THE DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF MAGNESIUM BY ATOMIC ABSORPTION.

By

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C O N T E N T S.

/(ii)....5. Results...

/(iii)....

SUMMARY.

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This thesis includes a description of modifications of the Hilger atomic absorption apparatus, which was used for most of the work. These modifications were restricted to the atomiser and burner, which were replaced by a modified "Eel" flame photometer atomiser-burner, and resulted in improved sensitivity and instrumental stability for the atomic absorption of magnesium. A comparison of the performance of this unit with that of the unmodified Hilger apparatus is given. A "Handigas" (butane-propane mixture)-air flame was used for most of this work, but a coal-gas-air flame was also studied and found to give slightly greater sensitivity. The method was found to be subject to interference from many elements. Strontium salts, employed as releasing agents to overcome the effect of other elements, were not completely effective as milligram amounts of several elements interfered even when strontium was present. Among the more serious interfering elements are: aluminium, iron, manganese and zirconium (less than 20 p.p.m. interfere); the alkali and alkaline earth metal salts (more than 200-500 p.p.m. interfere); phosphate (more than 100 p.p.m. P_2O_5); uranium (more than 4,000 p.p.m.); arsenate and vanadate. An attempt is made to explain the mechanism of some of these interfering effects. A combination of strontium salt and acetyl acetone was found to overcome the effects of small amounts of several elements that form complexes with acetyl acetone (e.g. iron and aluminium) far more effectively than strontium alone. Larger amounts of many interfering elements are removed by a solvent extraction procedure employing acetyl acetone and chloroform. Elements which cannot be removed by this means may be separated by anion-exchange, volatilisation, electrolysis or precipitation. A spiking technique, which compensates

for the effects of small amounts of interfering elements, is described and enables many samples to be analysed without prior separations.

The method described has good sensitivity (the limit of determination is approximately 1 microgram of magnesium in 50 ml. of solution). It has been applied to the analysis of clay samples, iron ore, limestone and uranium metal, oxides and processing solutions. The coefficient of variation of the method was determined using two clay samples and results of 2.0 and 4.6 percent, at magnesium oxide concentrations of 0.65 and 0.22 percent respectively, were obtained. The speed of the method compares favourably with others described for the determination of microgram amounts of magnesium, but increases if large amounts of interfering elements are present.

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3 /INTRODUCTION....

1. INTRODUCTION.

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This work was undertaken in order to establish a reliable method for the determination of magnesium, particularly in low concentrations. Some of the materials to be analysed include uranium metal and uranium concentrates; zirconium metal and concentrates; clay and siliceous ore samples and aluminium metal. Typical magnesium concentrations in the metal samples are frequently 10 p.p.m. or less, while most ore samples contain more than 0.01 percent of the element. Thus in the analysis of metal samples it is essential that the method should be sensitive and be able to deal with reasonably large amounts of sample. In the case of ore samples the chief problem is the variable and often uncertain composition of the material to be analysed. It is important, therefore, that the effects of other elements on the method should be studied and that efficient means of overcoming their interference should be provided.

A literature survey indicated that the atomic absorption method for the determination of magnesium had the desired sensitivity (see Section 2). The effects of other elements were claimed to be easily overcome by the addition of a "releasing agent." Insufficient information on the effects of other elements was given, however, for the method to be applied without further investigation. Most results available in the literature were obtained using a coal-gas-air or air-acetylene flame. As it was desired to use "Handigas" in this work a detailed investigation of the effects of other elements was necessary.

/2. LITERATURE SURVEY

2. LITERATURE SURVEY.

2. LITERATURE SURVEY.

2.1. Methods available for the determination of magnesium.

Most existing methods for the determination of macro amounts of magnesium employ the precipitation of magnesium ammonium phosphate after the separation of calcium and other interfering elements. Smaller quantities are usually determined either by titration with EDTA[1,2]. or by a colorimetric method.

The EDTA titration methods are commonly applied to the determination of macro (milligram) amounts of magnesium, although methods have been proposed for the estimation of a few micrograms. Most interfering elements can be complexed, but the endpoints are not sharp if large amounts of interfering elements are present. Usually solvent extraction has to be employed to remove interfering elements.

Titan Yellow[3,4,5]. is the most popular colorimetric reagent, but attempts by the author to employ it for the analysis of clay samples have so far been unsuccessful as consistently low results were obtained. The cause of this error was not investigated. Xylidyl Blue[6]. has also been proposed as a colorimetric reagent and is capable of good sensitivity (1 microgram of magnesium per 25 ml.), but the calcium content of the final aliquot must be between 10 and 300 micrograms and the sodium content must also be closely controlled.

The use of Phenazo[7]. for the colorimetric determination of between 0.02 and 0.7 percent magnesium in duralumin, high silicon alloys and other materials has also been described. This reagent, like Titan Yellow, depends on the adsorption of the dye onto magnesium hydroxide particles and is claimed to be superior to Titan Yellow. The sensitivity of this method, however, appears to be insufficient for the analysis of aluminium and uranium samples.

Magon[8]. gives the desired sensitivity (10 micrograms of Mg in 25 ml), as does Eriochrome Black T.[9]., but both these reagents also give colours with many other elements. Oxine[10]. appears to be the most promising colorimetric reagent for low concentrations of magnesium. From 10 to 80 micrograms of magnesium can be determined with an accuracy

/5.....of 5-10 percent....

of 5-10 percent in the presence of 0.1 mg. quantities of calcium, strontium, barium, tungsten, zirconium, beryllium, titanium, cobalt, molybdenum, vanadium, boron, aluminium, iron, chromium, copper and manganese. Limited amounts of most heavy metals are easily separated by solvent extraction with oxine or complexed with cyanide.

Flame photometric methods[11,12.] for the determination of magnesium in metallurgical samples have been described, but these methods generally suffer from the disadvantage that background correction is difficult. A sensitivity of 1 p.p.m. is claimed.[13.] The method is subject to interference by several elements, including iron, aluminium, manganese, phosphate, silicate and copper.

The application of atomic absorption techniques to the chemical analysis of terrestrial samples was first proposed by Walsh[14.] in 1953, although a similar technique had previously been used by astronomers to establish the composition of celestial bodies. Shortly after this Alkemade and Milatz[15.] also demonstrated the possibility of using atomic absorption measurements for analytical purposes and described a dual-beam instrument which they had devised for the purpose. Analytical procedures for the determination of low concentrations of magnesium in agricultural materials have been described by David[16,17.] and Allan.[18.] Willis has described the determination of magnesium in biological materials.[19-21.] During the course of this investigation a paper by Leithe and Hofer[22.] on the determination of magnesium in cements has been published. These authors also described a procedure[23.] for the determination of magnesium in aluminium metal and alloys by atomic absorption. They used calcium as a releasing agent. Andrew and Nichols[24.] described the determination of magnesium in nickel, The nickel in the sample acts as a releasing agent from silica and aluminium. A third procedure for the determination of magnesium in metallurgical samples by atomic absorption has been described by Belcher and Bray,[25.] who analysed cast iron samples, using strontium salts as releasing agents.

2.2 Atomic absorption instrumentation.

Russell, Shelton and Walsh[26] and Alkemade and Milatz[15] described double-beam instruments, neither of which is manufactured on a commercial basis. These instruments used chopped light beams and a.c. amplification. Box and Walsh[27] have described a simpler single-beam instrument, which is widely used and is manufactured by Techtron Appliances, Melbourne, Australia. This instrument employs a modulated light beam and a broad-band a.c. amplifier. It is direct-reading, the recitified signal being applied to an ammeter. The commercial version includes the amplifier and power supplies only; Australian workers have used it in conjunction with a Beckman DU monochromator[20] and a modified "Eel" (Evans Electroselenium, Ltd.) flame photometer burner and atomiser.

The Hilger instrument is described by Lockyer and Hames.[28] It uses an unmodulated light source and is built around the Hilger "Uvispek" spectrophotometer, which employs a d.c. system of measurement. This instrument like all other employing a d.c. system of measurement, has the disadvantage that the effect of emission by the element sought, in the flame, and of emission by the flame itself is not always adequately suppressed. It employs a water-cooled burner, constructed from brass, which gives a flame approximately 11 cm. in length.

More recently Leen and Attwood[29] have described a double-beam instrument now manufactured by Perkin-Elmer. It is claimed that this instrument gives somewhat better precision at low absorption than is usual with a single-beam system.

The Jarrell-Ash Company also market an atomic absorption apparatus[30] which employs five passes (with concave mirrors) through three Beckman flame photometer-type burners. It is a d.c., single beam instrument.

Malmstadt and Chambers[31] described a null-point instrument. Sample and standard are sprayed alternately and the standard concentration

/7...is adjusted....

is adjusted by titration until no difference in absorption from the sample is obtained. This system is slow and cumbersome, but the coefficients of variation obtained (0.1 to 0.4 percent) are better than usual.

Menzies[32.] described a ratio system, whereby the intensities of two lines emitted by the source, one of which is absorbed and one of which is not, are compared. This has the advantage that no beam splitting optical system is required, but the ratio of the intensities of the two lines does not remain constant when the lamp intensity is varied, as generally the two lines have widely different excitation potentials.

Clinton[33.] and Willis[34.] have described burners for use in atomic absorption analysis. These burners are of similar design both having a 12 cm. flame length and operate with air-coal-gas or air-acetylene. They are water-cooled. Clinton observed a slow decrease in sensitivity when an uncooled burner was used continuously for prolonged periods. Clinton constructed his burner from a cast aluminium alloy, while Willis used stainless steel.

As light sources, hollow cathode lamps or spectral discharge lamps have generally been used. Hollow cathode lamps are available from several sources (inter alia, Ransley Glass Instruments, Melbourne, Hilger and Watts and Westinghouse) and their construction and characteristics have been described by Walsh and his co-workers.[35,36.] Spectral vapour lamps are less commonly used and their application is generally confined to the alkali metals. These lamps give improved sensitivity when run at currents considerably lower than those specified by the manufacturers.

2.3 The interaction of the alkaline earth elements with other elements in the flame.

2.3.1 The nature of the molecule responsible for the band emission of the alkaline earth elements:

A considerable amount of work has been done on the nature of the molecule responsible for the band emission of the alkaline earth elements used in flame photometry. James and Sugden[37.] and Gaydon[38.] proposed that this emission was due to compounds of the

/8....type CaOH,

type CaOH, MgOH, etc., and produced evidence in support of this theory. It is unlikely, however, that these compounds will be stable, particularly under flame conditions and it has been suggested that these compounds may be the result of collision between alkaline earth atoms and hydroxyl radicles in the flame. Huldt and Lagerquist[39] attempted to confirm James' and Sugden's theory. They passed deuterium and calcium into an acetylene flame and reason that CaOD should be formed under these conditions. Observation of the spectrum using a spectrograph with high dispersion failed to reveal any isotopic wavelength shift for calcium and only a very small shift for strontium. These investigators concluded, therefore, that the problem is still unsolved. It is probable, however, that the hydrogen from the acetylene will swamp the effect of the deuterium in these experiments, as the ratio of H:D in the flame is 6:1. It would thus appear that the work of Huldt and Lagerquist is of doubtful value and does not disprove the theory advanced by James and Sugden and Gaydon.

Huldt and Knall[40] investigated the possibility of the formation of polymers of the type Ca_2, etc., by calcium and strontium in the flame. They conclude that polymers of this type cannot be responsible for the band spectra emitted by these elements.

It is generally accepted that the very great majority of alkaline earth metal in the flame is present as the oxide, MO[37,41]. This will be proved from thermodynamic data later in this report.

2.3.2 <u>The mechanism of aluminium, phosphate and silicate interference in flame photometry of the alkaline earth elements:</u>

A considerable amount of work has been done on the nature of the interference of phosphate, aluminium and silicate in the flame photometric determination of calcium. Mitchell and Robertson[42] attempted to explain the decrease in intensity of calcium emission in the presence of aluminium salts by the absorption of energy of excited alkaline earth atoms by aluminium atoms. These investigators used strontium salts to suppress this interference. This addition restored

/9....the calcium...

the calcium emission to within 4 percent of its value in the absence of aluminium. Baker and Johnson[43.] investigated the effect of various anions on the emission of calcium in an oxy-acetylene flame. They observed an enhancing effect in the presence of perchloric acid, while sulphate, phosphate and chromate depressed the emission, and suggested that the depressing effect of phosphate and sulphate, might be due to the formation of the pyrophosphate or pyrosulphate.

Margoshes and Vallee[44.] attribute the interference by phosphate, sulphate and aluminium in the flame photometry of calcium to the formation of compounds with high melting points. They claim that "interferences" are functions of the particular system used for the analyses, and state that interference can be predicted better by consideration of flame temperature and the boiling points of the compounds in the sample than by reliance on published data obtained with a different flame.

Kohnlein and Lücke[45.] found that there was a linear fall in calcium emission with increasing phosphate concentration up to a certain point, beyond which the emission was independent of the phosphate concentration. In a coal-gas flame, the initial fall in emission was more pronounced than in an acetylene-air flame and the final constant calcium emission was practically nil. Over the whole range of calcium concentrations the inflection in the emission curves occured at a point where the $CaO:P_2O_5$ ratio was 1.23:1, and it was suggested that a compound of this composition, which was only slightly excited in the acetylene flame and hardly at all in the coal-gas flame, was formed. These investigators also reported that the depressing influence of phosphate on calcium emission was affected by sodium and potassium and concluded that emission flame photometry was not a suitable technique for the determination of calcium.

Leyton[46.] confirmed the effect of phosphate observed by Kohnlein and Lücke, but found no evidence to support their claim that sodium and potassium influence the degree of phosphate interference. He attributes their results in the presence of sodium and potassium to the rather inefficient optical filter system which they used.

/10....Leyton...

Leyton suggests that the compound formed with calcium and phosphate is tri-calcium phosphate, $Ca_3(PO_4)_2$, whose composition corresponds to the points of inflection. Leyton examined the emission spectra of calcium chloride and tri-calcium phosphate and observed only the "calcium oxide" bands (possibly the CaOH bands, in view of subsequent work by James and Sugden). He suggests that the reduced emission of the phosphate is due to a smaller degree of dissociation into the oxide rather than to a different type of emission. His results were all obtained using an acetylene-air flame.

Huldt[47]. examined the depression of calcium emission by aluminium in the flame and concluded that aluminium and calcium combine as their oxides in the gaseous phase, i.e. after evaporation of their compounds in flame. This conflicts with the theory proposed by Margoshes and Vallee and other workers, who considered that this interference was due to involatile compounds, which arise directly from the solid aluminium and alkaline earth salts.

Alkemade and Jeuken[48]. used a two-atomiser technique in investigating these theories. They fed separate solutions of calcium and aluminium into the same air-acetylene flame through separate atomisers, and compared the results with those obtained by feeding one solution containing both elements into the flame through one atomiser. These investigators observed only a slight depression of calcium emission when aluminium nitrate was introduced via a separate atomiser and concluded that the interference of aluminium nitrate is due to the formation of a refractory compound in the solid or liquid aerosol particle. Tests with aluminium chloride, however, led these investigators to postulate the formation of an aluminium-calcium complex in the vapour phase in the presence of chloride.

Schuhknecht and Schinkel[49]. repeated some of the work of Alkemade and Jeuken, using a similar technique. They concluded, from their results, that there is no fundamental difference in the mechanism of the interference by various aluminium compounds in the emission of calcium in the flame. They produce evidence disproving

/11....the theory...

the theory proposed by Mitchell and Robertson mentioned earlier. They show that the formation of refractory compounds does not take place in the gaseous phase, but rather in the solid or liquid aerosol particle. They also investigated the effects of silicate and phosphate on the emission of calcium and concluded that these were also due to the formation of refractory compounds. This theory was supported by experiments using various types of flames, which showed that the interference of these substances decreases with increasing flame temperature. These investigators also came to the conclusion that the temperature attained by the aerosol particles is not solely dependent on flame temperature, but is also influenced by retention time of the particle in the flame and the size of the particles. Thus interference under otherwise identical conditions is far less in the flame of a burner with a spray chamber than in the flame of a total consumption burner. Schuhknecht and Schinkel also investigated the mechanism of the releasing effect of strontium reported by Mitchell and Robertson, and found that it was ineffective when sprayed through a separate atomiser to that carrying the solution of calcium and interfering element (e.g. aluminium). They, therefore, attribute the releasing action of strontium to the preferential formation of strontium aluminate, phosphate or silicate in the aerosol particle. At about the same time Alkemade and Voorhuis[50.] published a paper in which they reported the results of a similar investigation to that undertaken by Schuhknecht and Schinkel. They used similar techniques and came to virtually the same conclusions as the latter investigators.

In atomic absorption work similar interference effects have been observed. Thus in the determination of magnesium using a coal-gas flame aluminium, silicate, phosphate and sulphate have been reported to interfere[22,32.] but usually the latter two do not interfere in the hotter acetylene-air flame, although David[17.] reported depression by phosphate and sulphate in this flame. It is reasonable to expect that the mechanism of these interferences will be similar to those with calcium described earlier. In atomic absorption the elements which

/12 ....interfere with

interfere with magnesium affect calcium to a greater extent.

2.3.3 Methods of overcoming interfering effects.

Usually these interferences are overcome by adding a competing cation, which will combine with the offending anion. The element added is commonly called a "releasing agent." The use of strontium, calcium and nickel as releasing agents for magnesium in atomic absorption analysis has already been described. The use of lanthanum as a releasing agent was first suggested by Yofé and Finkelstein,[51.] who used it in the emission flame photometric determination of calcium. Subsequently David[17.] has used lanthanum as a releasing agent for magnesium in atomic absorption analysis. Yofé and Finkelstein also used iron as a releasing agent in the flame photometry of calcium, but found that it was less effective than lanthanum for this purpose. They suggest that the following reactions take place in the flame:

$$CaCl_2 + H_2O + E_1 \longrightarrow CaO + 2HCl \quad \text{.....(1)}$$

$$CaO + E_2 \longrightarrow Ca + O \quad \text{.....(2)}$$

$$2CaCl_2 + 2H_3PO_4 + E_3 \longrightarrow Ca_2P_2O_7 + 4HCl + H_2O \quad \text{.....(3)}$$

$$Ca_2P_2O_7 + E_4 \longrightarrow 2CaO + P_2O_5 \quad \text{.....(4)}$$

$$LaCl_3 + H_3PO_4 + E_3' \longrightarrow LaPO_4 + 3HCl \quad \text{.....(3')}$$

They claim that reactions 1, 3 and 3' can take place in the cooler area of the flame as the heats of reaction E_1, E_3, E_3', are relatively small, while reactions 2 and 4 can only occur in the hotter portions of the flame on account of large endothermic heats of reaction, E_2 and E_4. These investigators consider that the E_3' must be less than E_3 for lanthanum to act as a releasing agent i.e. lanthanum phosphate must be more stable than Calcium phosphate under flame conditions. They attribute the greater efficiency of lanthanum as a releasing agent to the fact that lanthanum phosphate has a greater heat of formation than ferric phosphate.

EDTA has also been used by Willis as a releasing agent in the atomic absorption determination of magnesium.[20.] Its action is attributed to the complexing of the magnesium or interfering element, thus preventing the formation of the involatile compound in the flame.

/13 ....Willis used it...

Willis used it in a slightly acidic solution.

L'Vov[52] investigated the atomic absorption of magnesium and other elements using a graphite tube furnace and an electric arc in an inert atmosphere to vaporise and decompose a dry sample. He operated the furnace at temperatures in the range 2000° - 3000°K, which are comparable with the temperature of an acetylene-air flame, but observed none of the interfering effects from phosphate, aluminium, etc., which occur in the flame photometry of the alkaline earths. This suggests that oxygen may be necessary for the formation of the involatile compounds formed with these elements in the flame. It is possible, however, that the arc which vaporises the sample will reach a somewhat higher temperature than that of the furnace, and that the refractory compounds of the alkaline earths will be effectively decomposed before passage into the furnace.

Further literature references will be given at relevant points in the text of this thesis.

/...3.THEORETICAL....

3. THEORETICAL BACKGROUND.

3. THEORETICAL BACKGROUND.

The absorption of discrete wavelengths of light, by various elements has been known for over a century. An example of this phenomenon is found in the "Fraunhöfer lines" in the sun's spectrum, which are dark bands in the bright emission spectrum, caused by the absorption of these wavelengths by elements in the sun's atmosphere. Astronomers have used these lines to identify the elements in the atmospheres of celestial bodies. The wavelengths of light which are absorbed correspond to emission lines in the emission spectrum of the absorbing element. Walsh's paper[14.] surveys the theoretical factors involved in atomic absorption analysis and gives as advantages of this technique over emission flame photometry: (i) atomic absorption is independent of the excitation potential of the electronic transition involved, and (ii) it is less subject to temperature variation and interference from extraneous radiation or energy exchange between atoms.

Atomic absorption analytical apparatus consists, essentially, of a suitable source of light emitting a line spectrum of the element, a device for vaporising the sample, a means of line isolation (monochromator or filter) and photo-electric detecting and measuring equipment. Various forms of this apparatus have already been described in the literature survey.

3.1 Factors affecting sensitivity in atomic absorption.

3.1.1. Population of energy levels.

The spectral lines used for atomic absorption measurements are all "resonance lines", i.e. those lines arising from an electronic transition ending in the ground state, as these lines are most strongly absorbed by the element sought at flame temperatures. The absorption line corresponding to the emission line used will, naturally, be caused by an electronic transition which begins in the ground state. These resonance wavelengths are listed in a paper by Meggers[53.] and, with the exception of the rare gases, hydrogen, mercury, the halogens and the metalloids, all elements have their most sensitive resonance lines in the range 2,000-9000 Å, i.e. at wavelengths which can be measured by conventional spectrophotometers. The reason for the greater absorption

/15.....of resonance...

of resonance lines is found in the denser population of the ground state. This becomes apparent on considering the emission of a resonance spectrum line due to the transition from an excited state j, of excitation energy Ej, to a ground state of energy Eo = o. If Pj and Po are the statistical weights for the excited state and ground state respectively, the number of atoms in the excited state, Nj, is related to the number of atoms in the ground state, No, by the relation:

$$Nj = No \frac{Pj}{Po} e^{-Ej/kT}$$, where k = the Boltzmann constant.

If self-absorption and induced emission are omitted, the intensity of the emission is proportional to Nj.

Walsh[14] gives values of Nj/No at temperatures between 2000°K and 3000°K for caesium, sodium, calcium and zinc and considers the excited state closest to the ground state (i.e. the state with a minimum Ej value) only. These values range from 7.29×10^{-15} for zinc at 2000°K to 6.82×10^{-2} for caesium at 5000°K, indicating that at these temperatures more than 90 percent of atoms are in the ground state. Since the amount of light of any wavelength absorbed is proportional to the number of atoms capable of absorbing light of that wavelength, it is obvious that resonance lines will be far more strongly absorbed than any other wavelength. While the percentage of atoms in an excited state varies exponentially with temperature, it is important to notice that the population of the ground state remains virtually constant in the temperature range up to 5000°K.

Multiplets, resulting from closely-spaced atomic energy-levels, exist in atomic line spectra. If, as for sodium, there is only a single ground-state level but a multiplet upper level, all free ground-state atoms are capable of absorbing light of any component of the multiplet. However, if, as in the case of transition elements, a multiplet ground state exists, the number of atoms, Nv, available for a given transition is diminished according to the expression:

$$N_v = \frac{N\ Pi\ e^{-Ei/kT}}{\sum Pj\ e^{-Ej/kT}}$$

where N is the total number of atoms available, Pi and Pj are the

/16.....statistical....

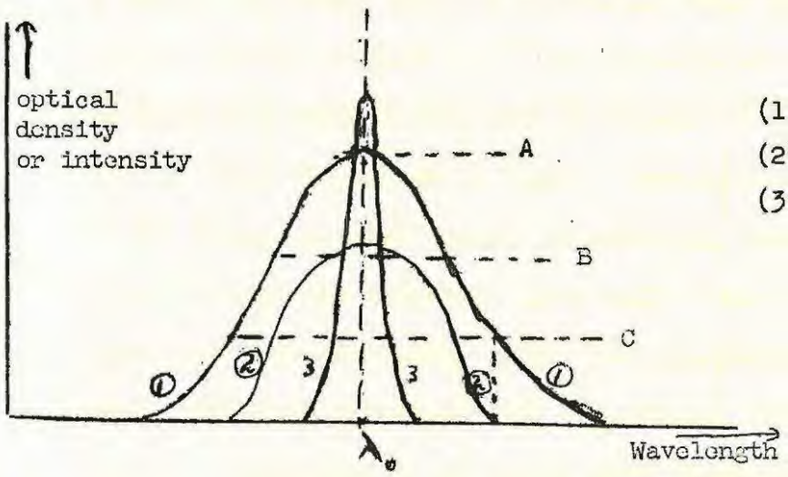
statistical weights for the states involved and Ei and Ej are the excitation energies of the transitions involved. Subscript i refers to the transition corresponding to the line absorbed; j covers all transitions for the multiplet..

3.1.2 Width of spectral lines used.

Another factor which influences the sensitivity of an atomic absorption method in which a line source is used is the relative widths of the line emitted from the source and the absorption line of the mass of atomic vapour. For maximum absorption the emission should be much narrower than the absorption line, so that peak absorption is measured. This is immediately evident from Figure 1, where typical contours are depicted.

FIGURE I.

Shapes of absorption and emission lines.



(1): absorption line
(2): broad emission line
(3): narrow emission line. Intensity and optical density scales not identical. Optical density refers to absorption line (1), Intensity to emission lines, 2 and 3.

The narrow emission line (3) will be absorbed in the region of maximum optical density corresponding to an optical density of A. The region in which the broader emission line, (2), is absorbed will be between A and C, with an average optical density at the point B, on account of the diminution of the absorption with increasing distance from the centre of the line.

David[54] states that the following factors determine the width of an absorption line:

(i) The natural width due to the finite life-time of an atom in the excited state (sic). This statement is not clear from

/17....Walsh's....

Walsh's treatment of the subject. It would appear that this broadening is due to variations in the excited-state life-times of individual atoms.

(ii) Doppler broadening due to thermal motions of the atoms.

(iii) Lorentz broadening due to collision with foreign gases.

(iv) Holtsmark broadening due to collision with atoms of the same kind

(v) Stark broadening due to electric fields, either internal or external.

Both David and Walsh express the opinion that only the first four factors will contribute to absorption line width at a low vapour pressure of an element in ordinary flames and furnaces, Doppler broadening probably predominating.

According to David, the same factors, as well as broadening due to self-absorption, influence the width of an emission line. How self absorption will broaden a spectral line is not clear to the author, but a line that is appreciably self absorbed will give reduced sensitivity. A good example of this is found in the determination of cadmium by atomic absorption.[55] The resonance line obtained from a cadmium hollow-cathode lamp is appreciably self-absorbed, the amount of self-absorption increasing with increasing lamp current. Thus the sensitivity obtainable with cadmium decreases sharply with increased lamp current.

As the emission line at high lamp current has most of its "middle" portion missing when appreciable self-absorptio n takes place, the reason for the resultant decrease in sensitivity of the atomic absorption method in this case is evident from Fig. 1, as the majority of the light in the emission line falls in the regions of low absorption.

According to Jones and Walsh[35] the half-width of resonance lines obtained from their hollow cathode lamps was approximately 0.01 Å (In order to obtain a comparable line-width from a continuous emitter (e.g. a tungsten lamp) a monochromator with resolution of at least 1 in 500,000 and a very intense source would be required).

/18....The advantages....

The advantages of running the hollow cathode lamp at the minimum current which will give sufficient light for the detector are apparent from the foregoing considerations, as increased current will result in an increase in temperature of the lamp and also give increased self-absorption of the emission line. The life of a hollow-cathode lamp is also increased by operating it at a minimum current.

The narrowness of the emission line obtained from a hollow cathode source is largely responsible for the almost complete freedom from spectral interference, i.e. interference due to absorption or emission of light by other elements, obtained in atomic absorption work. This is also why atomic absorption methods are generally more specific than emission flame photometric procedures for the same element: resolution is virtually equal to the width of the emission line used and is not determined by the resolution of the monochromator used.

