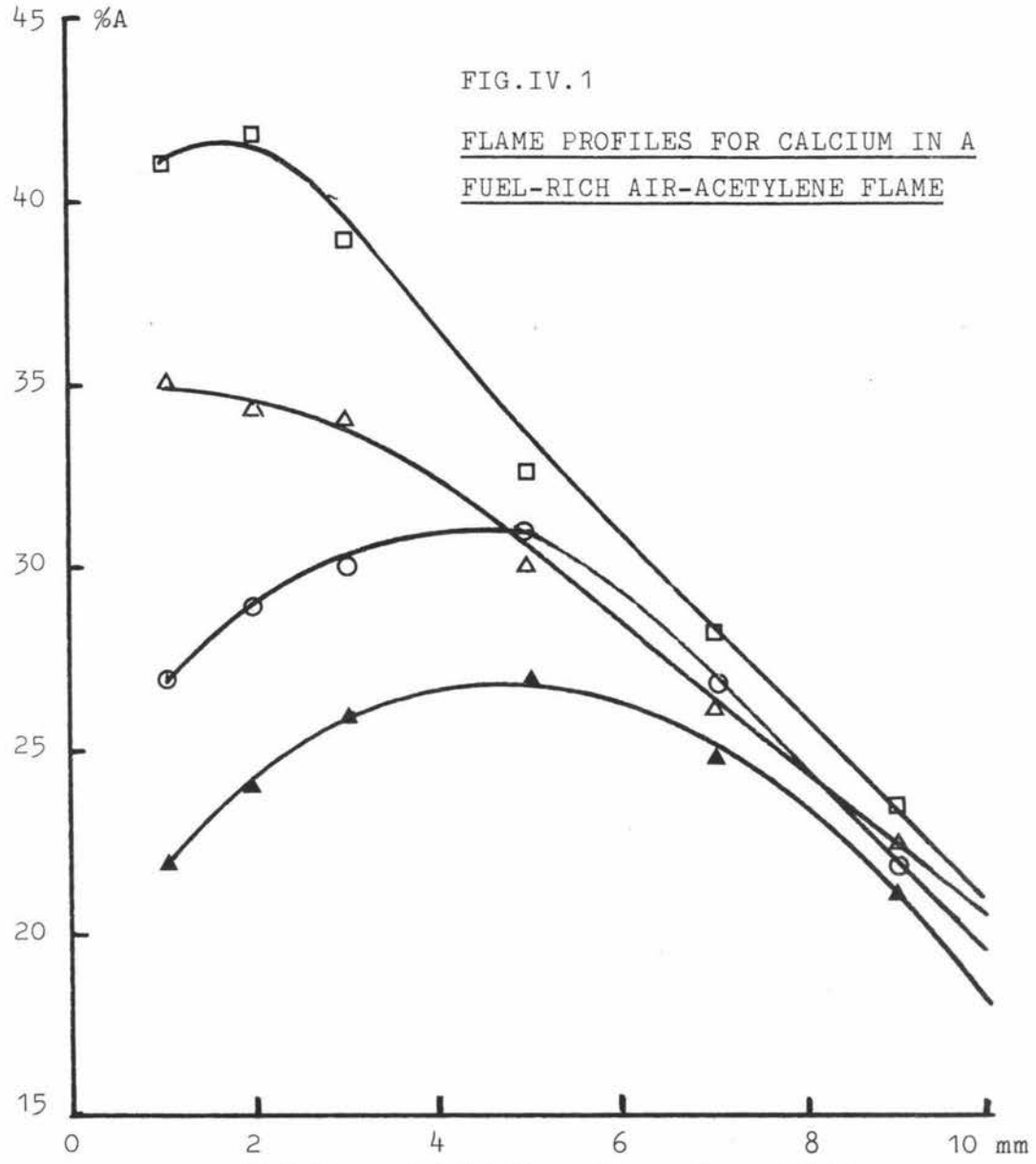
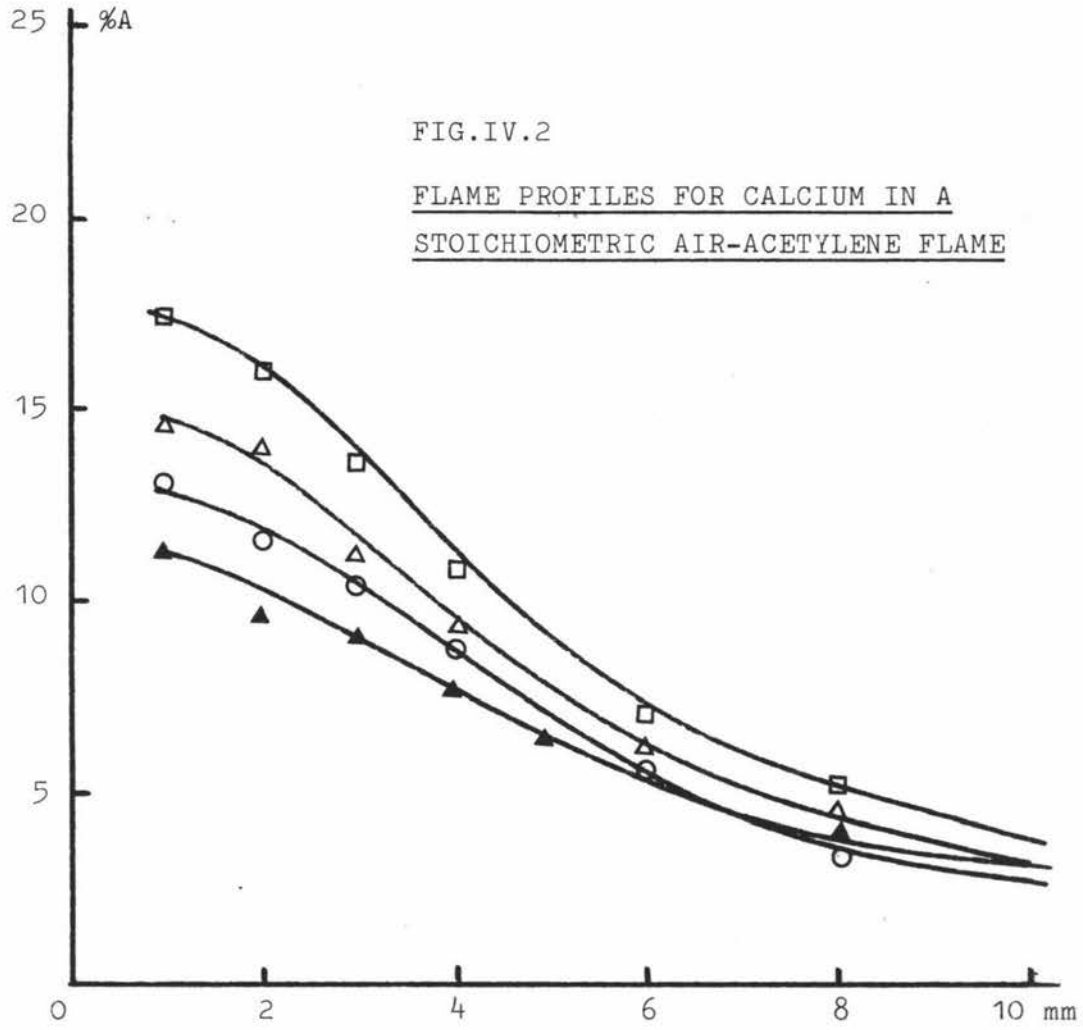


FIG.IV.2

FLAME PROFILES FOR CALCIUM IN A STOICHIOMETRIC AIR-ACETYLENE FLAME



Fluoride, sulphate, phosphate, molybdate and tungstate (as sodium salts) were added to aqueous Ca, Mg and Sr solutions (as chlorides or nitrates) to see if any interference occurred.

Calcium:

Data for the flame profiles with and without interfering ions in fuel-rich and stoichiometric flames are given in Table IV.2. Typical profiles are shown graphically in Figs. IV.1 and IV.2. The calcium ions are 10 ppm and interfering ions 25 ppm. It can be seen from the data and the graphs that the relative magnitudes of suppression by foreign ions, in increasing order, are:

$$F^- < MoO_4^{2-} < SO_4^{2-} < PO_4^{3-} < WO_4^{2-}$$

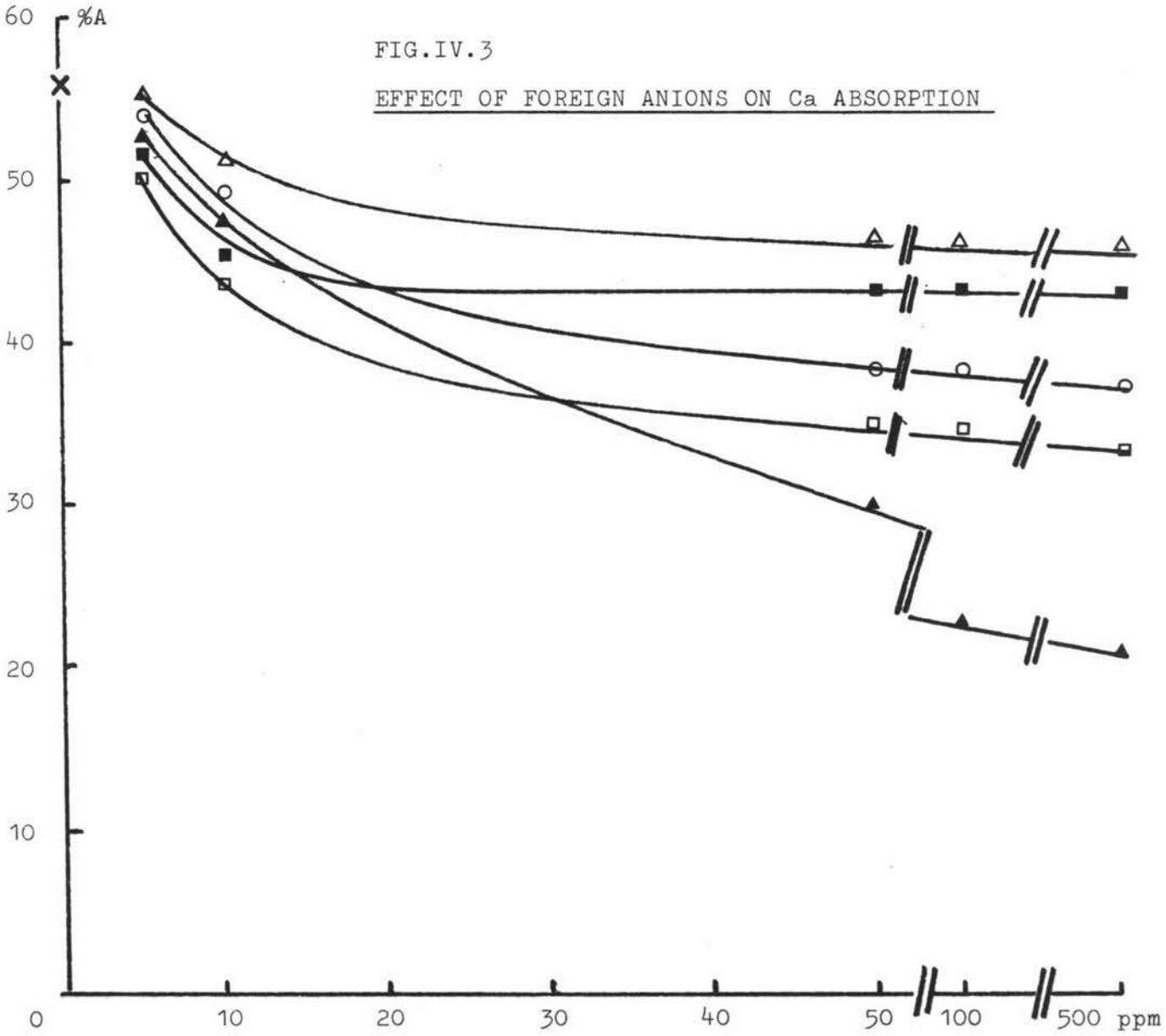
with the light beam 1-4 mm above the base of the flame. The flame profiles with F^-, MoO_4^{2-}, SO_4^{2-} and WO_4^{2-} are essentially similar to that found by Slavin *et al.*[13], in the case of PO_4^{3-}. In all cases, the extent of interference is smaller in the upper part of the flame, where the actual absorption is much smaller. This is in accordance with the thesis that atoms are produced by pyrolysis in the hottest part of the flame and are lost by secondary reactions higher in the flame.

Studies were made on the effect of increasing the concentration of the interfering agents. Solutions containing 10 ppm Ca and up to 500 ppm of the interfering agent were aspirated into a fuel-rich flame, which was examined 1 mm above the base, where the interference is relatively large. The results are shown graphically in Fig.IV.3

It can be seen that the extent of the interference tends towards a limiting value as the concentration of the interfering anion is increased. The amount of interference was in all cases

FIG.IV.3

EFFECT OF FOREIGN ANIONS ON Ca ABSORPTION



- ✕ Ca 10 ppm
- △ Ca 10 ppm + F^-
- ■ Ca 10 ppm + SO_4^{2-}
- ▲ Ca 10 ppm + WO_4^{2-}
- ○ Ca 10 ppm + MoO_4^{2-}
- □ Ca 10 ppm + PO_4^{3-}

TABLE IV.2.

