ATOMIC ABSORPTION SPECTROMETRY AND ITS APPLICATION IN GEOCHEMISTRY

A thesis submitted to the University of Cape Town for the degree of

Doctor of Philosophy

by

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I N D E X

SUMMARY

The atomic absorption method of analysis is reviewed. The theory describing the various phenomena such as atomic population, spectral line shapes, factors influencing absorption, analytical graph curvature, etc. are deduced.

The practical aspects of atomic absorption are discussed with respect to: Instrumentation:flame studies and an attempt to develop a "universal" flame; contamination; sources of errors, etc.

The method is applied to the analysis of silicate materials. Problems of sample dissolution and standards preparation are discussed.

Applications have been made on the determination of the alkali metals (including lithium isotope determination), magnesium and calcium, copper, zinc, iron, manganese, molybdenum and aluminium. Although certain geochemical aspects of these elements are discussed, the analytical problems are stressed. The interference effects by other elements were tested and techniques developed to enable interferences to be overcome.

It is concluded that atomic absorption spectrometry has significant uses for the geochemist, especially for the estimation of elements of the trace and minor concentration levels.

LIST of SYMBOLS USED IN THE TEXT

a	The "a" parameter of the Voigt profile, $a = \frac{\Delta\nu_N + \Delta\nu_L}{\Delta\nu_D} \sqrt{\log 2}$
A	Absorbance $\log I_o/I$
$A_{2\to1}$	The Einstein emission probability
$B_{2\to1}$	The Einstein absorption probability, and absorption probability (normal)
c	Speed of light, cm/sec.
C	Constant
δ	A variable from point $(\nu - \nu_o)$
$\Delta\nu_D$	Doppler half width
$\Delta\nu_L$	Collisional half width
$\Delta\nu_N$	Natural half width
E	Energy of atom E_i and E_j energy of excited state i and j
e	Electronic charge
f	Oscillator strength
g	Statistical weight (2J + 1)
h	Plank's constant
I	Intensity of light (I_o initial intensity, I_ν transmitted intensity at frequency ν)
J	Quantum number
K	Absorption coefficient (K_o, at centre and K_ν at ν)
λ	Wavelength of spectral line (λ_o at centre of line)
l	Pathlength, cm.

m	Atomic mass
N	Number of atoms in a particular state (e.g. N_i in state i)
ν	Frequency (ν_o frequency at centre of line profile)
R	Universal gas constant, erg/degree/gm-mol.
t	Time, also life-time of the excited state, sec.
T	Absolute temperature, degrees Kelvin
ψ	Lifetime of atom in the resonance state
ω	A parameter of the Voigt equation
$f(\phi_b)$	Function which describes chemical effect of analytical element
$f(\phi_p)$	Function which describes chemical effect of foreign element

ATOMIC ABSORPTION SPECTROMETRY AND ITS APPLICATION IN GEOCHEMISTRY

PART I: INTRODUCTION AND LITERATURE SURVEY

CHAPTER 1

INTRODUCTION

1.1 AIM OF THE THESIS

In this thesis a study has been made of atomic absorption spectrometry with a view to its application in geochemistry. The study has not been aimed at solving a particular analytical problem, but rather to investigate the method for general geochemical application, and to provide a clearer understanding of its advantages and disadvantages, its scope and its limitation.

For this reason more detailed studies have been made of those aspects of the subject considered of fundamental importance, such as:

(a) The use of flames and the attempt to develop a universal flame;

(b) a comparison of dissolution techniques to determine those most suitable for atomic absorption;

(c) the investigation of interference effects most likely to be encountered in geochemical analyses and the means used to overcome them, and

(d) the factors likely to affect precision and accuracy.

Certain elements have been more fully investigated in order to determine their most suitable conditions and also because these elements are representative of the behaviour of other elements in their group.

The final assessment of the methods has been by the analysis of various rock standards and samples.

1.2 GEOCHEMICAL ANALYSIS

Goldschmidt (1954) has pointed out that modern geochemistry studies the distribution and concentration of elements in all naturally occurring materials.

This includes all material from the earth and the universe, such as water from the oceans and rivers, rocks and minerals from the earth, and meteorites, from extra-terrestrial sources. The science of geochemistry depends significantly on chemical analysis, and considerable efforts are being made to improve existing methods and develop new ones.

To those acquainted with methods of chemical analysis, the analysis of the wide variety of geological material that exists such as ocean water, clays, rocks, minerals, and soils, is not easy, as wide variations occur in the composition of these materials. Chemical techniques, for instance those based on the chemical behaviour of atoms, molecules and radicals in solutions, as well as gravimetric methods etc. have been in use since the foundation of the science of geochemistry, and remain reliable and precise, especially for the determination of the major constituents. The accurate determination of elements present in minor and trace quantities presents difficulties, and it is not surprising that the sensitive emission spectrographic methods, based on the use of the D.C. arc (Ahrens and Taylor, 1961) and the flame (Lundegardh, 1934) became and remain popular. The geochemist today has the choice of many methods of analysis. These include

(a) the classical chemical methods;

(b) the more modern chemical methods, such as colorimetry, polargraphy, ion exchange, and

(c) physical methods, such as emission spectroscopy, flame photometry, spark-source mass spectroscopy, neutron activation, isotope dilution and mass spectrometry and x-ray fluorescence spectroscopy.

The choice depends on the degree of accuracy, precision, speed, sensitivity, the matrix and number and type of elements to be determined. Many of these methods overlap with regard to range of analysis, types of element which may be determined, precision and accuracy etc. so that other factors such as cost, speed and simplicity, may influence the geochemist's choice.

That geochemical analysis is still far from satisfactory has been well illustrated by the large discrepancies in analytical data obtained by the U S. Geological Survey (Stevans et al, 1960), when the two famous rock standards granite G-1 and diabase W-1 were released for analysis.

When the relatively new method of atomic absorption spectroscopy was first suggested by Walsh (1955) there was little reaction from geochemists. Since then, however, with its remarkable development and increasing popularity in other fields, this method has been seen as one which could well be of considerable value to geochemistry.

During the course of investigations by the author over the last nine years, it has been found that atomic absorption analytical spectrometry is extremely complementary to other methods, and in certain cases is more sensitive and precise. This has also been found to be true for geochemical analysis. The necessity to dissolve solid samples is time-consuming but the method efficiently fills gaps which are present in other available methods.

Because of its remarkable sensitivity coupled with good precision and accuracy, it will be of fundamental use for the estimation of trace metal concentrations in many types of geological materials. The high specificity of the method makes it ideally suitable for use with chemical enrichment techniques to increase sensitivity. This is of use for the analysis of ocean-water and natural waters where trace metal concentrations are very low, as well as for the determination of very low-abundance trace elements in rocks.

Although better suited for trace and minor element determination it has been found that the method may be used, with advantage, as a "rapid" method for the determination of major elements such as aluminium, iron, calcium, magnesium, sodium and potassium in silicate samples.

In these cases one or more of the methods available for reducing sensitivity may be used.

1.3 LITERATURE SURVEY

1.3.1 General

The phenomenon of atomic absorption has been known since the dark absorption lines in the spectrum of the sun were studied in detail by Kirchoff (1861), and the reversal of spectral lines emitted by a flame were noted by Bunsen and later flame spectroscopists. Apart from astronomers, who used the absorption spectra of the sun and planets for the study of planetary atmospheres, there is no record of atomic absorption spectroscopy having been used for analytical purposes until the brilliant work by Walsh in 1953. By suggesting the use of sealed hollow cathode lamps as light sources, he obviated the need for very high resolution spectrographs and thus opened the way to a method making use of simple, inexpensive, low dispersion spectrometers. In Holland, Alkemade had been working independently along similar lines and his publication with Milatz (1955) followed that of Walsh shortly after.

Not surprisingly the first applications of atomic absorption spectroscopy to practical analyses were made in Australia and New Zealand. Prominent among the scientists who foresaw the potential of the method were Willis (1959, 1960a, 1960b, 1962), David (1958, 1959, 1961, 1962) and Allan (1959, 1961, 1962a, 1962b). These applications were mainly for the determination of specific elements in biological and agricultural materials. Significant advances have been made during the last eight years in atomic absorption spectrometry, not only to extend the method for the determination of various elements in metals (Gidley, 1961), water (Platte and Marcy, 1965), cement (Capacho-Delgado et al, 1967), fertilizers (McBride, 1967), oil (Means and Ratcliff, 1965), foodstuffs (Slavin, 1965), wine (Zeeman and Butler, 1962), but also to improve limits of detection (Fuwa and Vallee, 1963).

Flames and combustion processes (Kirkbright et al, 1968), and atomizing phenomena (Willis, 1967) have been studied by several scientists, as it has long been realized that the flame plays an important role in affecting

precision, sensitivity and accuracy of the method. Perhaps one of the most significant advances made since atomic absorption was first suggested, has been the use of the nitrous oxide flame (Amos and Willis, 1966; Willis, 1965). Not only are many interference difficulties overcome, but the use of the flame has enabled many elements which form refractory oxides and hydroxides, to be determined.

Several techniques have been described to atomize solid samples (L'Vov, 1961; Walsh and Gatehouse, 1960), but most of these methods appear to have practical disadvantages.

Major advances in the improvement of instrumentation such as hollow-cathode lamps (Dawson and Ellis, 1967; Manning and Vollmer, 1967), nebulizers (Davies et al, 1965), and burners (Butler, 1962; Manning, 1965), spectrometers (Kahn, 1966) and readout systems (Boling, 1965; Keats, 1965) have been made. The high intensity lamps of Sullivan and Walsh (1965) aroused much interest, but these have not been found to improve analyses significantly except for the elements selenium and arsenic. Selective modulation (Walsh, 1966) and resonance spectrometers (Sullivan and Walsh, 1966) are receiving much attention at present and it is predicted that these devices may well revolutionize atomic absorption as well as emission spectroscopy within the next ten years.

The simultaneous determination of several elements (Butler and Strasheim, 1965) has been shown to be possible, applied mainly to specific problems, but research in this field continues.

A laser has been used successfully for the production of an atomic vapour for atomic absorption spectroscopy (Mossotti and Laqua, 1968), and solid fuels (Venghiattis, 1967) have been used for atomizing powdered ores, giving results which could be of use for rapid, semi-quantitative determinations.

Attention has been paid to the theoretical aspects of atomic absorption using flames as emission sources (Rann, 1968). The factors

influencing the shape of absorption lines have been studied (Lapp and Gallagher, 1967; Bleekrode, 1967) and it has been shown that the Voigt profile describes the absorption line shape better than the Doppler profile suggested by Walsh in his original paper. Attempts have been made to develop an absolute method using this theory, but have not been generally successful (Rann, 1967).

Research continues at a feverish pace in atomic absorption spectroscopy and its applications, as well as allied fields such as atomic fluorescence spectroscopy (Winefordner and Vickers, 1964).

1.3.2 Atomic Absorption in Geochemistry

Astrophysicists are perhaps the oldest users of atomic absorption spectroscopy for analytical purposes as this technique has been used for many years to determine the composition of solar and stellar atmospheres.

(a) Ores

One of the first applications of atomic absorption spectroscopy for the analysis of geological materials was that of Strasheim et al (1960) who determined copper in ores. Several other scientists have applied atomic absorption to ore analysis. Farrar (1966) has determined copper, zinc and cadmium in ores of these elements as well as in lead base ores. Rawling et al (1960) determined silver in lead sulphide concentrates and in silver and zinc ores, while Judy Bowman (1967) determined tin in tin ores and concentrates with a nitrous oxide acetylene flame.

Atomic absorption is used on a large scale for rapid analysis (Sampey, 1967) of soils, rocks and ores for geochemical prospecting, especially in Australia and the U.S.A.

(b) Water analysis

The method has been applied very successfully to water analyses probably because of the simplicity of sample preparation. Butler and

Brink (1963) determined magnesium, calcium, potassium, sodium, copper and iron in natural water. Burrell (1965a) determined nickel and cobalt by pre-concentration and solvent extraction, and Platte and Marcy (1965) described the atomic absorption method as a general tool for the water chemist.

Various elements in ocean water and brines have also been determined. Angino and Billings (1966) have determined lithium in sea water and have very recently published a useful book (Angino and Billings, 1967) describing the use of atomic absorption spectrometry in Geology. Fabricand et al (1966) have determined lithium, magnesium, potassium, rubidium and strontium in sea water and Joyner and Finley (1966) have determined magnesium and iron.