3.2 Theoretical value of the absorption coefficient in atomic absorption.

Walsh defined the maximum absorption coefficient, k_v, as follows:

$$I = I_o \; e^{-k_v l} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where I = intensity of light after passage through flame

I_o = Initial intensity of light

l = length of light path through flame, in cm.

k_v = absorption coefficient

This equation is identical to that obtained for molecular absorption of light by application of Beer's Law. Optical density may be substituted for the light intensities, giving the following equation:

$$2.303 \times \text{optical density} = k_v l \quad \ldots\ldots\ldots\ldots\ldots (2)$$

The theoretical maximum value of k_v, assuming the width of the emission line to be negligible compared with that of the absorption line and that the shape of the latter is determined by the Doppler broadening only, is given by Walsh as:

$$k_v = \frac{2}{D_\lambda}\sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\pi e^2}{mc^2} \cdot Nf \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where $$D_\lambda = \frac{1.67}{c}\sqrt{\frac{2RT}{M}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

/19....In these equations....

In these equations:

λ = wavelength of resonance line used, in Å

D_λ = Width of line due to Doppler broadening, in Å.

C = velocity of light in cm./sec.

N = concentration of absorbing atoms in flame, in atoms/cm.^{3}

f = oscillator strength for line (= 1.74 for magnesium)

m = mass of electron in gm.

e = charge on electron in E.S.U.

R = universal gas constant in ergs./mole/°C

M = molecular weight of absorbing species in molecular weight units.

3.3 Factors affecting linearity of the calibration curve.

These equations imply linear relationship between absorption and concentration, which is approached in practice only at low concentration. David suggests that the chief reason for this is that factors other than Doppler broadening also play an important part in determining the width of the absorption line at high concentrations. There are several other factors which can also cause departure from linearity in the calibration, the most important of which are:

(i) Another line close to the resonance line is emitted by the lamp but is not eliminated by the monochromator.

In this case, $I_o = I_1 + I_2$, where I_1 = intensity of resonance line before passage through the flame, and I_2 = intensity of unabsorbed interfering line and equation (1) becomes:

$$I = I_1 e^{-kcl} + I_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where $kc = k_\nu$ and c = concentration of absorbing species. This is not a linear relationship between concentration and optical density (which is $\log \frac{I_1 + I_2}{I}$ in this case).

(ii) Using similar reasoning, Menzies[32] calculated that inhomogeneity of the flame would also cause a non-linear calibration curve.

(iii) Russell, Shelton and Walsh[26] ascribe the departure from

/20....linearity at....

linearity at high concentrations which they observed in the calibration curves of several elements to pressure broadening, but do not supply mathematical proof of this.

(iv) The emission of the resonance line in the flame will also cause departure from linearity if it is detected. In general some emissioin will be detected when a d.c. system of measurement is used. The departure from linearity in this case may be proved as follows:

If I_1 = intensity of unabsorbed radiation from the lamp, after passage through flame

and I_2 = intensity of emission of resonance line from the flame,

I (as defined in equation (1) = $I_1 + I_2$.

In general $I_2 \doteqdot k'c$, where k' is a proportionality constant and c = conc. of emitting atoms. Equation (1) can be re-written:

$I_1 = Io\ e^{-kcl}$, where $kc = k_v$.

Substituting for I_1 and I_2:

$$I = Io\ e^{-kcl} + k'c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

This will not give a linear relationship between optical density and concentration.

The effect of variations in temperature on the absorption coefficient, according to equation 3, should be small, since temperature only appears in the equation for Doppler broadening as the square root. N, the concentration of ground-state atoms in the flame, will, however, also be temperature-dependent. This will be particularly true if a flame is used, as the combustion products will occupy a larger volume if the temperature is increased, causing dilution of the sample and reducing the value of N. Temperature will also have a pronounced effect on N if the compound from which the absorbing atoms is derived is not completely dissociated in the flame. In this case increasing temperature will generally increase N, the effect being greater the smaller the degree of dissociation of the compound.

3.4 Magnitude of pressure broadening in the flame.

When a flame is used to vaporise and dissociate the sample Lorentz broadening cannot be neglected in the derivation of the

21/absorption.....

absorption coefficient. Mitchell and Zemansky[56.] derived the following formula for the Lorentz broadening of an absorption resonance line:

$$\Delta\nu_L = P\left[1.95 \times 10^{19} \frac{2R}{\pi T}\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]\sigma_L^2 \quad \ldots\ldots\ldots\ldots (7)$$

where: $\Delta\nu_L$ = pressure broadening, in frequency units.

P = pressure of "foreign" gas, in mm. Hg.

R = Universal gas constant (8.314×10^7 ergs/mole/°C)

T = absolute temperature

M_1 = molecular weight absorbing species

M_2 = molecular weight of foreign gas.

σ_L^2 = effective cross-section for Lorentz broadening.

The Doppler broadening is given as:

$$\Delta\nu_D = \frac{2\sqrt{2R\ln 2}}{c}\,\nu_o\sqrt{\frac{T}{M_1}}$$

which simplifies:

$$\Delta\nu_D = \frac{1.67}{\lambda}\sqrt{\frac{RT}{M_1}} \quad \ldots\ldots\ldots\ldots (8)$$

where $\Delta\nu_D$ = Doppler broadening in frequency units

λ = wavelength of centre of line, in cm.

ν_o = frequency of centre of line

R, T and M_1 defined as before

Combining equations (7) and (8) gives:

$$\frac{\Delta\nu_L}{\Delta\nu_D} = \frac{1.168 \times 10^3 \lambda \sigma_L^2}{T} P\sqrt{\frac{1 + \frac{M_1}{M_2}}{\pi}} \quad \ldots\ldots\ldots\ldots (9)$$

Values of the effective cross-section, σ_L^2, for certain elements are also listed by Mitchell and Zemansky.

Mitchell and Zemansky define a further constant, a', as follows:

$$a' = \frac{\Delta\nu_N + \Delta\nu_L}{\Delta\nu_D}\sqrt{\ln 2} \quad \ldots\ldots\ldots\ldots (10)$$

where $\Delta\nu_N$ = natural width of line, due to finite life of the atom in the excited state.

If a' is known, the value of $\frac{k'_\nu}{k_o}$ can be deduced, where k'_ν is the absorption coefficient, taking both Lorentz and Doppler broadening into account, and k_o is the absorption coefficient when only

/22.. Doppler....

Doppler broadening determines the shape of the line.

Mitchell and Zemansky proved $\Delta\nu_N$ is usually small compared with $\Delta\nu_L$ and equation (10) then simplifies to:

$$a' = \frac{\Delta\nu_L}{\Delta\nu_D}\sqrt{\ln 2} \qquad \text{.....(10a)}$$

The correction to the absorption coefficient for Lorentz and Doppler broadening is introduced by considering a frequency band at a distance $(\nu - \nu_o)$ from the centre of a line showing only Doppler broadening. A variable distance, δ, from the point $(\nu - \nu_o)$ is chosen and integration is performed over all δ. The absorption coefficient is then given by -

$$k_\nu' = \frac{a'}{\pi} k_o \int_{-\infty}^{\infty} \frac{e^{-y^2}\,dy}{a'^2 + (\omega - y)^2} \qquad \text{.....(11)}$$

where $\omega = \frac{2(\nu - \nu_o)}{\Delta\nu_D}\sqrt{\ln 2}$ and $y = \frac{2\delta\sqrt{\ln 2}}{\Delta\nu_D}$

A solution of this equation is obtained by evaluating by series of numerical integration. Fortunately tables of k_ν'/k_o values for various values of ω and a' are given by Mitchell and Zemansky. As the width of the emission line from the hollow-cathode lamps is reputedly[35] very narrow (approximate half width = 0.01 Å), the value of k_ν' when $\omega = 0$ (i.e. $\nu - \nu_o = 0$) is of importance in this work. For the magnesium using the resonance line at 2852 Å, employed in this work, at a pressure of 620 mm Hg (average atmospheric pressure) and temperature of 1900° K (approximate flame temperature, according to Dean[57]), and assuming the foreign gas to be nitrogen, it may be calculated that:

$$a' = 0.48$$

This value is derived using the σ_L^2 value for sodium (6.89×10^{-15} cm^2), which is assumed to be equal to that for magnesium, as the latter value is not quoted by Mitchell and Zemansky.

This value of a' gives:

$$k_\nu'/k_o = 0.61$$

/23 This result.....

This result indicates that the effect of pressure broadening cannot be neglected when ordinary flames are used.

3.5 Effect of ionisation of the absorbing atoms.

The concentration of ground-state atoms in the flame, and hence the value of N in equation (3) and the value of the absorption coefficient will be reduced if an appreciable amount of the sample is ionised in the flame. The degree of ionisation may be calculated using the Saha equation[58]:-

$$\log. \frac{x^2 P}{1 - x^2} = \frac{-5040\ Vi}{T} + \frac{5}{2} \log. T - B \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

where: x = degree of ionisation

P = partial pressure, of all forms of the metal.

Vi = ionisation potential of the metal, in volts.

B = constant, 6.49 for alkali metals, 5.89 for alkaline earths.

For magnesium, Vi = 7.61 volts,[59] and the concentration of all forms of the metal in the flame, using a solution containing 0.4 p.p.m. Mg as the nitrate, will be shown later to be 1.4×10^{-17} grams per litre. At N.T.P., 24.3 grams of magnesium in the gaseous state would occupy a hypothetical 22.4 litres, or 191 litres at 1900°K and 620 mm. Hg (using the ideal Gas Laws). Thus the partial pressure of magnesium metal in the flame under these conditions is 1.15×10^{-16}. Using these values in the Saha equation, the degree of ionisation is found to be:

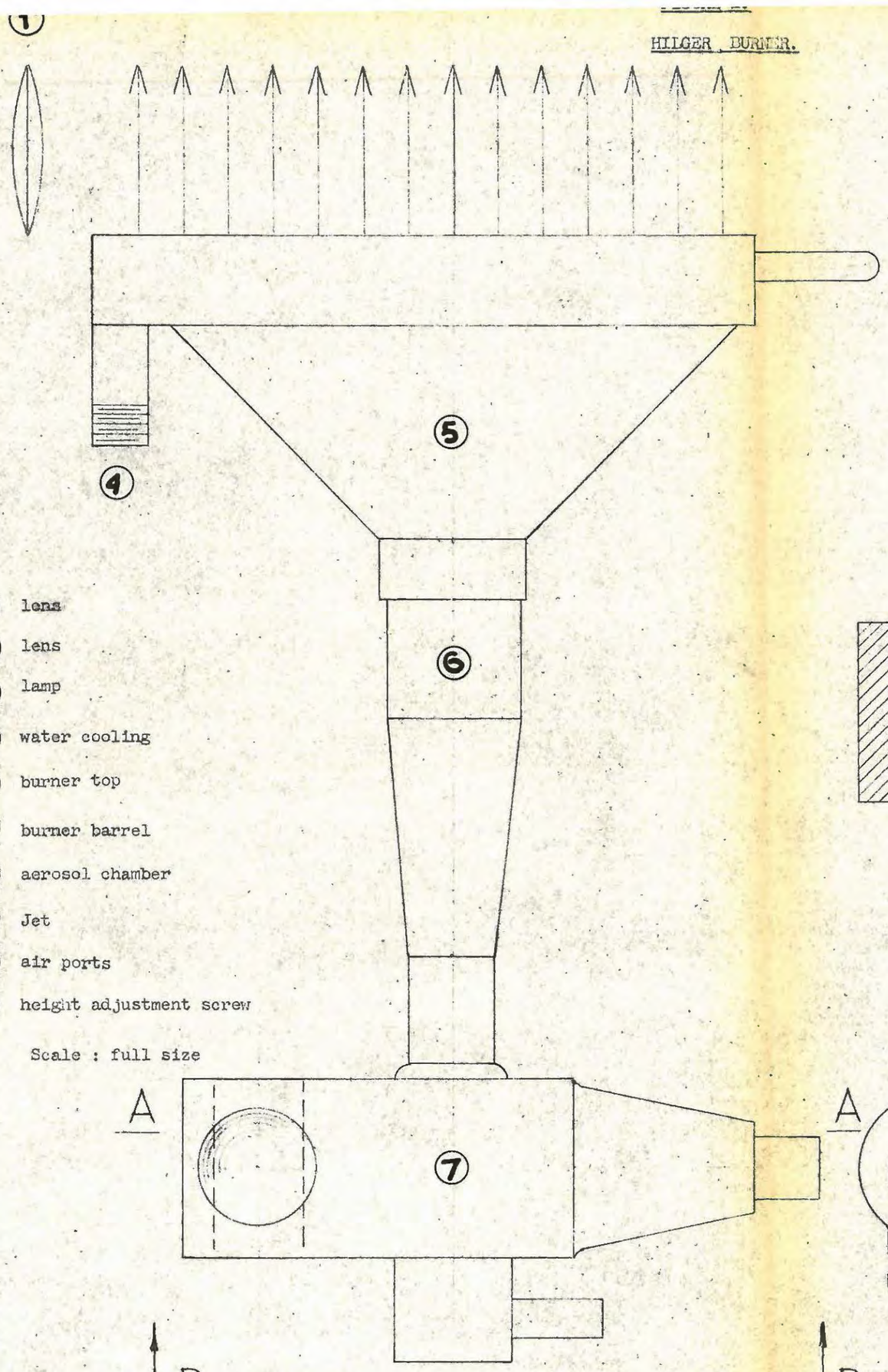
$x = 1.1 \times 10^{-1}$, or approximately 10 percent.

This calculation does not, however, take into account the high electron concentration of the hydrocarbon flame,[60] and the actual degree of ionisation may be expected to be lower in practice.

This result shows that ionisation may well have an effect on the absorbance of magnesium, particularly if a very high temperature flame is used to decompose the sample.

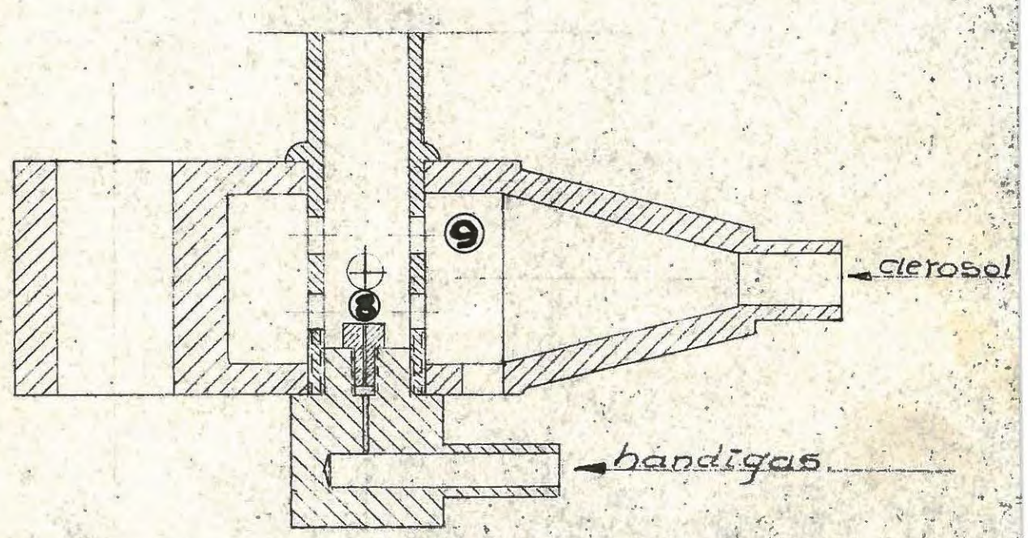
/4. EXPERIMENTAL....

HILGER BURNER.

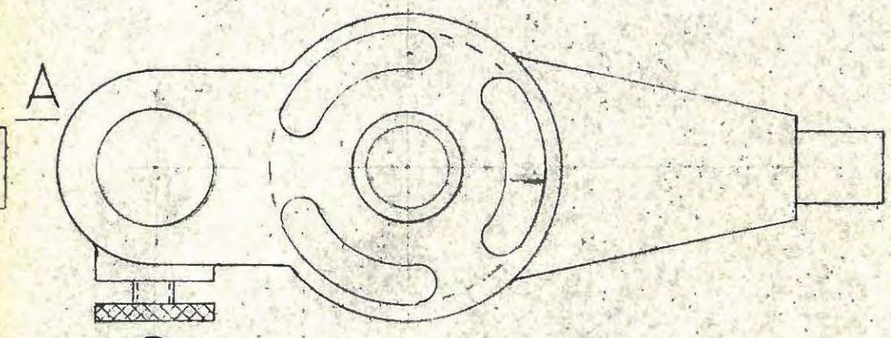


1. lens
2. lens
3. lamp
4. water cooling
5. burner top
6. burner barrel
7. aerosol chamber
8. Jet
9. air ports
10. height adjustment screw

Scale : full size



CROSS SECTION A-A.



VIEW B_B.

4. EXPERIMENTAL.

4. EXPERIMENTAL.

4.1 Description of the Hilger atomic-absorption apparatus.

In the early part of this work the standard Hilger apparatus, consisting of a "Uvispek" spectrophotometer, Hilger atomiser, burner, lamp assembly and the necessary power supplies, was used. The inside of the burner was painted with a plastic paint, to prevent chemical attack. "Epitar", an epoxy resin paint, was found to give adequate protection from acids. No contamination due to attack on the burner was detected at any time.

The burner was operated with "Handigas" (60 percent by volume of butane, 40 percent propane) and compressed air. The Handigas was obtained from a 20 lb. cylinder and the pressure adjusted by a diaphragm valve. A mercury manometer was used to control the pressure, and hence the flow-rate, of the Handigas. The compressed air was obtained from a storage tank fed by a compressor and was filtered before use. Its pressure was measured with a 0-80 p.s.i. dial-type gauge and adjusted with a diaphragm valve.

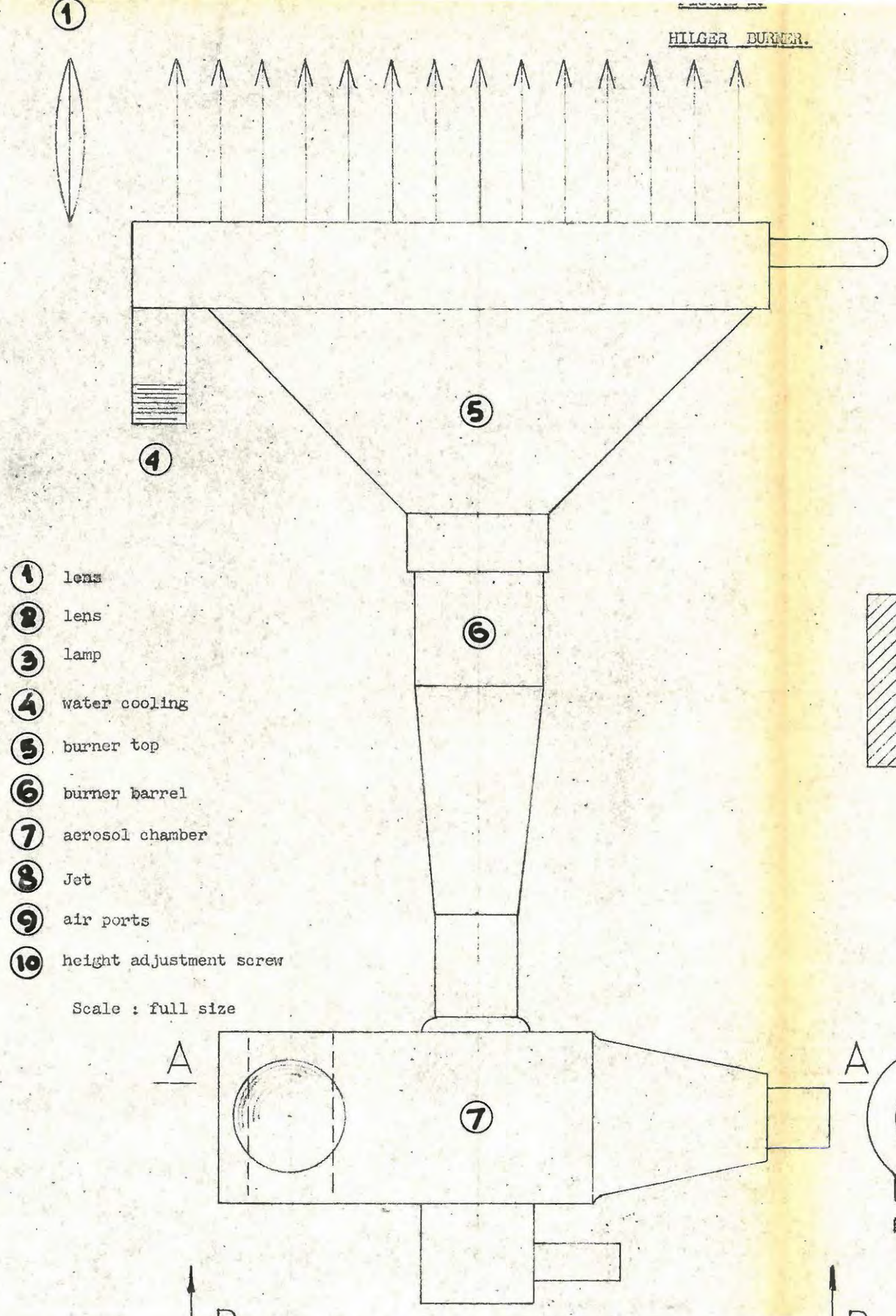
The burner is shown in Fig. 2. The similarity of basic design of the burner to the Meker pattern should be noted. Not all the aerosol formed is drawn up into the burner barrel and hence into the flame: some escapes through the holes in the bottom of the chamber surrounding the air ports.

Several jet sizes for the burner were tried. The original jet supplied with the instrument has a diameter of 0.019 inch and functioned satisfactorily, giving a steady flame. A jet of 0.032 in. diameter was found unsatisfactory as it gave a "ragged" flame. A jet of 0.022 inch diameter operated well and gave fractionally better sensitivity than the original: it was used for most of the work done with this burner. The height of the top of the jet in the burner was found to be critical; if placed too low an unsteady flame results. The original pattern of jet was found unsatisfactory on account of the deposition of salt in the screw-driver groove which obstructed the jet, causing a steady decrease in absorbance of a solution during operation.

/(25)....This...

FIGURE 1.

HILGER BURNER.



1. lens
2. lens
3. lamp
4. water cooling
5. burner top
6. burner barrel
7. aerosol chamber
8. Jet
9. air ports
10. height adjustment screw

Scale : full size

CROSS SECTION A-A.

VIEW B_B.

This fault was easily remedied by filing the top of the jet flat.

The efficiency of the Hilger atomiser-burner system was found to be very low: considerably less than 8 percent of the solution drawn through the atomiser eventually enters the flame. Condensation in the spray-chamber and tubing leading to the burner is the chief cause of this loss. This may be improved by using hot air to atomise the sample, but it was felt that the design of the burner and atomiser was basically unsound, mainly because of a long and tortuous path from the atomiser to the burner and the loss of aerosol at the base of the burner, and it was considered best to use a different type of atomiser.

During this investigation two Hilger hollow-cathode lamps were used. The first, used during the early part of this work only, had a magnesium-aluminium alloy cathode. The emission of the magnesium resonance line at 2852 Å from this lamp fell off with use. The second lamp, used for most of this work, had a cathode made of magnesium metal. Its performance was superior to that of the first lamp, but its life (less than 500 hours), although longer than that of the first lamp, was shorter than the usual life-time of hollow cathode lamps given by Jones and Walsh[35].

4.2 The use of an "Eel" atomiser.

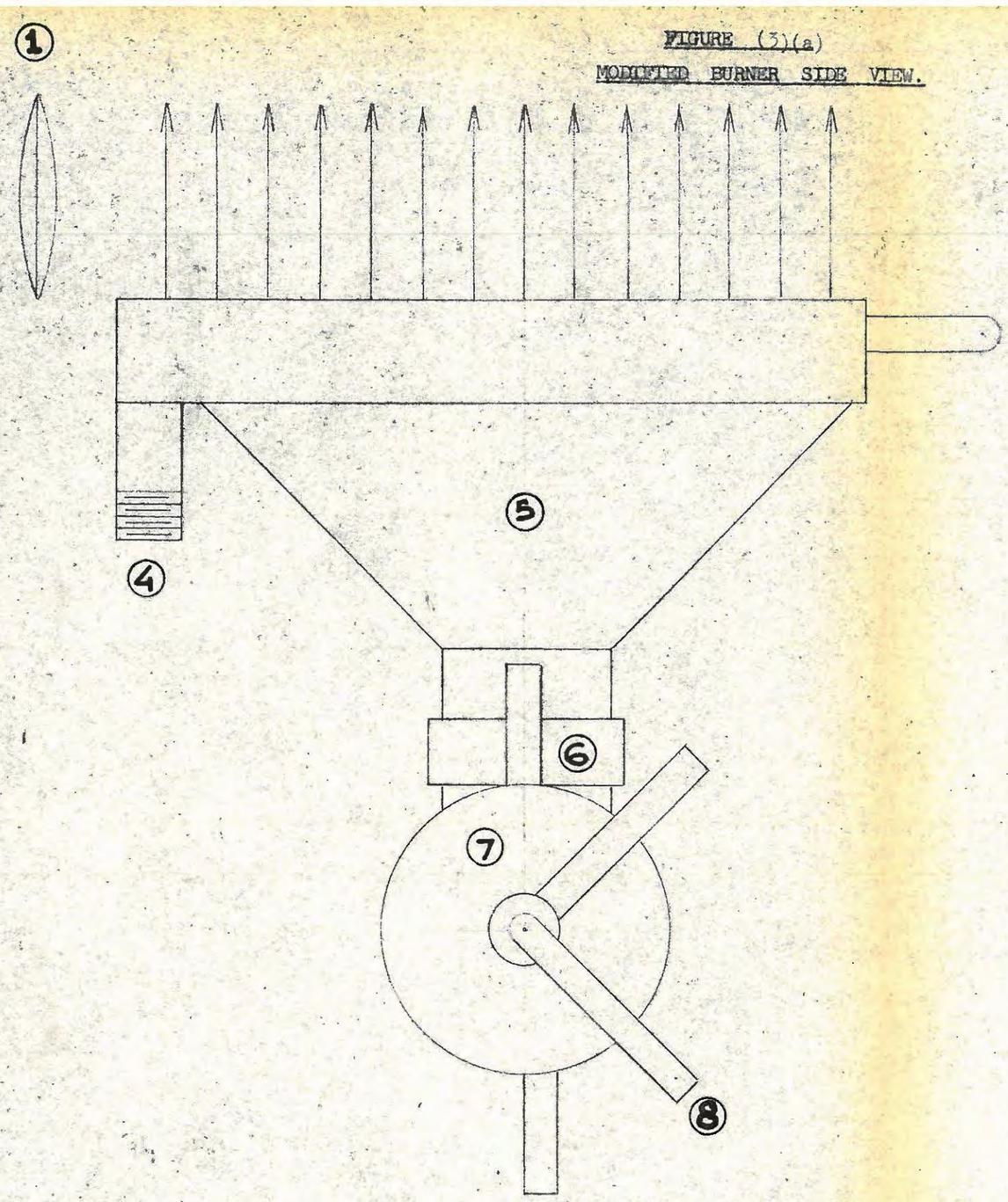
Reports by Willis[20] and other workers on the use of an "Eel" (Evans Electroselenium, Ltd.) flame photometer burner and atomiser indicate that somewhat better sensitivity for the determination of magnesium by atomic absorption is obtainable with it than with the Hilger apparatus. A burner unit incorporating the Eel atomiser was designed by the author and constructed in the Government Metallurgical Laboratory workshops. This unit is shown in Figure 3.

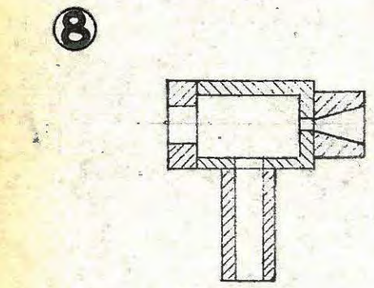
A disadvantage of the Eel atomiser is that it is attacked by fairly concentrated solutions of hydrochloric acid as it is made of stainless steel. Solutions containing up to 10 percent hydrochloric acid by volume have been aspirated with no apparent damage to the atomiser, but more concentrated solutions attack it, particularly if a little nitric acid is present as well. The original Hilger atomiser was adapted to fit

/(26)....the Eel...

FIGURE (3)(a)

MODIFIED BURNER SIDE VIEW.