Flame Profiles

Ca 10 ppm + Interfering ion, 25 ppm

Ca 10 ppm = 58% T Fuel inch $\begin{matrix} \text{air} = 15 \\ C_2H_2 = 5 \end{matrix}$

Burner position (mm)	Ca	Ca+F	$Ca+SO_4$	$Ca+PO_4$	$Ca+MoO_4$	$Ca+WO_4$
0	58%T	65	74	76	73	78
1	59	65	72	75.5	71	76
2	58	65.5	68	71	70	74
3	61	66	68	73	69	73.5
4	64	67.5	70	74	69	73
5	67.5	70	71	75	71	75.5
6	70.5	72.5	71.5	75.5	72	75
7	72	74	75	76.5	75	75
8						
9	76.5	78	78	80	78	79
10	80	80	80	82.5	80	81

Ca 10 ppm = 80%T Stoichiometric flame

Burner position (mm)	Ca	Ca+F	$Ca+SO_4$	$Ca+PO_4$	$Ca+MoO_4$	$Ca+WO_4$
0	80	81.5	82.5	88.5	83.5	86
1	82.5	85.5	85.5	90	87	88.5
2	84	86	86.5	90.5	88.5	90.5
3	86	89	87.5	91.5	89.5	91
4	89	91	90	92.5	91	92.5
5	92.5	93.5	93.5	94	92.5	93.5
6	93.5	94	93.5	95.5	94.5	94.5
8	95	95.5	95.5	96.5	96.5	96
10	96.5	96.5	96.5	97	96.5	96.5

FIG.IV.4

FLAME PROFILES FOR STRONTIUM IN A FUEL-RICH AIR-ACETYLENE FLAME

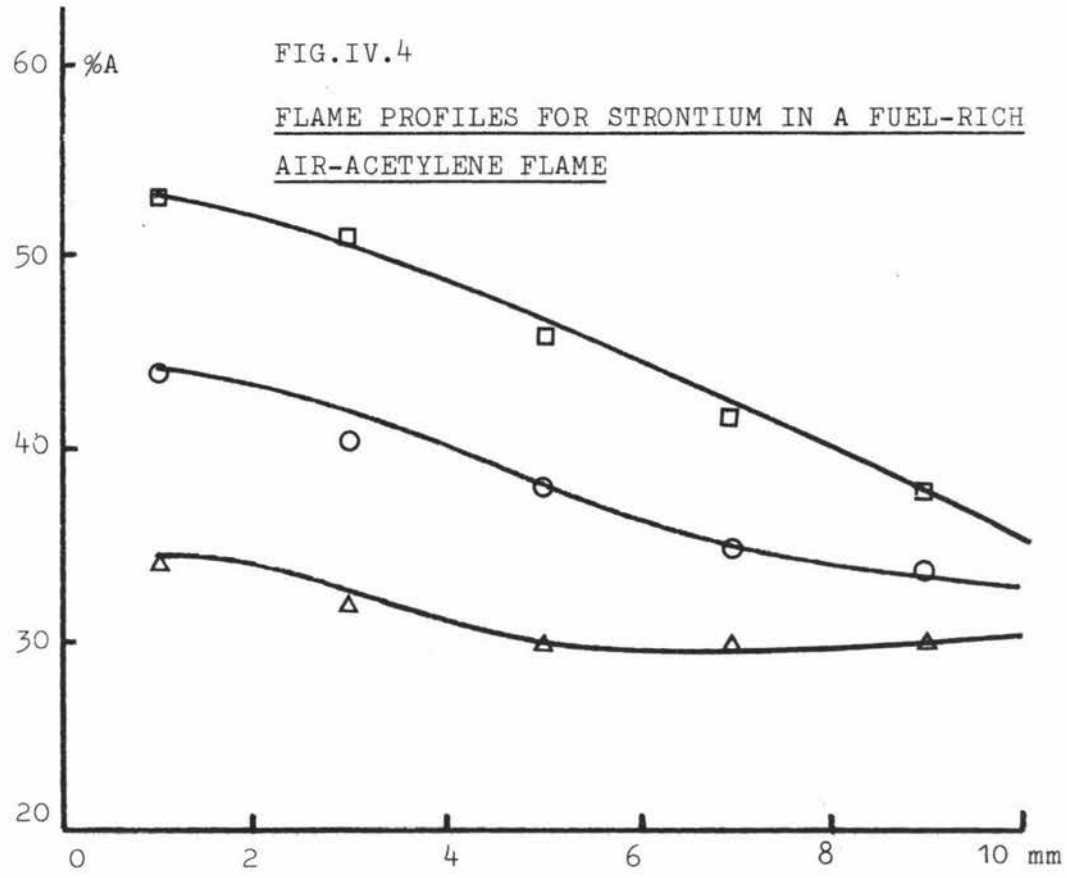
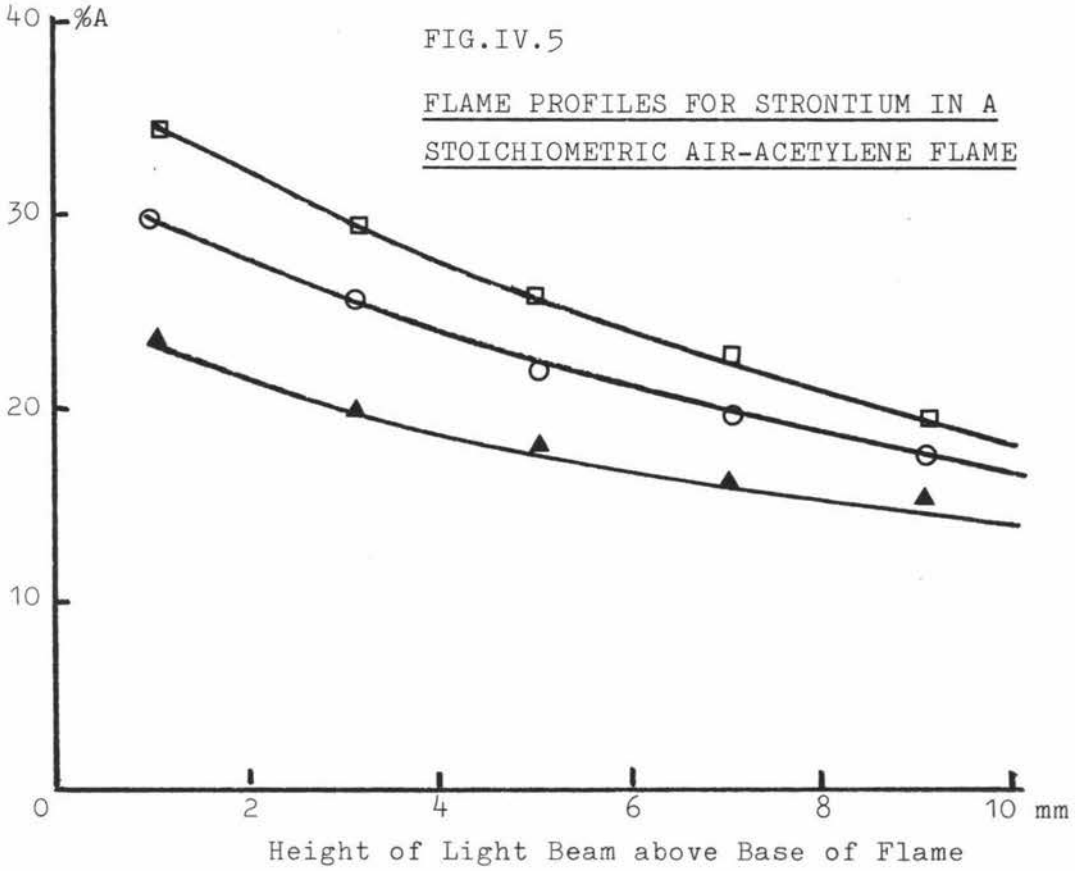


FIG.IV.5

FLAME PROFILES FOR STRONTIUM IN A STOICHIOMETRIC AIR-ACETYLENE FLAME



□ Sr 25 ppm

○ Sr 25 ppm + WO_4^{2-} 15 ppm

▲ Sr 25 ppm + PO_4^{3-} 15 ppm

virtually unaltered after addition of a ten-fold excess of the anion.

Strontium:

Similar observations on the profiles and the interferences can be made about the absorption by strontium. Data for the flame profile of strontium (25 ppm) with and without interfering anions (15 ppm) are shown in Table IV.3. Typical profiles are shown graphically in Figs. IV.4 and IV.5. The relative magnitudes of suppression by foreign anions increase in the order:

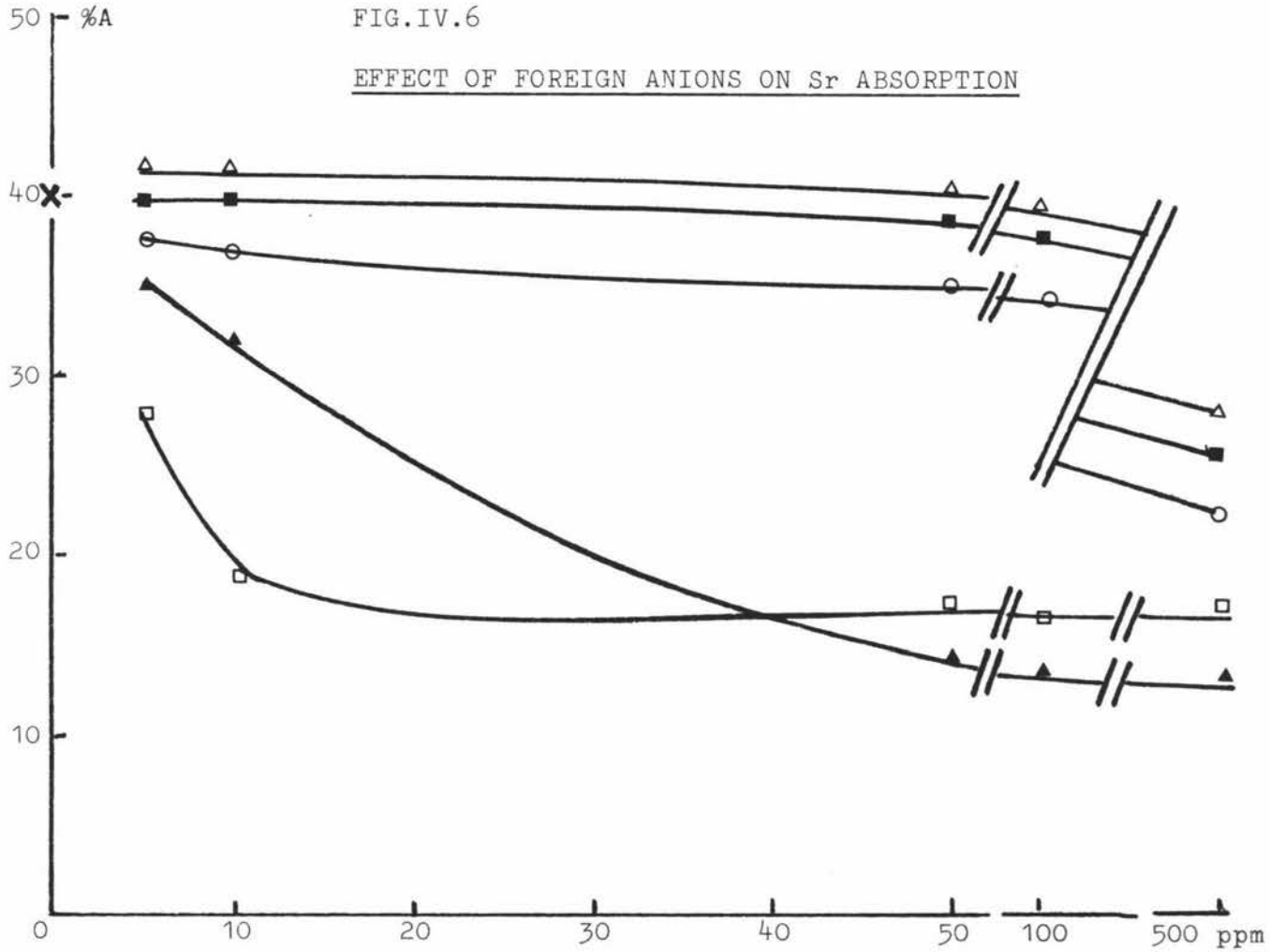
$$F^- < MoO_4^{2-} < SO_4^{2-} < WO_4^{2-} < PO_4^{3-}$$

throughout the greater part of the flame profile. The degree of interference decreases higher in the flame, where the actual absorption also decreases.

The effect of increasing the concentration of interfering anions is shown graphically in Fig IV.6. The solutions contained 25 ppm Sr and up to 500 ppm interfering agents. A fuel-rich flame, which gives better sensitivity than a lean flame, was used and examined 2 mm above the base, where the interference is comparatively large. It can be seen that F^-, SO_4^{2-} and MoO_4^{2-} do not interfere significantly except at high concentrations. The extent of interference by PO_4^{3-} and WO_4^{2-} tends to reach a limiting value, after which further addition of interfering ions does not alter the absorption. Parameters other than flame profile and flame composition which have already been discussed have little effect on the strontium absorption; these include lamp current and slit width. The resonance line 4607 Å, which is the most sensitive line, was used.

FIG.IV.6

EFFECT OF FOREIGN ANIONS ON Sr ABSORPTION



X Sr 12.5 ppm

△ Sr 12.5 ppm + SO_4^{2-}

■ Sr 12.5 ppm + F^-

▲ Sr 12.5 ppm + WO_4^{2-}

□ Sr 12.5 ppm + PO_4^{2-}

○ Sr 12.5 ppm + MoO_4^{2-}

TABLE IV.3.

Flame Profile

Sr 25 ppm + Interfering ions 15 ppm

Sr 25 ppm = 48%T Fuel rich $\begin{matrix}\text{air} = 15\\ C_2H_2 = 5\end{matrix}$

Burner position (mm)	Sr	Sr+F	$Sr+SO_4$	$Sr+PO_4$	$Sr+MoO_4$	$Sr+WO_4$
0	48	50	59	52	55	59
1	47	52	57	66	50	56
2	48	51	55	65	52	57
3	49	52	56	68	53	60
4	53	55	63	69	55	62
5	54	58	61	70	56	62
6	56	58	62	70	58	63
7	58	58	62	70	60	65
8	60	64	65	68	62	67
9	62	65	66	70	64	66
10	64	67	70	72	65	65

Sr 25 ppm = 60%T Stoichiometric flame $\begin{matrix}\text{air} = 15\\ C_2H_2 = 4\end{matrix}$

Burner position (mm)	Sr	Sr+F	$Sr+SO_4$	$Sr+PO_4$	$Sr+MoO_4$	$Sr+WO_4$
0	60	60	65	73	65	65
1	65	65	68.5	76	67.5	70
2	68	71	69	78	71	72
3	70	72	72	80	73	74
4	72	75	74	80	75	75
5	74	76	78	82	78	78
6	76	76	78	83	78	78
7	78	80	80	83	80	80
8	79	79	81	84	80	81
9	82	81	83	84.5	82	82
10	83	83.5	84	86.5	85.5	84.5

Magnesium:

No significant interference was exerted by F^-, SO_4^{2-}, PO_4^{3-}, MoO_4^{2-}, and WO_4^{2-} on the absorption of magnesium (0.5 ppm). Only at high concentrations (a thousand-fold excess) did WO_4^{2-} and MoO_4^{2-} interfere. (see Table IV.4.).

TABLE IV.4.

Anion interference on Magnesium absorption

Mg 0.5 ppm 48 %T

Anions	F^-	SO_4^{2-}	PO_4^{3-}	MoO_4^{2-}	WO_4^{2-}
5 ppm	46	47	47	47	47.5
10 ppm	47	47	47	47	47
50 ppm	47	47	47	47	48
100 ppm	47.5	47	48	48	48.5
500 ppm	48	49	49	50	50

This supports Allan's observation[3] that magnesium can be determined free of interference in an air-acetylene flame.

It is clear from this study that the compounds formed by magnesium with the interfering anions are much less stable than the corresponding calcium and strontium compounds.