Solvent extraction is ideal for concentrating trace elements (Mulford, 1966) and eliminating alkali and alkaline earth interferences. Lakanen (1962) has used chelating agents and solvents such as chloroform for this and Fabricand et al (1962) have used quinozaline-2, 3-Dithol for determining nickel. A P D C and Oxine are also well suited for this purpose as mentioned by Mansell and Emmel (1965). Orren (1967) has used A P D C successfully for extraction of trace elements from sea water.

(c) Organic Geochemical Analysis

Burrell (1965b) has used atomic absorption for determining cobalt, iron and nickel in organic (asphaltic) fractions in recent sediments, by extraction of these fractions with chloroform.

(d) Industrial

Cements have successfully been analysed by Manning et al (1963) for silicon, aluminium and titanium. Coal has been analysed by atomic absorption spectroscopy. Belcher and Brooks (1963) determined strontium in coal ash and Boar and Sullivan (1967) used a resonance

monochromator for the routine determination of magnesium in brown coal. Adams et al have published several papers (Adams, 1961; Adams, 1965; Adams and Passmore, 1966) on glass analysis by atomic absorption.

(e) Rocks

Relatively few papers have been published describing the use of atomic absorption for rock analyses and most of these have appeared within the last three years. Rubeska et al (1963) determined magnesium in various types of silicate samples. Butler and Mathews (1966) developed a method using solvent extraction for the determination of molybdenum in silicate materials. Trent and Slavin (1964a) described a method for determining sodium, potassium, calcium, magnesium, manganese and iron in the two rock standards G-1 and W-1. Surprisingly, very little interference was reported even from silicon when a fusion technique was used. These authors also described the use of atomic absorption for the determination of calcium, magnesium, manganese and iron in various types of silicate samples, as well as copper in G-1 and strontium in G-1 and W-1 (Trent and Slavin, 1964b).

Billings has probably made the greatest contribution to the application of atomic absorption to geochemical analysis. Apart from two very interesting papers (Billings and Adams, 1964; Billings, 1965a) describing some of his work, his recent book (Angino and Billings, 1967) provides a good source of reference. In the first of the papers, he describes the determination of ribidium, iron, strontium, potassium, sodium and calcium in the silicate minerals plagioclase, alkali feldspar, and nepheline and in the second discusses the accuracy of atomic absorption results. Belt (1964), has applied atomic absorption methods to the determination of copper and zinc in geological materials, and has suggested a method for the partial

analysis of silicate rocks (Belt, 1967).

Three books have been written to date (Elwell and Gidley, 1962;, Robinson, 1966; Ramirez-Munoz, 1968) and another by Slavin (1968) is in press. An excellent bibliography is published periodically in the Perkin Elmer Atomic Absorption Newsletter.

The conclusion which is reached after the literature survey is that while atomic absorption spectroscopy has been applied to many isolated problems, there has been little attempt to assess its use as a method for general geochemical application, and fully understand its scope. Most scientists working on the application of atomic absorption to geochemistry have used ordinary commercial equipment with little attempt to make improvements for the special problems encountered in geochemical analysis.

Some of the work presented is similar to work published by other scientists active in this field. This is not surprising as atomic absorption is a field which is developing at an enormous rate and duplication is inevitable.

PART II. GENERAL

CHAPTER 2

THE ATOMIC ABSORPTION METHOD

2.1 PRINCIPLES OF THE METHOD

Atomic absorption spectroscopy is based on the phenomenon whereby atoms which are unbound chemically may absorb electromagnetic radiation at specific wavelengths. The energy of these wavelengths corresponds to the energy difference of electronic transitions between allowable levels j and i*

$$\text{i.e.} \quad \Delta E = Ej - Ei = \frac{hc}{\lambda}$$

where Ej and Ei are the energies of states j and i,

h is Planks constant,

λ is the wavelength of the radiation, and

c is the speed of light.

At relatively low flame temperatures (2000 - 3000°K) most atoms are in non-ionized ground states and consequently the wavelengths most easily absorbed are those corresponding to the energy transitions between the ground state and the first allowable level. This radiation is usually termed resonance radiation. An atom will rapidly radiate the absorbed energy at precisely the same frequency at which it was absorbed.

The experimental technique used to harness this phenomenon for analytical purposes consists of (a) a light source, which is usually a hollow cathode lamp radiating light characteristic of the analytical element, (b) an absorbing medium, usually a flame into which is nebulized a fine aerosol of the sample solution, and (c) a spectrometer for isolating the selected spectral

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* A list of the symbols used is given at the beginning of this thesis.

line and measuring its intensity. Fig. 2.1 shows a schematic diagram of the apparatus.

An analysis is carried out by adjusting the spectrometer, lamp current, flame conditions, and burner to optimum setting, for the element to be measured. A blank solution is sprayed and the spectrometer adjusted to zero absorbance. Then standard solutions, with known concentrations of the analytical element, are sprayed and the absorbance is recorded for each, to establish the relationship between concentration and absorbance, usually represented graphically. Sample solutions with unknown concentrations of the analytical element are sprayed and the concentrations estimated from the graph.

There are many factors contributing towards the process of absorption and consequently towards the accuracy, precision and sensitivity of the method.

(a) The amount of aerosol which reaches the flame depends on the nabulizer, the shape and size of spray chamber, the air or gas pressure, and the size of burner aperture which determines the gas flow rates.

(b) The number of aerosol droplets which are dehydrated to salt particles depends on the droplet size distribution, number of droplets, temperature of the flame, latent heat of fluid evaporation and velocity of the flame.

(c) The rate at which atoms are produced from the salt crystals depends on the boiling point of the salt, or the dissociation energy of the salt crystals and on the velocity of the particles.

(d) The final number of atoms which are available for absorption depends on all these factors as well as on the chemical characteristics of the element, the combustion properties of the flames gases, the burning velocities, and the flame temperature.

Most of the many variables are kept as constant as possible, so that the factors which would influence absorbance for the analytical element would be the same for the standards as for the analytical element. The physical parameters which influence absorbance, are generally not difficult to

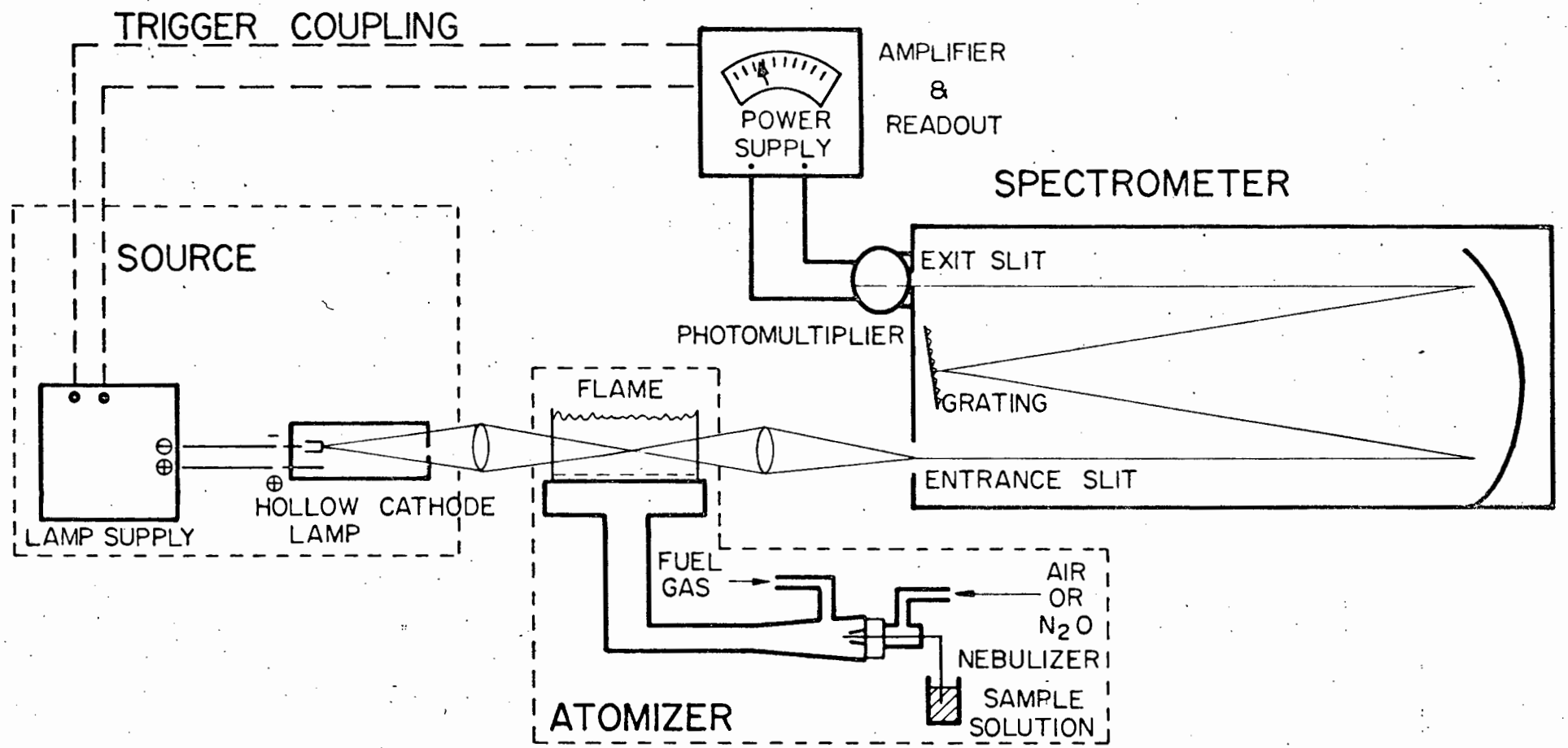


FIG. 2·1

Diagram of Atomic Absorption Apparatus.

PG4-1249

keep constant, but not so the chemical effects, especially where the compositions of the standards and sample differ markedly. In cases where the analytical element is not strongly affected by the presence of other elements, it may be possible to use aqueous solutions for standards. This is a significant advantage of the method, as it then becomes a semi-primary method, independent of pre-analyzed standards. However, in cases where chemical effects are present, there are several approaches, viz.:

(a) To use a flame which reduces or eliminates chemical and physical interferences;

(b) to add suppressing or inhibiting agents;

(c) to eliminate the interfering element by solvent extraction, precipitation or ion exchange; and

(d) to use standards which almost exactly match the samples in chemical composition.

All these factors have been studied in detail and their merits will be discussed later in this thesis.

2.2 THEORY

The treatment given here is to explain certain phenomena of atomic absorption spectroscopy and to provide a mathematical model. While the model may fail to encompass all the variables (e.g. chemical reactivity) it does form a basis for the understanding of the processes whereby atomic absorption occurs.

2.2.1 Concentration of Neutral Atoms

In an ideal atomic gas in thermal equilibrium the Maxwell-Boltzman theory may be applied with success to predict the states of partition of the constituents of the gas. This theory is also applicable in atomic absorption flames to explain the high sensitivity of the method, even though they may be far from the concept of ideal gases.

If the flame is considered to consist of an ensemble of atoms which have two allowable energy states E_1 and E_2

where $E_2 > E_1$

then the number of atoms N, in each state, may be given by

$$N_1 = Cg_1 e^{\frac{-E_1}{kT}}$$

and $$N_2 = Cg_2 e^{\frac{-E_2}{kT}}$$

The ratio is

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \cdot e^{\frac{E_1 - E_2}{kT}} \qquad \ldots\ldots\ldots\ (1)$$

where C is a constant independent of E,

k is the Boltzman constant,

T is the absolute temperature, and

g is the statistical weight of the energy level.

For a spectral term having a total quantum number

$$g = 2J + 1$$

In Table 2.1 this formula is applied to three elements to indicate that, at low temperatures, many more atoms are in a ground state than in all the other excited states together.

For resonance lines $E_1 = 0$ (the ground state)

and $E_2 = E_1$ (the first energy level)

also $N_1 = N_o$

$N_2 = N_1$

and $g_1 = g_o$

$g_2 = g_1$

$$E_1 - E_o = h\nu = \frac{hc}{\lambda}$$

where h is Planks constant,

c is speed of light, and

λ is the wavelength in air.