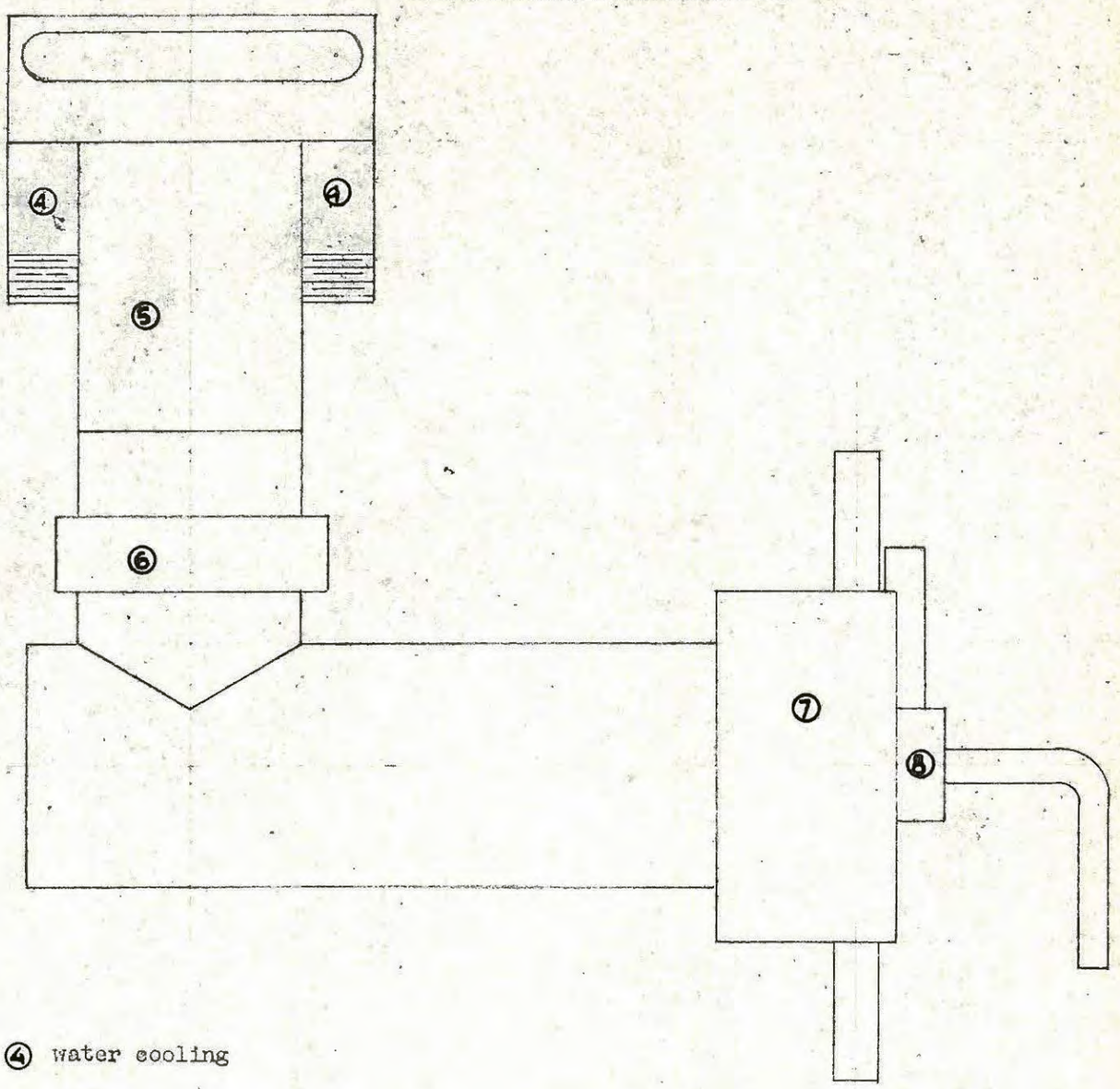




1. "Front Lens" (focussing lens).
2. "Back Lens" (collimating lens).
3. Hollow cathode lamp (size reduced).
4. Water cooling.
5. Burner top.
6. Adapting collar.
7. Spray chamber back.
8. atomiser.

FIGURE 3(b)

MODIFIED BURNER FRONT VIEW.



④ water cooling

⑤ burner top

⑥ adapting collar

⑦ spray chamber back

⑧ atomiser

the Eel spray chamber when such solutions were analysed. This modification reduced the sensitivity of the method by about 50 percent. The flame is much larger when the Hilger atomiser is used on account of the higher flow-rate of air with this atomiser. The performance of this burner and atomiser unit was considerably improved by removing the gauze and plastic mixer from the Eel spray chamber. Previously an accumulation of liquid on the gauze and "mixer" resulted in a restriction of the free flow of the aerosol, causing a progressive decrease in sensitivity and stability during operation.

4.3 Height of burner. For some elements, particularly calcium,[32] the absorbance varies with the position in the flame at which it is measured. This because a maximum concentration of atoms of the element sought occurs in one zone of the flame and best results are obtained when as great a percentage of light as possible passes through this zone. With magnesium optimum sensitivity was obtained when the light beam passed through the base of the flame; i.e. when the burner was raised to a point just below the bottom of the light beam from the hollow cathode lamp. Lowering the burner 1 cm. reduced the optical density reading for a solution containing 0.10 p.p.m. Mg and 2 percent (v/v) molar strontium nitrate solution by 22 percent, and that of a similar solution containing 0.40 p.p.m. Mg by 18 percent. Still better sensitivity can be achieved by raising the burner until it cuts off the lower half of the light beam, but this position was not used as it necessitated operating the lamp at too high a current.

4.4 The use of masks: For operation of the modified burner with "Handigas", particularly if aqueous solutions are used, it is essential to restrict the area of the light beam so that none of the light accepted by the detector misses the flame. This was accomplished by masking the focussing and collimating lenses of the burner housing. Cardboard masks were used, the mask on the lamp-side (collimating) lens (called the "back mask") having a slit 5/16" x ½" and the mask on the spectrophotometer side lens (the focussing lens) (also called the "front" mask) having a slit ⅛" x ½". A slightly larger front mask gave

/27...somewhat...

somewhat lower sensitivity for the atomic absorption of magnesium. Results are given in Table I. Using the smaller mask less meter fluctuation was observed while taking a reading than when the larger mask was used. This is probably because some of the light passes through the edges of the flame, where conditions are unsteady, when the larger mark is used.

TABLE I.

The Effect of masking on sensitivity.

Conc. Mg. (p.p.m.)	Optical density	
	Larger front mask ($\frac{3}{8}$" x $\frac{1}{4}$")	smaller mask ($\frac{1}{16}$" x $\frac{1}{2}$)
0.05	0.062	0.095
0.10	0.107	0.126
0.20	-	0.243
0.25	0.236	--
0.5	0.428	0.495

Coal gas-air flame. Air press. = 30 p.s.i. Lamp current = 15m A. for larger mask; 20 for smaller. Slit = 0.1 mm (large mask): 0.2 mm. (smaller mask). Solutions = aqueous, 1% (v/v) HNO_3, 2% $MSr(NO_3)_2$ Coal gas flowrate adjusted to give maximum optical density.

The flame which gave maximum sensitivity with the larger mask was noticeably larger than the flame which gave maximum sensitivity when the smaller mask was used. This explains the decrease in sensitivity when the larger mask is used: the greater flow-rate of fuel gas in this instance causes more dilution of the fixed amount of aerosol in the flame.

4.5 Comparison of the Hilger atomiser-burner with the modified "Eel" unit:

The first obvious difference between the two systems is that the flame of the Hilger atomiser-burner is far larger than that obtained with the modified apparatus. This has already been explained by the far greater air flow-rate for the former atomiser.

The Eel atomiser was found to draw up an aqueous solution at a rate of

/(28). 8.6 ml....

8.6 ml/min. at 25 p.s.i. air pressure. Efficiency of the atomiser, determined by collecting the "condensate" from the spray chamber after aspirating a known volume of water, was found to be 13 percent, compared with 8 percent for the Hilger atomiser-burner. The Hilger atomiser drew up solution at a rate of approximately 12 ml/min. at 20 p.s.i. air pressure. Thus solution enters the flame at a rate of approximately 1.1 ml./min. in the case of the modified unit, while less than 0.96 ml/min. reaches the flame of the original Hilger burner. With the latter unit some of the 0.96 ml./min. of solution leaving the spray chamber condenser in the burner and tubing leading to it. A considerable amount of this aerosol never enters the burner at all, as it escapes through the bottom of the chamber surrounding the burner air-holes.

Typical results obtained with the two atomiser-burner units are given in Table 2.

TABLE 2.

Comparison of results obtained with the original Hilger and modified apparatus.

Hilger Apparatus		Modified Apparatus	
Conc. Mg (p.p.m.)	Optical Density	Conc. Mg (p.p.m.)	Optical Density
0.51	0.083	0.051	0.044
1.02	0.160	0.102	0.060
2.05	0.316	0.153	0.114
3.07	0.431	0.205	0.159
		0.410	0.321
4.10	0.522		
6.15	0.632		
8.2	0.733		
10.2	0.801		

Air press. = 30 p.s.i. for modified unit, 20 for Hilger

Handigas fuel; Blanks subtracted

Solns.: 1% (v/v) HNO_3 ; 2% (v/v) $MSr(NO_3)_2$

/29.....These data

These data show an increase of sensitivity of roughly 5 times for the modified unit. This improvement is explained by the greater concentration of magnesium in the flame of the modified burner, resulting from increased atomiser efficiency and the smaller flow-rates of fuel gas and air.

4.6 Comparison of coal-gas and Handigas.

The performance of the modified atomic absorption unit was tested with coal-gas and Handigas as burner fuel. Fluctuations in the pressure of the municipal coal-gas supply which was used in this work necessitates some form of pressure regulator. The results reported here were obtained using a bleed with a constant head (9") of water. The pressure obtained with this system was not absolutely constant, but reproducible readings could be obtained by adjusting the coal-gas flow-rate during the measurement of each sample until a maximum optical density reading was obtained. Results obtained for magnesium absorption using the two fuels are given in Table 3.

TABLE 3.

Comparison of results with Handigas and coal-gas.

Conc. Mg. (p.p.m.)	Optical Density	
	Coal-gas	Handigas
0.05	0.096	0.074
0.10	0.127	0.103
0.20	0.246	0.199
0.30	0.321	0.262
0.4	0.416	0.341
0.5	0.495	0.400

Aqueous solutions; 2% (v/v) $MSr(NO_3)_2$; 1% HNO_3

Air press. = 30 p.s.i. lamp current = 20 m A. Slit = 0.2 mm.

These results indicate that coal-gas gives a sensitivity about 20 percent greater than Handigas for magnesium. It also appeared that the effect of varying the height of the burner was less pronounced in the case of coal-gas than when Handigas was used. This is evident from the results given in Table 4.

/(30)....Table 4...

TABLE 4.

Effect of varying the height of burner (coal-gas flame).

Conc. Mg. (p.p.m.)	Conc. $Sr(NO_3)_2$ % (v/v)	Optical Density	
		Optimum height	Burner approx. 1 cm. lower
0.1	0	0.082	0.081
0.2	0	0.134	0.145
0.4	0	0.202	0.204
0.5	0	0.234	0.208
0.1	2	0.127	0.113
0.2	2	0.416	0.388

Slit = 0.2 mm.; lamp current = 20 m A, modified burner, air press.=2 p.s.i. Solutions: aqueous, 1% (v/v) HNO_3

During the course of this investigation a Fisher Governor type S100-2, which has an output pressure that can be varied between $3\frac{1}{2}$" and $5\frac{1}{2}$" of water, became available. This regulator proved vastly superior to the bleed system previously used for coal-gas. It was found necessary to check the flow-rate setting about once in 10 minutes when this regulator was used and much smaller meter variation was observed while taking a reading.

Handigas was chosen in preference to coal-gas for this investigation as its flow-rate was easier to control. At the time when this decision was taken the Fisher regulator was not available and operation with coal-gas was tedious, as the coal-gas flow-rate had to be adjusted for each sample. A minor advantage of Handigas is that it is obtainable in cylinders while coal-gas is not, as a consequence of which a method which employs the latter as fuel can only be employed if a gasworks is close at hand.

4.7 Flow-rates of fuel gas and air.

The flow-rates for the operation of the burner were set by trial and error to give maximum optical density while passing a solution containing magnesium into the flame. The flow-rates of fuel gas and

/(31)....compressed air...

compressed air at the optimum settings were measured by displacement of water and the following results obtained:

1) Coal-gas : 6 litres/min.

2) Handigas: 630 mls./min.

3) Air, at 30 p.s.i. : 13 litres/min.

These figures are the means of 3 measurements and were obtained at a temperature of 22°C and a pressure of 621 mm. Hg. "Handigas" is a mixture of butane (approximately 60 percent by volume) and propane (approximately 40 percent by volume) containing small amounts of other hydrocarbons. It is a petroleum by-product, produced by the South African Coal, Oil and Gas Corporation, Ltd. (SASOL) and its composition varies slightly from batch to batch. On account of the difference between the boiling points of butane and propane the composition of the gas obtained from the cylinder will vary as the gas is used up. The first portions of gas drawn from the cylinder will be relatively rich in propane, while an almost empty cylinder will give a gas very rich in butane. This variation in composition did not affect the results obtained for magnesium noticeably, but as optical density readings became unsteady after approximately 90 percent of the capacity of the cylinder was used, it was replaced at this stage.

Assuming complete combustion to water and carbon dioxide, 1 volume of Handigas should require approximately 6 volumes of oxygen, i.e. 30 volumes of air. Thus, for complete combustion at a Handigas flow-rate of 0.63 litres/min., one would expect the flow-rate of air to be 19 litres/min. As the observed flow-rate for maximum sensitivity is only 13 litres/min., it would appear that a fuel-rich flame gives best results for the atomic absorption of magnesium. This is in agreement with the observations of Allan,[18] who attributed it to the reducing action of the "rich" flame, resulting in an increase of the magnesium metal concentration in the flame at the expense of magnesium oxide.

Coal gas is a complex mixture of somewhat variable composition. The following is a typical analysis (figures supplied by the Johannesburg Gasworks).

/(32)...Methane...

methane : 18.4% (v/v) nitrogen : 8% hydrogen : 45.9%

carbon monoxide: 20.4% ethylene: 2.6% carbon dioxide: 4.1%

oxygen: 0.6%

From these figures it may be calculated that 1 volume of coal-gas requires 4.9 volumes of air for complete combustion. This corresponds to an air flow-rate of 29.4 litres/min. Thus maximum sensitivity for magnesium is also obtained in a fuel-rich flame when coal-gas is used as fuel. From the appearance of the flame it was obvious that maximum sensitivity was obtained when the light beam passed through the reducing area of the flame.

At flow-rates of coal-gas slightly above the optimum, emission from the flame was detected by the spectrophotometer. This was probably due to the strong hydroxyl band emission in the region of the magnesium line. This emission did not affect this work seriously, however, as the flow-rate of coal-gas was kept below the level where emission was observed.

4.8 The Use of organic solvents.

In view of the improvement reported by Zeeman and Butler[61] in the atomic absorption determination of lead using ethanolic instead of aqueous solutions, it was decided to test the effect of acetone and alcohol on the absorbance of magnesium. Results obtained with the Hilger atomiser-burner are given in Table 5.

TABLE 5.

The effect of ethanol and acetone on the atomic absorption of magnesium.

Conc. Mg. (p.p.m.)	Conc. organic solvent (% v/v)	Nature of solvent	Conc. $Sr(NO_3)_2$	Optical Density*	Remarks
0.51	-	aqueous	0	0.058	-
0.51	20	ethanol-H_2O	0	0.117	solution cloudy
0.51	20	acetone-H_2O	0	0.10	-
0.51	-	aqueous	0.02 M	0.073	-
0.51	20	ethanol-H_2O	0.02 M	0.128	solution cloudy
0.51	20	acetone-H_2O	0.02 M	0.125	larger red area in flame then with ethanol

* blanks subtracted. Standard Hilger apparatus; air press.=20 p.s.i.; lamp current = 25 m A. Solutions: 1% (v/v) HNO_3. Handigas flame..

.33/...

The cloudiness of the ethanolic solutions was probably due to the presence of benzene in the absolute alcohol used. The results obtained indicate that 20 percent by volume of ethanol and acetone both increase the sensitivity of the atomic absorption of magnesium by approximately 100 percent in the absence of strontium. In the presence of strontium the optical density is increased by approximately 70 percent. As both ethanol and acetone enhance the absorption of magnesium to approximately the same extent, the former was chosen for further study on account of its lower volatility and the greater solubility of many inorganic salts in it. Results for varying concentrations of ethanol are given in Table 6.

TABLE 6.

The effect of various concentrations of ethanol.

Conc. alcohol (% v/v)	Optical density	Remarks
0	0.063	-
5	0.097	slightly cloudy solution
10	0.109	more " "
20	0.125	same as previous solution
30	0.144	" " " "
40	0.163	solution almost clear
60	0.197	clear solution

Standard Hilger apparatus; air press. 20 p.s.i., Handigas flame.

Solution: Mg. = 0.51 p.p.m,; HNO_3 = 1% (v/v); $Sr(NO_3)_2$ = 0.02 M.

These enhancements may be explained by atomisation efficiency differences, as subsequently also confirmed by Allan.[62] The atomiser efficiency was tested as described in section 4.5 and the results obtained here are liable to the same errors as those given in that section. The results obtained for mixtures of ethanol and acetone with water are given in Table 7.

/(34)...Table 7...

TABLE 7.

The efficiency of atomisation for organic-aqueous mixtures.

Nature of solvent	Conc. of organic solvent (% v/v)	Atomisation efficiency (mean of 3 readings)
		%
water	---	8
ethanol-water	20	16
acetone-water	20	20

Standard Hilger apparatus; air press. = 20 p.s.i. Solutions: 1% HNO_3; 0.02 M w.r.t. $Sr(NO_3)_2$.

As the feed-rate of solution to the Hilger atomiser is unaltered by the presence of acetone and ethanol in the above concentrations, it is evident from these results that twice as much solution enters the flame in a given time when 20 percent ethanol is used as when aqueous solutions are employed. This explains quantitatively the enhancement observed with 20 percent ethanol.

It was mistakenly assumed that 60 percent ethanol solutions would also improve the sensitivity when the modified burner was used, and a considerable amount of work was done on the effect of foreign elements on the absorption of magnesium using 60 percent ethanol and the modified burner. This, however, was found to be incorrect, as is evident from the results in Table 8. The rate at which the ethanolic solution (aerosol) entered the flame was determined in an attempt to explain this apparent anomaly. The efficiency of atomisation using 60 percent ethanol was found to be 30 percent, but solution was drawn up at the rate of only 3.7 ml./min. at an air pressure of 30 p.s.i., from which it may be calculated that the ethanolic aerosol enters the flame at a rate of 1.1 ml./min. It was shown in section 4.5 that an aerosol from an aqueous solution also entered the flame at a rate equivalent to 1.1 ml. of solution per minute. Thus it is reasonable to expect almost identical results for aqueous and 60 percent ethanol solutions when the modified apparatus is used. The reason for the lower flow-rate of the ethanolic solution was not investigated, but it probably results from differences in interfacial tensions as compared with an aqueous solution. Other factors,

/(35)...principally...

principally viscosity and density, should favour a higher flow-rate of the ethanolic solution.

As no advantage was obtained from the use of ethanolic solutions with the modified apparatus, further work was done with aqueous solutions.

TABLE 8.

Comparison of aqueous and alcoholic solutions with modified burner.

Conc. Mg. (p.p.m.)	Optical density*	
	Aqueous solution	60% (v/v) ethanol solution
0.05	0.062	0.068
0.10	0.108	0.105
0.25	0.236	0.224
0.5	0.428	0.392

* Blank not subtracted. Air press. = 30 p.s.i., coal-gas fuel. Slit = 0.05 mm. lamp current = 15 m A. Larger mask used. Solutions contain 1% HNO_3, 0.02 m w.r.t. $Sr(NO_3)_2$.

4.9 The Effect of other elements:

The effect of other elements was studied by measuring the optical density of a standard magnesium solution to which a known amount of foreign element was added and comparing the result with the optical density given by a solution of the magnesium salt of the same concentration. In most cases A.R. grade compounds of the foreign element were found sufficiently pure for use in these tests, but for lithium even the "Specpure" compound was found to contain too much magnesium and further purification had to be carried out. The methods employed for further purification, where necessary, are given in Appendix 2. The modified atomiser-burner was used for these tests. Handigas fuel and aqueous solutions were used excepting where indicated. All solutions employed in this work were prepared with de-ionised water.

/(36).....4.10 Two-atomiser tests.

4.10 Two-atomiser tests:

Tests using two atomisers were employed in an attempt to elucidate the mechanism of some of the inter-element effects observed in this work. This approach was suggested by the work of Alkemade and Jeuken and other investigators which was described in the literature survey.

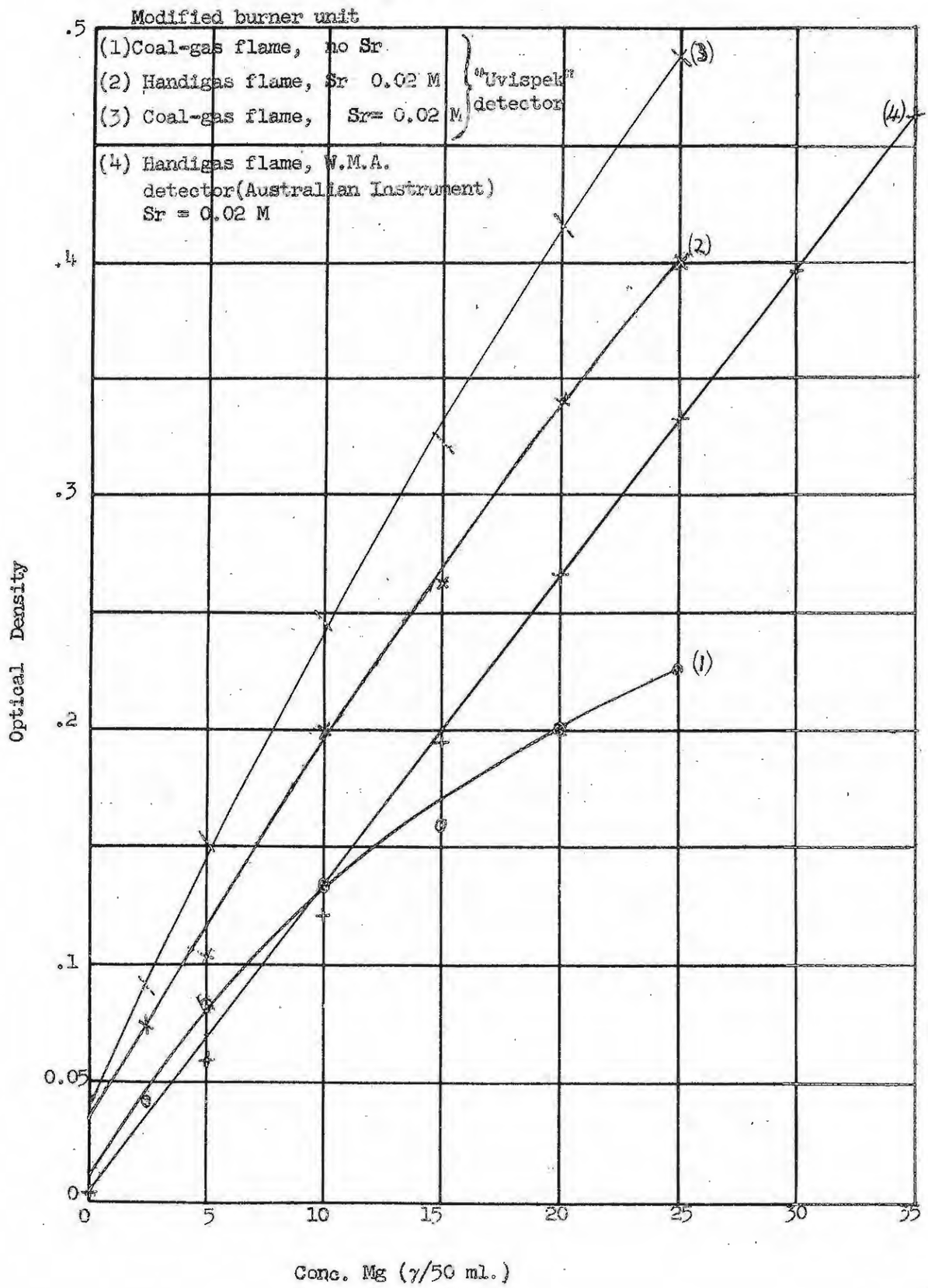
For these tests a new back for the Eel spray chamber was constructed from a plastic material. It was designed to accommodate two Eel atomisers which were operated at identical compressed air pressures (15 p.s.i.). Unfortunately the atomisers did not "match" (i.e. they gave different optical densities for the same solution of magnesium) but the results obtained showed the same effect regardless of which atomiser was used. The solutions used for these tests were those prepared for the inter-element effects described in section 4.9.

37./5. RESULTS AND DISCUSSION.....

5. RESULTS AND DISCUSSION.

FIGURE 4.

Calibration Curves for magnesium.



5. RESULTS AND DISCUSSION.

5.1 Calibration of instrument.

During the early part of this work a solution of magnesium sulphate (A.R. grade), which was standardised by gravimetric analysis, was used as standard. During the latter portion of the investigation, which includes the interference tests, a solution of magnesium chloride prepared from ignited A.R. grade magnesium oxide was used as a primary standard. The two solutions were checked against each other after suitable dilution: identical readings were obtained for their absorbance.

Typical calibration curves are given in Figure 4. A curved calibration line was always obtained, the curvature being least for the most sensitive systems. Thus magnesium nitrate without strontium gave a calibration curve which flattened at low concentrations, while in the presence of strontium or lanthanum salts the curvature was vastly reduced. The calibration curve with a coal-gas flame was less curved than that obtained with Handigas. The causes of departure from linearity listed in the theoretical section were investigated. In order to test if another emission line caused this non-linearity (cause (i)), the light from the magnesium hollow-cathode lamp was examined using a Hilger large glass-quartz (Littrow type) spectrograph. The lamp was clamped in position about 2 inches from the slit of the spectrograph and operated at a current of 30 m A. Light from the lamp was collimated using the quartz collimating lens (the "back" lens) from the burner housing. A slit width of 20 microns was used and the spectrum photographed on an Ilford thin-film, half-tone plate (N 50 emulsion). Exposure times of 1, 3, 20 and 60 minutes were used and an iron spectrum recorded as reference. A photograph (negative) of these spectra is shown in Figure 5. The line closest to the magnesium resonance line at 2852.1 Å was a magnesium line at 2848.4 Å, the intensity of which was a mere fraction of a percent of that of the resonance line. The magnesium line at 2851.7 Å, listed in most tables of spectra, was not observed. It is unlikely that it could have been obscured by the resonance line. The resolution of the Uvispek spectrophotometer at 0.2 mm. slit width is

/(38)...insufficient.....