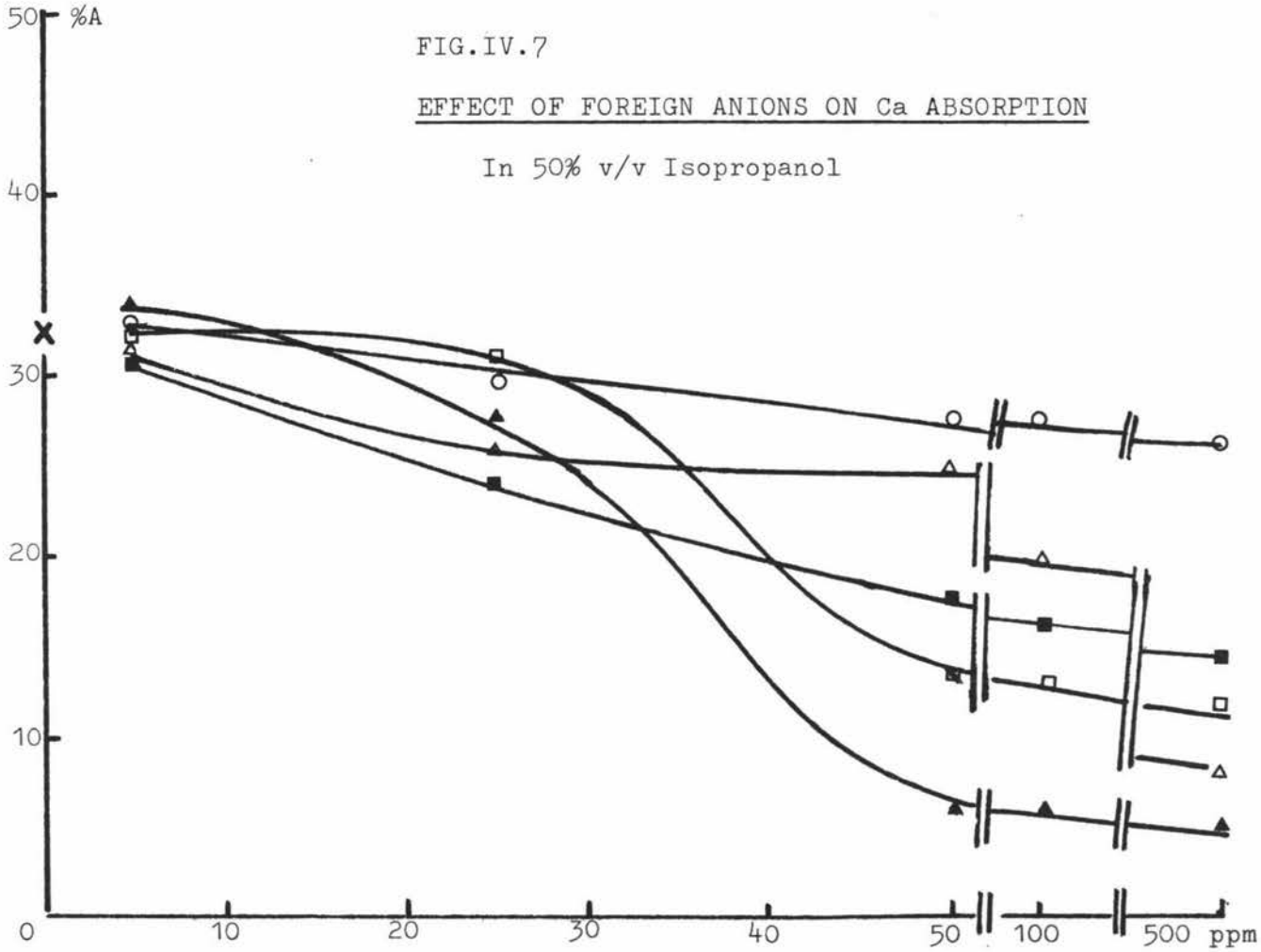
Interferences in the presence of organic solvents

The reported effects of organic solvents on the intensity of the absorption signal have been discussed in Section I.4(d). It is of interest to know whether the anionic interference effects remain in aqueous-organic solvent mixtures.

FIG.IV.7

EFFECT OF FOREIGN ANIONS ON Ca ABSORPTION

In 50% v/v Isopropanol



✕ Ca 10 ppm

○ Ca 10 ppm + SO_4^{2-}

△ Ca 10 ppm + F^-

■ Ca 10 ppm + PO_4^{3-}

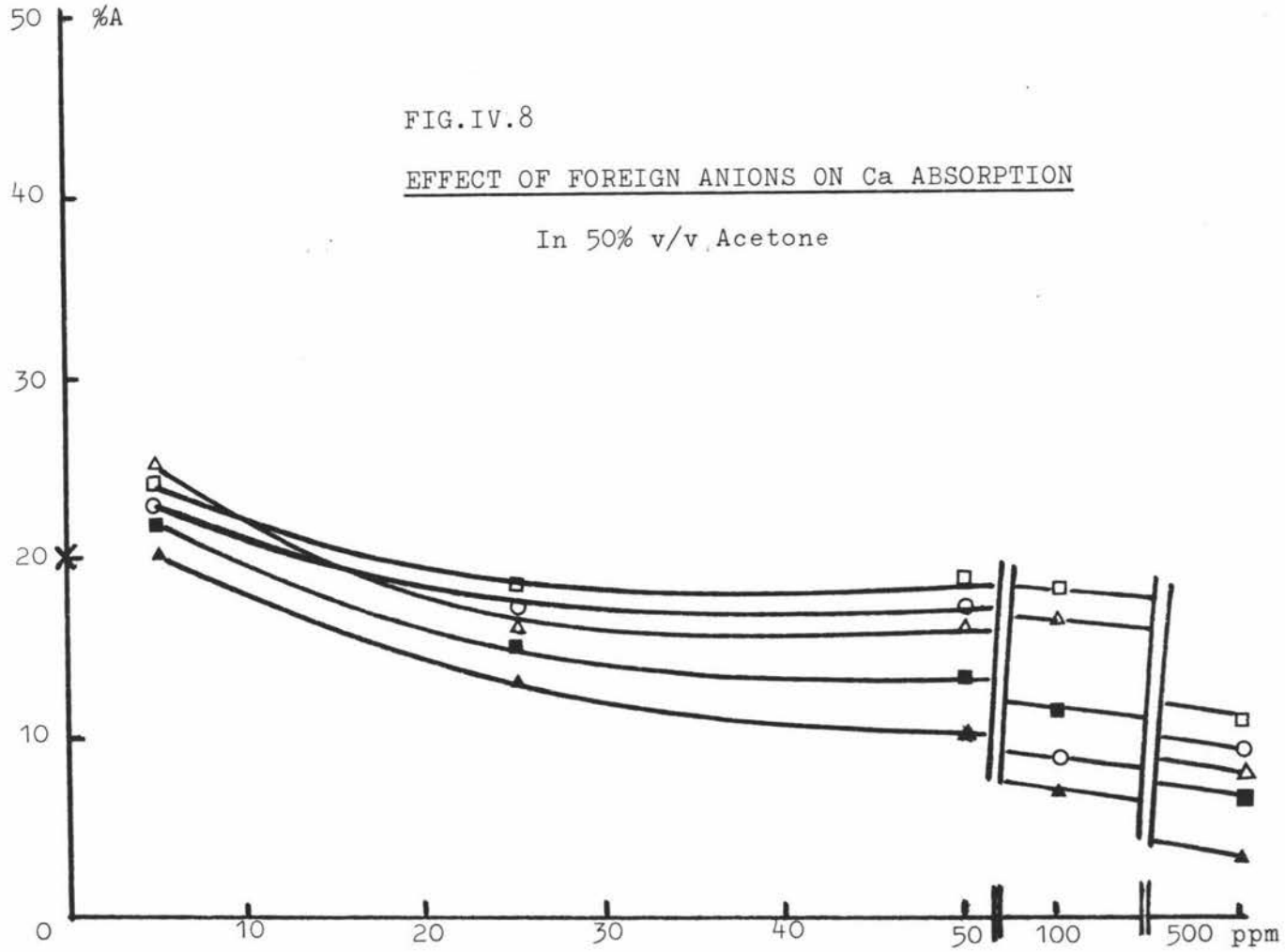
□ Ca 10 ppm + MoO_4^{2-}

▲ Ca 10 ppm + WO_4^{2-}

FIG.IV.8

EFFECT OF FOREIGN ANIONS ON Ca ABSORPTION

In 50% v/v Acetone



X Ca 10 ppm

△ Ca 10 ppm + F^-

□ Ca 10 ppm + MoO_4^{2-}

■ Ca 10 ppm + WO_4^{2-}

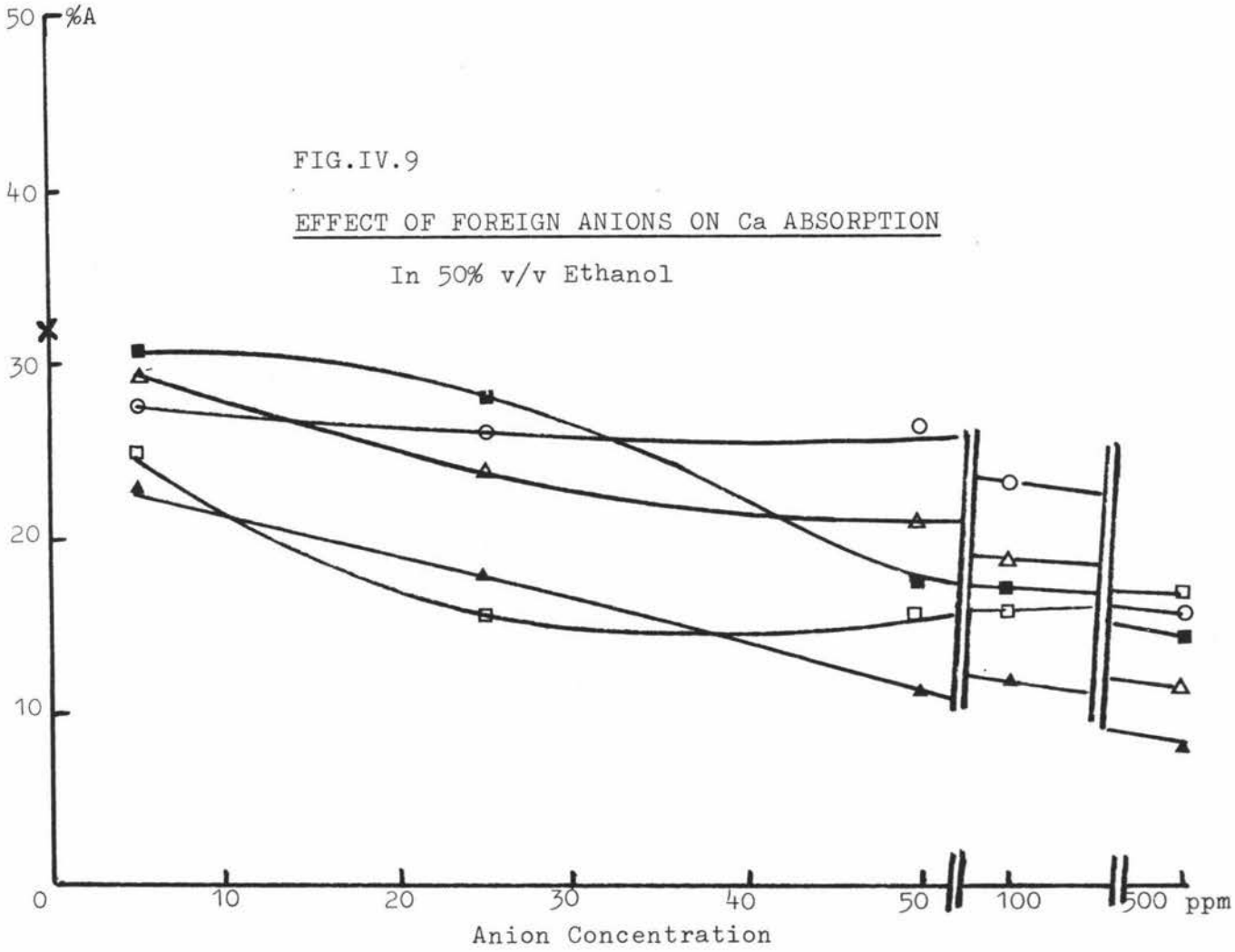
○ Ca 10 ppm + SO_4^{2-}

▲ Ca 10 ppm + PO_4^{3-}

FIG.IV.9

EFFECT OF FOREIGN ANIONS ON Ca ABSORPTION

In 50% v/v Ethanol



✕ Ca 10 ppm

○ Ca 10 ppm + SO_4^{2-}

△ Ca 10 ppm + F^-

□ Ca 10 ppm + MoO_4^{2-}

■ Ca 10 ppm + WO_4^{2-}

▲ Ca 10 ppm + PO_4^{3-}

The effects of foreign anions on Ca absorption in 50% v/v aqueous ethanol, aqueous isopropanol, and aqueous acetone were studied. The results (Figs IV.7 - IV.9) lead to the following conclusions.

(a) The use of an organic solvent enhances the Ca absorption in general. In aqueous solution when the absorption of Ca (10 ppm) is 20%, in both 50% aqueous ethanol and 50% aqueous isopropanol solutions the same Ca concentration gives an absorption of 32.5%. No enhancement was found in 50% aqueous acetone solution, where the Ca absorption was 20%. All observations were made in a lean air-acetylene flame.

(b) The interference with Ca absorption persists in spite of the enhancement by organic solvent.

The relative magnitudes of the suppression effect of the anions increase in the order:

$SO_4^{2-} < F^- < MoO_4^{2-} < WO_4^{2-} < PO_4^{3-}$ in 50% ethanol solution

$SO_4^{2-} < F^- < PO_4^{3-} < MoO_4^{2-} < WO_4^{2-}$ in 50% isopropanol solution

$MoO_4^{2-} < SO_4^{2-} < F^- < WO_4^{2-} < PO_4^{3-}$ in 50% acetone solution

In all cases the anions are at 50 ppm concentration, and observations made with the light beam passing through the base of the flame.

Up to a certain point, the addition of organic compounds to a lean air-acetylene flame should help to increase the flame temperature and provide increased dissociation of moderately stable inorganic compounds. However, it appears that the combustion of the organic solvents used here has done little to dissociate the compounds responsible for interference.

ii) A search for anion interference in the determination of chromium, molybdenum and nickel.

The instrumental parameters involved in the atomic absorption of chromium, molybdenum, and nickel were investigated as detailed below.

Chromium:

(a) Absorption line:

The most sensitive line, 3580Å, was used.