TABLE 2.1

Ratio $\frac{N_1}{N_o}$ for different temperatures

Line	Transition	$\frac{g_1}{g_o}$	Temperatures*	
			2000°K	3000°K
Na 5890	$^2S_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$	2	9.86×10^{-6}	5.83×10^{-4}
Ca 4227	$^1S_o - {}^1P_1$	3	1.21×10^{-7}	3.69×10^{-5}
Zn 2138	$^1S_o - {}^1P_1$	3	7.29×10^{-15}	5.58×10^{-10}

* The given temperatures 2000°K and 3000°K are similar to the temperatures of the propane-butane/air (1800°C) and the acetylene/nitrous-oxide (2800°C) flames respectively.

It can be seen that the number of atoms in the ground state far exceeds the number of atoms in the first excited state. When calculated for all higher energy states, i.e. N_1, N_2, where $N_1 << N_o$ and $N_2 << N_1$ etc. the ratio becomes considerably less so that

$$N_o >> \sum_{j=1}^{j=n} N_j$$

From these results the following conclusions can be drawn:

(a) Many more atoms are available for absorption than for emission, as absorption involves atoms in the ground state. Absorption spectroscopy should therefore be more sensitive than emission spectroscopy at lower temperatures. This has indeed proved to be the case, especially for elements having their resonance lines at shorter wavelengths, e.g. Zn and Cd (2138 and 2288 Å).

(b) N_1 is so small compared to N_o at low temperatures that it can be assumed $\frac{N_1}{N_o} \neq 0$ and that all the atoms may be presumed to be in a

ground state.

(c) While the number of atoms in the ground state remains fairly constant over a wide temperature range, the number of atoms in the energized or emitting state varies exponentially with temperature. Absorption measurements are therefore much less dependent on temperature. Matrix, interelement, solvent effects and change in combustion properties which change the temperature of the flame have much less effect on absorption than on emission spectroscopy.

2.2.2 Relationship between Absorption and Atomic Concentration

If parallel light from a continuous source passes through an atomic vapour and a portion is absorbed at a frequency ν, the Beer Absorption law holds

$$\text{i.e. } I_\nu = I_o.e^{-K_\nu .1} \qquad \ldots\ldots\ldots\ldots (2)$$

where I_o is intensity of original beam,

I_ν is intensity of transmitted beam,

K is absorption coefficient at frequency ν,

1 is absorption path length.

K_ν varies with ν, and when these two variables are compared graphically, a Gaussian distribution curve similar to that in Fig. 2.2 is obtained. The total width of the graph, where K_ν has fallen to half its maximum value is called the half breadth and is denoted by Δ_ν.

K_ν and Δ_ν depend on the nature of the atoms, their motion and their interaction either with one another or with foreign molecules. This will be discussed more fully in a later section.

2.2.3 The Einstein Theory in Radiation

Consider an enclosure containing isotropic radiation with intensity I_ν and with frequency distribution between ν and $\nu + d\nu$. This radiation passes through a cloud of atoms capable of being raised from a normal state 1, to an excited state 2.

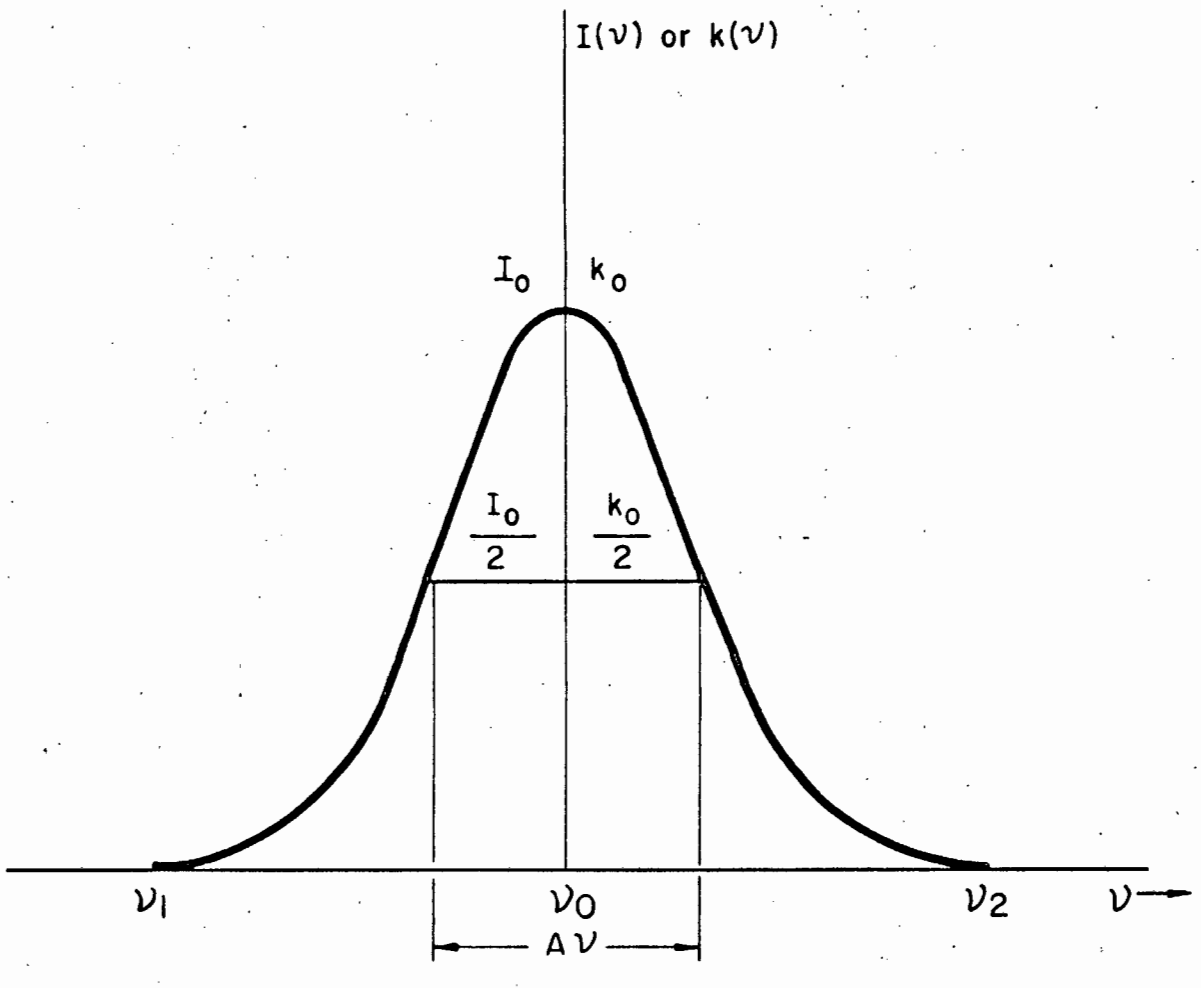


FIG. 2·2

Change of Absorption Coefficient (or Intensity) with Frequency.

Let $B_{1\rightarrow 2}.I_\nu$ = probability per second that atom in state 1 will absorb radiation quantum $h\nu$ and pass to state 2.

Let $A_{2\rightarrow 1}$ = probability per second that atom in state 2 will spontaneously emit quantum $h\nu$ in a random direction and pass to state 1.

Let $B_{2\rightarrow 1}.I_\nu$ = probability per second that the atom will undergo the transition $2\rightarrow 1$ and radiate a quantum $h\nu$ in the same direction as the incident quanta.

When these reactions are in thermodynamic equilibrium, Einstein showed that:

$$\frac{A_{2\rightarrow 1}}{B_{1\rightarrow 2}} = \frac{2h\nu^3}{c^2} \cdot \frac{g_1}{g_2} .$$

and $$\frac{B_{2\rightarrow 1}}{B_{1\rightarrow 2}} = \frac{g_1}{g_2}$$

where c is light velocity, and

g is statistical weight.

If Ψ is the lifetime of the atom in the resonance state 2, then

$$A_{2\rightarrow 1} \propto \frac{1}{\Psi}$$

$$= \frac{1}{\Psi} \quad \text{if the constants are correctly chosen.}$$

B coefficients may be defined either as radiation intensity or as radiation density, where

$$B \text{ (density)} = \frac{c}{4\pi} .B. \text{ (intensity)}$$

These Einstein probabilities are applied to the absorption by a layer of atoms dx thick with N normal atoms per ccm of which δ N are capable of absorbing radiation between ν and $\nu + d\nu$.

In this layer there are also N_1 excited atoms of which δN_1 are capable of emitting in this frequency range, and neglecting the effect of spontaneous re-emission in all directions, the energy of the original beam will

be decreased by:

$$-d\,(I_\nu \cdot \delta_\nu) = \delta N^o_\nu .dx.h.\nu.B_{1\to2}\cdot\frac{I_\nu}{4\pi} - \delta N^1_\nu .dx.h.\nu.B_{2\to1}\cdot\frac{I_\nu}{4\pi}$$

where $\frac{I_\nu}{4\pi}$ is the intensity of the equivalent radiation for

which $B_{1\to2}$ and $B_{2\to1}$ are defined,

then $$-\frac{1}{I_\nu}\cdot\frac{dI_\nu}{dx} : \delta_\nu = \frac{h_\nu}{4\pi}\{B_{1\to2}.\delta N^o_\nu - B_{2\to1}.\delta N^1_\nu\}$$

From equation 2:

$$K\nu.d\nu = -\frac{1}{I_\nu}\cdot\frac{dI_\nu}{dx}\cdot\delta_\nu$$

and by integration

$$\int K_\nu .d_\nu = \frac{\lambda_o^2 .g2}{8\pi .g_1}\cdot\frac{N_o}{\psi}\{1 - \frac{g_1}{g_2}\frac{N^1}{N^o}\}$$

but $$\frac{N_1}{N_o} \to o \quad \text{i.e.} \quad N_o \approx N.$$

then $$\int K_\nu .d_\nu = \frac{\lambda_o^2}{8\pi}\cdot\frac{g_2}{g_1}\cdot\frac{N}{\psi} \qquad \ldots\ldots\ldots\ldots \quad (3)$$

This equation gives the relation between the integrated absorption coefficient $K\nu$ and the number of atoms N. For one particular spectral line, ψ, λ_o, g_1, and g_2 are constant therefore

$$\int K_\nu . d_\nu = \text{constant} .N.$$

Since the intensities of spectral lines are usually expressed in terms of oscillator strength or f-values and not in terms of Einstein coefficients, it is necessary to determine the f-value and the lifetime ψ relationship.

2.2.4 Relation between f-values and lifetime

The f-value can be defined as the ability of an atom to absorb or emit light at a specific wavelength, as compared to the ability of the classical oscillating electron to absorb or emit light at the same wavelength.

From the classical electron theory

$$\int \frac{4\pi n.(n_K).d\nu}{\lambda_o} = \frac{\pi e^2}{mc}.N.f. \qquad \ldots\ldots\ldots\ldots \quad (4)$$

where n is refractive index (presumed = 1 for air),

n_K is the electron theory absorption coefficient and is related to the usual coefficient by

$$\frac{4\pi\ (n_K)}{\lambda_o} = K_\nu$$

e is electron charge,

m is electron mass.

Substituting for n_K, equation 4 becomes

$$K_\nu . d\nu = \frac{\pi e^2}{mc} . N.f. \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

If the oscillator strength f is known, then by substituting in the above equation, the atomic concentration can be calculated from the integrated absorption coefficient.

The relation between f-value and ψ can be calculated from equations 3 and 4

then $$\frac{\pi e^2}{mc} .N.f. = \frac{\lambda_o^2}{8\pi} . \frac{g_2}{g_1} . \frac{N}{\psi} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

and by substituting the values of the constants

$$\psi = 1.51 \ . \frac{g_2}{g_1} . \frac{\lambda_o^2}{f}$$

This equation allows the lifetime to be calculated directly from the f-value which can in turn be calculated from equation 5, a knowledge of the integrated absorption and number of atoms, N. Alternately, knowing all the constants including f, N may be calculated, but values for f are only known accurately for a few lines and then the values are not reliable.

The above theory deals only with the INTEGRATED absorption $\int K_\nu \, d\nu$. The absorption coefficient depends on the shape of the absorption line $\Delta\nu$.

2.2.5 Line shape and absorption coefficient

In the flame, which is the usual means for obtaining an atomic vapour, the shape, or broadening of the absorption line (see also Section 3.1.1), is almost entirely due to

(a) Doppler broadening;

(b) pressure broadening, which includes Lorentz and Holtzmark (Resonance) broadening.

The Doppler half width of a line may be calculated from the equation

$$\Delta \nu_D = \frac{2 \nu_o}{c} (\log 2. \frac{2 RT}{m})^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots \quad (8)$$

where ν_o is frequency at 1 mc centre,

T is absolute temperature,

R is universal gas constant, and

m is atomic mass.