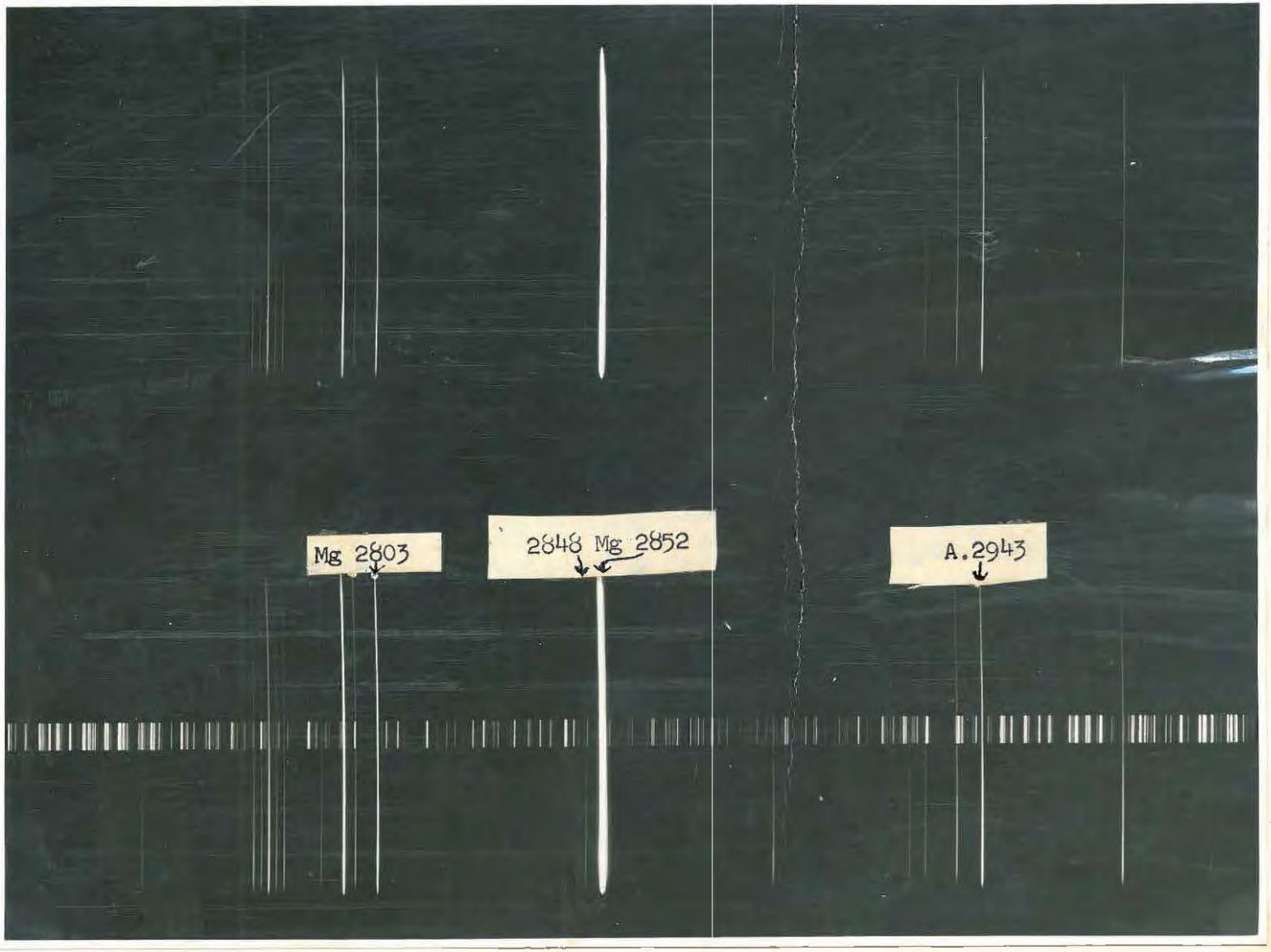


FIGURE 5. SPECTRUM OF LIGHT FROM MAGNESIUM LAMP.

insufficient to eliminate the magnesium line at 2848.4 Å, but its intensity is so low that it is unlikely to have any effect in this work. It appears, therefore, that cause (i) is not responsible for the departure from linearity of the calibration curve in this work. The resonance line did not show any signs of self-absorption (the microphotometer showed no decrease in intensity at the centre of the line).

Cause (iv) (the detection of emission of the resonance line in the flame) was examined next. For this purpose the apparatus described by Box and Walsh[27] was used. With this apparatus steady emission from the flame is not detected, as a modulated light source and a.c. amplifier is used. It was found, however, that any flicker from the flame was detected when a spectral region of high flame emission intensity was examined. This was especially pronounced when an oxy-acetylene flame, which emits very strongly at 2852 Å and flickers slightly, was used. Earthing the input signal to the amplifier through a tuned parallel resonance circuit (choke and condenser in parallel) eliminated nearly all of this emission noise from the flame. This modification resulted in some loss of gain in the amplifier, but sensitivity was still adequate for this purpose. With this apparatus the Hilger Uvispek monochromator, modified atomiser-burner (Handigas flame) and RCA 1 P28 photomultiplier tube were used. The Hilger magnesium hollow-cathode lamp was used and was operated with unsmoothed, half-wave rectified a.-c. current (from the mains). The calibration curve obtained with this apparatus is included in Figure 4 and shows good linearity. This indicates that cause (iv) is probably responsible for the departure from linearity of the calibration curve obtained with the d.c. system of detection.

The day-to-day reproducibility of the calibration curve was generally about 2 percent, providing flow-rates of the gases were controlled carefully. The calibration was seriously affected by dismantling the atomiser for cleaning. For accurate work it was considered essential to measure standards with each batch of samples.

Strontium salts are included in the solutions used in

/(39)....this work....

this work as releasing agents (see literature survey). The nitrate or chloride were used in most cases. The A.R. grade salts were found sufficiently pure and addition to samples at the rate of 2 percent by volume of a molar strontium salt solution was found to give best results. Strontium was found to enhance the absorbance of magnesium as well as "releasing" it from interfering elements. As the magnitude of the enhancement is dependent on the strontium concentration the addition of strontium must be carefully controlled. Details of the effect of strontium salts are given later in this thesis.

5.2 The effect of other elements.

The effects of other elements or compounds are expressed as the enhancement due to the foreign substance, which is defined as

$$\frac{\text{optical density of (Mg + foreign substance)}}{\text{optical density of solution with same concentration of magnesium}}$$

In most cases the foreign substance added contains a measurable amount of magnesium and the optical density due to this must be subtracted before calculation of the enhancement. An enhancement of more than 1 may be interpreted as meaning that the optical density due to a magnesium solution is increased by the introduction of the foreign substance, while an "enhancement" of less than 1 means that the optical density due to the magnesium solution is depressed by the introduction of the foreign element.

In this investigation the effect of other elements was studied both in the presence and absence of strontium salts. For purposes of calculating the enhancement in the presence of strontium salts the following definition is used:

$$\text{Enhancement} = \frac{\text{optical density (Mg + Sr + foreign substance)}}{\text{optical density (same conc. Sr + same conc. Mg)}}$$

Allowance must also be made for the optical density due to magnesium contained in the strontium and foreign substance here (blank corrections).

/(40).....5.2.1 Mineral Acids....

5.2.1 Mineral Acids.

The effects of nitric, hydrochloric, sulphuric, perchloric, hydrobromic and hydriodic acids were tested. The results obtained are given in Table 9.

TABLE 9.

The Effects of mineral acids.

Substance added	Conc. of foreign subst.	Conc. Mg (p.p.m.)	Conc. Sr (molarity)	Optical density* Mg soln. without foreign substance	Enhancement	REMARKS
HNO_3 (A.R. grade) S.G. = 1.39	5% (v/v)	0.4	0	0.158	0.582	Mg added as nitrate. Compared with neutral Mg solution.
	20% (v/v)	0.4	0.02	0.292	1.00	Compared with neutral Mg. + $Sr(NO_3)_2$ soln.
HCl (A.R.) S.G. = 1.18.	5% (v/v)	0.4	0	0.176	1.08	Mg added as chloride. Compared with neutral Mg Cl_2.
	20% (v/v)	0.4	0.02	0.292	0.99	Mg + Sr both as chloride
HCl + 100 vol. H_2O_2 (A.R.)	5% (v/v) of each	0.4	0	0.176	0.29	Mg. as chloride.
H_2SO_4 (A.R.) S.G.=1.84	5% (v/v)	0.4	0	0.059	0.763	Mg added as sulphate Compared with neutral Mg SO_4
$HClO_4$ (A.R.) 70-72% (w/w)	5% (v/v)	0.4	0	0.305	0.944	Mg added as perchlorate compared with neutral $Mg(ClO_4)_2$
	20%	0.4	0.02	0.292	0.96	Sr as $Sr(ClO_4)_2$
HBr (A.R.) S.G.=1.38	1.1% (w/v) HBr	0.4	0	0.096	1.08	Mg added as nitrate. Compared with neutral Mg $(NO_3)_2$
	0.01%(w/v)	0.4	0.02	0.250	0.97	Sr added as $Sr(NO_3)_2$
	0.05%(w/v)	0.4	0.02	0.250	1.00	
	0.11%(w/v)	0.4	0.02	0.250	0.96	
	0.22%(w/v)	0.4	0.02	0.250	0.906	

/(41) Table contd....

TABLE 9 (contd.).

Substance added	Conc. of foreign subst.	Conc. Mg (p.p.m.)	Conc. Sr (molarity)	Optical density* Mg. soln. without foreign substance	Enhance-ment	REMARKS
H I(A.R.) S.G.=1.70	1.9%(w/v)	0.4	0	0.096	1.07	Mg. added as nitrate
	0.019	0.4	0.02	0.250	1.00	
	0.097	0.4	0.02	0.250	0.804	
	0.19	0.4	0.02	0.250	0.76	

* represents O.D. of Mg. + Sr or La if used. Handigas flame.
Air = 30 p.s.i. Lamp current = 20 m A.
Sr as nitrate, if not otherwise indicated.

In the absence of strontium, however, the absorbance of magnesium is very dependent on the nature of the anion present in solution. For the concentration of magnesium tested, the order of sensitivity is perchlorate $\rangle$ chloride $\rangle$ nitrate $\rangle$ sulphate. Increasing nitric, sulphuric and perchloric acid concentrations decrease the absorbance of magnesium, while increasing hydrochloric acid concentration has the opposite effect. Excess perchloric acid has the smallest effect on the absorbance while sulphuric acid is the most powerful depressant.

The mechanisms of these inter-element effects are best explained by considering the decomposition of these acids and their salts in the flame. At flame temperatures nitric acid decomposes into nitric oxide, steam and oxygen according to the reaction:

$$4\ HNO_3 \longrightarrow 4\ NO + 2\ H_2O + 3\ O_2 \quad \ldots\ldots(5)$$

Magnesium nitrate decomposes on heating as follows:

$$2\ Mg(NO_3)_2 \longrightarrow 2Mg\ O + 4\ NO + 3\ O_2 \quad \ldots\ldots(6)$$

Sulphuric acid also decomposes with liberation of oxygen:

$$2\ H_2SO_4 \longrightarrow 2\ H_2O + 2SO_2 + O_2 \quad \ldots\ldots(7)$$

Magnesium sulphate first forms basic sulphates on heating the hydrate. These do not give the anhydrous salt on heating, but eventually

/42....decompose...

decompose yielding magnesium oxide, oxygen and sulphur dioxide.

The decomposition of perchloric acid by heat also involves the liberation of oxygen, steam and oxides of chlorine, which are unstable. Magnesium perchlorate decomposes at approximately 300°C according to the equation :

$$Mg(ClO_4)_2 \longrightarrow Mg\,Cl_2 + 4\,O_2 \quad \ldots\ldots(8)$$

Hydrochloric acid and magnesium chloride, however, react differently in the flame. Some of the reactions which may be expected to take place in the flame are :

$$4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2 \text{ - (the Deacon Process reaction)} \quad \ldots\ldots(9)$$

$$2\,Mg\,Cl_2 + O_2 \rightleftharpoons 2\,Mg\,O + Cl_2 \quad \ldots\ldots(10)$$

$$Mg\,Cl_2 + H_2O \rightleftharpoons Mg\,O + 2\,HCl \quad \ldots\ldots(11)$$

$$Mg\,Cl_2 + MgO \rightleftharpoons Mg_2O\,Cl_2 \quad \ldots\ldots(12)$$

$$Mg\,O \longrightarrow Mg + \tfrac{1}{2}\,O_2 \quad \ldots\ldots(13)$$

$$Mg\,Cl_2 \rightleftharpoons Mg + Cl_2 \quad \ldots\ldots(14)$$

As all these acids give rise to some oxide in the flame, by one or other of the above reactions, reaction (13) will take place no matter which acid is present in the solution. Reactions (10), (11), (12) and (14) will also take place in perchloric acid solutions, which give rise to chloride in the flame.

The concentration of magnesium atoms in the flame, which determines the absorbancy will be affected by the above reactions. Gaydon and Wolfhard[60] point out, however, that it is unlikely that true chemical equilibrium is achieved in the flame, basing their statement on the fact that the concentration of electrons in the flame is far greater than that predicted by equilibrium values. If this is true, exact calculations based on equilibrium constants may be misleading. Even if true equilibrium is not attained in the flame, the above reactions should still show a trend and explain some of the observed phenomena.

Any factor which reduces the free oxygen concentration in the flame should increase the concentration of magnesium atoms according to reaction (13), and consequently increase the absorbancy of magnesium.

/(43)....Thus increasing...

Thus increasing hydrochloric acid concentration increases the sensitivity, as would be expected from reaction (9). Conversely increasing nitrate, sulphate and perchlorate concentrations increase the oxygen concentration of the flame and depress the absorbance of magnesium. Peroxides, which decompose with the liberation of oxygen in the flame, depress the absorption of magnesium (present as chloride), as expected from reaction (13).

If the magnesium is present as nitrate or sulphate, all will decompose to form the oxide, which may undergo further reaction. The greater sensitivity of the chloride and perchlorate may be explained by the existence of a certain amount of magnesium chloride, which decomposes to give the metal more readily than the oxide in the flame and by a decrease in the oxygen concentration of the flame due to reactions (9), (10) and (11). Haber and Fleischmann[63.] showed that the hydrolysis reaction (11) is more nearly complete at higher temperatures and is very slow to approximately 500°C. Thus it is likely that reaction (11) will still be in progress in the hotter portion of the flame. This means that at least some magnesium chloride will reach the hotter region of the flame, where it can dissociate directly to the free element.

The fact that magnesium perchlorate gives better sensitivity than an equimolar solution of magnesium chloride is anomalous. According to reaction (8) the perchlorate should behave like the chloride with excess oxygen, i.e. it should give lower sensitivity for magnesium than the chloride. It is suggested, therefore, that the mechanism of decomposition of magnesium perchlorate in the flame must differ from that of the chloride. As perchlorates frequently decompose violently on heating, the explanation may lie in an explosive decomposition of the dry aerosol particle (Magnesium perchlorate decomposes at approximately 270 to 300°C, at which temperature the particle should be dry). Such a decomposition would result in smaller particles of magnesium chloride then would be formed by evaporation of the aerosol from the chloride solution. As the concentration of magnesium salt is very low, however, it is not reasonable to expect large aerosol particles after evaporation of moisture

/44 .....and this....

and this explanation does not seem plausible if size reduction is the only factor involved. It is possible, however, that the exothermic decomposition of the perchlorate will heat the aerosol particle to a higher temperature than otherwise attained in the flame and that the magnesium chloride formed will be more completely dissociated to the free metal.

The very low magnesium absorbance observed in the presence of sulphate cannot be explained in terms of liberated oxygen alone, as nitrate, which should yield the same amount of oxygen in the flame, gives much greater sensitivity. Possibly this is due to the formation of basic magnesium sulphates, which do not decompose readily, in the flame.

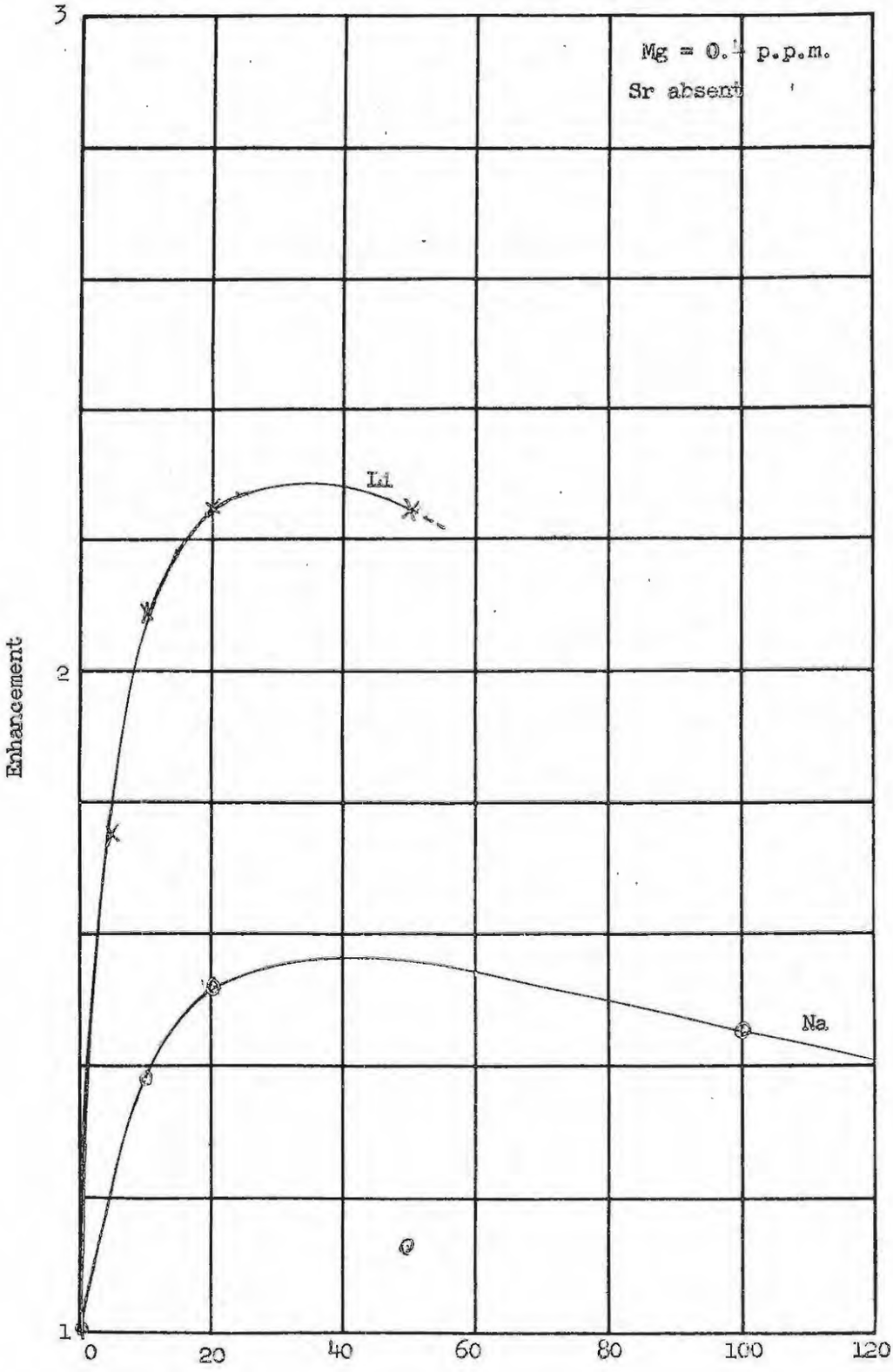
Comparison of the results obtained with and without strontium salts shows that strontium increases the absorbance of magnesium when present as magnesium nitrate, chloride, and perchlorate, the effect being least for perchlorate and greatest for nitrate. The effect of strontium on the absorbance of a magnesium sulphate solution was not tested on account of the insolubility of strontium sulphate. It will be shown later (under the effects of strontium) that the enhancement due to strontium in perchlorate medium is virtually 1, i.e. strontium has a negligible effect if the magnesium is present as the perchlorate. It is very likely that the effect of strontium in the presence of nitrate and chloride is due to a reduction in the free oxygen concentration of the flame. It will be shown later, from thermodynamic considerations, that this is theoretically possible.

The results obtained for hydrobromic and hydriodic acids show that, in the absence of strontium, an approximately 1 percent (w/v) solution of either acid enhances the absorbance of magnesium slightly. In the presence of strontium nitrate small amounts of these acids depressed the absorption, the threshold for interference by hydrobromic acid (approximately 0.1 percent (w/v) being considerably higher than that for hydriodic acid (about 0.05 percent). As varying concentrations of hydrogen ions do not affect the absorbance of magnesium significantly

/(45).....this effect...

FIGURE 6.

The effect of lithium and sodium on the absorbance of magnesium.



this effect is probably due to bromide and iodide ions. The effect of these ions is not likely to be serious in the determination of magnesium in ore and metallurgical samples, as they can be removed easily by fuming with perchloric acid on the rare occasions when they are encountered.

5.2.2 The alkali metals.

The results obtained for the absorbance of magnesium in the presence of various amounts of several of the alkali metals are given in Table 10.

TABLE 10.

Effect of the alkali metals.

Subst. added	Conc. foreign subst.	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	Optical Density Mg soln. without foreign subst.	Enhancement	Graph No.	REMARKS
Li as chloride (Purified)	5 mg Li/ 50 ml.	0.4	0	0.071	1.75	Fig.6	Mg added as chloride
	10 " "	0.4	0	0.071	2.10		
	20 " "	0.4	0	0.071	2.25		
	50 " "	0.4	0	0.071	2.25		
	5 " "	0.4	0.02	0.258	1.00		
	10 " "	0.4	0.02	0.258	0.952		
	20 " "	0.4	0.02	0.258	0.82		
	50 " "	0.4	0.02	0.258	0.934		
Na as nitrate (A.R.)	10 mg. Na/ 50 ml.	0.4	0	0.084	1.36	Fig.6	Mg added as nitrate
	20 mg. "	0.4	0	0.084	1.52		
	50 " "	0.4	0	0.084	1.13		
	100 " "	0.4	0	0.084	1.46		
	500 " "	0.4	0	0.084	0.73		
	1000 " "	0.4	0	0.084	0.52		
	10 " "	0.4	0.02	0.325	0.98		
	20 " "	0.4	0.02	0.325	0.90		
	50 " "	0.4	0.02	0.325	0.83		
	100 " "	0.4	0.02	0.325	0.65		
	500 " "	0.4	0.02	0.325	0.36		
	1000 " "	0.4	0.02	0.325	0.29		

Table contd. /46....

TABLE 10 contd.

Subst. added	Conc. foreign subst.	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	Optical Density Mg solution without foreign subst.	Enhancement	Graph No.	REMARKS
K as chloride (A.R.)	10 mg.K/ 50 ml.	0.4	0	0.069	1.71	-	-
	50 " "	0.4	0.	0.069	1.58		
	100 " "	0.4	0	0.069	1.50		
	500 " "	0.4	0	0.069	1.45		
	1000 " "	0.4	0	0.069	0.87		
K as chloride (A.R.)	10 " "	0.4	0.02	0.296	1.00		
	100 " ""	0.4	0.02	0.296	0.82		
	500 " "	0.4	0.02	0.296	0.58		
	1000 " "	0.4	0.02	0.296	0.54		
Rb as carbonate	2 mg.Rb/ 50 ml.	0.4	0	0.070	0.16		Mg added as nitrate-orange-coloured flame
	2 " "	0.4	0.02	0.254	1.03		

Same conditions as Table 9.

In the absence of strontium the absorbance of magnesium is enhanced by lithium in the concentrations tested, maximum enhancement occurring at a Mg:Li ratio of 1:1000. Low concentrations of sodium and potassium also enhance the absorbance of magnesium in the absence of strontium, but higher concentrations act as a depressant. The behaviour of rubidium is anomalous, as a large depression was observed in the presence of only 40 p.p.m. of rubidium. Too few readings were taken to be able to suggest a reason for this effect.

In the presence of strontium moderate amounts of the alkali metal salts tested depressed the absorbance of magnesium. The threshold of this effect occurred at 10 p.p.m. of lithium, 200 p.p.m. of sodium, 200 p.p.m. potassium and more than 4 p.p.m. of rubidium. The depression observed with potassium was less than that produced by an equal concentration of sodium.

/47...The results....

The results obtained for sodium contradict previous work done with the original Hilger apparatus, using a Handigas flame, where no interference was observed from 4,000 p.p.m. of sodium in the presence of strontium. Allan[18.] reports that sodium does not affect the absorbance of magnesium, even when present at a concentration of 17,000 p.p.m. The magnesium concentration used in his tests was 2 p.p.m. and he employed an air-acetylene flame.

The reason for the depression of the absorbance of magnesium in the presence of strontium by sodium and potassium was not investigated, but it seems likely that it may be due to changes in the properties, particularly the melting point and size, of the solid aerosol particles. Sodium is known to cool an electric arc discharge,[64.] probably on account of ionisation, and it may also be expected to reduce the flame temperature, but the fact that moderate concentrations of sodium have an enhancing effect in the absence of strontium suggests that temperature lowering is not the explanation of the effect observed in atomic absorption work.

The enhancing effect of these elements in the absence of strontium may be due to a reduction in the free oxygen content of the flame (Na_2O has a free energy of formation of -40 Cal. per mole at 1900°K),[65.] but free energy values indicate that reactions of the type:

$$2\ M + MgO \rightleftharpoons M_2O + Mg$$

have unfavourable equilibrium constants at flame temperatures. It seems likely that this enhancement is, therefore, due to changes in the properties of the solid aerosol particles.

5.2.3 The alkaline earth elements.

The effects of calcium, strontium and barium salts were tested. Beryllium was excluded on account of the poisonous nature of its compounds. Results obtained are given in Table 11.

/48...Table 11...

FIGURE 7.

The Effect of calcium on the absorbance of magnesium.

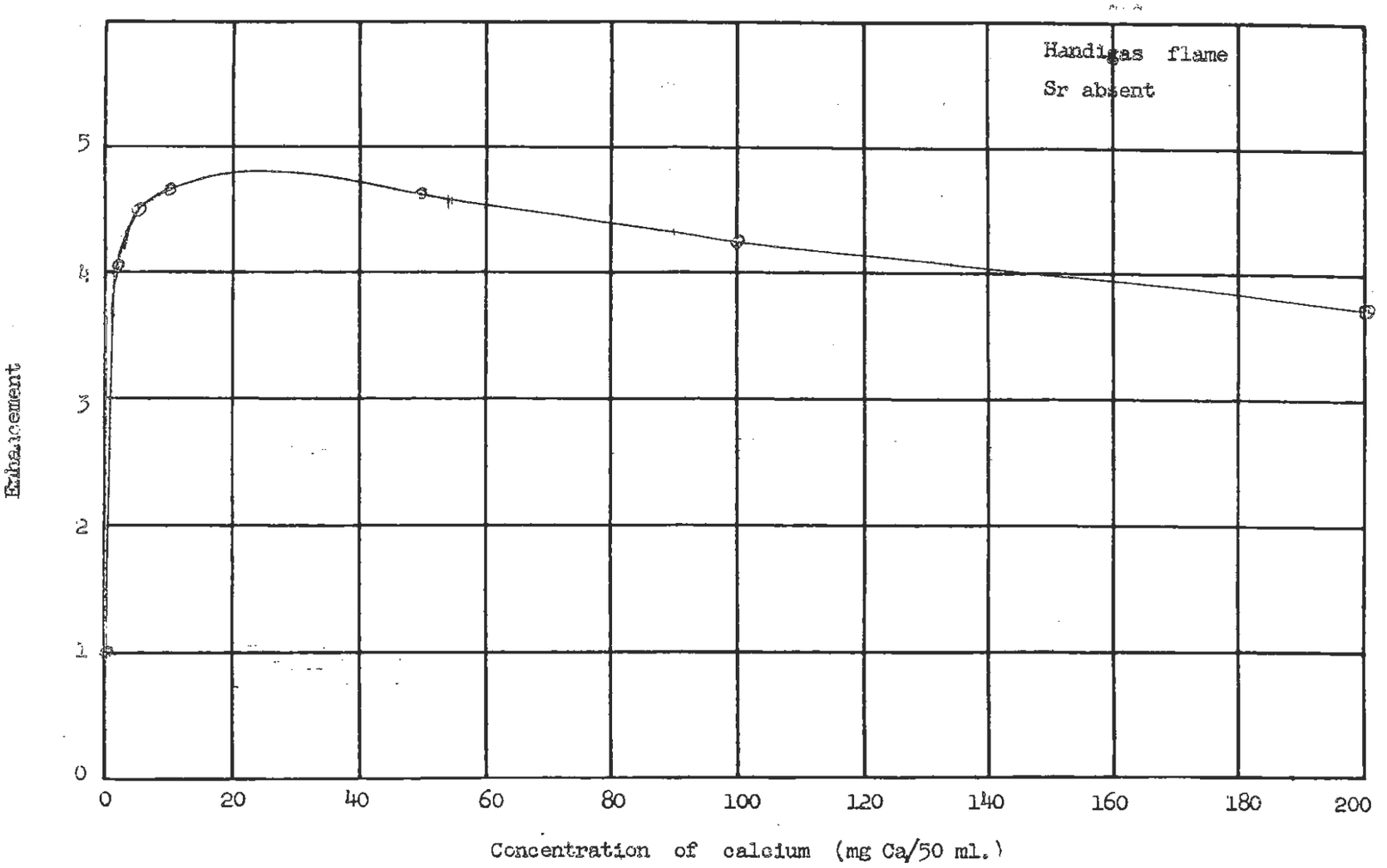


TABLE 11.