(b) Lamp current:

There was no appreciable effect when the current was increased from 5 to 15 mA. 10 mA was used.

(c) Slit width:

No significant changes occurred when the slit opening was changed.

(d) Flame Profile:

Absorption decreased when the burner position was lowered. The zero position gave the highest absorption. (The zero position was chosen as the highest position the burner could be raised without obstructing the passage of light from the hollow cathode tube to the monochromator).

(e) Flame composition:

A fuel-rich acetylene flame favoured absorption.

Molybdenum:

(a) Absorption line:

The most sensitive line, 3132Å, was used.

(b) Lamp current:

10 mA was used; no appreciable change in absorption was observed when the current was changed.

(c) Slit width:

No significant change in absorption was observed when the slit opening was changed. 100 μ was used.

(d) Flame profile:

The % transmission increased when the burner position was lowered. The highest absorption occurred in the zero position.

(e) Flame composition:

A fuel-rich flame gave more sensitivity than a stoichiometric flame. The absorption by Mo is critically dependent on the air to fuel ratio.

Nickel:

(a) Absorption line:

The most sensitive line, 2320Å, was used.

(b) Lamp current:

A high intensity hollow cathode tube was used. The operating currents were: primary 10 mA, secondary 400 mA.

(c) Slit width:

A 100 μ opening was used.

(d) Flame profile:

When the burner position was lowered the absorption decreased. The zero position gave the maximum absorption.

(e) Flame composition:

No change in absorption occurred when the stoichiometric flame was changed to a fuel-rich flame. This means Ni can be satisfactorily determined in a lean acetylene flame.

The operating conditions used for the three elements are summarised in Table IV.5.

TABLE IV.5.

Experimental conditions for Chromium, Molybdenum and Nickel			
	Cr	Mo	Ni
Wavelength (Å)	3580	3132	2310
Lamp current (mA)	10	10	10
Secondary current (mA)	-	-	400
Slit width (μ)	100	100	100
Burner position (mm)	0	0	0
Flame composition	Fuel-rich	Fuel-rich	Stoich-iometric
Air pressure (p.s.i.)	15	15	15
C_2H_2 flow rate (meter reading)	5	5	4

Interference studies

Chromium:

Fluoride, sulphate, phosphate and tungstate (100 and 500 ppm) were added to chromium solution (20 and 50 ppm as nitrate) to test if any interference occurred. No significant interference was

was observed, as shown in the table below:

TABLE IV.6.

Effect of Anions on Chromium Absorption		
Interferent	% Transmission (20 ppm Cr)	% Transmission (50 ppm Cr)
None	60	42
F^- 100 ppm	60	42.5
500 ppm	59	43
SO_4^{2-} 100 ppm	60	42
500 ppm	59	43
PO_4^{3-} 100 ppm	60	43
500 ppm	60	43
MoO_4^{2-} 100 ppm	60	43
500 ppm	59	42.5
WO_4^{2-} 100 ppm	60	43
500 ppm	60	43

Molybdenum:

Interferences were sought in solutions containing 50 and 100 ppm molybdemum (as sodium molybdate). Fluoride, sulphate, tungstate and phosphate were the interfering ions studied. Appreciable interference was only observed with fluoride and tungstate at high concentration (500 ppm) and then only with molybdemum at the lower concentration (50 ppm). The results are shown in Table IV.7.

TABLE IV.7.

Effect of anions on Molybdemum absorption		
Interferent	%T(Mo 50 ppm)	%T(Mo 100 ppm)
None	92	81
F^- 50 ppm	91	82
100 ppm	92	82
200 ppm	93	83
500 ppm	95	82
SO_4^{2-} 50 ppm	91	82
100 ppm	91.5	82
200 ppm	92	82
500 ppm	92.5	82
PO_4^{3-} 50 ppm	91	82
100 ppm	93	82.5
200 ppm	93	82
500 ppm	93	82
WO_4^{2-} 50 ppm	91	83
100 ppm	92	83
200 ppm	93	82
500 ppm	94	82

Nickel:

Fluoride, sulphate, phosphate, molybdate and tungstate were added to 50 and 100 ppm nickel solution (as chloride). No significant interference was observed. The results are given in Table IV.8.

TABLE IV.8.

Effect of anions on Nickel absorption			
Interferent		%T(Ni 50 ppm)	%T(Ni 100 ppm)
None		78	60
F^-	50 ppm	78	60.5
	100 ppm	77	60
	500 ppm	76	62
SO_4^{2-}	50 ppm	78	60
	100 ppm	77	59
	500 ppm	76	60
PO_4^{3-}	50 ppm	77	60
	100 ppm	76	60
	500 ppm	78	61
MoO_4^{2-}	50 ppm	77	60
	100 ppm	77	60
	500 ppm	77	60
WO_4^{2-}	50 ppm	77.5	60
	100 ppm	78	60
	500 ppm	76	59.5

iii) Chemical Interference of Gallium and Indium

Gallium and indium can be easily determined from an aqueous solution by use of an air-acetylene flame, though very few applications have been published. The following potential interfering ions and compounds were studied.

Group 1. Li^+ Na^+ K^+ Ag^+ Cu^{2+}

Group 2. Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+} Zn^{2+} Cd^{2+} Hg^{2+}

Group 3. BO_3^{3-} Al^{3+} Ce^{4+} Th^{4+}

Group 4. Ti^{4+} Sn^{2+} Pb^{2+}

Group 5. NH_4^+ NO_3^- HPO_3^{2-} VO_4^{3-} Bi^{3+} As^{3+}

Group 6. Cr^{3+} SO_4^{2-} SeO_3^{2-} MoO_4^{2-} WO_4^{2-} UO_2^{2+}

Group 7. F^- Br^- I^- Mn^{2+}

Group 8. Fe^{3+} Co^{2+} Ni^{2+}

Miscellaneous: Hydrochloric acid, nitric acid, sulphuric acid, and phosphoric acid (5% v/v in each case), di-sodium salt of ethylene diaminetetraacetic acid (EDTA), citric acid and oxalic acid (1000 ppm in each case).

The instrumental parameters involved in the atomic absorption of gallium and indium were investigated as detailed below.

Gallium:

(a) Absorption line:

Mulford[51] lists six analytical lines. The first four lines were tested and sensitivity decreases in the following order: 2874 Å, 2944 Å, 4172 Å and 4033 Å. The most sensitive line, 2874 Å, was used.

(b) Lamp current:

No appreciable change in absorbance was observed when the current was increased from 4 to 8 mA. The highest recommended current is 8 mA, but 6 mA was used here.

(c) Slit width:

An increase of slit width did not affect the absorbance of Ga (50 ppm).

(d) Flame profile:

The absorbance decreased as the burner was lowered. The zero position was used.

(e) Flame composition:

A rich acetylene flame gave slightly more sensitive absorption than a lean flame.

Indium:

(a) Absorption line:

The first two of six analytical lines[51] were studied. The line at 3039 Å was found slightly more sensitive than the 4356 Å line. Line 3039 Å was used.

(b) Lamp current:

There was no appreciable change in absorbance when the current was increased from 4 to 8 mA. 6 mA was used.

(c) Slit width:

No appreciable effect was observed when the slit width was increased.

(d) Flame profile:

Absorption decreased as the burner was lowered. The zero position gave the highest absorption.

(e) Flame composition:

Fuel-rich flame gave slightly more sensitive absorption.

The operating conditions used for the two elements are summarised in Table IV.9.

TABLE IV.9.

Experimental conditions for Gallium and Indium		
	Ga	In
Wavelength (Å)	2874	3039
Lamp current (mA)	6	6
Slit width (μ)	100	100
Burner position (mm)	0	0
Flame composition	Fuel-rich	Fuel-rich
Air pressure (p.s.i.)	15	15
C_2H_2 flow rate (meter reading)	5	5

Interference studies

Gallium:

Of twenty-eight cations (as chlorides or nitrates), 10 anions (as sodium salts), three complexing agents and four acids, the following interfered in the absorption of 50 μg/ml gallium (as perchlorate).

TABLE IV.10.

Interference with Gallium

Interfering ions (1000ppm)	%T (50 ppm Ga)	Interfering ions (1000 ppm)	%T (50 ppm Ga)
None	88.5	F^-	90.0
Mg^{2+}	90.0	SO_4^{2-}	90.0
Ca^{2+}	91.0	HPO_4^{2-}	90.0
Sr^{2+}	90.5	MoO_4^{2-}	90.0
Ba^{2+}	90.0	WO_4^{2-}	90.0
Ce^{4+}	90.0	BO_3^{3-}	92.0
Th^{4+}	90.0		
Ti^{4+}	90.0	H_3PO_4(5%)	91.0
Fe^{3+}	90.0	H_2SO_4(5%)	90.0
Co^{2+}	90.0		

Only Ca^{2+}, Sr^{2+}, BO_3^{3-} and phosphoric acid definitely interfere.

Indium:

The 28 cations (as chlorides or nitrates), 10 anions (as sodium salts) and three complexing agents at concentrations 1000 µg/ml respectively, and four acids at 5% v/v were tested with 25 ppm indium in aqueous solution as chloride. The figures in the following table are % transmission.

TABLE IV.11.

Interference with Indium

Group 1.	None	Li^+	Na^+	K^+	Ag^+	Cu^{2+}	
	75	70	69	69	70	69	
Group 2.	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
	72	72	71	70	78	70	72
Group 3.	BO_3^{3-}	Al^{3+}	Ce^{4+}	Th^{4+}			
	75	69	70	69			
Group 4.	Ti^{4+}	Sn^{2+}	Pb^{2+}				
	70	72	68				
Group 5.	NH_4^+	NO_3^-	HPO_4^{2-}	VO_4^{3-}	Bi^{3+}	As^{3+}	
	69	70	69	68	75	74	
Group 6.	Cr^{3+}	SO_4^{2-}	SeO_3^{2-}	MoO_4^{2-}	WO_4^{2-}	UO_2^{2+}	
	70	68	68	69	70	70	
Group 7.	F^-	Br^-	I^-	Mn^{2+}			
	68	78	76	68			
Group 8.	Fe^{3+}	Ni^{2+}	Co^{2+}				
	77	68	72				
Miscellaneous:	HCl	HNO_3	H_2SO_4	H_3PO_4	EDTA	Citrate	Oxlate
	78	73	72	75	68	70	70

Of all the ions tested, As^{3+}, Bi^{3+}, and BO_3^{3-} did not interfere. Fe^{3+}, Zn^{2+} and Br^- and HCl supressed the indium signal. The rest of the ions gave 4 to 8 % enhancement. The experiment was repeated and the same interference pattern was found. A Techtron AA5 Atomic Absorption Spectrophotometer was available in the later part of this work. The same interfering ions were tested with the new instrument, and no significant enhancement or suppression was found. This may

be due to the different fuel and air flow rates, and hence the different sample feed rate, the difference in the geometry of the burner and nebuliser design; all these factors lead to a different combustion pattern in AA3 and AA5 atomic absorption spectrophotometers. This may account for the difference in interfering behaviour. The experimental conditions when the AA5 atomic absorption spectrophotometer was used are given below.

Wavelength: 3039 Å

Lamp current: 6mA

Slit width: 100μ

Burner position: 7mm

Flame composition: Stoichiometric flame

Air pressure: 15 p.s.i.

Air flow rate: 6.5 (meter reading)

C_2H_2 flow rate: 3.0 (meter reading)

A further interference study was made by examining the effect of various concentrations of interfering ions on a 50 ppm indium solution. The results are given in the following tables.

TABLE IV.12.

Interference on Indium

	%T(Na)	%T(Sr)	%T(F)	%T(SO_4)	%T(WO_4)
None	60	60	60	60	60
50 ppm	58	58	56	57	58
100 ppm	56	56	56	57	57
500 ppm	56	59	57.5	57	57
1000 ppm	58	60	57	57	57

The following results were obtained from the AA5 Atomic Absorption Spectrophotometer:

TABLE IV.12(A).

Interference on Indium

	%T(Na)	%T(Sr)	%T(F)	%T(SO_4)	%T(WO_4)
None	51	51	51	51	51
50 ppm	52.5	52	49	50	51
100 ppm	51	51	49.5	50	51
500 ppm	52	52	51	50	51
1000 ppm	52	53	51	50	51

Small enhancement was found from the data from the AA3. No significant interference was obtained from the data from AA5.

IV. 2. THE POSSIBILITY OF ANION DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY

One approach to the determination of anions by atomic absorption spectrometry involves the quantitative precipitation of the anion by a suitable reagent, followed by the determination of the metallic portion of the precipitate. For example, chloride can be precipited as silver chloride, and atomic absorption spectrometry used to determined the silver. The method is limited by two factors. Firstly, the solubility product of the salt precipitated imposes a limit on the proportion of anion which can be precipitated. Secondly, it is necessary to ensure that other insoluble salts of the same metal are not precipitated, or are removed before the atomic absorption determination.