Equation (8) has been applied to calculate the width of a number of lines.

TABLE 2.2

Values of D at various temperatures

Element	λ(Å)	m	ΔD_λ (Å)		
			1000°K	2000°K	3000°K
Na	5890	22.3	0.028	0.039	0.048
Cu	3247	63.6	0.0092	0.013	0.016
Zn	2138	65.4	0.0060	0.0085	0.010

If a temperature of 2000°K is required to produce an atomic vapour then the Doppler linewidth is of the order of 0.01 Å, but at 3000°K, it may be twice to three times that, i.e. 0.03 Å.

The absorption coefficient for Doppler broadening alone is

$$K_\nu = K_o e^{-\left(\frac{2(\nu - \nu_o)}{\Delta \nu D}\right)^2 \log 2} \quad \ldots\ldots\ldots (9)$$

where K_o is the maximum absorption coefficient at the centre of the absorption line.

Integrating equation (9)

$$\int_o^\infty K_\nu \, d\nu = \tfrac{1}{2}\left(\frac{\pi}{\log 2}\right)^{\frac{1}{2}} . K_o . \Delta\nu D. \quad \ldots\ldots\ldots (10)$$

But equation (5) gave

$$\int K_\nu \, d\nu = \frac{\pi e^2}{mc} . N.f$$

If equations (5) and (10) are combined:

$$K_o = \frac{2}{\Delta\nu_D} . \left(\frac{\log 2}{\pi}\right)^{\frac{1}{2}} . \frac{\pi e^2}{mc} . F.N. \quad \ldots\ldots\ldots (11)$$

Substituting the value for $\nabla \nu_D$ from equation (8) and also

$$\frac{c}{\lambda_o} \text{ for } \nu_o$$

$$K_o = \frac{1}{(2\pi R)^{\frac{1}{2}}} . \frac{\pi e^2}{mc} . \frac{\lambda_o}{(T/m)^{\frac{1}{2}}} . F.N. \quad \ldots\ldots\ldots (12)$$

or K_o = Constant. N.F. for a given spectral line and element.

The essential difference between equations (12) and (3) is that in equation (3) the integrated absorption $\int K_\nu \, d\nu$ gives a linear relationship with the number of atoms, whereas in equation (12) the absorption at the peak of the absorption line K_o does this.

To utilize equation (3), i.e. using a continuous radiation source, would require a spectrograph with very high resolution (500,000 or more) to resolve the absorption line. If, however, a sharp line source is used, then equation (12) is applicable.

Walsh (1955) suggested the use of a hollow cathode lamp which is known to give a very narrow emission line, and in this case it is not necessary

to resolve the absorption line.

2.2.6 The Voigt Function

Walsh originally suggested that equation (12) could be applied to calculate the number of atoms N and that this would place atomic absorption spectroscopy as an absolute method not requiring the use of standards, but only a knowledge of the oscillator strength f.

Rann (1967) has investigated this possibility in some very carefully planned experiments, using silver, copper and gold as elements which could be considered:

(a) Fully atomized in the flame;

(b) not prone to any element interferences; and

(c) with f values reasonably well known.

Curves of growth using calculated and measured values differed widely. His results proved that the assumption of absorption line shape being caused by Doppler broadening alone was erroneous.

Rann (1967) and Lapp and Gallagher (1967) have suggested the use of the Voigt function, which takes into account broadening processes caused by collision as well as Doppler and natural effects (see also Mitchell and Zemansky, 1961).

The Voigt equation for the absorption coefficient is given by

$$K_\nu = Ko.\frac{a}{\pi} \cdot \int_{-\infty}^{+\infty} \frac{e^{(-y^2)}}{a^2 + (w - y)^2} .dy \qquad \ldots\ldots\ldots\ldots \quad (13)$$

where $y = (\log 2)^{\frac{1}{2}} . \frac{2\,\delta}{\Delta\nu_D}$

$$\omega = (\log 2)^{\frac{1}{2}} \left(\frac{\nu - \nu_o}{D}\right)$$

and $$a = (\log 2)^{\frac{1}{2}} \frac{\Delta\nu_N + \Delta\nu_L}{\Delta\nu_D}$$

$\Delta\nu_N$, $\Delta\nu_L$, and $\Delta\nu_D$ are the natural, Lorentz and Doppler half-widths and δ is a variable distance from the point $(\nu - \nu_o)$. The parameter "a" is proportional to the ratio of collisional to Doppler broadening.

$\Delta\nu_N$ is so small that it may be considered insignificant.

Assuming a Voigt profile for both emission and absorption lines, and using a computer to evaluate the integral for various "a" values, Rann showed that calculated curves of growth closely matched experimental curves for the three elements mentioned (gold, copper and silver).

His conclusion, however, was that many controllable factors would limit the use of a formula to calculate the concentration of atoms causing absorption.

2.3 FLAME FACTORS

All the assumptions made in the model of the absorbing medium may be partly erroneous when the practical factors are considered.

The most serious cause of error could be that of presuming the absorbing medium to be a perfect gas, in thermal equilibrium. In practice, the absorbing medium is a highly chemically reactive flame into which many chemically reactive substances are being introduced. While conditions of local thermal equilibrium are presumed for the outer regions of the flame for temperature measurements, there is little doubt that thermal equilibrium does <u>not</u> exist in the reactive zones of the flame. The statistical assumptions may therefore be incorrect.

The number of atoms in the ground state may be depleted or increased depending on the presence of other elements or radicals, and this again may depend on the factors mentioned in 2.1.

It is therefore postulated that equation (12) may be modified to

$$K_o = C.f.\ e^{-(f(\phi b) + f(\phi p))}.N \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

where the functions $f(\phi b)$ and $f(\phi p)$ describe the influence of chemical reactivity of the analytical element b and the interfering element or radical p.

These functions may be positive or negative depending on whether the interference causes enhancement or depression, and will be different for

different flames and for different combustion conditions. In the case where no interference exists, both functions are zero.

The functions will be difficult to determine accurately except in certain isolated cases, and for practical purposes this will be unnecessary, although of interest academically.

The normal procedure of preparing analytical working curves is the acceptable solution to the problem of determining the concentration of atoms in an unknown sample, and works well.

2.4 CURVATURE OF THE ANALYTICAL GRAPH

One of the disadvantages of the atomic absorption method is the relatively limited useful analytical range, which is seldom more than two orders of magnitude, i.e. 1.0-100 ppm or 0.1-10 ppm.

This is caused by curvature from linearity of the graph of absorbance against concentration. (Note: When absorption $\frac{1}{T}$ is plotted instead of absorbance, $\log \frac{1}{T}$, curvature must result as the Beer law is an exponential function).

The reason for deviation may be seen in the Voigt plot of the absorbing line profile against the emission line profile. Fig. 2.3(a) shows the Voigt profile for a = 0.0 and various absorbance values.

Where the emitted line is broadened by Doppler broadening only, the a value = 0.

This may be presumed to be the case at low lamp currents, but as lamp currents increase, the "a" values increase because of collision effects. (Self absorption will also increase, but for the purpose of this argument it is presumed that lamp current is not increased to the stage where significant self reversal occurs in the lamp itself.)

The detection will indicate the signal shown as the shaded portion (Fig. 2.3(a)). It is seen that some signal will be measured even when maximum absorption occurs ($K_\nu = 6$). This will be greater for values of higher "a" (Fig. 2.3(b)), which will cause the emission line to broaden.

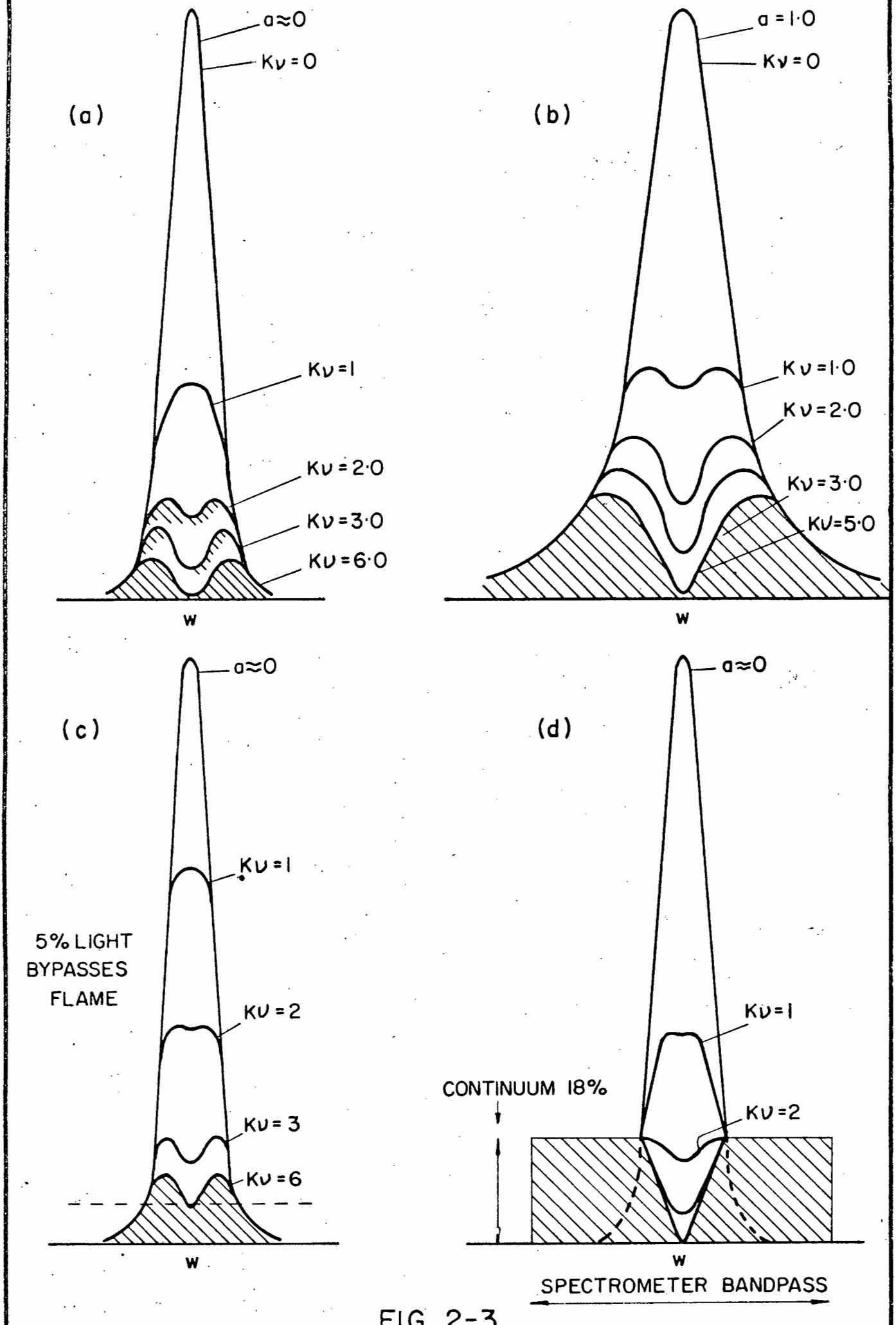


FIG. 2-3.

Voigt Plots of Emmission Line Profiles with Absorption.

Another factor which causes premature curvature of the analytical graph is when all the light from the cathode does not pass through the flame and consequently even at maximum absorption ($K_\nu = 6$) a signal is measured. This will, in effect, move the absorbance away from the co-ordinate, as shown in Fig. 2.3(c).

Similarly, if the source has a high background, the measured signal will be as shown in Fig. 2.3(d). By making the spectral band pass smaller, the curve can be made more linear, when background is high.

The Voigt distribution produces a symmetrical profile, whereas it is known that line profiles become asymmetric and are subject to wavelength shift at high levels of atomic concentration. This may well be a contributory reason for deviation of the working graph from linearity. (See also section 3.2.)

It is postulated that the use of selective modulation of the light from a hollow cathode lamp by another absorbing lamp, will improve the linearity, and thus the analytical range of atomic absorption. This is readily seen by studying Fig. 2.3(a). If the spectrometer "sees" only the <u>difference</u> between the graph where $K_\nu = 6$ (i.e. maximum absorbance) and the actual absorbance ($K_\nu < 6$) the difference will be very small and the actual absorbance; concentration graph, should be linear up to total absorbance of the line at the centre.