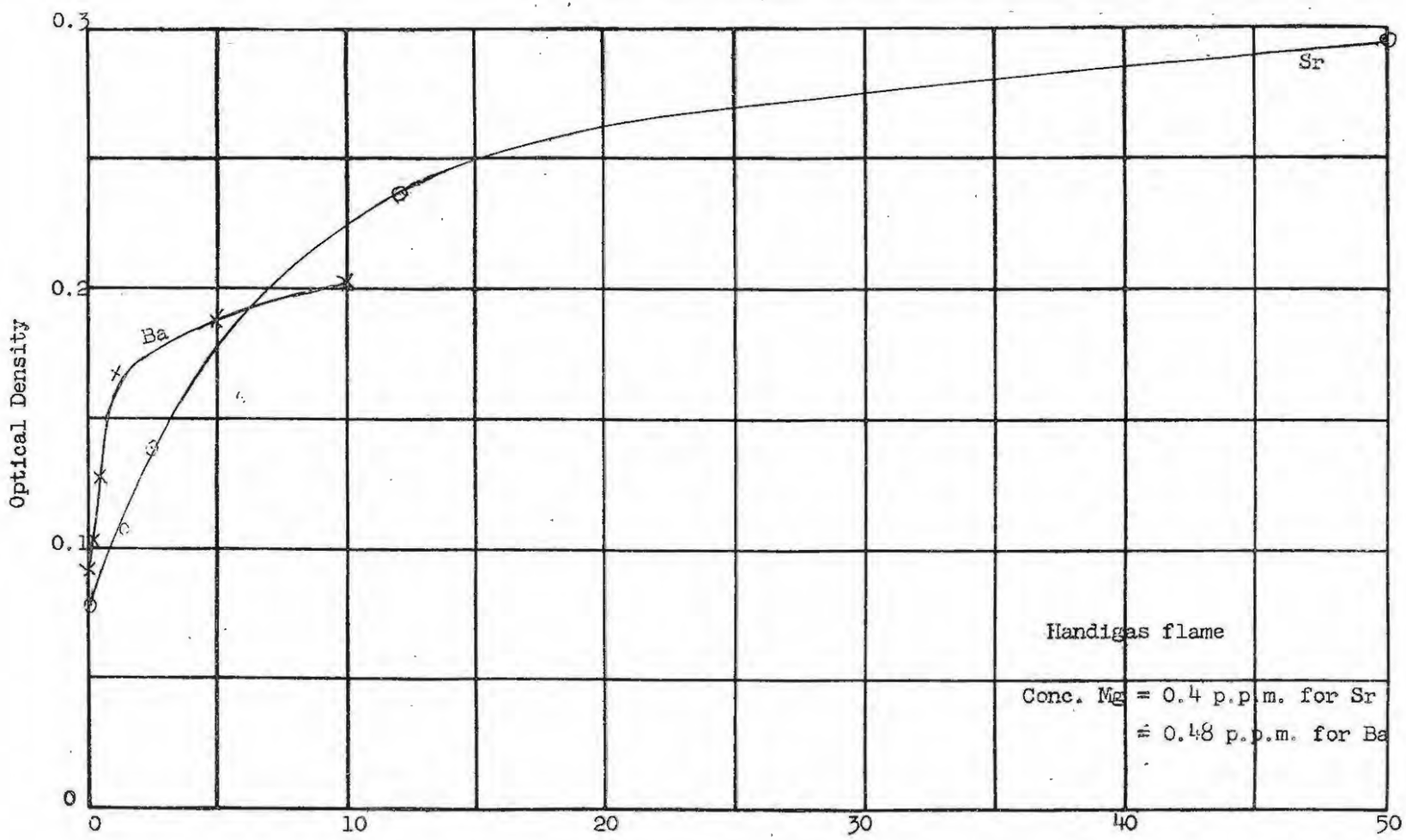
Effect of other alkaline earth elements.

Subst. added	Conc. foreign subst.	Conc. Mg (p.p.m.)	Conc. Sr salt(molarity)	O.D.Mg. soln. without foreign subst.	Enhancement	Graph No.	REMARKS
Ca, as nitrate (ex "Specpure" $CaCO_3$)	2 mg. Ca/50 ml	0.4	0	0.071	4.02	Fig. 7	Mg added as nitrate
	5 " "	0.4	0	0.071	4.49		Red Ca colour in flame
	10 " "	0.4	0	0.071	4.64		
	50 " "	0.4	0	0.071	4.60		
	100 " "	0.4	0	0.071	4.25		
	200 " "	0.4	0	0.071	3.71		
	10 " "	0.4	0.02	0.248	1.00		
	20 " "	0.4	0.02	0.248	0.97		
Sr, as nitrate (A.R.)	8.76 γ Sr/50 ml	0.4	--	0.077	1.39	Fig. 8	Mg added as nitrate. Bright red colour due to Sr in flame
	17.5 " "	0.4	--	0.077	1.80		
	43.8 " "	0.4	--	0.077	2.06		
	87.6 " "	0.4	--	0.077	3.09		
	438 " "	0.4	--	0.077	3.83		
	87.6 mg Sr/50 ml	0.4	--	0.077	4.59		
	87.6 " "	0.4	--	0.069	4.47		
	175 " "	0.4	--	0.069	4.30		
	350 " "	0.4	--	0.069	3.70		
	526 " "	0.4	--	0.069	3.44		
	376 " "	0.4	--	0.069	2.96		
	1.75 g.Sr/50 ml.	0.4	--	0.069	2.39		

/49.....Table 11 contd.

FIGURE 8.

The Effects of strontium and barium on the absorbance of magnesium.



molar concentration ratio, $\frac{(Sr)\ total}{(Mg)\ total}$ or $\frac{(Ba)\ total}{(Mg)\ total}$

TABLE 11.

Subst. added	Conc. foreign subst.	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhancement	Graph No.	REMARKS
Sr, as ClO_4	87.6 mg Sr/ 50 ml.	0.4	--	0.305	0.99	--	Mg added as perchlorate
Ba, as chloride (A.R.)	0.0137 mg Ba/ 50 ml.	0.48	0	0.091	1.03	Fig.8	Mg added as nitrate
	0.027 " "	0.48	0	0.091	1.12		
	0.068 " "	0.48	0	0.091	1.41		
	0.137 " "	0.48	0	0.091	1.75		
	0.274 " "	0.48	0	0.091	1.90		
	0.68 " "	0.48	0	0.091	2.06		
	1.37 " ""	0.48	0	0.091	2.22		
	0.137 " "	0.48	0.02	0.271	1.00		
	1.37 " "	0.48	0.02	0.271	1.01		
	10 " "	0.48	0.02	0.271	1.00		
	50 " "	0.48	0.02	0.271	0.96		

Same conditions as in Table 9.

The results in Table 11 show that calcium, strontium and barium all enhance the absorbance of magnesium. In the case of calcium and strontium maximum enhancement was observed at a molar $\frac{M^{++}}{Mg}$ concentration ratio of about 1000, larger concentrations giving a decreased enhancement. The tests with barium were not performed over as wide a range of concentrations as with calcium and strontium and, consequently, the peak in enhancement was not observed.

In the presence of 0.02 M strontium salt moderate concentrations of both calcium and barium have a depressing effect on the absorbance of magnesium. This effect is observed at concentrations of greater than 200 p.p.m. Ca and about 400 p.p.m. Ba.

/50....The concentration....

The concentration of magnesium in most materials containing high percentages of calcium is fairly high and separation will not be necessary in many instances. On occasions where the calcium concentration in the final solution exceeds 200 p.p.m. it may be separated by double precipitation as calcium oxalate.

When the barium concentration exceeds the tolerance of the method it is best separated by precipitation as the sulphate. Care must be taken not to add an excess of sulphate, as this will form a precipitate with the strontium salt added later as releasing agent.

The effects of these alkaline earth elements were also tested using 60 percent ethanol solutions and a coal-gas flame. The results obtained were very similar to those reported in Table 11.

In order to gain an understanding of the mechanism of the enhancing effect observed with these elements two-atomiser tests were conducted. These tests have been described in the literature survey and in section 4.10. The validity of the conclusions drawn from these tests depends on the assumption that the aerosol particles from the two atomisers do not coalesce. This was proved by passing separate, fairly concentrated, solutions of ferric chloride and potassium ferrocyanide through separate atomisers into the "Eel" spray chamber and allowing the aerosol issuing from the unlighted burner to impinge on a piece of paper, held approximately 1 inch above it, for 30 seconds. Equal portions of the two solutions were mixed and diluted approximately 5 times. This solution was sprayed through both atomisers simultaneously and the spray from the burner was allowed to impinge on a second piece of paper, held in the same position as the first, for 30 seconds. The two pieces of paper were examined under a microscope (X72 magnification) and the number of blue specks on the first piece was found to be considerably less than 10 percent of that on the second, proving that at most only a small amount of coalescence takes place. Quite possibly the few blue specks on the first sheet were due to a droplet from atomiser A impinging on a spot where a droplet from B had struck previously. The specks produced on each sheet were well separated and clearly defined under the microscope. The results of these

/51...tests are given...

tests are given in Table 12.

TABLE 12.

Two-atomiser tests with strontium.

Solution thru' atomiser A	Solution thru' atomiser B	Optical density	Enhancement	REMARKS
0.04 M $Sr(NO_3)_2$	H_2O	0.003	--	---
H_2O	0.04 M $Sr(NO_3)_2$	0.004	--	---
1 p.p.m. Mg (as NO_3^-)	H_2O	0.074		
1 p.p.m. Mg	0.04 M $Sr(NO_3)_2$	0.169	2.28	....
H_2O	1 p.p.m. Mg	0.110	---	---
0.04 M $Sr(NO_3)_2$	1 p.p.m. Mg	0.287	2.61	---
.002 M $Sr(NO_3)_2$	1 p.p.m. Mg	0.229	2.08	---
H_2O	1 p.p.m. Mg	0.100	---	readings taken ± 3 hrs. after those reported above
H_2O	1 p.p.m. Mg + 0.002 M $Sr(NO_3)_2$	0.324	3.24	
H_2O	1 p.p.m. Mg + 0.04 M $Sr(NO_3)_2$	0.319	3.19	

The results indicate that the enhancement of the absorption of magnesium by strontium is principally a vapour phase effect, as it is observed both when two atomisers are used and when only one atomiser is employed. There is a difference between the enhancements observed with one and two atomisers, when solutions of the same concentrations of strontium and magnesium were atomised. These may be due to concentration differences in the flame as a result of the different flow-rates of the two atomisers. Possibly a greater strontium concentration in the immediate vicinity of the aerosol particle when one atomiser is used is also partly responsible for this difference in enhancement. It should be borne in mind that the aerosol particles in the flame will be solid: both magnesium oxide and strontium oxide have melting-points considerably higher than the flame temperature.

/52...It is suggested...

It is suggested that this enhancement is due to a reduction in the free oxygen concentration of the flame. In the flame a little strontium oxide is decomposed as follows:

$$SrO(s) \longrightarrow Sr(g) + \tfrac{1}{2} O_2(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

It will be shown later that the amount of strontium oxide decomposed at flame temperature is very small, but its concentration in these tests far exceeds that of magnesium. Thus the concentration of strontium (metal) in the flame may approach that of magnesium atoms when 0.02 M strontium salt is used. Magnesium oxide will tend to decompose in the flame according to reaction (13).

$$Mg\ O\ (s) \longrightarrow Mg(g) + \tfrac{1}{2} O_2(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

It is suggested that the strontium atoms in the flame will produce a greater concentration of magnesium atoms, as the concentration of oxygen that can exist in equilibrium with strontium and strontium oxide is smaller than the equilibrium oxygen concentration for magnesium oxide and reaction (13) will proceed further to the right. This is equivalent to reaction (16):

$$Mg\ O(s) + Sr\ (g) \rightleftharpoons Sr\ O(s) + Mg\ (g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

It will be shown later that this reaction has a favourable equilibrium constant at the assumed flame temperature.

One of the disadvantages of this mechanism is that it seems that strontium cannot remove more oxygen from the flame than is introduced as a result of reaction (15), which is the reaction which leads to the presence of strontium atoms in the flame. Unless some other reducing agent, e.g. the fuel, removes at least some of the oxygen produced by the dissociation of the strontium oxide it is difficult to see how this mechanism will account for the observed enhancement.

The mechanism of the enhancement observed with calcium and barium is probably similar to that with strontium. It will later be shown that the reaction:

$$Mg\ O(s) + Ca(g) \rightleftharpoons CaO(s) + Mg(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

also has a favourable equilibrium constant.

/53 ....Yet another...

FIGURE 10.

The effect of variations in concentration of strontium nitrate on interference by aluminium.

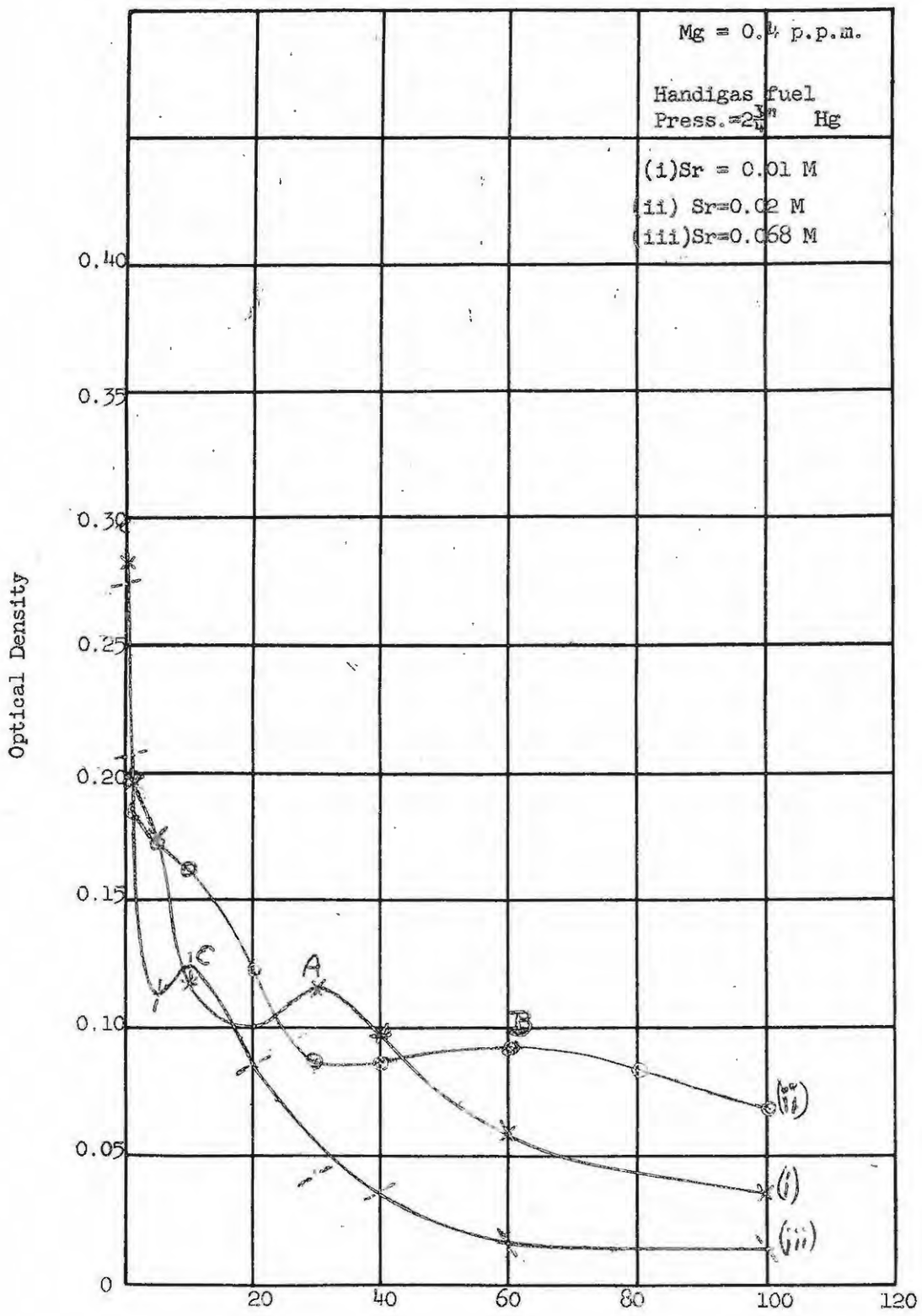
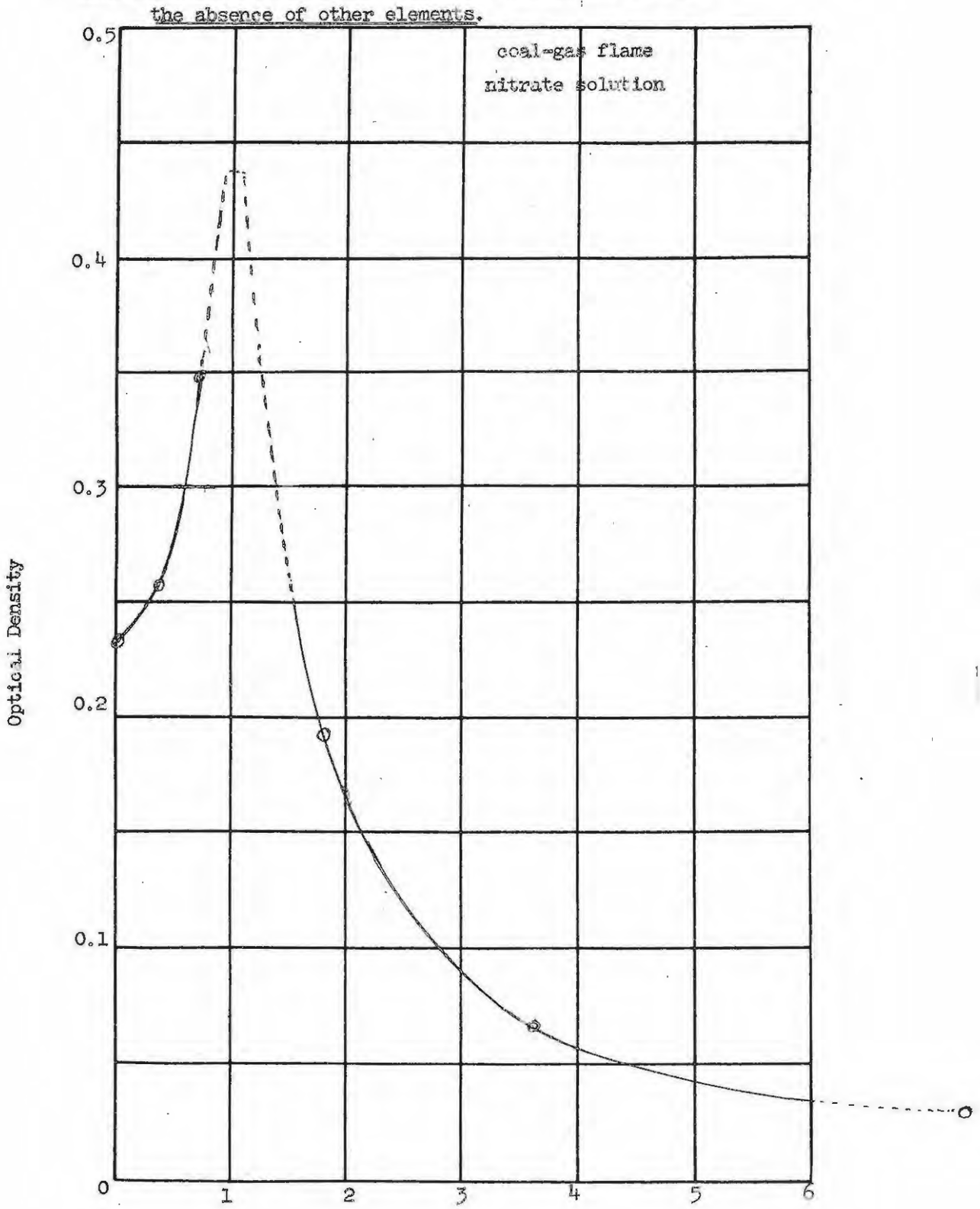


FIG.9.

The Effect of aluminium on the absorbance of magnesium in the absence of other elements.



Yet another difficulty raised by this mechanism is the reason for the depressing effect of calcium in the presence of strontium. If both calcium and strontium enhance the absorbance of magnesium by a gaseous phase process when present alone, it is not reasonable to expect a mixture of the two to enhance to a lesser extent. The most probable explanation of this lies in the variation of melting point of the solid aerosol particle with changing composition and concentrations.

5.2.4 Aluminium.

As has been shown in the literature survey, the interference of aluminium in both the emission and absorption flame photometry of the alkaline earth elements has been extensively investigated. Results obtained in this work are given in Table 13.

TABLE 13.

The Effect of Aluminium.

Form of Al added	Conc. Al(mg/50 ml.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhancement	Graph	REMARKS
A.R.-grade nitrate	0.01	0	0.233	1.11	Fig.9	Conc. Mg = 0.51 p.p.m.
	0.02	0	0.233	1.5		
	0.05	0	0.233	0.82		
	0.10	0	0.233	0.28		coal-gas flame used for these tests
	0.20	0	0.233	0.12		
A.R.-grade nitrate	0.1	0.02	0.292	0.87	Fig. 10(i) + Fig. 11A	Conc. Mg = 0.4 p.p.m.
	0.2	0.02	0.292	0.80		
	0.5	0.02	0.292	0.69		Nitrate solutions. Handigas flame Sr colour in flame becomes paler as conc. Al increases
	0.7	0.02	0.292	0.67		
	1.0	0.02	0.292	0.66		
	5	0.02	0.292	0.59		
	10	0.02	0.292	0.39		
	20	0.02	0.292	0.34		
	30	0.02	0.292	0.36		
	40	0.02	0.292	0.32		
	60	0.02	0.292	0.20		
	100	0.02	0.292	0.08		

/54...Table 13...contd.

FIG. 11.

The effect of aluminium on the absorbance of magnesium.

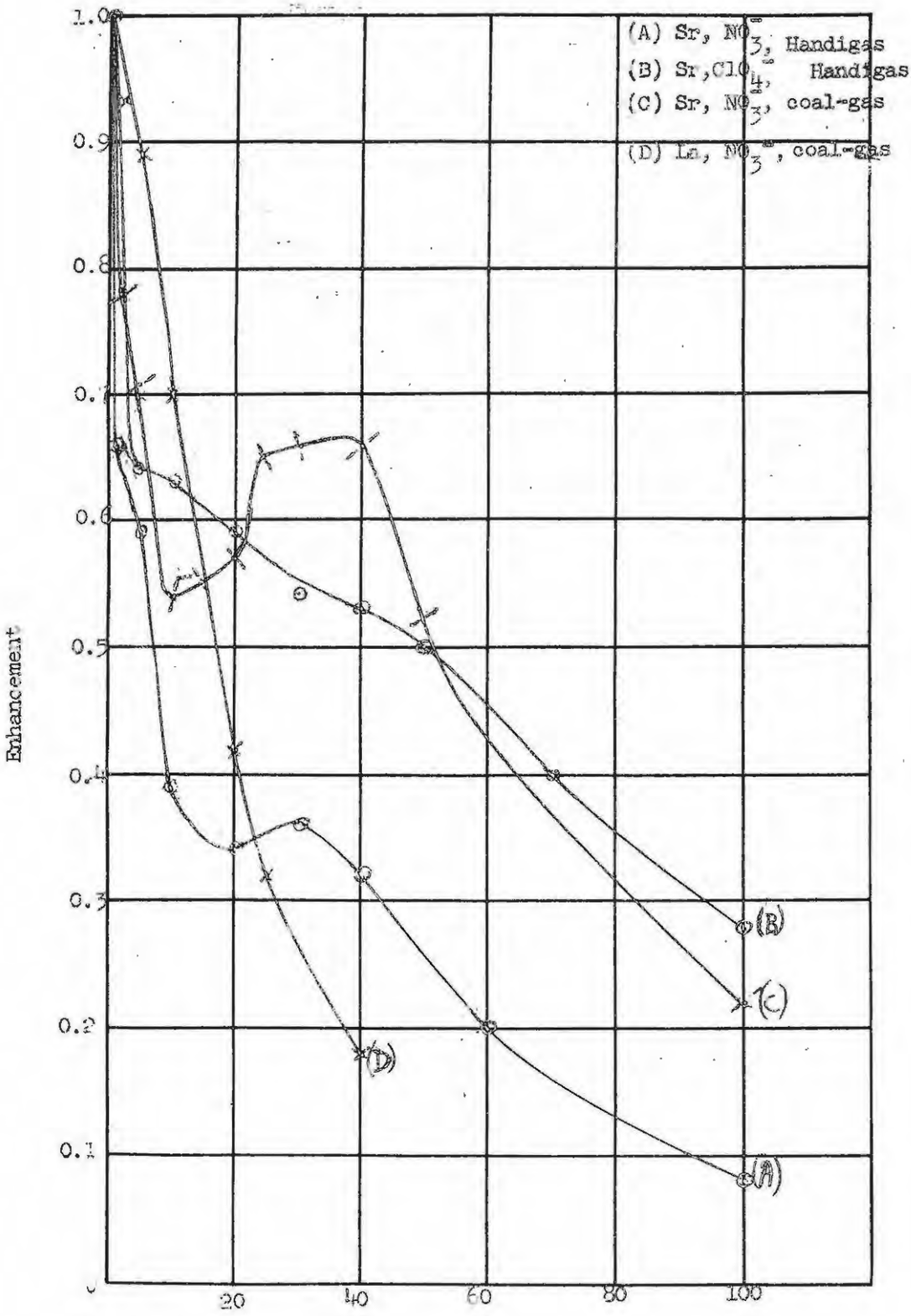


TABLE 13.(contd.).

Form of Al added	Conc. Al (mg./50 ml.)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhancement	Graph	Remarks
perchlorate	1	0.4	0.02	0.270	0.78	Fig. 11B	Perchlorate solutions: Al and Mg added as nitrate, converted to perchlorate by fuming with A.R. $HClO_4$ Sr colour again decreases with increasing Al
	5	0.4	0.02	0.270	0.64		
	10	0.4	0.02	0.270	0.63		
	20	0.4	0.02	0.270	0.59		
	30	0.4	0.02	0.270	0.54		
	40	0.4	0.02	0.270	0.53		
	50	0.4	0.02	0.270	0.50		
	70	0.4	0.02	0.270	0.40		
	100	0.4	0.02	0.270	0.28		
	1	0.4	0	0.265	0.40		
	5	0.4	0	0.265	0.24		
A.R. nitrate	1	0.5	0.02	0.386	0.86	Fig. 11c	Coal-gas flame, nitrate solutions
	2	0.5	0.02	0.386	0.78		
	5	0.5	0.02	0.386	0.71		
	10	0.5	0.02	0.386	0.54		
	15	0.5	0.02	0.386	0.55		
	20	0.5	0.02	0.386	0.57		
	25	0.5	0.02	0.386	0.65		
	30	0.5	0.02	0.386	0.66		
	40	0.5	0.02	0.386	0.66		
	50	0.5	0.02	0.386	0.52		
	100	0.5	0.02	0.386	0.22		
A.R. nitrate	1	0.5	0	0.476	0.96	Fig. 11d	Coal-gas flame $La(NO_3)_3$ added as releasing agent: Solns. 0.02 M w.r.t. $La(NO_3)_3$
	2	0.5	0	0.476	0.93		
	5	0.5	0	0.476	0.89		
	10	0.5	0	0.476	0.70		
	20	0.5	0	0.476	0.42		
	25	0.5	0	0.476	0.32		
	40	0.5	0	0.476	0.18		

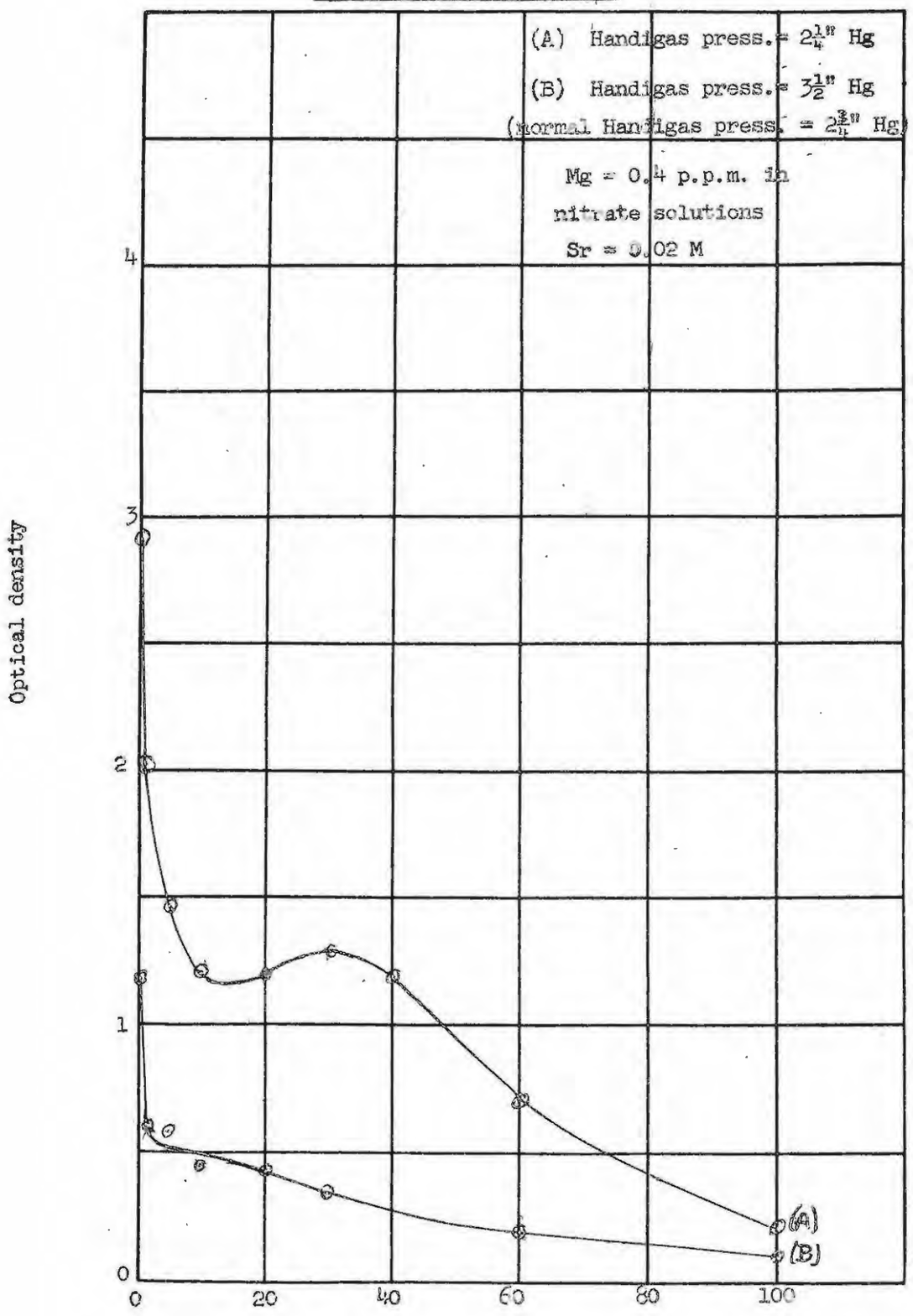
Conditions as in Table 9 (excepting where another fuel specified).