FIG. IV. 10

EFFECT OF PHOSPHATE ON CALCIUM ABSORPTION

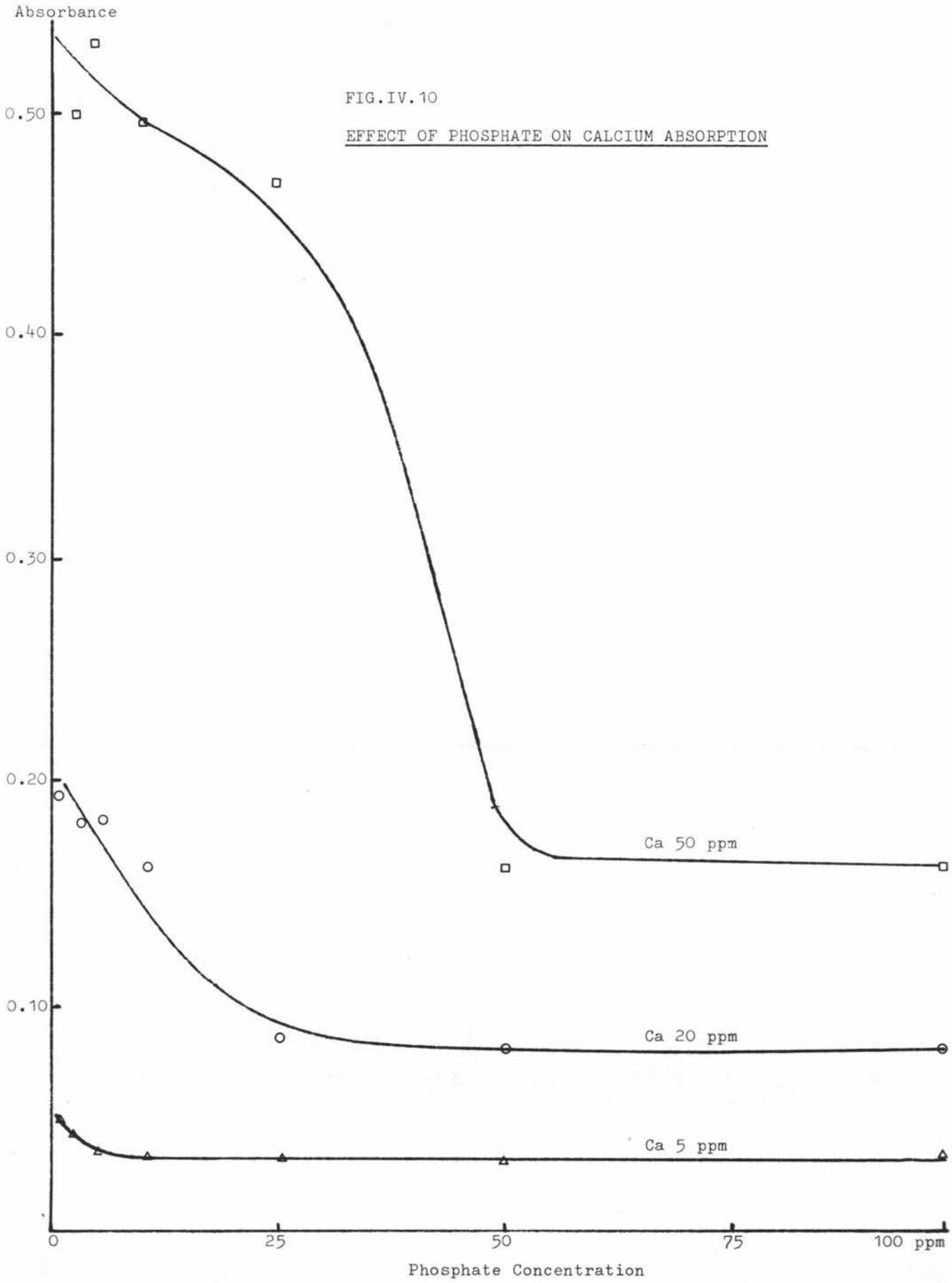
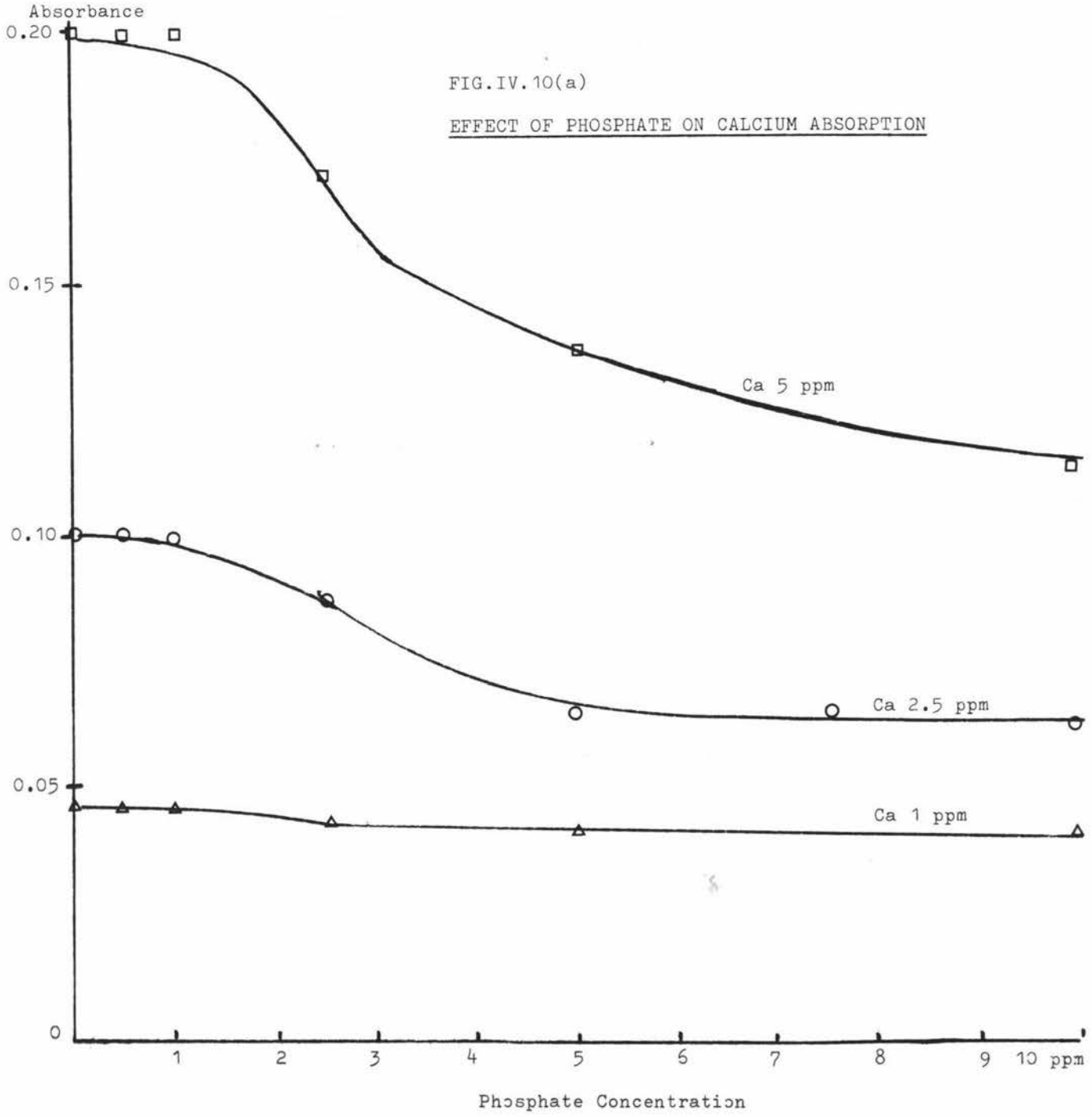


FIG. IV. 10(a)

EFFECT OF PHOSPHATE ON CALCIUM ABSORPTION



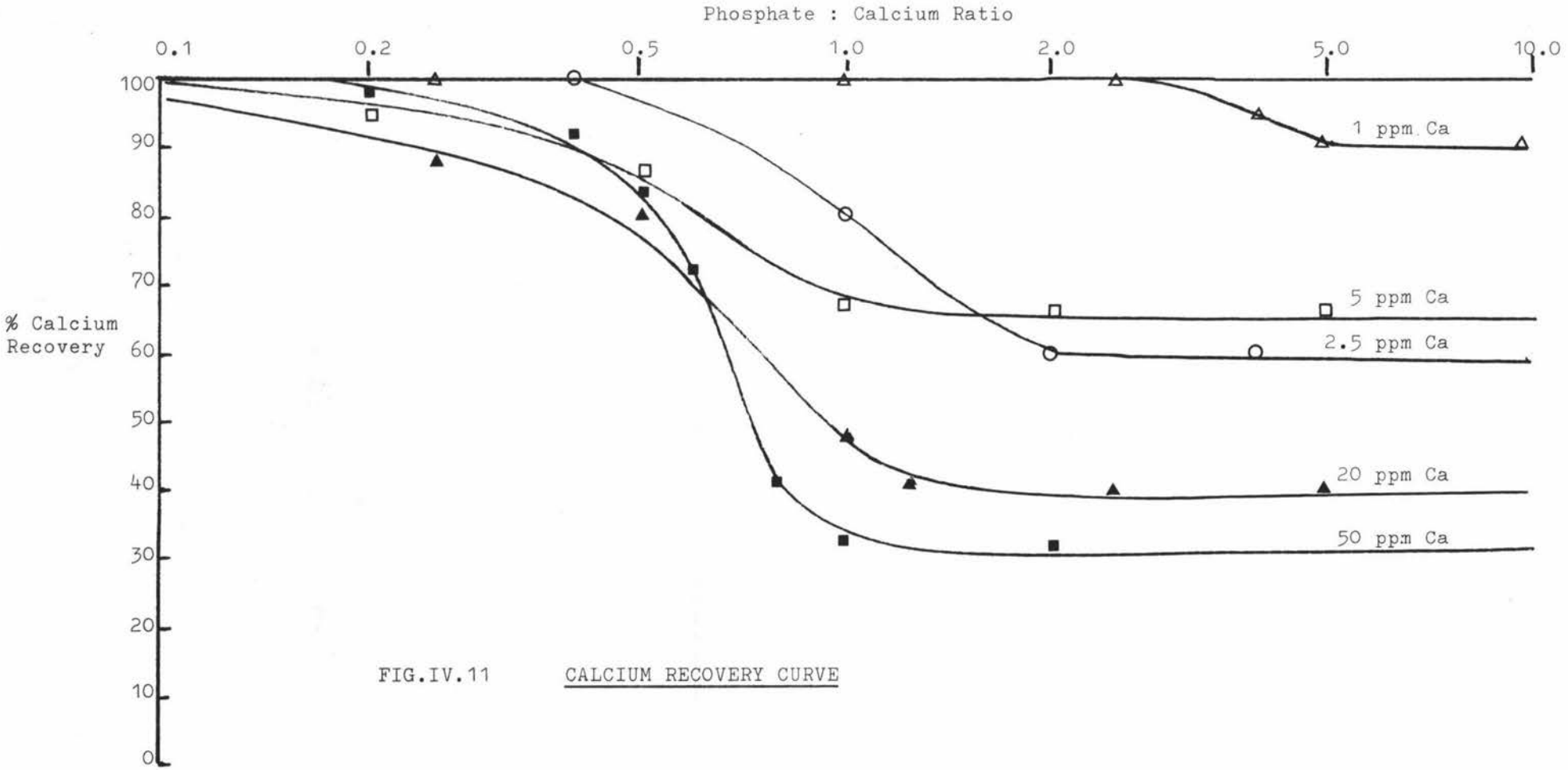


FIG.IV.11 CALCIUM RECOVERY CURVE

The approach using interference effects has already been investigated by flame emission. The present study involves examination of atomic absorption interferences by phosphate, tungstate and molybdate on calcium absorption, to find the conditions under which these anions might be determined quantitatively.

The depression of Ca absorption by phosphate is shown in Table IV.13 and Figs IV.10 and IV.10(a). The calcium salt is present as chloride and phosphate as the di-sodium salt.

The figures show that the depression of the calcium absorption is relatively insignificant until the phosphate concentration reaches a value of the order of 10-20% of calcium concentration. A regular decrease of calcium absorption follows until a limiting depression is reached. The limiting depression depends on the absolute calcium and phosphate concentrations, but is reached when the PO_4^{3-}/Ca^{2+} ratio is in the range 1.0 - 5.0 in the present experiments (covering the Ca concentrations of 1-50 ppm).

The effect of the PO_4^{3-}/Ca^{2+} ratio on the calcium absorption is shown in Fig IV.11. The vertical axis of this graph is labelled "% Ca recovery" and represents the apparent percentage of calcium in the flame which is still in the atomic form. The precise shape of these curves is somewhat sensitive to variations of the flame composition and the height of the light path in the flame.

At low phosphate concentrations, the calcium absorption declines almost linearly with increasing phosphate concentration (Fig IV.10). This linear depression can be used as the basis of indirect determination of phosphate. However the concentration range

TABLE IV.13.

Phosphate Depression of Calcium

Ca(ppm)	Phosphate(ppm)	%T	A	Ca(ppm)*	Phosphate(ppm)	%T	A
1	0	90	0.0458	5	0	89	0.0506
	0.5	90	0.0458		1	89	0.0506
	1	90	0.0458		2.5	90.5	0.0434
	2.5	90.5	0.0434		5	92	0.0362
	5	91	0.0410		10	92.5	0.0339
					25	92.5	0.0339
2.5	0	79.5	0.0996		50	92.5	0.0339
	0.5	79.5	0.0996		100	93	0.0315
	1	79.5	0.0996				
	2.5	82	0.0862	20	0	64	0.194
	5	86	0.0655		1	64	0.194
	7.5	86	0.0655		2.5	65	0.184
	10	86.5	0.0630		5	66	0.181
					10	68.5	0.164
5	0	62.5	0.204		25	82	0.0862
	0.5	62.5	0.204		50	82.5	0.0835
	1	63	0.201		100	82.5	0.0835
	2.5	67.5	0.171				
	5	73	0.137	50	0	29	0.538
	10	77	0.114		1	29	0.538
					2.5	31	0.509
					5	28.5	0.545
					10	32	0.495
					25	34	0.469
					50	68	0.164
					100	68	0.164

*Measurements in this column were with burner rotated to decrease sensitivity.