CHAPTER 3

APPARATUS

3.1 THE SOURCE

The source is one of the most important components of atomic absorption apparatus. This was realized early in the use of atomic absorption in South Africa, when commercial hollow cathode lamps were extremely unreliable. Not until hollow cathode lamps were self-built (Strasheim and Butler, 1962), could dependable results be obtained.

The requirements of the source for atomic absorption are:

(a) Narrow emission line profile;

(b) purity of spectrum (i.e. no interfering lines from other elements within the band pass of the spectrometer);

(c) sufficient intensity;

(d) constancy of emission;

(e) long life and low background.

3.1.1. Spectral Line Shapes

The factors which govern the shape of spectral lines hold for both emission and absorption. The processes which contribute are:

(a) Natural broadening due to the fact that the finite lifetime of the excited state is not the same for all atoms. It gives rise to such a small effect that for all practical purposes it may be ignored.

(b) Doppler broadening is due to the motions of the atoms as a result of thermal activity. Similarly excited atoms will radiate similar frequencies, but when they are moving at different velocities in different directions, the frequencies reaching the observer will have a distribution (Maxwellian) with a halfwidth

$$\Delta\nu_D = 2(2 \log 2. \frac{RT}{mc})^{\frac{1}{2}} \quad . \quad . \quad cm^{-1}$$

For a given atom line

$$\Delta\nu_D = 1.67. \frac{}{c} (2 \frac{RT}{m})^{\frac{1}{2}}$$

$$= \text{Const. x } T^{\frac{1}{2}}$$

If narrow lines are required it is therefore necessary to keep the temperature as low as possible. This is done by keeping the lamp current low. With a properly designed hollow cathode lamp, a current of 5-10 mA should provide sufficient intensity and give little Doppler broadening.

(c) Lorentz broadening is caused by collisions of the excited atoms with foreign gas particles, and, as not all atoms are affected similarly, broadening and line shift results. Forces acting are of the Van der Waal type, i.e. inversely proportional to distance $()^6$.
It has been seen (in Chapter 2.2.6) that Lorentz broadening plays an important role in the flame, but in the hollow cathode lamp where low gas pressures are used, Lorentz broadening is relatively small, affecting the emission line to be broadened little more than 0.01Å.

(d) Holtzmark (or Resonance) broadening is also a collisional effect, but is due to collisions of the radiating or absorbing atoms with each other. At low atomic pressures or low concentrations of atoms, the broadening effects are relatively small. At higher atomic pressures the collision, and thus resonance processes, cause significant broadening and distortion of the line shape. In a hollow cathode lamp operating at low current, Holtzmark broadening is small. In an atomic absorption flame however, Holtzmark effects may cause the absorption line to shift and cause bending of the analytical graph.

Lorentz and Holtzmark broadening collectively are often called Pressure Broadening.

(e) Stark effect broadening is caused by non-uniform electrical fields perturbing the energy levels of emitting atoms. Little Stark effect broadening is found for the absorption line in the flame. In sources where strong electrical field gradients are present, e.g. high voltage spark, Stark effect broadening is appreciable. In the hollow cathode lamp, however, in the negative glow region, the electrical potential gradients are very low, consequently, spectral lines originating in this region show little Stark broadening. Stark broadening will cause atoms with low mass numbers to be affected more than those with high mass numbers, e.g. the lines from a lithium lamp are not as sharp as those from a gold lamp. Some electrical fields exist in the flame and are caused by the presence of ions and electrons (Gaydon, 1957) and although appreciable, they are randomly distributed.

(f) Self-absorption broadening is due to absorption of radiation by non-radiating atoms in the source. For sources of extended depth such as hollow cathode lamps or Geissler tubes, broadening depends on the length of the non-emitting atomic cloud through which the radiation must pass. The intensity of an emission line, at the centre of the line decreases and the intensity in the outer regions remains the same.

The halfwidth of a line has already been defined as

$$\nabla\nu = \frac{I_o}{2}$$

If I_o is decreased only at ν, $\nabla\nu$ becomes larger and the line emitted by the source is broadened.

The emitted line may be similar to the line shown in Fig. 2.3(a) where $K\nu = 1$.

This type of broadening is only evident in emission sources and can be reduced by shortening the source length and vapour concentration.

In hollow cathode lamps, self absorption can cause the line to be severely changed and this has an influence on sensitivity. For this

reason it is necessary to reduce cathodic sputtering to a minimum by working at as low a lamp current as possible.

Another means for reducing self absorption is to concentrate the discharge into the centre of the cathode. This may be done by reducing the front diameter of the cathode or limiting the discharge with a non-conductive material.

3.1.2 Hollow Cathode Lamps

The hollow cathode lamp has been found to be the most satisfactory source for atomic absorption. A great deal of published data exist (Slavin, 1968), describing hollow cathode discharges and explaining the various factors of importance in their design.

Small sealed hollow cathode lamps are obtainable commercially from several overseas firms. Although the design of these lamps is similar, performance and lifetime characteristics often differ considerably. As the shelf-life of hollow cathode lamps is limited, large stocks of lamps are seldom held in South Africa.

The ability to manufacture lamps in the laboratory has thus been of considerable advantage, as new lamps or special lamps can be made at short notice.

Most of the lamps used for this thesis were self-built. Although the techniques used have been described in previous publications (Strasheim and Butler, 1962; Butler, 1963), certain improvements have been made. The purpose of this section is to describe these improvements and to sketch the technical details of manufacture. As much of the "know-how" is not available, the methods used are the result of many years of experiment.

(a) Lamp construction: The latest design of lamp is shown in Fig. 3.1. The cathode is formed from a cylinder of the analytical element, closed at one end, Fig. 3.1(a).

In cases where the element has a low melting point, the cylinder

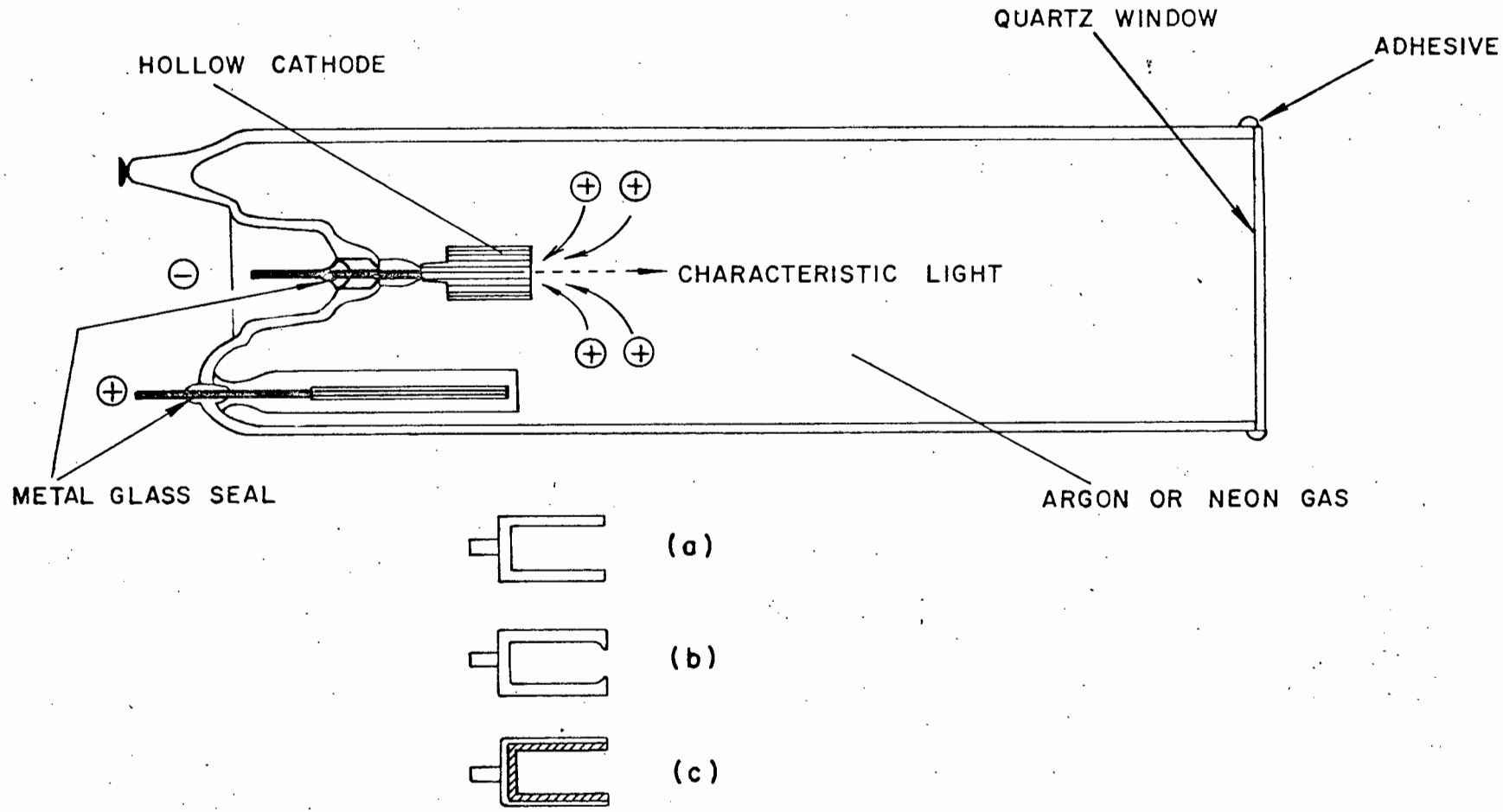


FIG. 3-1.

Diagram of Hollow Cathode Lamps and Cathode Types.

is made from a stable metal such as copper or stainless steel. The analytical element is then introduced as chips or powder and melted To prevent molten metal from running out of the cathode, the front is partly closed. This also has the effect of concentrating the discharge and reducing sputtering from the molten metal. When a lamp of a precious metal is required, a thin liner of the metal is placed inside a carrier cathode as shown in Fig. 3.1(c).

The metal feed through for the electrical connection to the cathode or anode has, in the past, been tungsten sealed into a pyrex glass tube. Because of the difficulty of making a satisfactory metal-to-glass seal, and because of the difference in the expansion properties of the two materials, an intermediate uranium glass has been used. Although these seals withstand much larger thermal changes, many lamps still fail because of glass cracking at the seal. For this reason "Kovar" (28% nickel, 18% cobalt, rem. iron) is now being used with a specially manufactured glass with similar expansion properties.

TABLE 3.1

Coefficient of Expansion for Materials used for Hollow Cathode Lamps

Material	Coefficient of Expansion (Linear) for range 20-300°C
Tungsten	4.6
Kovar (28% Ni, 18% Co, 54% Fe)	5.0
Pyrex type glass	3.2
Schott 8243 (special sealing glass)	5.0
Fused quartz	0.54

The cathode, which is relatively massive, requires a sturdy seal to provide rigidity and prevent fracture of the seal.

The cathode cylinder is attached to the feedthrough by means of a small brass threaded section which is hard-soldered to the metal

feedthrough.

The anode is used to hold the "getter". This metal, zirconium or titanium, which absorbs foreign gases at higher temperatures, is spot welded to the anode feedthrough. If the polarity of the electrodes is reversed and the anode operated as the cathode, it becomes very hot, absorbing any hydrogen or other gases which may have leaked into the lamp. In this way the background radiation may be reduced and the lifetime of the lamp extended.

An important detail of construction is the sealing of the quartz plate to the glass tube. Fused quartz has a different coefficient of expansion (Table 3.1) from the other materials. If a quartz window is used, the sealing material should have sufficient plasticity to prevent cracking and leakage of gas at this point. Dow Corning 806A-Resin adhesive has been found to work satisfactorily although it is necessary for the end of the glass tube to be polished flat and smooth. Plasticized epoxy resins have also been used, but curing time is relatively long.

At present, experiments are being conducted to replace the adhesive with a graded quartz-to-glass seal which will enable the quartz window to be melted or "glass soldered" directly onto the tube.

A glass connecting piece and a vacuum tap enable the lamp to be connected to a vacuum system.

(b) Lamp filling and conditioning

The cathode is connected to the "feedthrough" inside the lamp. In cases where the element is one which is easily oxidized or readily forms hydrides, e.g. calcium or lithium, the whole procedure of charging the cathode with the metal and attaching the quartz or glass window is done within a special transparent glove box (Plate 1). The box is evacuated and flushed with dry argon or nitrogen. The lamp may be

PLATE I.