These data show that in the absence of strontium low concentrations of aluminium enhance the absorbance of magnesium considerably, maximum enhancement being obtained at an approximately equimolar concentration

/55....of the two....

FIG. 12.

The Effect of variations in Handigas flow-rate on interference by aluminium.



of the two elements. Higher concentrations of aluminium depress the absorbance, which falls off asympototically to almost zero with increasing aluminium concentration. The enhancement by aluminium has not been reported by other investigators. The sharp peak in the graph of enhancement versus concentration ratio at a molar $\frac{[\text{aluminium}]}{[\text{magnesium}]}$ concentration ratio of 1 is rather suggestive of compound formation. An examination of the $MgO-Al_2O_3$ phase diagram[66,67] indicates a eutectic at this concentration ratio. The difference between the melting-points of this eutectic mixture and the most common magnesium aluminate, $Mg(AlO_2)_2$, is only 100°C, which would seem too small to account entirely for this pronounced enhancement.

The results given in Table 13 indicate that the interference by aluminium is not adequately suppressed by the addition of a releasing agent. Even 2 p.p.m. of aluminium interfere seriously in the presence of strontium as a releasing agent, using nitrate solutions. The results obtained using a coal-gas flame with lanthanum as releasing agent indicate that the effect of low concentrations of aluminium is less pronounced when this system is used. The threshold of aluminium interference in this case is approximately 10-20 p.p.m., but at 40 p.p.m. of aluminium the depressing effect is greater than with a Handigas flame and strontium as releasing agent. Comparison of the interference by aluminium using Handigas and coal-gas flames indicates that the degree of depression is somewhat lower when the latter is used, but the general shapes of the optical density-aluminium concentration graphs are very similar.

The reduced depression of the magnesium absorbance by aluminium in perchlorate medium, particular at higher aluminium concentrations, supports the theory proposed for the greater sensitivity of magnesium perchlorate (viz. explosive decomposition), as higher temperatures can be expected to decompose more magnesium aluminate.

The influence of various flame conditions on the effect of aluminium in the presence of strontium was also studied and the results are given graphically in Figure 12. It is evident from this graph that variations in the Handigas flow-rate do not affect the shape of the optical density - aluminium concentration graph significantly, but some

/56...of the...

of the maxima in the graph obtained at optimum Handigas flow-rate were not present at a slightly higher flow-rate. No significance is attached to this, however, as overall sensitivity was reduced considerably at the higher flow-rate.

The results of variations in strontium content are given in Figure 10. It is important to note that the maxima A, B and C in curves (i), (ii) and (iii) respectively, all occur at a molar strontium concentration ratio of approximately 1. As other aluminium alkaline earth oxides with aluminium oxide give a eutectic point in their phase diagrams[66, 67]. at this concentration ratio, it is reasonable to expect that this point will correspond to a eutectic concentration for aluminium oxide and strontium oxide as well.

EDTA was tested as a releasing agent for magnesium from aluminium. A concentration of 5,000 p.p.m. EDTA (di-sodium salt) was added to solutions containing 0.4 p.p.m. Mg and 200 p.p.m. Al and the pH set at values ranging from 1 to about 10. The same absorbance was obtained for this solution as for the blank (optical density less than 0.01). The failure of EDTA as a releasing agent is in contradiction to the favourable reports by other investigators, mentioned in the literature survey. Iron was also tested as a releasing agent from aluminium, but was not effective.

A possible advantage of strontium as a releasing agent for magnesium from aluminium is that a "plateau" is formed in the optical density - aluminium concentration curve. Thus if the approximate concentration of aluminium in the sample is known and if it lies in the "flat" portion of the graph, an equivalent amount can be added to the standards. This method of correcting for aluminium interference reduces the sensitivity of the method and has the added disadvantage that in most cases the aluminium concentration is unknown. For these reasons it was decided to rather remove the aluminium before determination of magnesium. Work done on this separation is described later in this report.

Two-atomiser tests were also performed with aluminium. The results obtained are given in Table 14.

/57....Table 14....

TABLE 14.

Two-atomiser tests with aluminium.

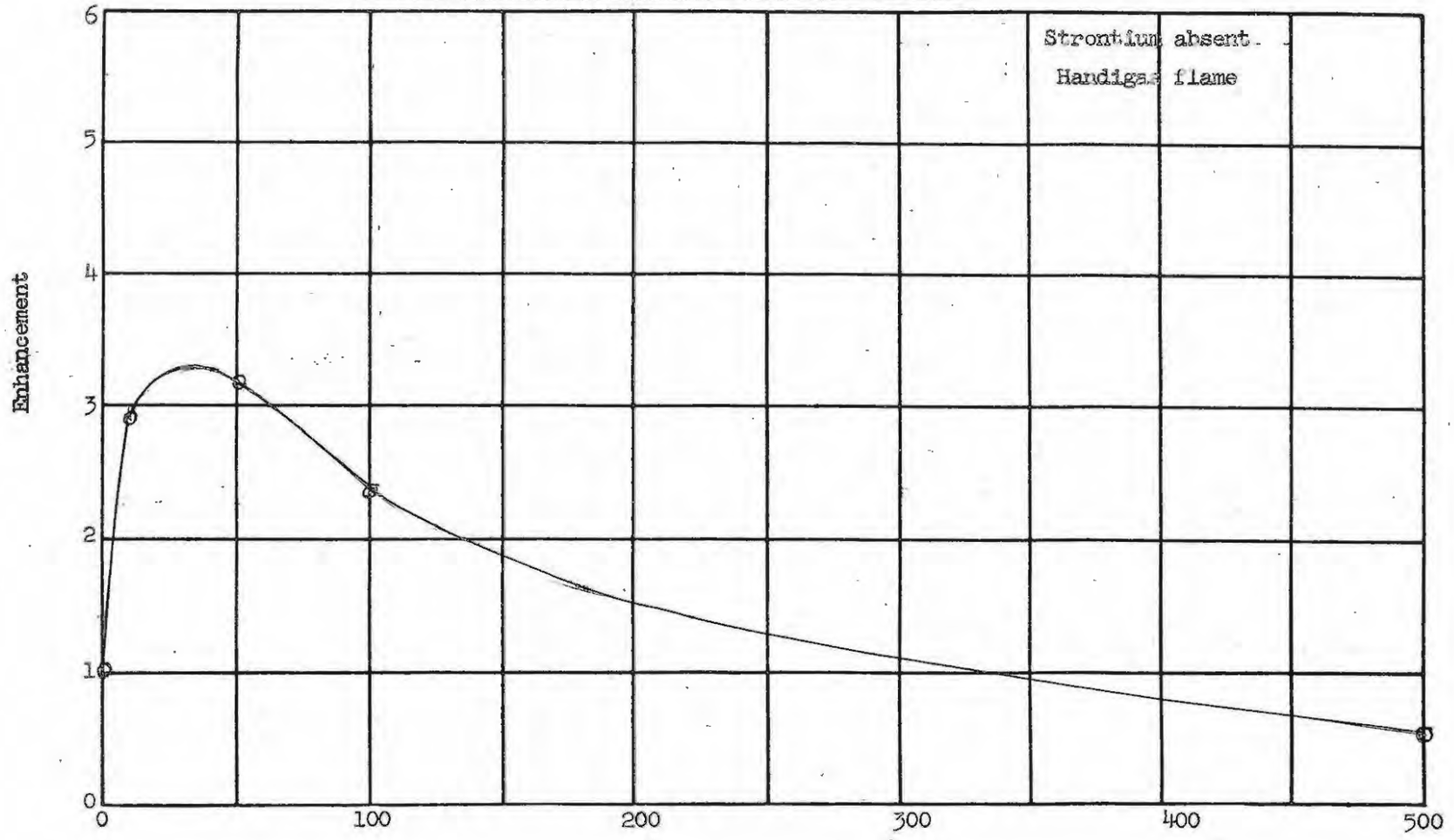
Solution thru' atomiser A	Solution thru' atomiser B	Optical density	Enhancement	Remarks
H_2O	1 p.p.m. Mg(as NO_3)	0.106	—	—
2 mg Al/100 ml	1 p.p.m. Mg	0.087	0.82	Al added as nitrate
4 mg Al/100 ml	1 p.p.m. Mg	0.079	0.74	
10 mg Al/100 ml	1 p.p.m. Mg	0.074	0.70	
40 mg Al/100 ml	1 p.p.m. Mg	0.055	0.52	
H_2O	1 p.p.m. Mg + 2 mg Al/100 ml	0.009	0.08	
H_2O	1 p.p.m. Mg + 10mg Al/100 ml	0.005	0.05	

These data show that interference by aluminium is vastly reduced when the magnesium and aluminium solutions are sprayed by separate atomisers. This in agreement with the results of similar tests, using calcium instead of magnesium, conducted by other investigators (see literature survey for details), and indicates that the interference by aluminium is probably due to the formation of a refractory compound with magnesium in the solid aerosol phase. The depression observed when the aluminium and magnesium solutions were atomised separately is probably due to a small amount of coalescence of theaerosol particles from the two atomisers. It may also be due to the combination of magnesium and aluminium to a slight extent in the gaseous phase, although this seems unlikely in view of the work of Schuhknecht and Schinkel and others.

/58 ...4.2.5 Iron....

FIG. 13.

The Effect of iron on the absorbance of magnesium.



4.25 Iron:

The results of interference tests with iron are given in Table 15.

TABLE 15.

The Effect of Iron.

Form of Fe added	Conc. Fe (mg./50 ml)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhance-ment	Graph No.	Remarks
$Fe(NO_3)_3$ (A.R.)	10	0.4	0	0.075	2.9	Fig. 13	Nitrate solutions Streaky flame (straw-coloured). Streaks deepen in colour with increasing Fe conc.
	50	0.4	0	0.075	3.2		
	100	0.4	0	0.075	2.36		
	500	0.4	0	0.075	0.56		
	1000	0.4	0	0.075	0.29		
$Fe(NO_3)_3$ (A.R.)	0.1	0.4	0.02	0.249	0.92		
	0.2	0.4	0.02	0.249	0.88		
	0.5	0.4	0.02	0.249	0.83		
	1	0.4	0.02	0.255	0.79		
	2	0.4	0.02	0.255	0.67		
	5	0.4	0.02	0.255	0.57		
	10	0.4	0.02	0.260	0.35		Red colour of Sr in flame weakens with increasing Fe and finally disappears at 500 mg Fe/50 ml.
	50	0.4	0.02	0.260	0.29		
	100	0.4	0.02	0.260	0.28		
	500	0.4	0.02	0.260	0.11		
	2	0.4	0.	0.290	0.99		0.02 M $La(NO_3)_3$ as releasing agent-streaky yellowish flame
	10	0.4	0	0.295	0.81		
	20	0.4	0	0.295	0.78		

Same conditions as Table 9.

These results show that fairly low concentrations of iron enhance the absorbance of magnesium strongly in the absence of strontium, but larger amounts of iron have a depressing effect. The maximum enhancement was observed at a molar $\frac{\text{Iron}}{\text{Magnesium}}$ concentration ratio of about 500.

In the presence of strontium even 2 p.p.m. of iron had a significant depressing effect on the absorbance of magnesium. The strontium colour in the flame became fainter with increasing iron concentration, which is

/59.....suggestive....

suggestive of the formation of a refractory strontium-iron compound in the solid aerosol particle.

Two-atomiser tests were conducted to elucidate the mechanism of the interference by iron. The results obtained are given in Table 16.

TABLE 16.

Two-atomiser tests with iron.

Solution through atomiser A	Solution through atomiser B	Optical density	Enhancement	REMARKS
H_2O	1 p.p.m. Mg (as NO_3^-)	0.103	---	---
10 mg Fe/100 ml	1 p.p.m. Mg	0.154	1.50	Fe as $Fe(NO_3)_3$
50 mg Fe/100 ml	1 p.p.m. Mg	0.208	1.96	
100 mg Fe/100 ml	1 p.p.m. Mg	0.224	2.12	
1000 mg Fe/100 ml	1 p.p.m. Mg	0.185	1.74	
H_2O	1 p.p.m. Mg + 0.04 M.Sr	0.319	--	Sr as nitrate
500 mg Fe/50 ml.	1 p.p.m. Mg + 0.04 M.Sr	0.225	0.71	
H_2O	1 p.p.m. Mg + 10 mg Fe/100 ml.	0.337	3.27	Enhancement with respect to reading at top of list (0.103).
H_2O	1 p.p.m. Mg + 50 mg Fe/100 ml	0.323	3.15	
H_2O	1 p.p.m. Mg + 100mg Fe/100 ml	0.295	0.86	
H_2O	1 p.p.m. Mg + 1000mg Fe/100 ml.	0.102	0.99	

These data suggest that the enhancement by iron is due to a gaseous phase process. The maximum enhancement observed when the iron and magnesium were atomised separately is considerably lower than that obtained when only one atomiser was used. This may indicate that a solid phase process is also involved, but it is far more likely to be due to differences in flow-rates of the atomisers and the higher local iron (vapour) concentration around the magnesium oxide aerosol particle when one atomiser is used. It is probable that the mechanism of the

/60.....enhancement...

enhancement by iron is similar to that of strontium, i.e. it is also due to a shift in the equilibrium of reaction (13):

$$MgO \rightleftharpoons Mg + \tfrac{1}{2} O_2$$

The fact that a much smaller depression of the absorbance of magnesium was observed when iron was atomised separately from a solution of magnesium and strontium indicates that this effect is probably due to the formation of a refractory strontium-iron compound in the solid aerosol particle, which prevents the decomposition of magnesium oxide in the flame. Thus when one atomiser is used two competing processes, viz. enhancement due to a vapour phase process and depression due to a solid aerosol phase process are in operation. The former predominates at low iron concentrations and the latter at higher concentrations.

The depression of magnesium absorbance at high iron concentrations was not observed when the magnesium and iron solutions were atomised separately. Possibly this effect is due to increase in size of the dry aerosol particle with consequent reduced decomposition of the magnesium oxide in the flame.

The addition of ascorbic acid to reduce the iron, or of citric acid or EDTA to complex it did not alter the pattern of the interference. It appears, therefore, that iron must be removed before the determination of magnesium by atomic absorption. The extraction of iron with acetyl acetone is described in section 6 of this thesis. It may also be removed by mercury cathode electrolysis.

5.2.6 - Chromium.

Two chromium compounds, chromic chloride and chromic acid, were tested. Results are given in Table 17.

/61...Table 17....

TABLE 17.

Effect of chromium.

Form of Cr added	Conc. Cr. (mg Cr/50 ml)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign substance	Enhancement	REMARKS
A.R. grade $CrCl_3$	0.5	0.4	0	0.075	2.0	Mg added as nitrate
	2	0.4	0	0.075	3.15	
	100	0.4	0	0.075	1.70	Straw-coloured streaky flame
	0.5	0.4	0.02	0.255	1.00	Yellow streaks in red flame, yellowish colour becoming more intense with increasing chromium
	1	0.4	0.02	0.255	1.00	
	2	0.4	0.02	0.255	0.92	
	5	0.4	0.02	0.255	0.91	
	50	0.4	0.02	0.255	0.40	
$H_2Cr_2O_7$ ex CrO_3	50	0.4	0	0.084	0.50	
	50	0.4	0.02	0.248	0.57	

Same conditions as Table 9.

The results obtained with chromic salts in the absence of strontium show that chromic chromium has an enhancing effect on the absorbance of magnesium. The maximum enhancement was obtained at a molar $\frac{\text{chromium}}{\text{magnesium}}$ concentration ratio of about 100. Larger concentrations gave a reduced enhancement. A similar concentration of chromium, added as chromic acid, depressed the absorbance.

In the presence of strontium both forms of chromium depressed the absorbance of magnesium. The tolerance for chromium (as chromic chloride) in the presence of strontium was found to be approximately 20 p.p.m. Cr.

When the concentration of chromium in the final sample exceeds this value it may be removed by volatilization as chromyl chloride, using perchloric and hydrochloric acids. Chromium may also be removed by mercury cathode electrolysis.

/62....5.27 Lanthanum....

5.27 Lanthanum.

Purified lanthanum nitrate was tested: the results obtained are given in Table 18.

TABLE 18.

The effect of lanthanum.

Form of La added	Conc. La (mg/50 ml.)	Conc. Mg (p.p.m.)	Conc. Sr salt molarity	O.D. Mg soln. without foreign subst.	Enhancement	REMARKS
Purified C.P. nitrate	13.9γ La/50 ml.	0.48	0	0.086	1.24	Mg added as nitrate
	27.8 " " "	0.48	0	0.086	1.61	
	69.5 " " ""	0.48	0	0.086	1.81	
	139 " " "	0.48	0	0.086	2.29	
	278 " " "	0.48	0	0.086	3.20	
	695 " " "	0.48	0	0.086	3.53	
	1.39 mg La/50 ml	0.48	0	0.086	3.88	
	34.7 " " " "	0.48	0	0.086	3.95	
	139 " " " "	0.40	0.02	0.262	0.99	

Same conditions as Table 9.

These results show that lanthanum enhances the absorbance of magnesium strongly in the absence of strontium. It appears that lanthanum enhances the absorbance of magnesium more strongly than an equivalent amount of strontium. This is supported by results obtained with lanthanum given in Tables 13 and 15. Its properties as a releasing agent were not investigated extensively, but for iron and aluminium it would appear at least as effective as strontium.

In the presence of strontium 2,700 p.p.m. of lanthanum did not affect the absorbance of magnesium.

5.2.8 Zirconium.

The results obtained for tests on the effect of zirconium are given in Table 19.

/63....Table 19....The

TABLE 19.
The Effect of Zirconium.

Form Zr added	Conc. Zr (mg Zr/50 ml.)	Conc. Mg. (p.p.m.)	Conc. Sr (molarity)	O.D. Mg soln. without foreign substance	Enhancement	REMARKS
$ZrOCl_2$ A.R. grade	1	0.4	0	0.080	1.73	Mg added as nitrate
	0.1	0.4	0.02	0.246	1.01	
	0.5	0.4	0.02	0.246	0.95	
	1	0.4	0.02	0.246	0.89	
	10	0.4	0.02	0.246	0.65	

Same conditions as Table 9.

These results show that zirconium enhances the absorbance of magnesium in the absence of strontium but more than 4 p.p.m. of zirconium has a depressing effect when strontium is present. Tests performed with 60 percent ethanol solutions and a coal-gas flame showed that a plateau similar to that obtained with aluminium existed in the enhancement-zirconium concentration graph (strontium present). This "plateau" was also observed when the effect of zirconium was studied using aqueous solutions, a Handigas flame and the standard Hilger apparatus. The absorbance of a magnesium solution was constant over the zirconium concentration range 1,400 p.p.m. to 2,800 p.p.m. using 0.04 M strontium nitrate. The plateau occurred at half the zirconium concentration when the strontium concentration was halved.

The interference by zirconium could be overcome by working in the concentration range of the "plateau" and adding an equivalent amount of zirconium to the standards, but this has the same disadvantages as described for aluminium. It was decided to remove zirconium by liquid-liquid extraction with acetyl acetone. This separation is described later in this thesis.

5.2.9 Uranium.

The results obtained for the effect of uranium on the absorbance of magnesium are given in Table 20.

/64....Table 20....

TABLE 20.

The effect of uranium.

Form of U added	Conc. U (mg U/50 ml.)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. Mg soln. without uranium	enhancement	REMARKS
$UO_2(NO_3)_2$ ex purified	100	0.4	0	0.080	0.45	Straw-coloured streaks in flame.
U_3O_8 and A.R. HNO_3	100	0.4	0.02	0.264	0.99	Red Sr colour of flame becomes paler with increasing U, finally get orange-yellow streaky flame
	200	0.4	0.02	0.264	1.01	
	500	0.4	0.02	0.264	0.59	
	1000	0.4	0.02	0.264	0.40	

Conditions same as Table 9.

These results show that 2,000 p.p.m. of uranium depress the absorbance of magnesium in the absence of strontium. In the presence of strontium up to 4,000 p.p.m. of uranium has no effect, but greater concentrations depress the absorbance. These results are similar to those obtained with 60 percent ethanol solution and a coal-gas flame. With this system it was found that the tolerance for uranium was doubled by doubling the strontium concentration.

As uranium is readily separated by liquid-liquid extraction with acetyl acetone and chloroform, as will be described later in this thesis, the interference of uranium in larger concentrations is not a serious disadvantage.

5.2.10 Cerium, thorium and titanium.

Results of the tests of the effects of these elements are given in Table 21.

/65.....Table 21...

TABLE 21.

The effect of cerium, thorium and titanium.

Foreign substance	Conc. foreign subst. (mg/50 ml)	Conc. Mg (p.p.m.)	Conc.Sr (molarity)	O.D. Mg soln. without foreign subst.	Enhancement	REMARKS
Ce, as $CeCl_3$ (C.P.grade)	10	0.4	0	0.097	2.97	
	10	0.4	0.02	0.278	0.99	
Th, as purified C.P.$Th(NO_3)_4$	100	0.4	0	0.096	1.12	
	100	0.4	0.02	0.278	0.99	
Ti, as sulphate (ex C.P.grade TiO_2, fused with $K_2S_2O_7$)	2(TiO_2)	0.4	0.	0.084	0.61	Mg added as nitrate
	1(TiO_2)	0.4	0.02	0.283	1.00	slight ppt. of $SrSO_4$ formed. (Sr added as nitrate)

Conditions as for Table 9.

These results show that cerium enhances the absorbance of magnesium strongly in the absence of strontium. Thorium enhances the absorbance only very slightly, while titanium has a depressing effect. The effect of titanium may be partly attributed to the presence of sulphate, but the amount of sulphate present is insufficient to account for the entire depression.

In the presence of 0.02 M strontium nitrate the concentrations of foreign elements tested did not affect the absorbance of magnesium.

Titanium may be removed by liquid-liquid extraction with acetyl acetone and chloroform.

The effects of other rare earth elements may be expected to resemble those of cerium and lanthanum.

5.2.11 Manganese.

The results obtained for the effect of manganese on the absorbance of magnesium are given in Table 22.

/66....Table 22...

TABLE 22.

The effect of manganese.

Form of Mn added	Conc. Mn mg/50 ml	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhance-ment	REMARKS
$MnCl_2$ ex A.R.	500	0.4	0	0.071	0.65	Mg as nitrate K present as well as Mn
K MnO_4 + HCl (contains KCl)	0.1	0.4	0.02	0.246	0.96	
	0.5	0.4	0.02	0.246	0.86	Conc. K = 0.71 conc. Mn
	500	0.4	0.02	0.246	0.10	

Conditions same as Table 9.

The results in Table 22 are complicated by the presence of potassium chloride in the manganous chloride solution. Other manganese salts available at the time of this investigation contained too much magnesium for use in this work. The depression of the magnesium absorbance by 10,000 p.p.m. of manganese in the absence of strontium is definitely due to the manganese, as a solution containing the same amount of potassium chloride alone was found to have an enhancing effect.

In the presence of strontium more than about 1 p.p.m. of manganese depresses the absorbance of magnesium. Manganese may be partially removed by liquid-liquid extraction with acetyl acetone. A more efficient separation is effected by mercury cathode electrolysis at pH 2.75 in sulphate medium.

5.2.12 Copper, silver and gold:

Only one concentration of each of these elements was tested. The results obtained are given in Table 23.

/67...Table 23....Effects of

TABLE 23.

Effects of copper, silver and gold.

Substance added	Conc. foreign subst. (mg/50 ml)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. of Mg solution without foreign subst.	Enhancement
Cu, as chloride (A.R.)	500	0.4	0	0.084	2.40
	500	0.4	0.02	0.283	0.93
Ag, as A.R. nitrate	500	0.4	0	0.084	3.90
	500	0.4	0.02	0.283	1.01
Au, from pure metal and aqua regia	10	0.4	0	0.081	3.25
	10	0.4	0.02	0.257	1.04

Conditions as in Table 9.

In the absence of strontium all these elements enhance the absorbance of magnesium. This phenomenon cannot be explained by a reduction of the free oxygen content of the flame as these elements do not form particularly stable oxides. Silver does dissolve oxygen, even at its melting-point (960°C), where the solubility is 20 volumes of oxygen (at atmospheric pressure) per volume of metal.[59] The volume of silver metal in the flame is so small, however, that this is not likely to have a noticeable effect on the oxygen concentration.

In thepresence of strontium 10,000 p.p.m. of copper had a slight depressing effect on the absorbance of magnesium. The effect of 10,000 p.p.m. of silver was negligible. 200 p.p.m. of gold enhanced of the absorbance very slightly. All these elements may be removed by electrodeposition when their concentration is excessive. Copper is also removed by acetyl-acetone liquid-liquid extraction.

/68...5.2.13 ...Zinc,

5.2.13 Zinc, Cadmium and Mercury.

Only one concentration of each of these elements, viz. 10,000 p.p.m., was tested. The results obtained are given in Table 24.

TABLE 24.

Effects of zinc, cadmium and mercury.

Substance added	Conc. foreign subst. (mg/50 ml)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. of Mg soln. without foreign substance	Enhancement
Zn as $Zn(NO_3)_2$ ex Zn + HNO_3	500	0.4	0	0.084	3.45
	500	0.4	0.02	0.279	0.95
Cd, as $CdCl_2$ (A.R.)	500	0.4	0	0.071	1.31
	500	0.4	0.02	0.288	0.96
Hg as $HgCl_2$ (A.R.)	500	0.4	0	0.084	0.92
	500	0.4	0.02	0.298	1.04

In the absence of strontium zinc enhanced the absorbance of magnesium strongly, cadmium enhanced it slightly and mercury had a slight depressing effect. In the presence of strontium, the concentration of zinc and cadmium tested had very slight depressing effects, while mercury enhanced the absorbance slightly. Zinc is partially removed by acetyl acetone extraction and mercury is eliminated by ignition of the dry sample at approximately 900°C.

5.2.14 Nickel and cobalt.

The results obtained for the effects of these elements are given in Table 25.

/69....Table 25....The

TABLE 25.

The Effects of cobalt and nickel.

Foreign substance	Conc. foreign subst. (mg/50 ml)	Conc. Sr salt (molarity)	O.D. of Mg soln. without foreign substance	Enhance-ment	Remarks
Ni, as A.R. nitrate	100	0	0.071	4.35	ochre, streaky flame
	10	0.02	0.249	1.01	orange, streaky flame
	20	0.02	0.249	0.86	
	50	0.02	0.249	0.86	
Co, as A.R. chloride	100	0	0.071	3.45	greenish-yellow flame
	10	0.02	0.250	0.93	orange, streaky, yellow-edged flame
	20	0.02	0.250	0.74	
	50	0.02	0.250	0.52	

Conc. of Mg = 0.4 p.p.m.