FIG.IV.12

EFFECT OF TUNGSTATE ON Ca ABSORPTION

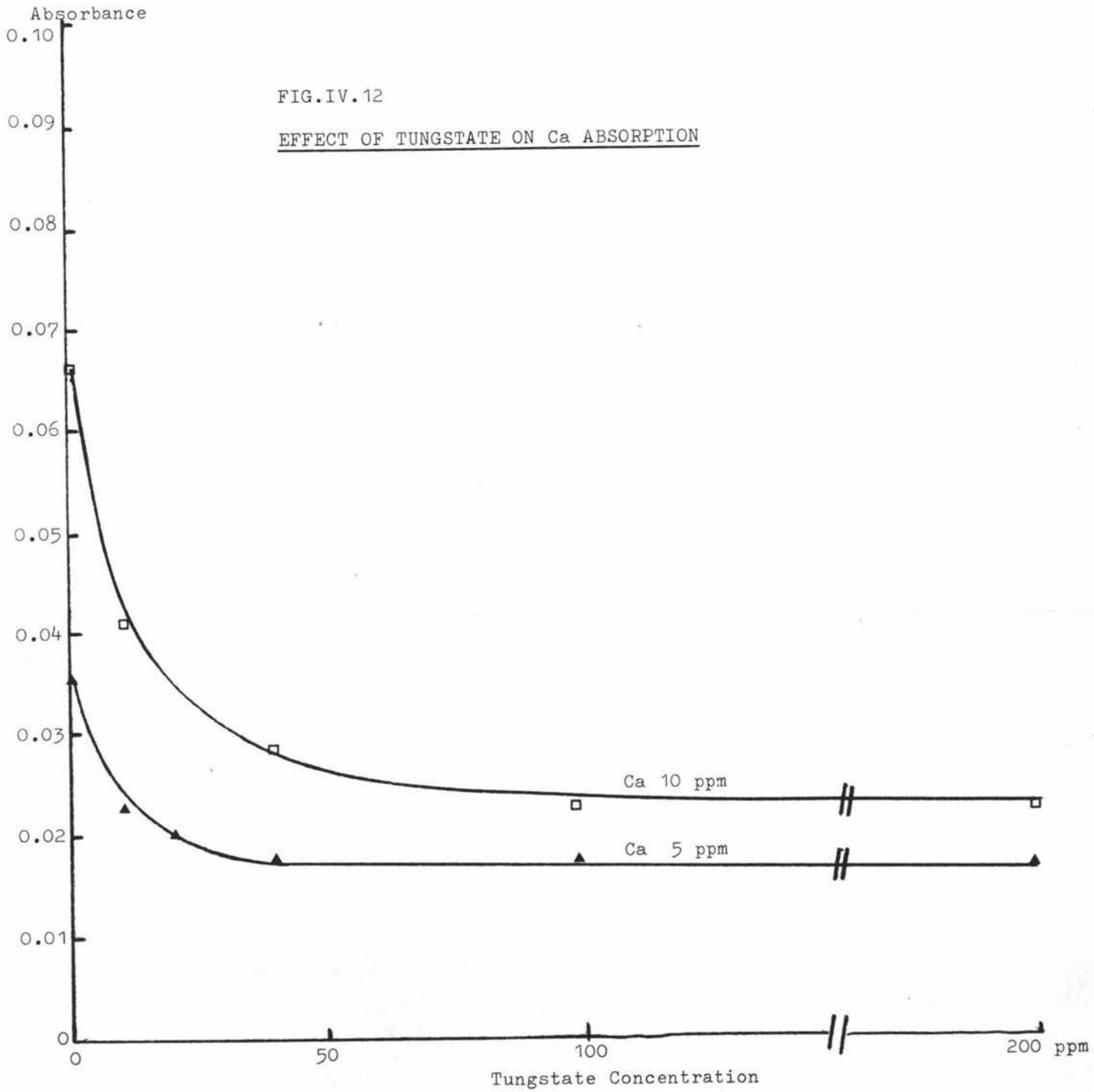
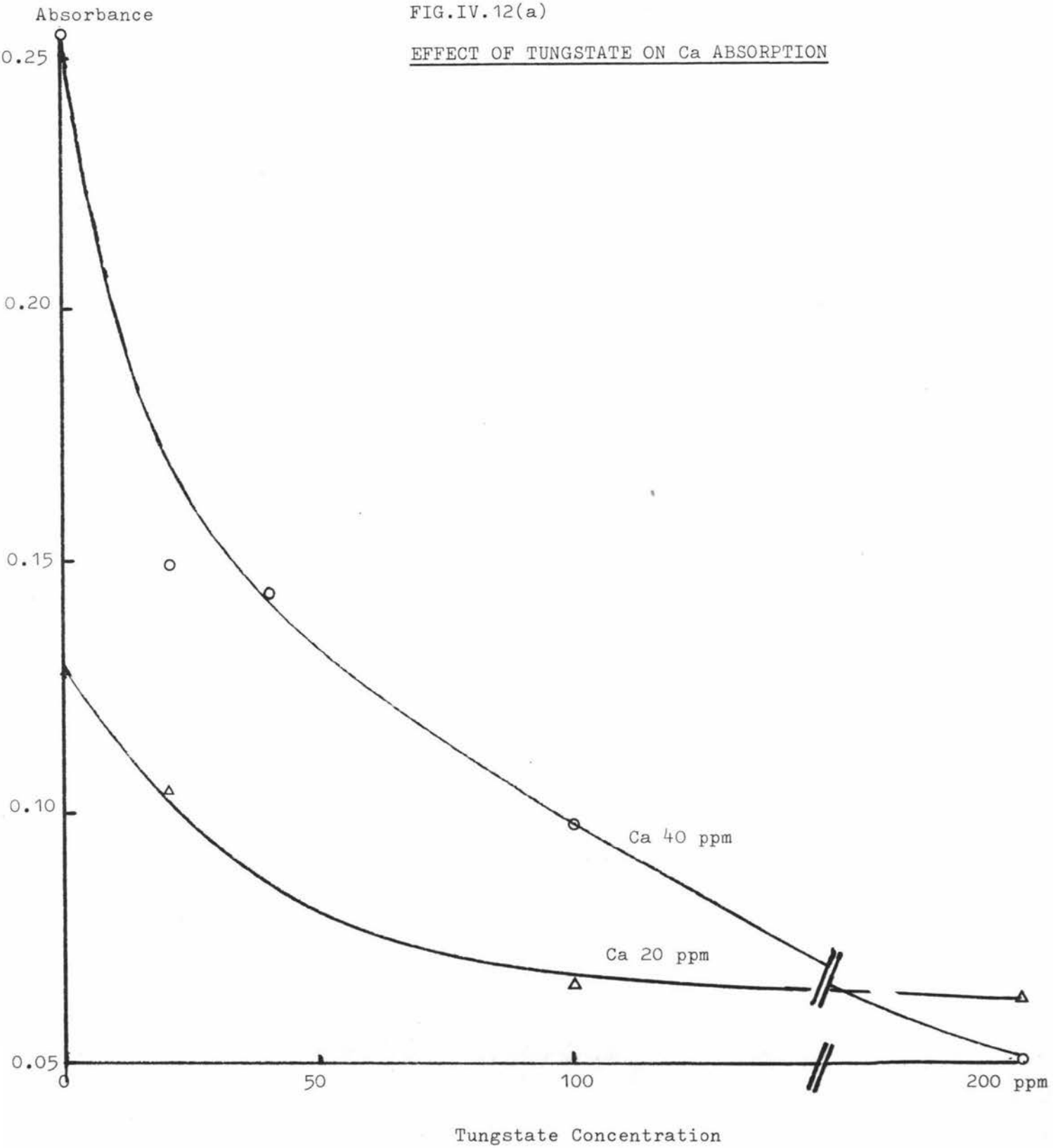


FIG.IV.12(a)

EFFECT OF TUNGSTATE ON Ca ABSORPTION



is quite limited. Moreover, other ions that interfere with the calcium determination must be absent, e.g., sulphate, silicate, aluminate and zirconium.

TABLE IV.14.

Tungstate Depression of Calcium Absorption

Ca^{2+}	$/WO_4^{2-}$	%T	A	Ca^{2+}	$/WO_4^{2-}$	%T	A
5	0	92	0.0362	20	0	74.5	0.128
	10	95	0.0223		10	79	0.102
	20	95.5	0.0200		20	78.5	0.105
	40	96	0.0177		40	82	0.0862
	100	96	0.0177		100	86	0.0655
	200	96	0.0177		200	86.5	0.0630
10	0	86	0.0655	40	0	55.5	0.256
	10	91	0.0410		10	70.5	0.152
	20	92	0.0362		20	71	0.149
	40	93.5	0.0292		40	72	0.143
	100	95	0.0233		100	80	0.0969
	200	95	0.0233		200	89	0.0506

Tungstate (as the disodium salt) inhibits calcium absorption in a similar manner (Table IV.14, Figs IV.12 and IV.12(a)). However, the concentration range of the linear depression is also quite small and other interfering ions must be absent.

Molybdate (as the disodium salt) does not interfere with the calcium absorption up to 100 ppm.

In a recent paper, Bond and O'Donnell[55] showed the determination of fluoride by atomic absorption spectrometry. Fluoride ion

TABLE IV.14(A).

Molybdate Depression of Calcium Absorption

Ca^{2+}	MoO_4^{2-}	%T	Ca^{2+}	MoO_4^{2-}	%T
5	0	96	25	0	82
	5	96		5	82
	10	96.5		10	82
	25	97		25	82
	50	97		50	83.5
	100	97		100	85
10	0	92	50	0	65
	5	92		5	66
	10	92		10	66
	25	93		25	66
	50	93.5		50	67
	100	91		100	69

depresses the absorption of magnesium in the air-coal gas flame, the change in absorbance of the Mg resonance line at 2852Å being proportional to the fluoride concentration over the concentration 0.2 - 20 ppm. In the absence of interfering ions, principally sulphate and phosphate, the effect can be used to determine fluoride in this concentration range.

IV. 3. ATTEMPTS TO IDENTIFY THE SPECIES CAUSING INTERFERENCE

i) Investigation of Flame Emission Spectra.

A variable-speed motor was attached to the wavelength setting control of the Techtron AA3 atomic absorption spectrophotometer. A Techtron FE 1 burner was used instead of the AB 41 type used in the absorption method, and a chopper was placed between the lens and the

monochromator. The emission spectra were obtained by slow scanning of the wavelength range of the instrument while spraying the solution into the flame. A permanent record was obtained with the aid of a recorder.

The following solutions were sprayed in turn into the air-acetylene flame.

1. Ca (as chloride), 50 ppm.
2. Phosphate (as phosphoric acid), 500 ppm.
3. Ca, 50 ppm, plus phosphate, 500 ppm.

The peaks and bands[56] obtained in the emission spectra are listed below, together with identification of the species responsible.

TABLE IV.15.

Emission Spectra of Calcium and Phosphate

Ca		Phosphate	Ca + Phosphate	
Wavelength(Å)	Species		Wavelength(Å)	Species
4227 (very strong peak)	Ca	Molecular bands at 5100, 5262, 5600 Å were not observed in the air-C_2H_2 flame Atomic line of P at 1775 Å is outside range of detection	4227 (strong peak)	Ca
4360 (weak peak)	C_2		4360 (weak peak)	C_2
5550 (medium band)	CaOH		5550 (medium band)	CaOH
5890 (strong peak)	Na impurity		5890 (strong peak)	Na
6200-6500 (diffuse band)	CaOH		6200-6500 (diffuse band)	CaOH

The phosphate bands referred to in the above table have been reported[57] in the argon-hydrogen flame, but were not observed in the present work. The higher temperature of the air-acetylene flame causes extensive decomposition of the phosphate radicals responsible for these

bands.

It is noteworthy that no new emitting species were found when the mixture containing calcium and phosphate was examined. However, the peaks and bands arising from calcium-containing species were reduced in intensity. The diffuse CaOH orange band system (6200-6500Å) was better resolved, showing separate maxima at 6230 and 6208 Å.

Quantitative measurements were made by comparing the emission signal of Ca 500 ppm with that of Ca 500 ppm plus phosphate 5000 ppm. The ratio of Ca singal at 4227 Å to that of Ca plus phosphate was 100 : 65 while at 5550 Å the ratio was 100 : 50 and at 6200 Å 100 : 52.

It is clear that the chemical form of the calcium in the flame has been modified by the presence of phosphate. Not only is there a reduction in the proportion existing as ground state and excited state atoms, but also there is a reduction in the concentration of other calcium-containing molecular species such as CaOH. It appears, therefore, that approximately 30-50% of the calcium normally present as Ca and CaOH is combined in one or more molecular species containing Ca and P (and probably O, possibly H).

The fact that no new molecular bands were observed in the emission spectrum seems to indicate either that any transitions involving these species lie outside the wavelength range examined, or that they are of insufficient intensity to have been recorded with the concentration used.

Emission spectra of Sr, (500 ppm), and Sr 500 ppm plus phosphate 5000 ppm were also obtained. The emission peaks and bands for the Sr solution[56] were:

4359 Å, C_2 emission from the flame

4607 Å, resonance line of atomic Sr

5890 Å, Na emission

6060 Å, SrOH band

No extra peak or band was observed for the Sr plus phosphate solution. The ratio of Sr signal to that of Sr plus phosphate at 4607 Å was 100 : 35 while at 6060 Å the ratio was 100 : 20. This indicates that the Sr-phosphate molecular species are even more stable than the corresponding Ca species.

ii) Investigation of Solids in the Flame Gases.

Solutions were aspirated into the flame and solid particles entrained in the flame gases were collected with the aid of a micro-slide mounted approximately 1-2 cm above the top of the flame where the temperature of the flame gases is approximately 600 K. Infra-red spectra were obtained from solid particles by compressing the sample into a potassium bromide disc. X-ray powder diffraction photographs of the solid particles collected were also obtained.

(a) Solid from the aspiration of $Ca(NO_3)_2$.

The solution aspirated contained 10% $Ca(NO_3)_2$. The X-ray powder photograph , shown in Plate 3(a), corresponded very closely to the data available for calcite, $CaCO_3$, as shown in the following table.

TABLE IV.16.

X-ray Data from Plate 3(a)

Experimental sample		Calcite	
d-spacing(Å)	Intensity	d-spacing(Å)	Intensity
3.79	weak	3.86	12
2.99	very strong	3.035	100
2.85	very weak	2.845	3
2.46	medium	2.495	14
2.25	medium	2.285	18
2.07	medium	2.095	18
1.89	medium	1.927 1.913	5 17
1.85	medium	1.875	17

In every case, (apart from the very weak line), the experimental d-spacings are lower than the literature values by 1.2 - 1.8%, with an average of 1.4%. This may reflect a personal error in the measurement of the positions of the lines, or may be the result of a small inaccuracy in the mounting of the film in the holder.

Confirmation that the sample was calcite was obtained from the infra-red spectrum of the solid. A clean and simple spectrum was obtained, with peaks at 1430 cm^{-1} (very strong, rather broad) and 869 cm^{-1} (medium, very sharp). Spectra of simple inorganic carbonates recorded in the literature show a strong peak at 1470 - 1420 cm^{-1} and a medium peak at 890 - 820 cm^{-1}. Bhangarantam and Venkataryudu[58] quote maxima of 1429 cm^{-1} and 879 cm^{-1} for calcite.

It is evident that, in the region where the sample was collected, calcite is the predominant stable product from the reactions

involving the aqueous calcium nitrate sample introduced into the flame. Species present in the flame itself include, among others, Ca, CaO, CaOH, C, C_2, CO, O_2, and CO_2. At the relatively low temperatures just above the flame, calcium carbonate is thermodynamically stable. (The dissociation pressure is 1 atmosphere at 900 C). The partial pressure of CO_2 is sufficiently high, and the reaction $CaO + CO_2 \longrightarrow CaCO_3$ sufficiently fast, that only $CaCO_3$ (and no CaO) is found to be deposited.

(b) Effect of addition of H_3PO_4.

In a second experiment, 25 ml of conc. H_3PO_4 was added to 250 ml of 10% $Ca(NO_3)_2$ solution, and the solid material in the flame gases sampled as before.

The X-ray powder diagram (Plate 3(b) shows the sample to be a totally different compound from that obtained previously. The strongest calcite line (at a d-spacing of 3.035 A) is absent. The powder diagram, however, does contain a number of sharp lines, indicating the formation of a regular cyrstalline compound. In view of the positive identification of calcite in the previous experiment, it was considered justifiable to correct all subsequent measurements of d-spacings by adding 1.4% to the value obtained. This should be appropriate, regardless of whether the discrepancy is a personal error or one due to the instrument.