The Glove Box used for handling Elements which are Affected by Air or Atmospheric Water Vapour.

partly evacuated in the glove box by means of a rotary pump and connecting tubes. Once the window has been attached, the lamp is connected to the vacuum system and thoroughly evacuated. The glass components should be treated in a vacuum oven at 600°C to drive off absorbed water beforehand and the lamp should be made as soon as possible after this.

The cathode is heated by cathodic sputtering to a temperature as high as possible without melting the hard solder. Many metals defy outgassing at temperatures below 500°C. under high vacuum. The ideal would be to heat the cathode with an induction furnace under high vacuum. As an induction furnace is not available, it is heated by operating the lamps on the vacuum system, using a relatively high current at low gas pressure. While the cathode is still hot the lamp is strongly evacuated. Some elements, notably the alkalis, the alkaline earths, and metals which absorb gas, require the process to be repeated several times. When no background is seen, the lamp is filled with spectroscopically pure (99.999%) argon or neon at pressures 1.5-2.0 or 5.0-7.0 Torr respectively. The pressure is critical and depends on the cathode material, cathode dimensions and anode to cathode distance.

The type of carrier gas used depends on the element being excited. Although argon has been used for most lamps, neon has been found more satisfactory for many elements e.g. copper, lead, iron. Not only is the background lower, but intensity of the resonance lines is higher. Spectral interference of carrier gas spectral lines with those of the analytical element, in some cases, prevent one or other of the gases from being used.

3.2 THE SPECTROMETER

The requirements for the spectrometer used for atomic absorption spectroscopy

are:

(a) It should transmit light from at least 2000 Å or less to 10,000 Å.

(b) It should have sufficient dispersion to separate closely adjacent spectral lines. A minimum band pass of about 2 Å is necessary to separate the resonance lines of iron, cobalt, nickel and chromium from other non-resonant lines.

(c) It should have a relatively high aperture to transmit the low light intensities from hollow cathode lamps.

(d) The wavelength must be reproducibly adjustable and have minimum backlash.

(e) It should have reproducible adjustable slit openings.

(f) It should have a good line to background factor.

Generally the instruments sold as atomic absorption spectrometers meet most of these specifications.

Two types of dispersive media are used in commercial spectrometers, viz.:

(a) Prisms. These provide relatively uniform intensity over the whole wavelength range, but the dispersion changes with wavelength, the dispersion and resolution being considerably poorer at long wavelengths.

(b) Gratings. Linear dispersion over the wavelength range is obtained, but intensity of reflectance changes. The intensity depends on the blaze angle. Broad blaze gratings have reduced this difficulty by spreading the reflectance over a wider range.

During the course of several years it has been possible to test both types of dispersive media using several different makes of spectrometer. The tests have indicated that, for the general application of atomic absorption to the detection of as many elements in the periodic table as possible, grating spectrometers are better suited than prism spectrometers. An example of one of the tests is given below:

3.2.1 Test of monochromators

Several solutions were prepared of ainc, copper, calcium, sodium and potassium. The resonance spectral lines of these elements cover the spectral range from 2138-7665 Å. The solutions were sprayed under identical conditions using two different monochromators, viz. a Zeiss PMQ II and a Techtron AA3. This was done by adapting the Zeiss spectrometer to work with a modulated hollow cathode lamp and interchanging all the components for each set of measurements, i.e. burner, nebulizer and lamp. The results of this test are shown in Table 3.2

TABLE 3.2

Comparative Absorbance Values of Various Elements Using Grating and Prism Spectrometers

Element	Wavelength Å	Conc. ppm	Techtron				Zeiss			
			Disp. Å/mm	Slit micron	Band Å	Abs.	Disp. Å/mm	Slit micron	Band Å	Abs.
Zn	2138	0.1	33	200	6.7	.014	19	200	3.8	.015
		0.5				.066				.066
		1.0				.133				.134
		5.0				.641				.640
Cu	3247	0.5	33	50	1.7	.032	92	50	4.6	.030
		2.5				.15				.15
		5.0				.30				.29
		20.0				.92				.86
Ca	4228	0.5	33	50	1.7	.035	210	50	10.5	.025
		2.5				.145				.120
		5.0				.268				.219
		10.0				.425				.370
Na	5890	0.5	33	50	1.7	.067	590	50	29.5	.05
		2.5				.315				.12
		5.0				.555				.30
		10.0				.86				.495
		0.5						10*	5.9	.055
		2.5								.24
		5.0								.421
		10.0								.656
K	7665	1.0	33	200	6.7	.06	1200	200	240	.032
		5.0				.299				.145
		10.0				.58				.22
		1.0						50*	60	.045
		5.0								.226
		10.0								.340

*Minimum slit value at which stable measurements could be made.

The bandpasses used were those recommended for the elements listed. For the sodium and potassium measurements on the Zeiss, two sets of readings were taken, one set at the same slit setting as the Techtron, and the second with as narrow a slit as possible without introducing fluctuations by increasing the gain of the amplifier.

The bandpass of each instrument was calculated from:

$$\text{Bandpass} = \frac{\text{Dispersion at wavelength (Å/mm)}}{\text{Slitwidth (mm)}}$$

The dispersion of the Techtron is linear at 33 Å/mm, and the dispersion of the Zeiss which varies with wavelength was read off a graph obtained from the manufacturers.

(a) Results: The results of this test show:

(i) Once sufficient resolution is provided to isolate the resonance line, no gain in sensitivity is obtained by increasing resolution. The resolution of the prism spectrometer is greater at the zinc wavelength than the grating spectrometer, but sensitivity is the same.

(ii) A considerable increase in sensitivity is obtained with the grating spectrometer for potassium and sodium. The calibration curve is also far more linear. This may be attributed to the higher resolution.

(iii) Even at those wavelengths, where the dispersion is similar, the line to background ratio of the grating spectrometer is better than the prism instrument. This may be because of the Littrow mounting used in the Zeiss, whereas in the Techtron an Ebert mounting is used.

These results indicate that a grating monochromator is better suited for obtaining higher sensitivity and a longer concentration analytical range in the visible and red regions of the spectrum. A dispersion of 30 to 40 Å/mm with a resolution of 32,000 is considered a minimum.

For all the work described in this thesis, two types of atomic absorption spectrometers were used:

(a) A Techtron AA-3 which was later converted to an AA-4.

(b) A Perkin Elmer model 303 double beam.

Although other instruments were used and tested, these two instruments were found to be the most suitable for geochemical applications.

The Techtron AA-4 readout operates with a lock-in amplifier. The pulse which triggers the lamp (frequency 285 cycles/sec) also triggers the amplifier. This electronic system provides an electronic band which is very small as only the 285 cycle frequency is eventually amplified, and registered on the readout meter. No emission from the flame reaches the meter, even when a highly luminous acetylene/nitrous-oxide flame is used.

The Perkin Elmer 303 makes use of a relatively broad band amplifier (50 cycles/sec), but the band pass is not so narrow that flame emission will normally cause any difficulty. It is only when a highly luminous acetylene/nitrous-oxide flame is used that care must be exercised to prevent saturation of the amplifier. If a narrow slit is used in conjunction with this flame the difficulty is avoided.

The standard photomultiplier supplied with the Techtron (Hamamatsu R 106) was replaced with an R-136, which has higher sensitivity in the red region of the spectrum. However, even with this photomultiplier, sensitivity for the deep red regions is poor. A special holder was made so that when caesium was determined, a photomultiplier with an S-1 (red sensitive) cathode was used.

The Perkin Elmer has two gratings with blaze angles to give maximum reflectance at 2500 Å and 5000 Å respectively. This feature is of decided advantage when the alkali metals, which have their most sensitive lines in the red region of the spectrum, are to be determined.

Apart from the hollow-cathode lamps and burners, the instruments

used for all the analytical work in this thesis were standard.

3.3 THE FLAME

In atomic absorption spectrometry the flame has proved to be the most convenient and popular means for bringing a sample into the required atomic state. In spite of its usefulness, the flame is the source of most of the difficulties which are experienced in applying this technique to geochemical analysis. It is not surprising, therefore, that much attention has been given to the understanding of the chemical and physical processes of combustion, as well as to the reactions which involve metallic species in flames (Pungor, 1967).

When atomic absorption was first suggested, a pre-mixed coal-gas/air flame, burning from a simple Meker burner, was used. The disadvantages of the burner's short length, the low flame temperatures, and the difficulty in controlling combustion conditions, rapidly led to the use of a pre-mixed acetylene/air flame burning from a long, narrow, slot burner. This type of flame has been, and remains, the most popular for the determination of the majority of elements.

Relatively high temperature hydrocarbon/oxygen and alkyne/nitrous oxide flames have been shown to have significant advantages, especially with regard to enabling those elements which form stable refractory oxides, to be determined. Forced diffusion or total consumption hydrogen/oxygen flames have also been used, but these flames have not proved to be very successful, mainly because of the difficulty in controlling combustion, the short flame length and interference difficulties.

The use of the lower temperature pre-mixed flames has the advantages of high sensitivity (Butler, 1962) - see Section 2.2.1 - and freedom from "ionization interference". This interference occurs when an element or radical with relatively low ionization energy is introduced into a high temperature flame, together with the analytical element. The resultant increase in electron pressure causes reactions of the type

$$x^+ + e^- \rightarrow x^o$$

where x^+ is an ionized atom of the analytical element. The result is a shift in the equilibrium state of ionized and neutral atoms towards the state of lower energy (and temperature) and more neutral atoms are available for absorption. This causes an absorption enhancement. The low temperature flame suffers from chemical interferences, and certain elements and compounds fail to be sufficiently atomized at the relatively low flame temperature.

With the use of higher temperature pre-mixed flames, many of the chemical interferences experienced with low temperature flames, are overcome. When acetylene is used as fuel, with either oxygen or nitrous oxide, the chemical reactions in the flame are conducive to the determination of refractory elements. However, ionization interference may be a serious obstacle, especially in geochemical analysis where solutions with relatively high concentrations of alkali metals are nebulized into the flame.

The aim of the work described in this section was to investigate thoroughly the flames used in atomic absorption to determine their advantages and disadvantages. An attempt was also made to develop a "universal" flame, with temperature and atomic absorption properties intermediate between the low and high temperature flame types. This would give a flame which would combine their advantages and reduce their disadvantages. In practice, such a flame would reduce the number of burners and gases which must be kept at hand if a wide range of elements is to be determined.

The proposed fuel was commercial propane-butane gas (sold in South Africa as "Handigas") consisting of 40% butane and 60% propane. The oxidizing gas was nitrous oxide. The flame from this gas combination was studied in detail.

Certain tests were also carried out on the use of acetylene with nitrous oxide diluted with various amounts of air. The flame from this mixture was described by Fleming (1967) who showed that several interferences on

magnesium could be overcome by its use. His results and those obtained from the experiments described below indicate that this flame holds much promise as the envisaged "universal flame".

3.3.1 Flame Velocity Measurements

An important consideration regarding the choice of a flame in analytical flame spectrometry is safety in use. The lower burning velocity of the acetylene/nitrous oxide flame in comparison with the acetylene/oxygen flame has been an important factor in the successful, and safe use of this flame.

The flame velocities of several flames were determined using standard Techtron burners. The method used was the particle-track method, described by Lewis and von Elbe (1951), and Alkemade (1954). A diagram of the apparatus is shown in Fig. 3.2. The burner was positioned side-on to the optical axis and a clear glass screen interposed between the camera and the flame to prevent flame fluctuations caused by the 3000 rpm rotating disc. Very fine particles of iron were introduced into the gas stream and the resulting incandescent tracers photographed through the rotating disc. In order to obtain an accurate measurement of the tracer lengths, a ruler with a fine scale was photographed, without the flame burning, and placed vertically at the burner slot. Care was taken not to disturb the apparatus, and thus the magnification, before photographing the flame with the tracers. The photographs showed the tracers as a number of short lines separated by dark spaces. The distance from the start of one line to the start of the next was used to calculate the flame velocities. This was done as follows:

Speed of rotation = 3000 rpm = 50 rev/sec.