In the absence of strontium both these elements enhanced the absorbance of magnesium strongly when present at a concentration of 2,000 p.p.m. In the presence of strontium more than 200 p.p.m. of nickel or 100 p.p.m. of cobalt depressed the absorbance. Nickel and cobalt are most conveniently removed by electrodeposition or mercury cathode electrolysis.

5.2.15 Tin and lead.

The results obtained for the effects of these elements are given in Table 26.

TABLE 26.

The Effect of tin and lead.

Foreign substance	Conc. foreign subst. (mg./50 ml).	Conc. Sr salt (molarity)	O.D. of Mg soln. without foreign substance	Enhance-ment	REMARKS
Sn, as A.R. $SnCl_2$	500	0	0.080	1.03	$MgCl_2$ and $CrCl_2$ used to avoid nitrates
	0.5	0.02	0.248	0.95	
	1	0.02	0.248	0.93	
	2	0.02	0.248	0.92	
	5	0.02	0.248	0.88	
	200	0.02	0.248	0.94	
	500	0.02	0.267	0.93	

/70....Table contd...

TABLE 26 (contd.).

Foreign substance	Conc. foreign subst. (mg./50 ml.)	Conc. Sr salt (molarity)	O.D. of Mg soln without foreign substance	Enhance-ment	REMARKS
Pb, as nitrate, ex A.R. Pb shot and HNO_3	5	0	0.071	4.23	
	5	0.02	0.285	0.89	

Conc. of Mg = 0.4 p.p.m.

These results show that tin, present at a concentration of 10,000 p.p.m., has a negligible effect on the absorbance of magnesium in the absence of strontium. Lead at 100 p.p.m. enhances the absorbance strongly under these conditions.

In the presence of strontium even 10 p.p.m. of tin depresses the absorbance of magnesium. The degree of depression is almost constant over a wide range of tin concentrations (20-10,000 p.p.m.). Tin may be conveniently removed by volatilization with ammonium iodide or by mercury cathode electrolysis.

In the presence of strontium, lead at the concentration tested (100 p.p.m.) depressed the absorbance of magnesium. It would appear that the tolerance of the method for lead is well below this level, probably at about 20 p.p.m. These results disagree with those obtained using 60 percent ethanol and a coal-gas flame, where up to 10,000 p.p.m. of lead did not affect the absorbance in the presence of strontium. Lead may be removed by mercury cathode electrolysis when its concentration exceeds the tolerance.

5.2.16 Phosphate, arsenic, antimony and bismuth.

The results obtained for these elements are given in Table 27.

/71....Table 27....

TABLE 27.

The effect of phosphate, arsenic, antimony and bismuth.

Foreign subst.	Conc. foreign substance (mg/50 ml.)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhance-ment	REMARKS
P_2O_5 as $NH_4H_2PO_4$ (A.R.)	5 (P_2O_5)	0	, 0.075	0.88	
	5	0.02	0.251	0.99	Sr colour in flame becomes paler with increasing P_2O_5
	10	0.02	0.251	0.92	
	50	0.02	0.251	0.88	
As, as A.R. As_2O_5 in H_2O	10	0	0.081	1.35	
	1	0.02	0.251	1.01	
	2	0.02	0.251	0.94	
	5	0.02	0.251	0.91	
	10	0.02	0.251	0.89	
Sb, as $SbCl_3$	5	0	0.071	2.10	
	5	0.02	0.263	1.03	
Bi, as $Bi\ ONO_3$ in dil. HNO_3	10	0.	0.096	0.79	Very faint yellow colour in flame from Bi soln.
	5	0.02	0.246	1.01	
	10	0.02	0.273	0.95	

Conc. of Mg = 0.4 p.p.m.

In the absence of strontium 100 p.p.m. of phosphate (as P_2O_5) depressed the absorbance of magnesium. More than 100 p.p.m. of phosphate also had a depressing effect in the presence of strontium. The separation of larger amounts of phosphate from magnesium is most easily effected by anion exchange.

200 p.p.m. of arsenic as arsenic acid had a slight enhancing effect on the absorbance of magnesium in the absence of strontium. In the presence of strontium more than 20 p.p.m. of arsenic acted as a depressant. The separation of larger amounts of arsenic is easily accomplished, either by volatilization or by anion exchange.

/72...In the absence...

In the absence of strontium 500 p.p.m. of antimony enhanced the absorbance of magnesium moderately strongly, but this concentration of antimony had a negligible effect when strontium was present.

Bismuth had a depressing effect on the absorbance of magnesium in the absence of strontium. When strontium was present more than 150 p.p.m. of bismuth also acted as depressant. Bismuth may be removed by mercury cathode electrolysis.

5.2.17 Vanadium and molybdenum.

The results obtained for the effects of these elements are given in Table 28.

TABLE 28.

The Effect of vanadium and molybdenum.

Foreign subst.	Conc. foreign substance (mg/50 ml)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhancement	REMARKS
V as NH_4VO_3 (A.R.)	50	0	0.080	0.50	yellow-ochre, streaky flame
	5	0.02	0.248	0.98	
	10	0.02	0.248	0.96	
	50	0.02	0.248	0.60	
Mo, as A.R. ammonium molybdate	500	0	0.071	0.75	yellow-ochre flame
	10	0.02	0.271	1.02	
	50	0.02	0.271	0.99	
	100	0.02	0.271	0.98	
	500	0.02	0.287	0.08	yellow-ochre flame, no Sr colour

Conc. of Mg = 0.4 p.p.m.

In the absence of strontium 1000 p.p.m. of vanadium and 10,000 p.p.m. of molybdenum both had a depressing effect. In the presence of strontium more than 100 p.p.m. of vanadium or 2,000 p.p.m. of molybdenum depressed the absorbance of magnesium. Tri- and quidrivalent vanadium are separated from magnesium by liquid-liquid extraction with acetyl acetone and chloroform. Vanadate and molybdate may also be removed by anion exchange.

/73....5.2.18 Boron....

5.2.18 Boron:

Boric acid was used to test the effect of boron. The results are given in Table 29.

TABLE 29.

The Effect of boron.

Form of boron added	Conc. boron (mg B/50 ml)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign subst.	Enhancement
A.R. grade H_3BO_3	10	0	0.076	1.72
	100	0	0.076	3.23
	5	0.02	0.248	1.00
	10	0.02	0.248	1.00
	20	0.02	0.248	0.88
	50	0.02	0.248	0.70
	100	0.02	0.248	0.61

Conc. of Mg = 0.4 p.p.m.

These results show that boric acid enhances the absorbance of magnesium strongly in the absence of strontium. More than 200 p.p.m. of boron (as boric acid) depress the absorbance in the presence of strontium. Removal of boron is most easily accomplished by volatilization as methyl borate or anion exchange.

5.2.19 Silica:

The results obtained for the effect of sodium silicate are given in Table 30.

TABLE 30.

The effect of silica.

Form of Si added	Conc. silica (mg SiO_2/50 ml)	Conc. Sr salt (molarity)	O.D. Mg soln. without foreign substance	Enhancement	REMARKS
Na_2SiO_3 from C.P. grade SiO_2 fused with Na_2CO_3 and leached with H_2O	0.5	0	0.075	0.17	0.2 ml HNO_3 added to all samples to neutralise Na_2CO_3. conc. Na = 1.7 x SiO_2 conc.
	1	0	0.075	0.12	
	2	0	0.075	0.11	
	0.5	0 02	0.280	1.00	
	1	0 02	0.280	0.93	
	2	0 02	0.280	0.86	

Conc. of Mg = 0.4 p.p.m.

/74....The results....

The results given in Table 30 for the effect of soluble silicate on the absorbance of magnesium should not be affected by the sodium present, as the sodium concentration is well below the tolerance of the method for it.

Even 10 p.p.m. of silica has a strong depressing effect on the absorbance in the absence of strontium, while more than 10 p.p.m. of silica also act as depressant in the presence of strontium. This is probably due to the formation of magnesium and strontium silicates with high melting points in the flame. These results show the necessity of removing silica almost quantitatively when determining magnesium by atomic absorption. The most convenient method of separation is by volatilization with hydrofluoric acid.

5.2.20 Ammonia and sulphate.

The results of interference tests with ammonium chloride and ammonium sulphate are given in Table 31.

TABLE 31.

Effect of ammonia and sulphate.

Foreign substance	Conc. foreign substance (mg/50 ml.)	Conc. Mg (p.p.m.)	Conc. Sr Salt (molarity)	O.D. of Mg soln. without foreign substance	Enhancement	REMARKS
NH_4^+ as A.R NH_4Cl	500 (NH_4)	0.4	0	0.081	1.12	--
	500	0.4	0.02	0.248	1.00	--
$SO_4^=$ as $(NH_4)_2SO_4$, A.R. grade	1 ($SO_4^=$)	0.4	0.02	0.251	0.99	
	2	0.4	0.02	0.251	1.00	slight ppt. of $Sr SO_4$
	5	0.4	0.02	0.251	1.00	

These results show that 10,000 p.p.m. of ammonium ion has a slight enhancing effect in the absence of strontium. This is possibly due to the presence of chloride. In the presence of strontium, however, no change in absorbance of magnesium was observed upon the addition of this concentration of ammonium chloride.

The effect of sulphate was tested in the presence of strontium only in order to establish the maximum concentration that could be present without formation of a precipitate of strontium sulphate.

75 /(The....

(The effect of sulphate in the absence of strontium has been discussed earlier in this thesis). Up to 100 p.p.m.of sulphate did not affect the absorbance of magnesium, but larger concentrations gave a precipitate. Sulphate in excess of this concentration can be removed by anion exchange.

5.2.21 Rhenium, thallium and indium.

As these elements are seldom encountered in the samples to be analysed by this method, only one concentration of each was tested. The results obtained are given in Table 32.

TABLE 32.

Effect of rhenium, thallium and indium.

Foreign substance	Conc.foreign substance (mg/50 ml)	Conc. Sr salt (molarity)	O.D. of Mg soln. without foreign subst.	Enhancement	REMARKS
Re, as A.R.grade nitrate	1	0	0.084	1.06	
	1	0.02	0.256	1.01	
Tl, as sulphate	10	0	0.070	0.76	light pink flame
	10	0.02	0.257	1.03	
In as nitrate in dil. HNO_3	5	0	0.070	1.03	light orange-pink flame
	5	0.02	0.257	1.00	

Conc. of Mg = 0.4 p.p.m.

The effects of 20 p.p.m. of rhenium 200 p.p.m. of thallium or 100 p.p.m. of indium on the absorbance of magnesium in the presence of strontium were found to be negligible. In the absence of strontium rhenium and indium enhanced the absorbance very slightly, while thallium sulphate acted as a depressant. This effect of thallium, however, may be partly due to the presence of sulphate, which acts as a depressant in the absence of strontium.

5.2.22 Selenium and tellurium:

As these elements are also rare in the samples to be analysed by this method, their effects were not extensively investigated. The results obtained are given in Table 33.

/76....Table 33....The

TABLE 33.

The effect of selenium and tellurium.

Foreign substance	Conc. foreign subst. (mg/50 ml)	Conc. Sr salt (molarity)	O.D. of Mg soln. without foreign substance	Enhancement
Se, as H_2SeO_3	2	0	0.084	1.50
	2	0.02	0.254	1.00
Te as soln. of the element in dil. HNO_3	5	0	0.084	2.21
	5	0.02	0.244	1.03

Conc. of Mg = 0.4 p.p.m.

Both selenium (at 40 p.p.m.) and tellurium (at 100 p.p.m.) enhanced the absorbance of magnesium in the absence of strontium. In the presence of strontium the effect of these elements at the above concentrations was negligible.

5.2.23 Fluoride.

The results obtained for the effect of fluoride on the absorbance of magnesium are given in Table 34.

TABLE 34.

The Effect of fluoride.

Form of fluoride used	Conc. F^- (mg F/50 ml)	Conc. Mg (p.p.m.)	Conc. Sr salt (molarity)	O.D. of Mg solution without fluoride	Enhancement	REMARKS
A.R. NaF	10	0.4	0	0.080	1.50	Na conc. = 1.2 x F conc.
	5	0.4	0.02	0.276	0.98	
	10	0.4	0.02	0.276	0.71	

The enhancement observed in the absence of strontium is probably due to the sodium added with the fluoride. The depression of the absorbance of magnesium in the presence of strontium is greater than can be

/77...accounted for...

accounted for by the presence of sodium alone. The tolerance for fluoride in the presence of strontium is,therefore, about 100 p.p,m. Amounts of fluoride in excess of this may be removed by fuming with perchloric or sulphuric acid. The presence of fluoride in this work is also objectionable as, in the slightly acidic solutions used, it would cause contamination due to attack on the glassware.

5.2.24 Ruthenium, platinum and palladium.

The results of intereference tests with these elements are given in Table 35.

TABLE 35.

The Effects of Ruthenium, palladium and platinum.

Foreign subst. added	Conc. foreign subst. (mg/50ml)	Conc. Sr salt (molarity)	O.D. of Mg soln. without foreign subst.	Enhance-ment	REMARKS
Ru, as chloride	1	0	0.085	2.72	Yellow-orange flame, even in presence of Sr, suggestive of Na contamination
	1	0.02	0.250	1.00	
Pd, as nitrate in dil. HNO_3	1	0	0.083	2.06	
	1	0.02	0.254	1.00	---
Pt, as $PtCl_4$	5	0	0.080	1.46	Faint yellow colour in flame
	1	0.02	0.245	1.00	
	5	0.02	0.245	0.98	

All these elements enhanced the absorbance of magnesium in the absence of strontium. Ruthenium and palladium were tested at 20 p.p.m. and platinum at 100 p.p.m. In the presence of strontium 20 p.p.m. of ruthenium and palladium did not affect the absorbancy but more than 100 p.p.m. of platinum had a depressing effect.

5.3 General notes on interference effects.

It is noteworthy that on no occasion was an appreciable enhancement of magnesium absorbance observed in the presence of 0.02 molar strontium nitrate or chloride. This may be mistakenly interpreted as meaning that enhancement is at a maximum in 0.02 molar strontium nitrate solution.

/78.... Numerous elements...

Numerous elements, however, enhance the absorbance of magnesium more strongly than strontium.

If the enhancing effect of other elements is due to a reduction in the free oxygen content of the flame, the observed enhancements should be proportional to the free energies of formation of the oxides of the elements which exhibit this effect. The correlation of free energy and enhancement is given in Table 36. Unfortunately the optimum enhancement is not always available; figures from the interference tests are used.

TABLE 36.

Correlation of enhancement and free energy of formation of oxides.

Element	Enhancement (observed)	ΔG° at 1900°K in K cals/mole	Element	Observed Enhancement	ΔG° at 1900°K
Calcium+*	4.65	-100.2	Ruthenium+	2.72	large positive
strontium	4.5	- 92.6	Copper*	2.40	-11.6
nickel*	4.35	-13	barium+*	2.3	-90
lead*	4.23	-81.5			
lanthanum+	4	-287	lithium	2.25	-77
silver*	3.9	large, positive	antimony*	2.1	-50.2
			palladium	2.1	large, positive
Cobalt*	3.45	-82.5	zirconium*	1.73	-172.5
Zinc*	3.45	-20.2	potassium	1.71	small, negative
gold*	3.25	large, positive	sodium	1.52	-40.9
boron*	3.23	-200.1	aluminium	1.5 ?	-254.5
iron	3.2	-120			
chromium*	3.15	-153.8	cadmium*	1.31	+4.4
Cerium*	2.97	-284	thorium*	1.12	-200.9

* Best result not available - usually only 1 concentration tested.

\+ Probably a higher figure would have been obtained at a different concentration.

These results indicate that the correlation is certainly not straight-forward. Where an element gives a lower enhancement than would be expected from the free energy of formation of its oxide, the discrepancy may be due to the formation of a refractory compound in the solid aerosol phase. Examples of this are found in the cases of aluminium, zirconium and thorium. Far more difficult to explain is the abnormally

/79....high enhancement....

high enhancement observed with certain elements whose oxides have a low negative, or even positive, free energy of formation, e.g. nickel, silver, copper, gold, platinum, palladium, ruthenium and zinc. The enhancing effect of other elements is not due entirely to a reduction of the free oxygen content of the flame, however, and certain abnormally high enhancements may be due to the formation of eutectic mixtures in the solid aerosol phase. The enhancement observed with low concentrations of aluminium appears to confirm this. It is also possible that the mechanism proposed for the enhancement by strontium, viz. reduction in oxygen content of the flame, is incorrect: no direct evidence in support of this has been obtained. The catalytic properties of nickel and the platinum metals in particular in gaseous phase reactions lead one to wonder if these may not also be responsible for the abnormally high enhancements observed with these elements.

It is convenient at this stage to summarise the tolerances for other elements in tabular form. This is done in Table 37. Results are given for solutions which ~~0.02~~ are 0.02 molar with respect to strontium.

TABLE 37.

Maximum permissible amounts of foreign elements.

Element	Tolerance (p.p.m.)	Suggested separation when present in excess
Bromide	1000	Fume with perchloric acid
iodide	500	" " " "
lithium	100	---
sodium	200	---
potassium	200	---
rubidium	$>$ 40	---
calcium	200	double precipitation as oxalate
barium	400	Precipitation as sulphate
ammonium salts	$>$ 10,000	Heat dry sample
aluminium	$<$ 2	acetyl-acetone solvent extraction
iron	$<$ 2	" " " "

/80....Table 37 contd.

TABLE 37 (contd.).

Element	Tolerance (p.p.m.)	Suggested separation when present in excess
chromium	20	volatilize as chromyl chloride ($HClO_4$ + HCl)
lanthanum	> 2,800	---
cerium	> 200	---
thorium	> 2,000	---
zirconium	10	acetyl acetone solvent extraction
manganese	2	mercury cathode electrolysis; acetyl acetone solvent extraction
rhenium	> 20	--- ---
titanium	> 20	acetyl acetone solvent extraction
copper	±1,000	electrolysis, or acetyl-acetone solvent extraction
silver	> 10,000	electrolysis
gold	> 200	electrolysis
zinc	±5,000	---
cadmium	±5,000	---
mercury	> 10,000	Ignition of dry sample
nickel	200	Electrolysis
cobalt	100	Mercury cathode electrolysis
uranium	4,000	acetyl-acetone-chloroform solvent extraction
silica	10 (SiO_2)	Volatilization with HF
tin	10	Volatilization with NH_4I or mercury cathode electrolysis.
lead	±20	Mercury cathode electrolysis
phosphate	100 (P_2O_5)	Anion exchange
arsenic	20	Anion exchange or volatilization
antimony	> 500	Ignition of dry sample
bismuth	150	mercury cathode electrolysis
vanadium	100	anion exchange
molybdenum	2,000	anion exchange
boron	200	Volatilize as methyl borate or anion exchange

/81....thallium...

TABLE 37 (contd.).

Element	Tolerance p.p.m.	Suggested separation when present in excess
thallium	> 200	---
indium	> 100	---
sulphate	100	anion exchange
selenium	> 40	Volatilize by heating dry sample
tellurium	> 100	
fluoride	100	anion exchange or by fuming with $HClO_4$
ruthenium	> 20	H_2S precipitation
palladium	> 20	H_2S precipitation
platinum	100	H_2S precipitation

5.4 Theoretical considerations.

In this section an attempt will be made to obtain theoretical justification for some of the theories proposed earlier. A comparison of the observed sensitivity with that expected in theory will also be attempted. Activity coefficients will be neglected in these calculations and simple concentrations used.

5.4.1 Degree of dissociation of magnesium oxide in the flame.

Consider the formation of magnesium oxide from its elements:

$$Mg\ (g) + \tfrac{1}{2}O_2(g) \longrightarrow MgO(s)$$

The standard free energy of formation, at 1900°K, ΔG°, is given as -81.37 Kcals/mole.[65] The equilibrium constant, K_1, for the formation of magnesium oxide is defined as:

$$K_1 = \frac{P_{MgO(s)}}{P_{Mg} \cdot P_{O_2}^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (A)$$

where the P terms represent partial pressures. From thermodynamic considerations the free energy of formation of a compound is related to the equilibrium constant by the equation:

$$\text{Log } K = \frac{-\Delta G^\circ}{2.303\ RT}$$

where R = universal gas constant in cals./°K/mole and T = absolute temperature

/82....Substituting....

Substituting in this equation, it may be deduced that :

$$K_1 = 2.24 \times 10^9$$

Dean[68.] gives the theoretical partial pressure of oxygen in the stoichiometric air-acetylene flame as 0.016 atmospheres for molecular oxygen (O_2) and 0.0022 atmospheres for atomic oxygen (O). This value is based on theoretical calculations of equilibria at flame temperature. This oxygen concentration will be used (as an approximation) in this calculation, although it is reasonable to expect the oxygen concentration in the lower-temperature Handigas flame to differ somewhat from this value. Furthermore the oxygen concentration is likely to vary with the position in the flame at which it is measured.

Calling the degree of dissociation x and substituting in equation (A) gives:

$$2.24 \times 10^9 = \frac{(1 - x)\ P}{x\ P.0.127}$$

where P is the hypothetical partial pressure of solid MgO in the flame. (Equal to the vapour pressure of MgO in the flame)

Since $x \ll 1$, $(1 - x) \doteq 1$, and $\underline{\underline{x = 3.5 \times 10^{-9}}}$

Thus only a minute fraction of the total amount of magnesium oxide in the flame is decomposed to elementary magnesium at the assumed temperature and oxygen concentration.

The degree of dissociation of magnesium oxide increases with temperature. At 2500°K it is 2.16×10^{-4}, while at 3000°K it is approximately 3.68×10^{-2}. As the temperature of an oxy-acetylene flame is of this order[57.] (approximately 2600°C, when aspirating water), one would expect a large increase (at least a factor of 10^5) in the sensitivity of the atomic absorption of magnesium, compared with an air-Handigas flame, if an oxy-acetylene flame is used, other things being equal. Naturally, there are factors that will counteract this increase.

Chief among these are: (i) an increase in volume of combustion products, due to the higher temperature, which will cause a reduction in the magnesium concentration of the flame; (ii) an increase in the degree of ionisation of magnesium in the flame; (iii) an increase in the Doppler broadening of the absorption line. (iv) an increase in the

/83.....oxygen concentration...

oxygen concentration of the flame.

The effect of ionisation appears to outweigh all the others. At a partial pressure of magnesium metal in the flame of 10^{-16} (which is the concentration in the Handigas-air flame when a solution containing 0.4 p.p.m. of magnesium as the nitrate is atomised), the Saha equation predicts that 100 percent of the metal will be ionised at 3,000°K. This result will be reduced by the high electron concentration of the hydrocarbon flame, but the degree of ionisation will, nevertheless, be very large.

Two oxy-acetylene burners, viz. a Beckman flame photometer burner and a Warren-type burner,[69] were tested with magnesium. Both these burners have smaller flame lengths (about 1 cm. and 8 cm. respectively) than the modified burner used for most of this work. With the Beckman burner optical density readings of less than 0.01 were obtained for two solutions containing 0.4 p.p.m. of magnesium, one with and one without strontium. The Warren-type burner gave optical densities of about 0.03 for the same two solutions. The reason for this reduced sensitivity appears to lie largely in the ionisation of the magnesium in the oxy-acetylene flame. It may be calculated that the total effect of the other three factors contributing to reduced sensitivity at the higher temperature will be small.

5.4.2 Concentration of magnesium in the flame.

The volume of combustion products arising from 13 litres of air and 600 ml. of Handigas is approximately 108 litres at flame temperature (1900°K) and atmospheric pressure (620 mm. Hg). The volume of solution entering the flame in the same time is 1.1 ml. This will give rise to 10.6 litres of steam in the flame. Thus the total volume of combustion products per minute at flame temperature is 119 litres. For purposes of this calculation a figure of 120 litres will be used. This is justified, as the calculation of combustion product volumes does not take into account the dissociation of carbon dioxide, steam, etc., at the flame temperature.

/84....Consider

Consider a solution containing 0.4 p.p.m. of magnesium as the nitrate. This solution carries 0.44 micrograms of magnesium per minute into the flame. Thus the total concentration of magnesium in the flame is approximately 0.0037γ/litre. The concentration of magnesium atoms in the flame is given by the product of the total quantity of magnesium in all forms in the flame and the degree of dissociation of magnesium oxide. It is assumed that all the magnesium is initially present as oxide in the flame and that chlorides, etc., are absent. The concentration of magnesium atoms in the flame is, therefore:

$$1.3 \times 10^{-17} \text{ g Mg/litre}$$

As 6.023×10^{23} (Avogadro's number) of magnesium atoms weighs 24.3 g, the concentration expressed in atoms/litre is:

$$3.21 \times 10^{5} \text{ atoms Mg/litre}$$

It says much for the sensitivity of the method that so small a concentration of absorbing species gives an appreciable reading.

5.4.3 Comparison of theoretical and observed absorption Coefficients.

The value of the absorption coefficient, k_v, as defined in equation (2) is:

$$k_v = \frac{2.303 \times \text{optical density}}{\text{length of flame}}$$

As a solution containing 0.4 p.p.m. of magnesium as the nitrate gave an optical density of 0.16, the value of k_v for this solution, using an 11 cm. flame, is:

$$k_v = \frac{2.303 \times 0.16}{} = 0.034.$$

This is the observed value of k_v.

Naturally the value of k_v will depend on the composition of the solution tested. The result for magnesium nitrate was used as the nitrate is sure to produce pure magnesium oxide in the flame. Chloride, perchlorate or strontium would only complicate the issue.

The theoretical value for k_v, taking Doppler broadening into account, is given by equations (3) and (4). Substituting 3.21×10^{2} atoms Mg/cc. for N, 1.74 for f, 1900°K for T and 2852 Å for λ gives:

$$k_v = 0.207$$

85./ Correcting...

Correcting for pressure broadening gives :

$$k_v' = 0.207 \times 0.61$$
$$= \underline{\underline{0.126}}$$

This is till more than 3 times the observed value. It is likely that this discrepancy is due to the approximations used in this calculation, especially the assumptions of flame temperature and oxygen concentration. The accuracy of the temperature value is particularly important. It may be shown that at 1800°K the equilibrium constant for the formation of magnesium oxide drops to 3.02×10^{10} and the value of k_v' at this temperature is only 0.0097.

5.4.4 The effects of strontium and calcium:

The enhancing effects of strontium and calcium salts can be explained thermodynamically. The equilibrium constant for the formation of strontium oxide from its elements at 1900°K, i.e. the reaction:

$$Sr\ (g) + \tfrac{1}{2}\ O_2(g) \longrightarrow Sr\ O(s)$$

may be calculated in the same way as that for the corresponding reaction for magnesium. Since the free energy of formation of strontium oxide is -92.6 K cals/mole at 1900°K, the equilibrium constant, K_2, for the formation of strontium oxide is $4.38 \times 10^{10} = \dfrac{P_{SrO}}{P_{Sr} \cdot P_{O_2}^{\frac{1}{2}}}$,

where the symbols have the same significance as for magnesium.

Combining this with the equilibrium constant K_1, for the formation of magnesium oxide, we get:

$$K_3 = \frac{K_2}{K_1} = \frac{4.38 \times 10^{10}}{2.24 \times 10^{9}} = \frac{P_{SrO} \cdot P_{Mg}}{P_{Sr} \cdot P_{MgO}} = 19.5$$

K_3 is the equilibrium constant for the reaction:

$$MgO\ (s) + Sr\ (g) \rightleftharpoons Sr\ O(s) + Mg\ (g)$$

The value obtained for K_3 indicates that, under flame conditions, there would be a tendency for strontium to reduce magnesium oxide to the metal, and hence increase the absorbance of magnesium.

If the activities of the solid phase components, magnesium oxide and strontium oxide, are taken as 1or if they are equal, the equation

/...86...for

for K_3 simplifies to:

$$K_3 = \frac{P_{Mg}}{P_{Sr}} = 19.5$$

Thus, if equilibrium were reached, one would expect the magnesium atom concentratin in the flame to be doubled by doubling the concentration of strontium atoms. The graph of optical density (which is roughly proportional to the elementary magnesium concentration) versus total strontium concentration is curved, but the early portion of the graph approximates to a straight line of slope 1.26 (instead of a theoretical 2). Possibly the reason why the enhancement by strontium never reaches its theoretical value is that, since the concentration of strontium atoms in the flame is exceedingly low, it cannot reduce the free oxygen content of the flame by a significant amount.