The d-spacings are shown in the table below, together with 'corrected' values. The only calcium-phosphate crystal form whose powder photograph bears a resemblance to the unknown solid is secondary calcium orthophosphate, $CaHPO_4$ (X-ray powder diffraction file, card 9/80). The d-spacings and intensities from the Powder

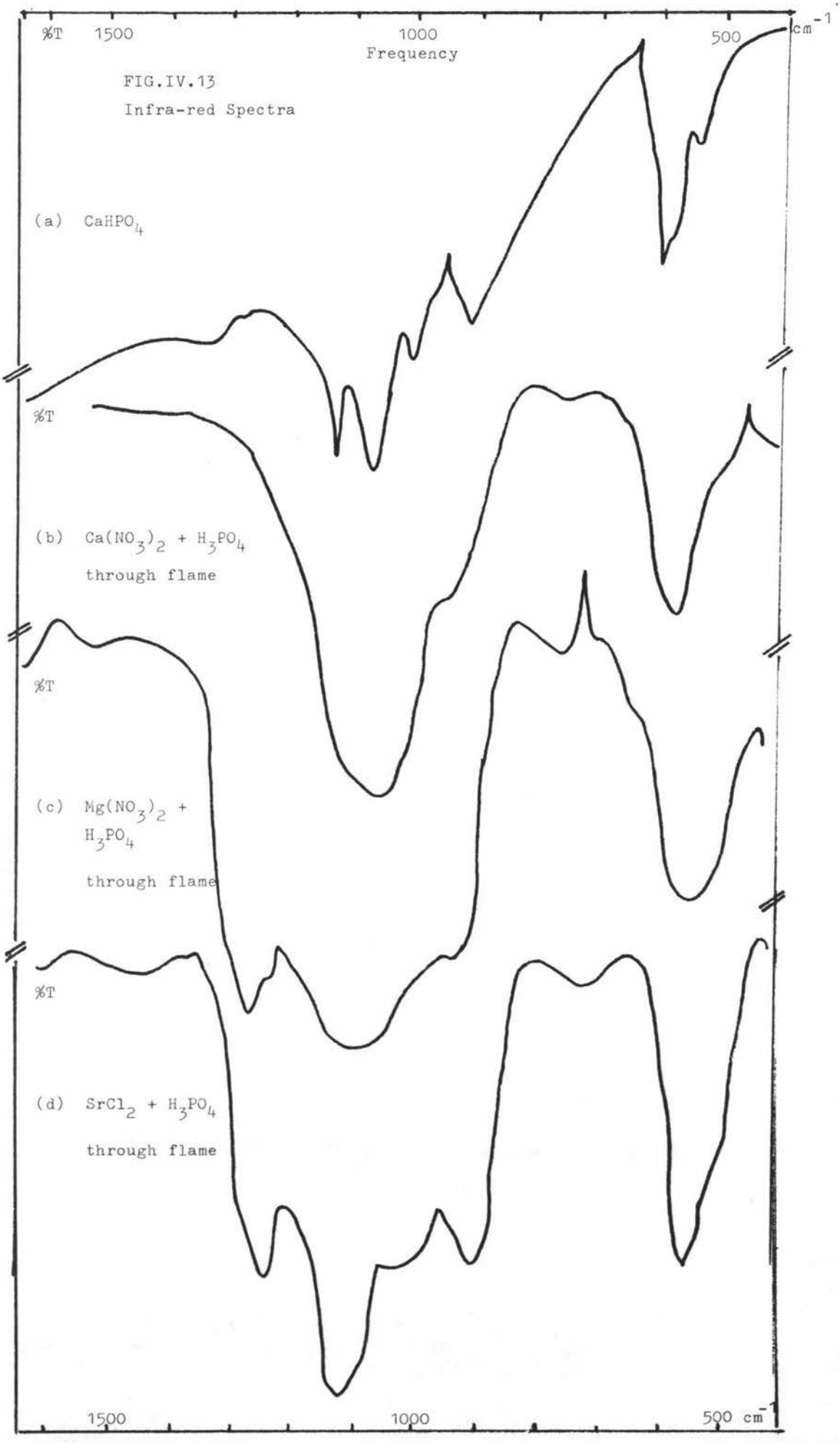


FIG.IV.13
Infra-red Spectra

Diffraction File are recorded in the table below for comparison.

TABLE IV.17.

X-ray Data from Plate 3(b)

Sample			$CaHPO_4$	
d-spacing Å	'Corrected' d-spacing	Intensity	d-spacing Å	Intensity
3.325	3.37	strong	3.37 3.35 3.33	70 75 <20
3.09	3.135	weak	3.13	20
2.885	2.925	medium	2.96 2.94	100 35
2.67	2.705	medium	2.75 2.72	<20 35
2.455	2.49	weak		
2.225	2.255	weak		

The infra-red spectrum of this solid is shown in Fig IV.13(b), and is discussed on page 63, together with similar spectra from $Mg(NO_3)_2 + H_3PO_4$ and $SrCl_2 + H_3PO_4$. Fig IV.13(a) is the spectrum from a known sample of $CaHPO_4$.

iii) Effect of H_3PO_4 with $Mg(NO_3)_2$ and with $SrCl_2$.

The X-ray powder diagrams (Plate 3(c), (d)) of the solids obtained from aspiration of these solutions (25 ml conc. H_3PO_4 in 250 ml 10% $Mg(NO_3)_2$ solution, 25 ml conc. H_3PO_4 in 250 ml 10% $SrCl_2$, respectively) do not correspond to any compound of magnesium and strontium previously recorded. The X-ray photographs were, in these

cases, not as sharp and simple as those obtained previously. The major lines are recorded below.

TABLE IV.18.

X-Ray Data from Plate 3(c),(d)

$Mg(NO_3)_2$- H_3PO_4			$SrCl_2$- H_3PO_4		
d-spacing Å	'corrected' d-spacing	Intensity	d-spacing Å	'corrected' d-spacing	Intensity
4.83	4.90	weak	5.00	5.07	strong
4.42	4.46	medium	4.64	4.705	strong
3.92	3.975	medium	4.30	4.36	weak
3.66	3.71	weak	3.87	3.92	very strong
3.32	3.36	strong	3.54	3.59	strong
3.13	3.17	weak	3.43	3.48	strong
2.86	2.90	strong	2.97	3.01	medium
			2.81	2.85	medium
			2.58	2.62	weak
			2.36	2.39	strong

In the case of the strontium compound, some of the observed lines correspond to lines recorded in the Powder Diffraction File for 'strontium hydrogen phosphate' (card 12/364), 'α-strontium hydrogen phosphate' (card 12/359), and 'β-strontium hydrogen phosphate' (card 12/368), but other lines, especially the strong ones at 5.07 Å and 4.71 Å, remain unaccounted for.

The solid obtained in this experiment may therefore be (i) previously unrecorded crystal forms of compounds of known formula; (ii) complex mixtures of several compounds or several crystal modifications of a single compound.

This conclusion is supported by the evidence from the infrared spectra. All three spectra (Fig IV.13(b),(c),(d)) show the characteristic features of derivatives of ortho-phosphoric acid. These include, particularly, a medium-strong peak in the vicinity of 540-580 cm^{-1}, associated with O-P-O bending modes in the ortho-phosphate derived anions[59], medium strong peaks at 890-930 cm^{-1}, strong peaks at 1050-1120 cm^{-1}, and medium strong peaks at 1120-1260 cm^{-1}, the last three absorptions being associated with P-O stretching vibrations[60].

There are general similarities to the spectrum of the known sample of $CaHPO_4$ (Fig IV.13(a)), but the spectra of the solids from the flame show greater broadening and overlapping of absorption peaks. This is consistent with the presence of more than one compound of this type, or with crystal imperfections which could easily arise in a solid deposited from flame gases.

iv) Solids from aspiration of solutions containing Ca, Cl and PO_4.

A solution was prepared by dissolving 25g of $Ca_3(PO_4)_2$ in 25 ml of conc. HCl and diluting to 250 ml with water. (Approximate concentrations of ions were therefore Ca 0.9 m/l, Cl 1.1 m/l, total phosphate 0.6 m/l). The X-ray powder-diffraction photograph (Plate 3(e)) was found to be consistent with that which would be expected from a mixture of chlorapatite, 3 $Ca_3(PO_4)_2$. $CaCl_2$ and α-calcium orthophosphate, $Ca_3(PO_4)_2$. Two sets of X-ray powder photograph data

are available[61,62] (Powder Diffraction File cards 2-851, 12-263). As these determinations show some disagreement in the relative intensities of the weaker lines, both sets of data are listed below.

TABLE IV.19.

X-Ray Data from Plate 3(e)

Sample			Chlorapatite				$Ca_3(PO_4)_2$	
d-spacing Å	'corrected' d-spacing	intensity	2-851		12-263		d-spacing Å	intensity
			d-spacing Å	intensity	d-spacing Å	intensity		
11.3*	11.4*	w						
8.4*	8.5*	w			8.32	10		
7.3*	7.4*	w					7.31	25
3.84	3.89	m	3.92	5			3.91 3.88	40 40
3.64	3.69	w					3.69	40
3.38	3.43	w	3.42	20	3.39	14		
3.11	3.15	vw	3.08	10	3.15	10		
2.87	2.91	ms					2.91	100
2.80	2.84	ms	2.85	90	2.86	60	2.86	30
2.73	2.77	s	2.76	100	2.78	100		
2.59	2.63	m	2.64	20	2.63	6	2.62	50
		(diffuse)	2.55	10			2.59	30
2.28	2.31	w	2.31	30				
2.14	2.17	w						
1.93	1.96	m	1.95	50	1.98	18		
1.89	1.92	vw	1.91	20	1.91	10		
1.81	1.84	m	1.84	50	1.84	20		

*These lines could not be measured to better than ± 0.2 Å

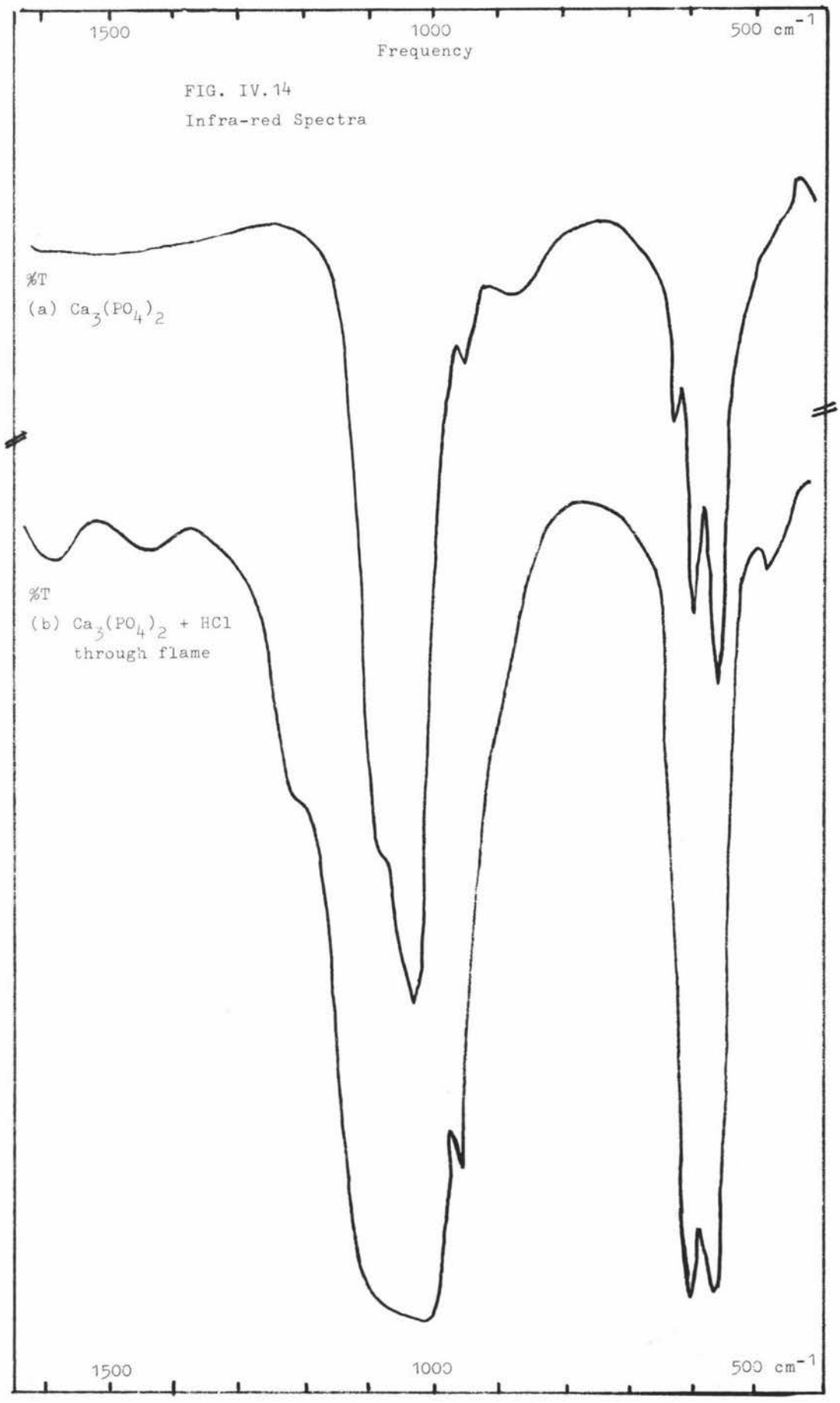


FIG. IV.14
Infra-red Spectra

The identification from the X-ray data is supported by the infra-red spectrum of the solid. A mixture of chlorapatite and α-calcium orthophosphate would be expected to show essentially only those vibrations characteristic of the orthophosphate anion, with possible modifications due to the presence of the chloride ion in the lattice, and peak broadening as observed previously. This is in fact observed, as the spectra in Figs IV14(a) and (b) show. Fig IV.14(a) is the spectrum from a known sample of $Ca_3(PO_4)_2$. The major absorption regions for $Ca_3(PO_4)_2$ are 950-1100cm^{-1} (P-O stretching) and 550-640 cm^{-1} (O-P-O angle bending). The major features of the two spectra are tabulated below.

Known $Ca_3(PO_4)_2$		Sample	
Frequency (cm^{-1})	Remarks	Frequency (cm^{-1})	Remarks
559	medium intensity	568	medium intensity
595	sharp	602	sharp
621	weak, sharp	-	
955	weak, sharp	960	weak, sharp
1030	strong, rather broad	1023	strong, very broad
1080	weak	-	

Under the conditions prevailing after the passage of the solution through the flame it appears that both chlorapatite and α-calcium orthophosphate are sufficiently stable to be deposited. It is clear that, when other anions are present with phosphate, these anions help to determine the nature of the compounds deposited.