The disc has 8 slots $\therefore$ slots are separated in time by

$$\frac{1}{8} \times \frac{1}{50} = \frac{1}{400} \text{ sec.}$$

$$\text{Velocity} = \frac{\text{distance (cm)}}{\text{time (sec)}}$$

$\therefore$ Velocity of particle = 400 x (length of tracer + dark space)

By enlarging the negative 20 times, the distances could be

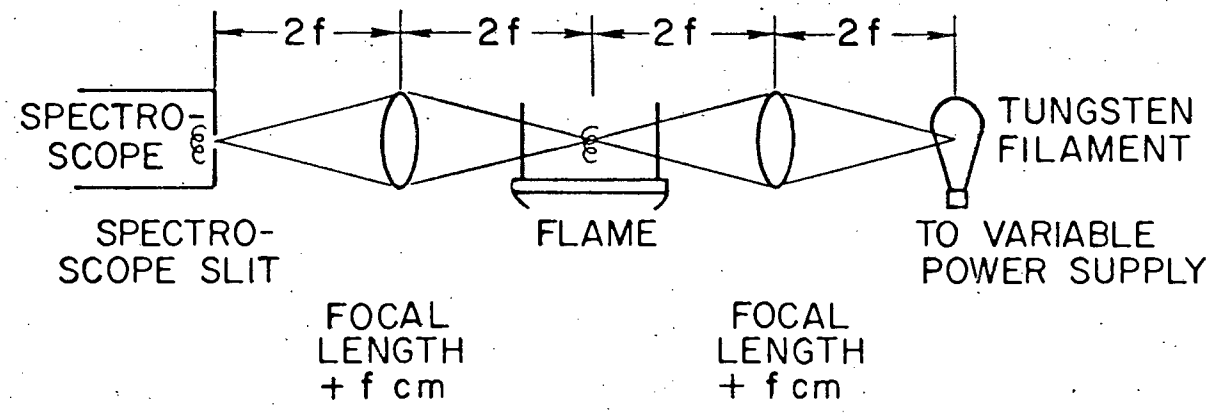


FIG. 3-3.

Diagram of Optical Arrangement for Flame Temperature Measurement.

measured to an accuracy of 3%.

It was assumed that the particle velocity is the same as the velocity of the gas which carries it. This assumption was found to be inaccurate as some larger particles gave lower velocities than smaller particles. For this reason, only the higher velocities were considered representative of the flame velocity. If an error is still present, the measured velocities should be lower than the true velocity of the flame. However, measured values are higher than the values published by Amos and Willis (1966),

Flame velocity of a given gas combination depends on:

(a) The initial temperature of the mixture;

(b) the size and shape of the orifice through which the mixture is issuing, and

(c) the heat conductive properties of the burner jaws and their smoothness.

The results of these measurements are given in Table 3.3 together with values published by Amos and Willis.

TABLE 3.3

Burning Velocities of Various Flames

Fuel	Support	Height Range of Tracers above Burner cm	Burning Velocity cm/sec	
			Measured	Published
Acetylene	air 100%	1.1 - 3.9	286	160
Acetylene	air 85% N_2O 15%	1.3 - 4.5	317	
Acetylene	air 9% N_2O 91%	5.5 - 10.4	658	
Acetylene	N_2O 100%	5.0 - 8.4	680	180
Propane-butane	N_2O 100%	0.7 - 5.1	296	

Discussion of Results

(a) The measured velocities exceed the published values of Amos and

Willis by a factor of 1.8 for the acetylene/air and 3.6 for the acetylene/nitrous oxide flame. This can be attributed to the different method of measurement and a difference in the types of burners.

(b) A large difference exists between the burning velocities of the acetylene/air (286 cm/sec) and the acetylene/nitrous oxide flames (680 cm/sec). This difference is strongly supported by practice, as the acetylene/nitrous oxide flame will flash back very readily on a burner designed for acetylene/air.

The results are confirmed by a crude test of burning velocity, viz. that of reducing the gas flow through the burner until flash-back occurs and then calculating the gas velocity at the burner orifice.

(c) It is seen that the burning velocities of the acetylene/air and the propane-butane/nitrous oxide flames are similar. This confirms experience that the latter flame can burn on a standard acetylene/air burner with safety.

(d) The burning velocity of the "mixed flame" i.e. nitrous oxide + air, increases rapidly as the nitrous oxide content of the mixture is increased. For safety reasons it is advisable when using this mixture to use a high temperature burner.

The reason for the increase in burning velocity is probably because a higher ratio of nitrous oxide gives rise to more molecular oxygen in the primary combustion zone.

3.3.2 TEMPERATURE MEASUREMENTS

The process whereby sample aerosol droplets, sprayed into a flame, reach the stage of free atoms is not clear. It is certain, however, that the temperature of the flame plays an important role in dehydration of the droplets, and dissociation of the salts. It is also known that droplet size is important for

the atomizing process (Willis, 1967).

As temperature is an important parameter, measurements of the temperature gradients in several flames were made, using standard burners.

The method used was the wellknown spectrum line reversal method (Reck et al, 1956: Gaydon and Wolfhand, 1953), using sodium as the element introduced into the flame. This technique measures only the effective electronic excitation temperature, not the translational temperature. As departure from thermal equilibrium is significant mainly in the primary reaction zone, the method is accepted as reliable for measurements in other flame zones.

It was found that the apparent temperature varied with sodium concentration. Above 1000 ppm, temperatures measured in the acetylene/air flame remained constant with increasing concentrations of sodium. With the propane-butane/nitrous-oxide and the other "hot" flames a temperature plateau was not reached. A concentration of 1000 ppm was thus selected. The temperatures measures in the"hot" flames must therefore be considered relative to the acetylene/air flame temperature.

A schematic diagram of the apparatus is shown in Fig. 3.3. The lamp used was a 24 volt 150 watt quartz iodine lamp which could be over-run by 15% without melting the filament. In this way, source temperatures of up to 2900°C could be obtained. It was suspected that this type of lamp might give rise to a non-continuous spectrum, but comparison tests with a standard strip filament lamp gave identical temperatures. Both filaments suffered from local uneven heating, but as a visual spectroscope was used for comparing intensities of the 5890 and 5897 Å sodium lines with the continuum at these wavelengths, it was possible to select only the brightest part of the filament.

The filament temperature was measured by means of an optical pyrometer calibrated by the "gold-point" method (Carte, 1954).
Errors due to the change in emissivity of tungsten with wavelength are cancelled out by light losses at the first lens.

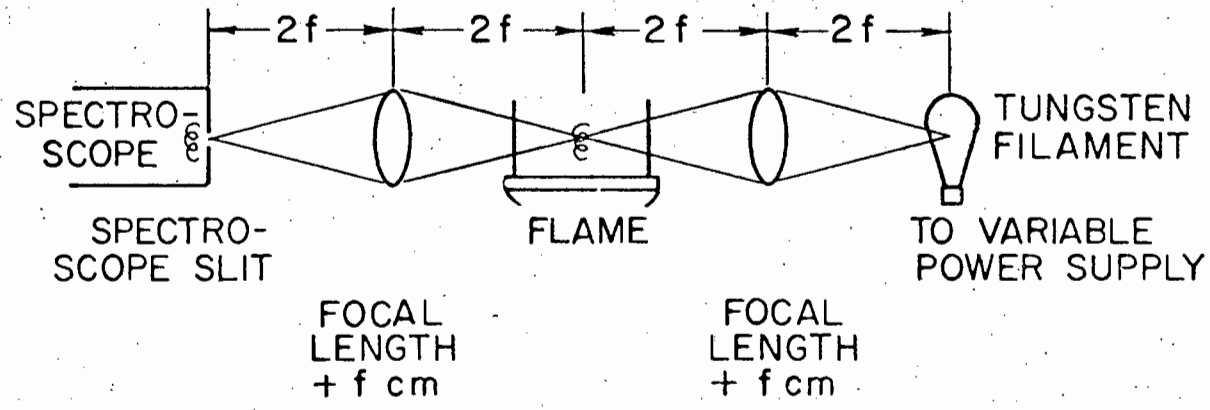


FIG. 3-3.

Diagram of Optical Arrangement for Flame Temperature Measurement.

The optical arrangement was found to be critical. It was essential that the solid angle of light subtended by the filament was identical to that subtended by the flame. Consequently, a reduced image of the filament could not be formed in the flame. As a result, the temperature values obtained did not pertain to as small a portion of the flame as desired. Overall precision of measurement was calculated for different temperatures and found to be approximately $\pm$ 1%. The values accepted were the average of at least four measurements.

Fig. 3.4 shows the temperature profiles of the propane-butane/nitrous-oxide flame under two burning conditions with the acetylene/air flame for comparison. Similar profiles were obtained for the other flames. The maximum temperatures measured in various flames are shown in Table 3.4.

TABLE 3.4

Maximum Spectroscopic Temperatures of Atomic Absorption Flames

Flame Type	Max. Temp. °C	Height above Burner Edge (mm)
1. Acetylene/Air, Fuel Rich	2060	8 - 12
Acetylene/Air, Stoichiometric	2150	2.0
Acetylene/Air, lean	2145	0.5
2. Propane-Butane/Nitrous-oxide, Rich	2480	10 - 14
Propane-Butane/Nitrous-oxide, Stoichiometric	2550	4
Propane-Butane/Nitrous-oxide, Lean	2535	0.5
3. Acetylene/Nitrous-oxide, Stoichiometric	2795	4
Acetylene/Nitrous-oxide, Lean	2740	0.5

In Fig. 3.5 is shown a diagram of the apparatus developed for the mixing of the nitrous-oxide and air. The flowmeter tubes used were standard "Rotameters", type 7X and 7, with A series floats. By using these tubes, which have a flow ratio of 8:10, the density factor differences between nitroux-oxide and air is very nearly compensated, i.e. 0.81 : 1.0 respectively The linear metric calibration can thus be used to indicate the relative

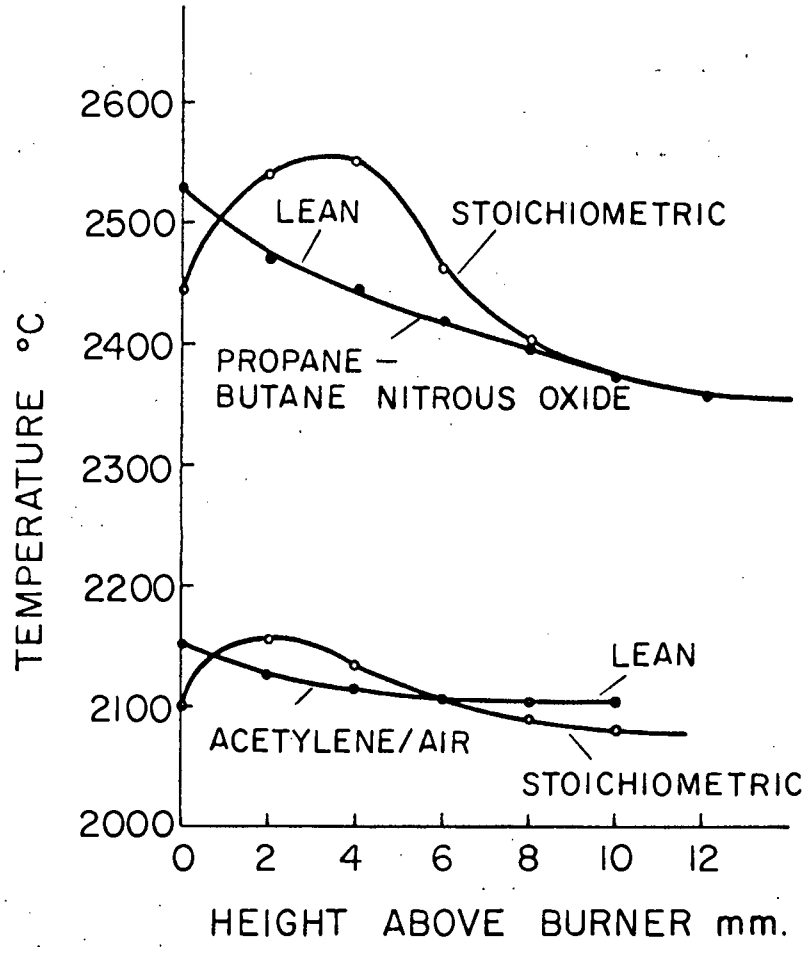


FIG. 3-4.