The effect of calcium can be treated in an analogous manner. Calcium oxide has a stability constant, K_4, of 3.47×10^{11} at 1900°K (derived from the free energy of formation of calcium oxide) which gives rise to an equilibrium constant, K_5, of 155 for the reaction:

$$Ca(g) + Mg\ O(s) \rightleftharpoons Ca\ O(s) + Mg(g)$$

The enhancement of the absorbance of magnesium by calcium is only fractionally greater than that observed with strontium, which is contrary to the predictions from K_5 alone. It must be remembered, however, that, at equivalent solution concentrations, the concentration of elementary calcium in the flame is still lower than that of strontium, which in turn is only $\frac{1}{20}$ of that of magnesium when equilibrium is attained.

/6...Acetyl....

6. ACETYL ACETONE SOLVENT EXTRACTION.

6. ACETYL ACETONE SOLVENT EXTRACTION.

On account of the large number of elements which were found to interfere in the determination of magnesium by atomic absorption, it was felt that some form of separation was essential if the method were to be of any use in the analysis of ore samples. The separation by extraction of cupferrides at pH5 with chloroform seemed promising, but no more than a few milligrams of interfering elements could be extracted on account of the formation of a bulky precipitate.

Acetyl acetone[70.] is reported to extract aluminium, beryllium, cerium, chromic chromium (with refluxing), copper, iron, molybdenum, titanium, uranium, vanadium, zinc, zirconium and manganese. It was decided to test this extraction, with particular emphasis on aluminium.

6.1 Purity of reagent: A C.P.-grade acetyl acetone was found to give high blank values (optical density 0.05-0.06) when used as extractant. The A.R. grade reagent used subsequently gave somewhat lower blanks (optical density 0.03 - 0.04).A.R. grade chloroform was used.

It was found that the neutral and alkaline solutions used in this work dissolved magnesium from the glass-ware if soda-glass apparatus was used, but no contamination was observed if slightly acidic solutions were stored in soda-glass volumetric flasks for 48 hours. For this reason it was decided to perform the extraction in Pyrex separating funnels and to acidify the solution before transfer to volumetric flask. Either hydrochloric acid or nitric acid (generally the latter) was used to acidify the solution.

6.2 Extraction conditions.

The optimum pH value for the extraction of aluminium was first determined. In these tests, the aqueous solution containing 100 mg Al as nitrate was diluted to approximately 15 ml.in a 100 ml. separating funnel, a few drops of methyl red and 5 ml. acetyl acetone were added and the pH was adjusted, using universal indicator paper, by the addition of ammonia or nitric acid. This solution was shaken to mix the two phases, 10 ml. chloroform was added and the solution again shaken for 1 minute. The phases were allowed to separate and the chloroform layer was discarded. The extraction was repeated with 10 ml. of 5 percent acetyl acetone in

/88...chloroform...

chloroform. The aqueous phase was then acidified with nitric acid, filtered through a wet Whatman no. 541 filter-paper and diluted to 50 ml. A 5 ml. portion of this solution was fumed with nitric and perchloric acids to destroy organic matter and the aluminium was determined by a spectrophotometric method using "Aluminon" as colourimetric reagent. The results obtained are given in Table 38.

TABLE 38.

Effect of pH on extraction of aluminium.

Approximate pH	Residual aluminium (mg Al).
3	3
4	3
7	0.67
8	0.1
9	2.6*
9.5	0.3
10	0.6

* Result doubtful.

The extraction appears to be fairly constant over the pH range from 7 to 10. The adjustment of pH in the presence of aluminium is easy, using methyl red as indicator. When coloured solutions are encountered, the pH may be adjusted using universal indicator paper.

The optimum shaking time was also determined and it was found that the extraction was constant for shaking times of more than 30 seconds. It was decided to use a shaking time of 1 minute.

The number of extractions necessary for efficient separation was tested, starting with 200 mg. of aluminium and using similar conditions to those described for the previous test, excepting that the pH was adjusted by adding ammonia until the methyl red turned yellow (pH approximately 7) and 20 ml. of chloroform were used for the first extraction. Intermediate extractions were performed with 10 ml. of 10 percent acetyl acetone in chloroform and the solution was finally washed with 10 ml. of chloroform, which was also counted as one extraction. The results obtained are given in Table 39.

/89...Table 39.

TABLE 39.

Effect of number of extractions.

Number of extractions	Residual Aluminium (mg Al)
2	3
3	0.15
4	0.23
5	0.1

As these results indicate that the percentage of aluminium extracted decreases when more than 3 extractions are used, it was decided to use 3 extractions.

The effect of various intervals between the pH adjustment and the first extraction with chloroform was also tested, as it was felt that possibly the complex formation was slow. Results indicated that this was not the case and that the first chloroform extraction could be performed immediately after the pH adjustment.

6.3 Effect of residual aluminium.

As these amounts of unextracted aluminium are above the threshold of aluminium interference, the effect of residual aluminium on the absorbance of magnesium was determined. 5 ml. of acetyl acetone were used and the extractions performed as described previously, excepting that 10 ml. of 30 percent acetyl acetone were used for the second extraction. Three extractions were performed. The results obtained are given in Table 40.

TABLE 40.

Effect of residual aluminium.

Conc. Mg (γ/50 ml)	Amount Al added (mg)	Residual Al(mg)	Optical Density	O.D. sample - O.D. blank
0 (not extracted)	0	0	0.009	--
20 (" ")	0	0	0.292	0.283
20 (extracted)	0	0	0.310	± 0.265
20 (")	100	0.25	0.301	0.254
0 (")	100	(0.25)	0.047	---

/90.... Table 40 contd....

TABLE 40 (contd.).

Conc. Mg (γ/50 ml)	Amount Al added (mg)	Residual Al(mg)	Optical density	O.D. sample - O.D. blank
20 (extracted)	200	0.62	0.303	0.254
0 "	200	(0.62)	0.049	--
20 "	300	1.45	0.307	0.257
0 "	300	(1.45)	0.050	--

The results show that a fairly constant recovery of magnesium is obtained over a fairly wide range of aluminium concentrations. Previously (see Table 13) 0.1 mg Al/50 ml was found to reduce the absorbance of magnesium by about 13 percent, while 1 mg. Al/50 ml reduced it by about 34 percent. Clearly the residual aluminium after extraction must be in some form in which it cannot react with magnesium after the acetyl acetone extraction. Probably the residual aluminium is still present as the acetyl acetone chelate after acidification (just enough concentrated nitric acid was added to turn the methyl red red), and this chelate apparently does not react with magnesium to give a refractory compound. The direct addition of 0.1 ml. of acetyl acetone to a solution containing 5 mg. Al and 20 γMg/50 ml. in acidic solution did not reduce the interference at all; it appears the complex must first be formed in neutral or alkaline solution.

This was tested using standard magnesium solutions to which an impurity and acetyl acetone were added. The solution was made just alkaline to methyl red with ammonia, re-acidified after about 3 minutes with concentrated hydrochloric acid, diluted to volume and the absorbance measured. Results are given in Table 41.

/91....Table 41....

TABLE 41.

Effect of acetyl acetone on interference by certain elements.

Conc. Mg (γ/50 ml.)	Conc. acetyl acetone (ml/50ml)	Conc. strontium nitrate % v/v M soln.	Nature foreign element	Conc. foreign element (mg/50 ml.)	Enhancement
20	0.2	2	Al(as NO_3)	1	0.96
20	0.1	2	Al(as NO_3)	5	0.69
20	0.2	0	Al(" ")	1	0.87
20	0.2	0	Fe(as NO_3)	2	1.26
20	0.2	2	Fe(")	2	0.93
20	0.2	0	Mn(as Cl)	2	1.00
20	0.2	2	Mn(" ")	2	0.93

The addition of 0.2 ml. acetyl acetone to a solution containing 0.4 p.p.m. magnesium did not affect the absorbance, both in the presence and absence of strontium nitrate.

These results show that the effects of some foreign elements are partially overcome by the addition of a little acetyl acetone to the solution, providing that the solution is first made alkaline to form the acetyl acetone complex.

6.4 The extraction of other elements.

The extraction of several other elements was tested under slightly different conditions. 10 ml. of acetyl acetone were used and the pH adjusted to pH 6-8 with ammonia. The solution was extracted with 20 ml. of chloroform and a second extraction performed with 10 ml. of 5 percent acetyl acetone in chloroform. The aqueous phase was filtered through a wet Whatman No. 541 filter paper before acidification. The results obtained are given in Table 42.

/92.....Table 42..

TABLE 42.

The extraction of several elements with acetyl acetone-chloroform.

Element tested	Amount taken	Amount unextracted	REMARKS
Fe, as nitrate	200 mg Fe	$<$0.05 mg	
" " "	300 mg Fe	$<$0.05 mg	
Al, as nitrate	300 mg Al	0.4 mg	
TiO_2, as sulphate	100 mg TiO_2	$<$ 0.25 mg	A trace of ppt. in aqueous phase - removed by filter
Zr, as chloride	200 mg Zr	$<$ 0.01 mg	
" " "	300 mg Zr	0.06 mg	
U, as (NO_3^- + Cl^-)	300 mg U	1 mg	
U, as nitrate	1 g U	0.7 mg	
Mn, as chloride	200 mg Mn	36 mg	Required 35 ml $CHCl_3$ for 1st extraction

These results indicate that the extraction is useful for the removal of aluminium, titanium, iron, zirconium and uranium in quite large amounts. In a further test conducted with uranium, 1.5 g U was found to be removed almost quantitatively using 5 ml. of acetyl acetone and 20 ml. chloroform for the first extraction; 10 ml. 30 percent acetyl acetone in chloroform for the second and a final scrub with 10 ml. of chloroform. Unfortunately, the extraction of manganese is not efficient enough to overcome its interference as even 0.1 mg. of manganese per 50 ml. of solution has a significant effect on the absorbance of magnesium.

6.5 Losses of magnesium during extraction:

To test the loss of magnesium during the extraction procedure, 5 to 35γ aliquots of magnesium were transferred to Pyrex separating funnels, a drop of methyl red added and the solutions diluted to approximately 15 ml. 5 Ml. of acetyl acetone were added and ammonia added until the indicator turned yellow. The solutions were then diluted to approximately 25 ml., shaken to mix and 20 ml. of chloroform added. The solutions were then shaken for 1 minute, the phases allowed to separate for 15 minutes and the

/93...(lower)

(lower) organic layer discarded. This extraction was repeated with 10 ml. of 20 percent acetyl acetone in chloroform and finally with 10 ml. of chloroform. A further drop of indicator was added to each solution and nitric acid added until the indicator just turned red. The solutions were then filtered through a wet Whatman 541 filter paper (9 cm.) directly into a 50 ml. volumetric flask. 1 ml. of molar strontium nitrate solution was added, the solutions diluted to 50 ml. and mixed. The absorbance of these solutions was measured in the usual manner (see Appendix 1 for details) and the results compared with similar solutions of magnesium which had not been extracted with acetyl acetone. The results obtained are given in Table 43.

TABLE 43.

Recovery of magnesium after solvent extraction.

Mg Conc. (γ Mg/50 ml.)	% Recovery $\frac{\text{(O.D. extracted soln.-O.D.blank) x 100}}{\text{(O.D. unextracted soln.-O.D.of its blank.)}}$
5	100, 95.7
10	93.6
15	94.0, 93.1
20	96.0, 94.0
30	95.6, 93.7

These results indicate that the percentage recovery of magnesium is fairly constant over the concentration range studied. Discarding the values for the 5γ aliquot (these are likely to be less accurate than the others as a 0.5 ml. portion of st ndard magnesium solution was taken for this solution, using a microburette), a mean recovery of 94.3 percent is obtained. Later work on actual samples showed that this recovery varied with the concentration and type of other salts present in the solution. The recovery is best determined separately for each sample in accurate work, particularly if the samples are of variable composition. This may be done by spiking a separate aliquot portion of the sample solution with a known amount of magnesium before extraction and calculating the percentage recovery of the added magnesium.

/94...We thus...

We thus have two sources of error introduced by this extraction, viz. the introduction of magnesium from reagents and apparatus, corrected by the blank, and a proportional loss of magnesium, corrected by a spiking technique.

If the calibration curve were linear, and if errors due to the depressing effect of other elements were proportional to the magnesium concentration then the errors could be corrected by spiking and extrapolation, as employed in emission flame photometry. Where a non-linear calibration curve is obtained spiking may still be used, but each optical density reading must be converted to a magnesium concentration from the calibration curve. Often a fixed amount of impurity causes a depression which is proportional to the magnesium content over a wide range of magnesium concentrations. In this case a correction factor can be calculated from the recovery of added magnesium in a spiked sample, and the effect of foreign elements compensated by applying this factor. That foreign elements behave like this was proved by measuring the absorbance of solutions of magnesium to which sodium, iron, aluminium or magnesium was added. The results obtained are given in Table 44.

TABLE 44.

Effects of foreign elements in presence of varying amounts of magnesium.

Conc. Mg added (γ/50 ml)	Conc. foreign element (mg/50 ml.)	nature foreign element	Magnesium found (% of mg added)	REMARKS
10	1	Al, as nitrate	77	
20	1	" " "	75	All solutions contain 1 ml M.$Sr(No_3)_2$/50 ml.
30	1	" " "	75	
10	1	Fe as nitrate	75	Results corrected for blank
20	1	" " "	75	
30	1	" " "	76	
10	1	Mn as chloride	94	
20	1	" " "	95	
30	1	" " "	96	
10	40	Na as chloride	88	
20	40	" " "	87	
30	40	" " "	91	

/95....These results

These results show that the effect of the fixed amounts of the foreign elements tested is to give an apparent magnesium concentration which is virtually a fixed percentage of the true concentration over a fairly wide range of magnesium concentrations. This justifies the use of a factor, obtained by determination of the recovery of added magnesium, to correct the sample result for the effect of foreign elements, as the recovery of added magnesium will be equal to the magnesium recovery in the sample.

/96...7.. The..

7. THE ANALYSIS OF SAMPLES.

7. THE ANALYSIS OF SAMPLES.

To test the accuracy of the method, several standard samples, including clay samples, a magnetite and a uranium plant processing solution (actually a purified uranyl nitrate solution called an "O.K. Liquor"), and a limestone were analysed. The results are given in Table 45.

TABLE 45.

Analytical results by proposed method.

Sample	Certificate value	no. of determinations	Mean Result	Coeff. variation	Spike recovery
Flint Clay no. 97	0.26% MgO	10	0.223% MgO	4.6%	A)9.4γ from 10γ Mg B)19.2γ from 20γ
Plastic Clay no. 98	0.72% MgO	10	0.650% MgO	2.0%	A)10.4γ from 10γ B)20.4γ from 20γ
Iron ore 29a (magnetite)	0.095% MgO	4	0.090% MgO	--	10.2γ from 10γ Mg
Cupro-nickel "A"	0.02% Mg,	4	0.016% Mg	--	-- **
Limestone "A" (argilla-ceous)	2.19% MgO	2	2.21% MgO	--	-- **
O.K.Liquor AW 216	--	3	3.4(2) p.p.m. Mg*	--	A)4.8γ from 5γ Mg B)10.1γ " 10γ C)14.8γ " 15γ

* Result calculated on uranium basis.

** Where spike recovery not reported, 6% loss assumed and result corrected for loss.

The procedure followed in the analysis of these samples is described in Appendix I. Dissolution procedures followed for various types of samples naturally differ.

The iron ore, clay and argillaceous limestone samples are all U.S. Bureau of Standards standard samples. The cupro-nickel sample is a British Chemical standard, prepared by the Bureau of Analysed Samples, Ltd. No great accuracy is claimed for the magnesium

/97...figure..

figure given in the certificate for this sample; only one significant figure is quoted.

The acetyl acetone-chloroform solvent extraction was used in the analysis of all these samples and the observed standard deviation is probably due largely to errors resulting from this step.

The difference between the certificate and observed results for the clay samples in 10-15 percent, which is abnormally large in view of the coefficient of variation and spike recoveries obtained. As classical methods of analysis were used to obtain the magnesium results quoted in the certificate, it is quite possible that the certificate results, rather than the atomic absorption results, are at fault.

The experimental results for the other samples agree fairly well with the certificate values.

98 /8....CONCLUSIONS...

8. CONCLUSIONS.

8. CONCLUSIONS.

This investigation shows that the inter-element effects involved in the determination of magnesium by atomic absorption are very complex. Where possible, theories have been proposed for the mechanisms of these interferences. Most of these theories have not been conclusively proved in this investigation and must accordingly be accepted with caution.

The use of strontium salts to overcome the interference by other elements was thoroughly investigated. It was found that strontium alone was not completely effective as a releasing agent. Small amounts of several substances, e.g. aluminium and iron, interfere even in the presence of 0.02 molar strontium nitrate. A combination of acetyl acetone and strontium salt was found to be more effective as a releasing agent for magnesium from interfering elements that form complexes with acetyl acetone than the strontium salt alone. With many elements, however, even this mixture did not fully restore the magnesium absorbance to its value in the absence of the interfering element. This is particularly true of manganese, iron and aluminium. A spiking technique is proposed to overcome this residual interference, which is generally small.

The agreement between the theoretical and observed absorption coefficients obtained in this work leads one to conclude that equilibrium conditions are possibly attained in the flame, in spite of the views of other investigators, reported in the literature survey.

A solvent extraction procedure employing acetyl acetone and chloroform was developed and found to be useful in the removal of moderate amounts (up to about 0.5 gram) of several interfering elements, including aluminium, iron, uranium, zirconium and titanium. This separation has the disadvantage of lengthening the determination and increasing the blank correction, but is essential for the determination of magnesium in aluminium metal, uranium metal, and several other materials where the magnesium concentration is very low and the concentration of interfering elements is high. Other methods of separation are proposed for most of the elements studied. These are usually standard procedures and were not investigated in this work.

As a result of this investigation a method for the determination

/99...of microgram...

of microgram quantities of magnesium in a wide variety of materials has been developed. Even when solvent extraction or some other means of separation of interfering elements has to be employed, this method is probably at least as rapid as most others available for the determination of microgram amounts of magnesium. The precision of the proposed method, including solvent extraction, was determined using two standard clay samples. Coefficients of variation of 2.0 and 4.6 percent, at magnesium oxide concentrations of 0.65 and 0.22 percent respectively were obtained. The solvent extraction procedure is probably responsible for most of this variation on account of the relatively large and somewhat variable blank correction resulting from it. The precision of the method as judged from these results, is adequate for most purposes.

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APPENDIX I.

Procedure for the determination of magnesium.

Outline of method: The sample is dissolved, preferably by attack with acids, and, if necessary, interfering elements are removed by liquid-liquid extraction with acetyl acetone-chloroform, mercury cathode electrolysis or anion exchange. Strontium nitrate is added and the absorbance of the solution is measured after dilution to a suitable volume. Standard magnesium solutions are measured with the samples and optical densities plotted against magnesium concentration on linear graph paper.

Application: This method is applicable to the determination of more than 1 p.p.m. of magnesium in uranium metal, oxides and processing solutions; clay and siliceous ores; limestone; aluminium metal; iron ore; zirconium metal, concentrates and processing solutions and may also be adapted to the analysis of other materials.

Reagents:

Water: De-ionised water must be used. Store in polythene containers.

Acids: hydrochloric, sulphuric, nitric, perchloric and hydrofluoric. A.R. grade acids must be used.

Strontium nitrate solution, molar: Dissolve 212 g. A.R. strontium nitrate (Anhydrous) in de-ionised water and dilute to 1 litre.

Ammonium hydroxide: A C.P. grade reagent was found sufficiently pure and may be used.

Acetyl acetone: Use an A.R.-grade reagent. Riedel de Haën brand was found satisfactory.

Methyl red solution: 0.1% (w/v): Dissolve 0.2 g. of the acid form of the indicator in 200 ml. hot de-ionised water.

Chloroform: A.R. grade.

Standard magnesium solution: Heat A.R. grade magnesium oxide at 1100°C in an electric muffle furnace for 2 hours to remove carbonate. Cool in a well-sealed desiccator for approximately 30 minutes, weigh out 1.658, add approximately 25 ml. water and dissolve in a minimum amount of A.R. grade nitric acid (If the magnesium oxide effervesces the solution must be discarded and the magnesium oxide re-heated to

/105 ....remove....

remove residual carbonate). Dilute to 1 litre. This solution contains 1.000 mg. magnesium per ml. Prepare a solution containing 10γ Mg/ml. by diluting 10 ml. of this solution to 1 litre with 1 percent (v/v) nitric acid. This solution is stable for at least 1 month.

Other Reagents: may be necessary for some samples. Use A.R. grade wherever possible.

Amount of sample:

Optimum quantities aliquot samples are given in the following table. If the magnesium concentration is very low, particularly if it is below 10 p.p.m., there will frequently be too much interference from other elements if the optimum amount of sample is used.

SAMPLE SIZE.

Estimate (% Mg)	wt. of sample(g)	Dilution vol. (1) (ml.)	Aliquot(1) (ml)	Dilution vol.(2) (ml)	Aliquot (2) (ml)	Final volume (ml)
3-6	0.2	100	5	100	5	50
1.5-3	0.2	100	10	100	5	50
0.7-1.4	0.2	--	--	500	5	50
0.3-0.6	0.2	--	--	250	5	50
0.1-0.2	0.2	--	--	100	5	50
0.05-0.1	0.2	--	--	100	10	50
0.02-0.04	0.5	--	--	100	10	50
0.01-0.02	0.5	--	--	50	10	50
0.005-0.01	1.0	--	--	50	10	50
0.002-0.004	1.0	--	--	50	25	50
0.001-0.002	1.0	--	--	Take all.		50
0.0005-0.001	2.0	--	--	Take all.		50
0.0001-0.0005	5.0	--	--	Take all		50

/106....PROCEDURE....

PROCEDURE:

1) Dissolution of sample: (a) Clays and silicates:

Transfer a suitable weight of sample to a platinum basin or crucible. Add approximately 5 ml. water, 2 ml. perchloric acid, 1 ml. 1:1 sulphuric acid and 5 ml. of hydrofluoric acid for samples of up to 0.5 g. For larger samples increase the amounts of sulphuric, perchloric and hydrofluoric acids in the proportion of the sample weight, but the hydrofluoric acid added should not exceed 25 ml. Evaporate slowly on a sand-bath, with occasional swirling, until the sample fumes. Cool, add a further amount of hydrofluoric acid equal to that used initially and evaporate until fuming ceases. Cool, add 5 ml. nitric acid and heat to almost boiling. Transfer the sample to a small pyrex beaker, washing with water and using a policeman to remove any undissolved residue adhering to the basin. Boil until all soluble salts dissolve.

If the insoluble residue is large, filter the solution and wash the paper about 6 times with hot, approximately 1% (v/v) nitric acid. Burn off the paper in a platinum crucible, fuse with a minimum amount of sodium carbonate (note 1), and leach with a little dilute nitric acid. Combine this solution with the filtrate and dilute to a suitable volume, if it is necessary to take an aliquot of the sample.

b) Uranium metal or oxides: Transfer a suitable weight of degreased uranium metal or oxide (not exceeding 1.5g U) to a pyrex beaker and dissolve in a minimum amount of nitric acid. Cool and dilute to a suitable volume if it is necessary to take an aliquot portion of the sample.

c) Limestone: Dissolve a suitable weight of the sample in 1:1 hydrochloric acid in a covered pyrex beaker. If a large insoluble residue remains, filter the solution and fuse the residue as described in (a). If it is necessary to take an aliquot of the solution, dilute to a suitable volume.

d) Other solid samples: These must be considered individually. It is best, where possible, to use an acid attack in preference to a fusion as moderate amounts of the alkali metals interfere. Samples containing

/107....organic matter...

organic matter, arsenic, sulphides, etc., should be ignited before dissolution in order to destroy organic material and drive off the volatile impurities.

2) Solvent extraction (Note 2).

Transfer an aliquot of the sample solution, preferably containing between 10 and 25γ Mg, to a 100 ml. pyrex separating funnel. Add 5 ml. acetyl acetone, 2 drops methyl red indicator, dilute to approximately 20 ml.,stopper, and shake for a few seconds to mix. Add ammonium hydroxide with swirling until the indicator just turns yellow. If the solution is highly coloured adjust to pH 7 using universal indicator paper. Add 20 ml. of chloroform, shake for 1 minute and allow the phases to separate for about 15 minutes. Discard the chloroform layer. Repeat the extraction using 10 ml. of 20 percent (v/v) acetyl acetone solution in chloroform. Finally add 10 ml. chloroform, shake for 30 secs. and allow the phases to separate. Discard the chloroform.Add 1 drop of methyl red and just acidify the solution with nitric acid. Filter the solution through a wet 9 cm. Whatman no. 541 paper, and collect the filtrate in a 50 ml. volumetric flask. Rinse the paper 3 times with water, add 1 ml. of molar strontium nitrate solution, dilute to the mark and mix.

3. "Spiked" sample: To a portion of sample identical in size to that taken in paragraph 2, add 10γ Mg (from the standard magnesium solution). Treat in exactly the same way as the sample.

4. Blank determination.

Prepare a total blank solution, commencing from paragraph (1) and following exactly the same procedure as described for the sample.

5. Preparation of standards:

Transfer aliquots of the standard magnesium solution containing : 0, 5, 10, 15, 20, 25, 30 and 35γ Mg to 50 ml. volumetric flasks, add 1 ml. molar strontium nitrate solution, dilute to the mark and mix.

/108....6. Measure the

6. Measure the absorption of the samples and standards in optical density unit according to instructions supplied with the instrument. Use a magnesium hollow cathode lamp and set the wavelength to the peak at 2852 Å.

Calculation of result:

1. Plot the results for the standard solutions on linear graph paper. Use this graph to convert the optical density readings of sample, spike and blank to the corresponding magnesium concentrations.
2. Calculate a correction factor = F given by:

$$F = \frac{\text{Magnesium in spiked sample } (\gamma) - \text{magnesium in sample } (\gamma)}{10}$$

(NOTE 3).

3. Calculate true magnesium content of sample solution, given by:

$$\frac{\text{Magnesium in sample} - \text{magnesium in blank}}{F}$$

and use this result to obtain the magnesium concentration of the sample.

NOTES:

1. The amount of sodium carbonate used must be such that the sodium content of the final solution will not exceed 10 mg. Na per 50 ml. As the magnesium content of A.R. grade sodium carbonate is appreciable, a similar amount of sodium carbonate must be added to the blank solution.
2. Liquid-liquid extraction with acetyl-acetone is necesaary only when extractable interfering ions are present in more than their tolerable amount. Samples whose final aliquots contain more than about 2 mg. of aluminium or iron must always be extracted. When solvent extraction is not employed, the following procedure must be adopted:

i) Transfer the final aliquot of the sample to a 50 ml. volumetric flask. Add 0.2 ml. acetyl acetone, 1 ml. molar strontium nitrate solution and 1 drop of methyl red. Add ammonia, with thorough mixing, until the indicator just turns yellow (or adjust the pH to 7 with indicator paper). Allow to stand for approximately 5 minutes.

/(109) .....(ii)..Add...

ii) Add hydrochloric acid until the indicator just turns red (or pH 3-4), dilute to the mark with water and mix. Proceed as from paragraph 3 in the Procedure.

This modification of the Procedure will overcome the interference of 2 mg. of aluminium.

3. A factor of less than 0.70 is undesirable as it can cause inaccuracy in the result. When the spike recovery factor falls below this level, separation of impurities causing it is indicated. In very accurate work, spike and sample determination should be done at least in duplicate.

/110...APPENDIX 2.

APPENDIX 2.

Purification of salts.

1) Lithium chloride: "Specpure" lithium carbonate was found to contain 0.03% of magnesium, which is too much for it to be used in interference tests. A solution of lithium chloride of sufficient purity was prepared from this lithium carbonate as follows:

About 8 g. lithium carbonate was dissolved in a minimum of A.R. hydrochloric acid, the solution evaporated to dryness and the residue redissolved in approximately 150 ml. of water. This solution was passed slowly over about 25 ml. of Amberlite IR-120 resin in the hydrogen form and the effluent collected and evaporated to dryness. This lithium chloride was used for the tests reported in Table 9.

2) Lanthanum nitrate: Only a C.P. grade salt was available and this was purified by double precipitation with ammonia. The hydroxide was redissolved in A.R. grade nitric acid.

3) Uranyl nitrate: A solution of uranyl nitrate was prepared from purified U_3O_8 and A.R. grade nitric acid. This U_3O_8 was prepared from a sample of impure U_3O_8 (approximately 90 percent pure), obtained from Calcined Products, according to the method described in "Assay Practice on the Witwatersrand."[71].

4) Thorium nitrate: A C.P. grade salt was available, but contained too much magnesium for use in interference tests. It was purified by double precipitation with ammonia. The hydroxide was redissolved in concentrated nitric acid.