Furthermore, the exact nature of the compounds deposited is also influenced by the relative amounts of the cations and anions present. This is shown by an experiment similar to the previous one, but with the total phosphate concentration increased by a factor of approximately 2.5. In this case, there was no evidence of the formation of chlorapatite or α-calcium orthophosphate. The X-ray photograph of the compound deposited (Plate 3(f)) did not correspond to one for which X-ray data are available. The infra-red spectrum suggested the formation of a pyrophosphate or linear triphosphate, but identification was not possible.

In order to obtain yields of several milligrams of deposited solid material the concentrations used in these experiments are considerably higher than those of routine analytical solutions. It is possible that reduction in the concentrations of the ions would alter the composition of the solid deposited.

v) Effect of presence of strontium or lanthanum.

Two solutions were aspirated, one containing 10% of $Ca_3(PO_4)_2$ and 10% of strontium, the other containing 10% of $Ca_3(PO_4)_2$ and 10% of lanthanum. In both cases the solid material gave X-ray photographs without clearly defined lines. In the lanthanum case, particularly, the photograph was characteristic of an amorphous solid.

As indicated earlier (Section I.6), the addition of lanthanum is believed to release Ca^{2+} ions from the solution droplets in the flame by forming small crystals of lanthanum phosphate. The present experiment did not succeed in the isolation of a crystalline lanthanum phosphate. This could be due to relatively extensive disintegration

of crystals (by melting or sublimation), resulting in the later deposition of a material with very poor crystallinity.

IV. 4. GENERAL CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The interference studies carried out in the first part of this work have shown that serious chemical interference is to be expected with alkaline earth elements (other than magnesium) in solutions containing significant amounts of certain stable oxyanions. It is worth noting that chemical interferences arising from stable compound formation do not appear to occur with those elements for which the standard free energy of formation of the metal oxide at about 2300 K is less negative than about -100 kcal mol^{-1} (e.g., PbO: -50 kcal mol^{-1}, MgO: -80 kcal mol^{-1}). It seems to be a strong possibility with metals with standard free energy of formation of -100 to -180 kcal mol^{-1} at 2300 K (e.g., CaO: -170 kcal mol^{-1}). Elements with even more stable oxides can generally not be determined in the air-acetylene flame, but require the higher temperature of the nitrous oxide-acetylene flame.

The experiments with gallium and indium show that small interference effects, possibly not related to compound formation, may occur with other elements. The possibilities of matrix effects, including changes in the physical properties of the solution and of the combustion pattern in the flame, must be considered. In such cases, it is always advisable to use standard solutions with a composition similar to that of the solutions being analysed.

The restrictions on using major interference effects for quantitative determination of anions have already been noted. Nevertheless, some further work in testing the method, especially for

phosphate, would be useful. It would be necessary to know, for example if the curves obtained are reproducible in the presence of others ions (e.g., chloride) which do not themselves cause interference.

In the elucidation of the nature of compounds formed in flame reactions, the study of flame emission seems to hold little promise. A much more rewarding approach involves the separation and study of solids entrained in the flame gases. This work has shown the possibility of separating and identifying reaction products from a region just above the flame. The next step is to devise methods for collecting solid particles from the flame itself. It would be necessary to do this without causing too much disturbance to the flame - a number of tungsten wires placed across the flame might prove satisfactory. Comparison of the results of experiments of this kind with the present work would help to indicate, for example, whether relatively large crystals of stable compounds are formed in the flame itself or are only built up by deposition above the flame.

In the present work, in order to collect several milligrams of solid in a short time, the concentrations of solutions used were much higher than ordinary analytical concentrations. Before extrapolating the results to explain the behaviour of analytical solutions, it would be necessary to carry out some experiments involving more dilute solutions, with particles being collected over a much longer period of time. Any variation of products with solution composition and with flame composition should be examined.

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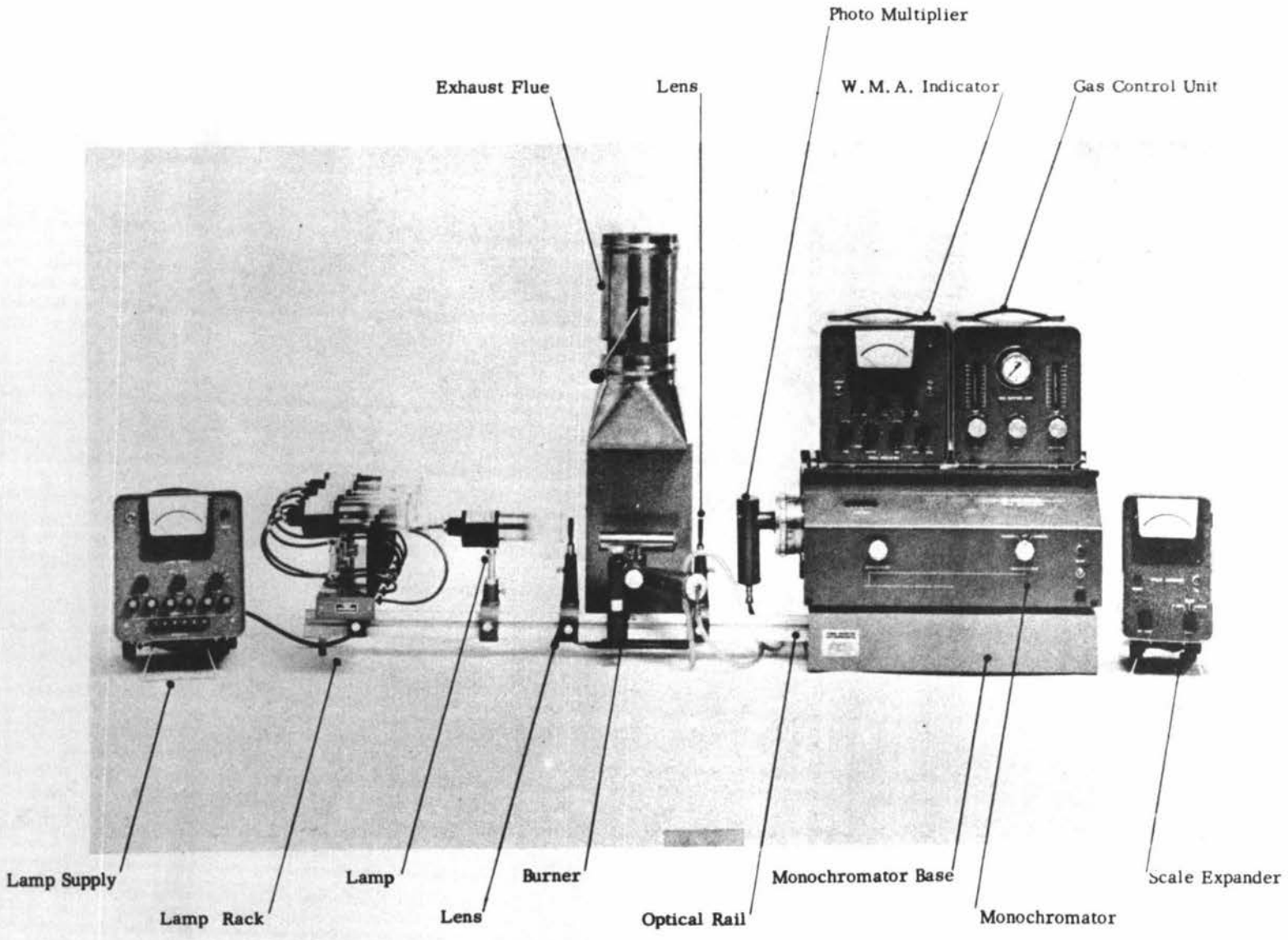
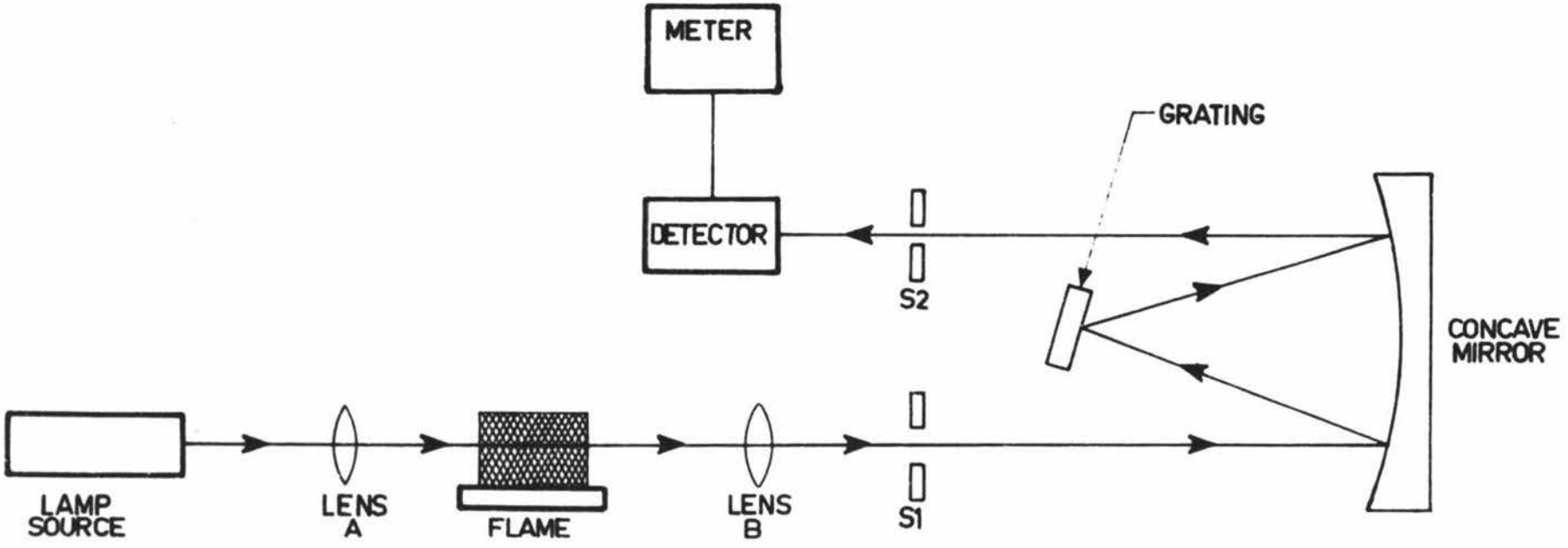


TYPE AA3 - ATOMIC ABSORPTION SPECTROPHOTOMETER WITH ACCESSORIES.

Plate 1. Techtron AA3 Atomic Absorption Spectrophotometer



OPTICAL SYSTEM

Plate 2. Optical System of Techtron AA3 Atomic Absorption Spectrophotometer

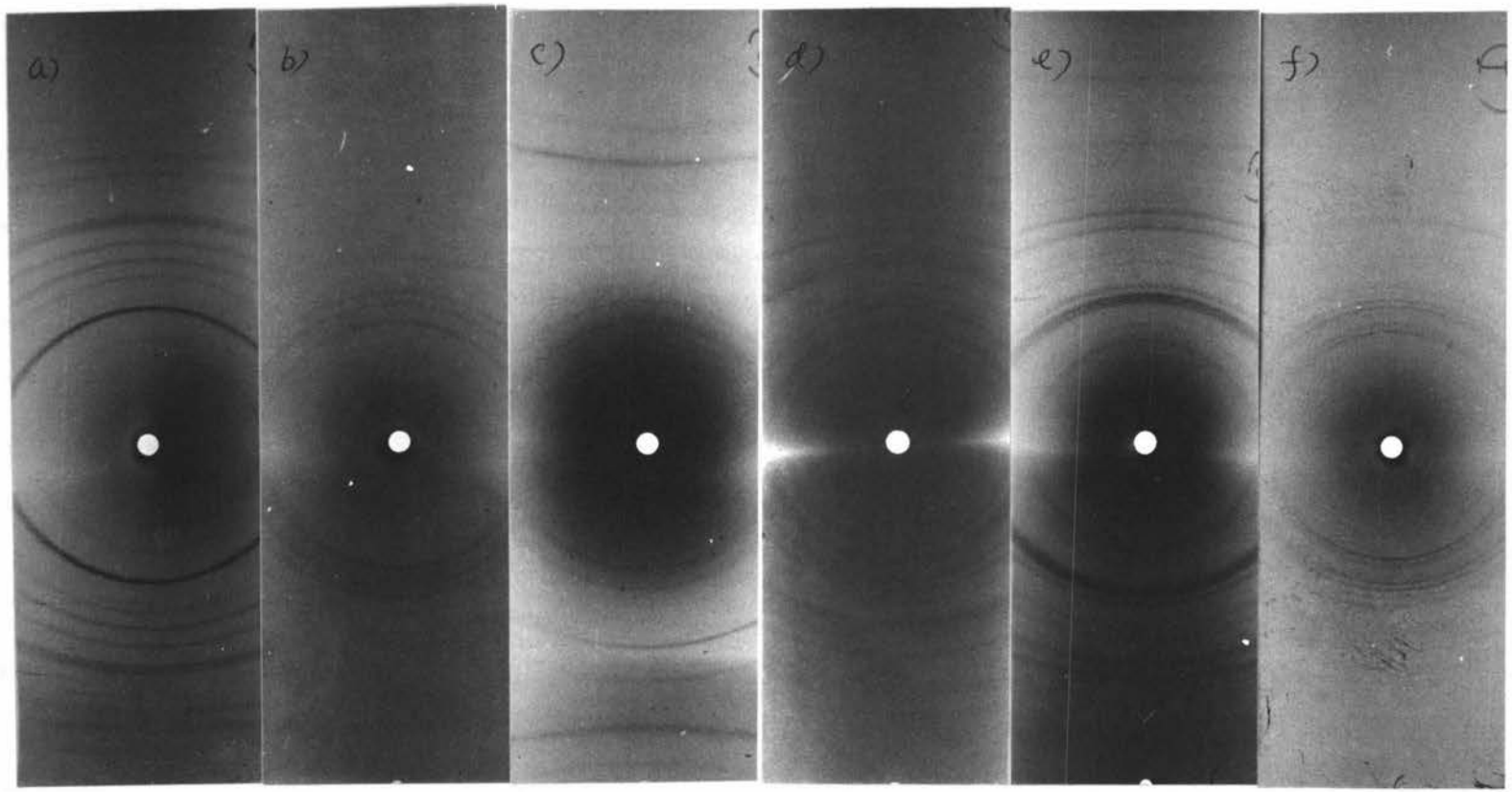


Plate 3. X-Ray Powder Diffraction Photographs of Solids from Flame Gases