Temperature Profiles of Prop-But/N_2O C_2H_2 / Air Flames

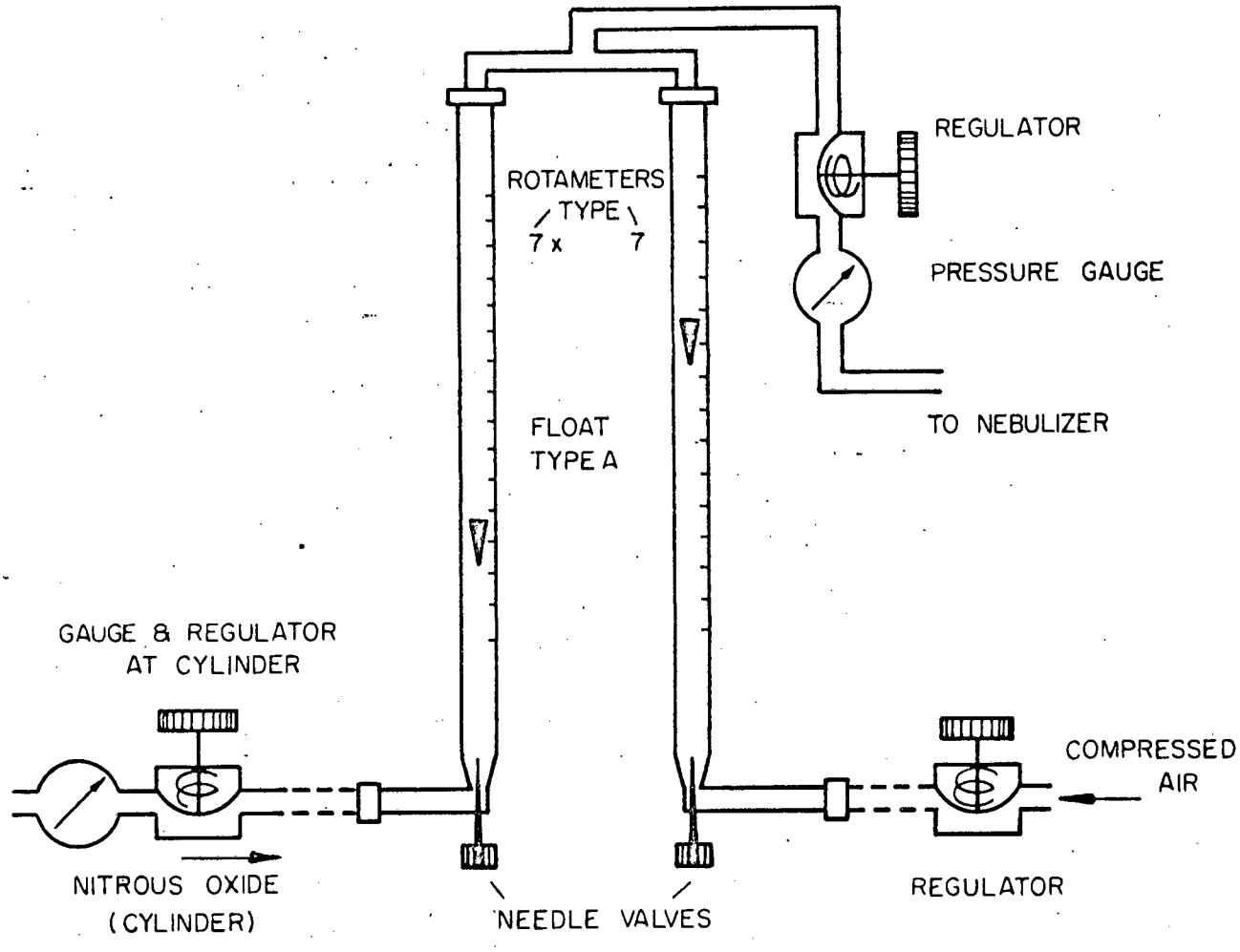


FIG. 3-5.

Gas Control Apparatus for varying N_2O and Air Ratios.

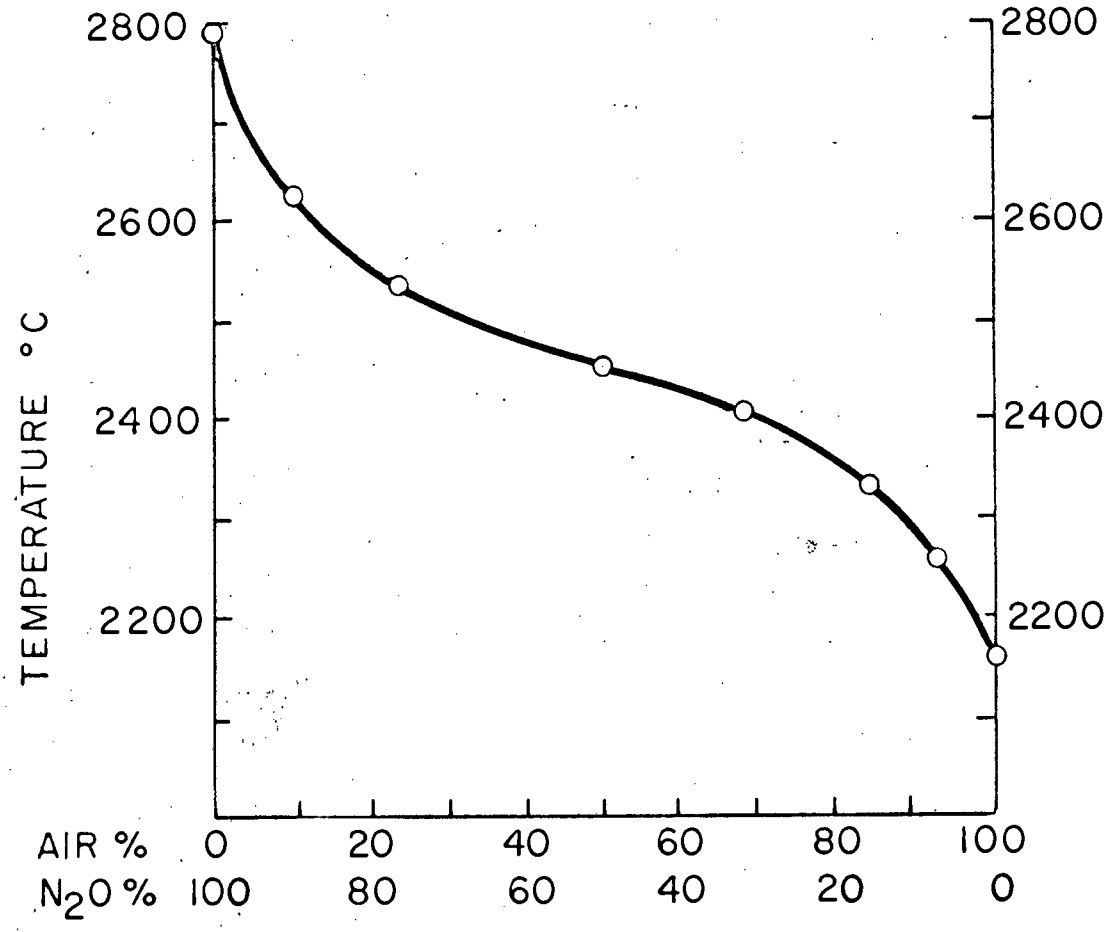


FIG. 3-6.

Change of Temperature of Mixed Flame with change in Gas Ratios.

TABLE 3.5

Comparison of Acetylene/Air Flame (Stoichiometric Temperatures, Measured by Various Methods

Temp. °C	Method	References
2150	Na 5890, 5896 line reversal	Butler and Fulton (1968) Nr 61
2237	"	Alekseeva (1947) 9
2232	"	Shuler (1950) 212
2000	"	Rann (1967) 194
2199	"	Alkemade (1954) 10
2257	K 4044.1, 4047.2 line reversal	Alekseeva (1947) 9
2257	Tl 5350.5 line reversal	" 9
2202	Li 6707.8 line reversal	Wolfhard (1939) 271
2327	OH rotational spectra ($A^2\Sigma$)	" 271
2247	Calculated thermodynamically	Gaydon (1948) 103

Discussion of Results

(a) It is interesting to note that the maximum measured temperature of the acetylene/nitrous-oxide flame is nearly 2800°C. which is lower than the value of 2950°C measured by Parker and Wolfhard (1952). Although this can be attributed to the relatively large image of the filament in the flame, which results in an "average" temperature that may be lower than the local maximum temperature at the small region separating the two flame zones, it is felt that the value obtained is not inaccurate. This has been confirmed by Willis (1968) who measured a similar temperature.

(b) It is evident that the temperature of the acetylene/nitrous-oxide and air flame may be varied quite easily between 2150°C and 2800°C. This feature is of fundamental importance for a "universal" flame, where temperature can be adjusted to provide optimum sensitivity and freedom from interference for a particular element.

(c) The temperature of the propane-butane/nitrous-oxide flame is intermediate between the acetylene/air and nitrous-oxide. This temperature is high enough to overcome several types of interferences but not so high as to cause severe ionization.

3.3.3 Sensitivity

The difference between detection limit and analytical sensitivity is often misunderstood by beginners using a new analytical technique. Early workers (Gatehouse and Willis, 1961) in atomic absorption defined detection limit as the concentration of the metal in water, required to give an absorbance of 0.004 (1%). This definition does not take into account any fluctuations in measurement. While the stability of atomic absorption apparatus is usually such that background fluctuation is usually of the order of 0.002 or less, certain elements, e.g. tin and zinc, may have significant background fluctuations. A far better definition of detection limit is that used by many spectrochemists, viz. a concentration which gives a signal equal to twice the magnitude of the background fluctuation.

Unfortunately, unless a recorder is used some difficulty may be experienced with ascertaining background fluctuation. The first definition, therefore, is generally accepted.

Analytical sensitivity is more difficult to define, as it often depends upon the presence and concentrations of other elements in the analytical solution. A certain concentration of an element may give an absorbance value which is easily measurable when a pure aqueous solution is sprayed. However, in the presence of an element or ion which causes depression, no absorbance may be measured for the same element concentration. Examples which will be mentioned later are lithium in the presence of iron, calcium and magnesium in the presence of aluminium. Some elements may cause enhancement of absorption, thus giving a greater analytical sensitivity, e.g. lanthanum or calcium in an acetylene/nitrous oxide flame.

As one of the chief criteria of any analytical technique is sensitivity, measurements were made to compare three flames, viz. propane-butane/nitroux-oxide, acetylene/nitrous-oxide, and the acetylene/nitrous-oxide+air, with the normal acetylene air flame.

This was done by determining the concentrations of elements in ppm in an aqueous solution, which would give absorbances of 0.004 and 0.1. Conditions were adjusted to give optimum absorbance for each element.

The results are shown in Table 3.6.

Discussion of Results

(a) The absorbance values obtained for the acetylene/air flame are of the same order as those which appear in the literature (Gatehouse and Willis, 1961).

(b) The values obtained for the propane-butane/nitrous-oxide flame are generally a factor 2 poorer than those of the acetylene/air flame. For the elements which form refractory oxides the absorbance is considerable poorer, and silicon gives no absorbance at all.

(c) The sensitivity of the acetylene/nitrous-oxide flame is worse than the acetylene/air flame for most elements except those which form refractory oxides where the sensitivity is very much better. For the other elements the poorer sensitivity may be attributed to the high temperature.

(d) For the mixed support gas flame, adjusted to optimum setting of air to nitrous oxide for each element, the sensitivity is higher for several elements. This is seen in Table 3.6, column 4. The lower the concentration required to give 0.1A the higher the sensitivity. The lower detection limit (0.004A) is also significant. For some elements (copper, gold, zinc, iron) the air + nitrous oxide mixture was nearly 100% air. For others (silicon, aluminium) the oxidant gas was nearly 100% nitrous-oxide, but for other elements (calcium, strontium,

TABLE 3.6

Comparison of Sensitivities in the Acetylene/Air, Propane-Butane/Nitrous-Oxide and Acetylene/Nitrous Oxide Flames

(Concentration in ppm which will give 0.004 and 0.1 Absorbance)

Element	C_2H_2/Air Flame		Propane-butane/Air Flame		C_2H_2/N_2O Flame		C_2H_2/N_2O + Air - Ratio N_2O:Air adjusted to give max. sensitivity for each element	
	0.004 Abs	0.1 Abs	0.004 Abs	0.1 Abs	0.004 Abs	0.1 Abs	0.004 Abs	0.1 Abs
Mg	0.005	0.2	0.01	0.4	-	-	0.005	0.2
Ca	0.03	1.50	0.05	3.65	0.02	1.10	0.02	0.90
Sr	0.08	2.8	0.2	7.25	0.15	6.0	0.03	2.53
Ba	4.0	177.5	8.0	245.5	2.5	46.5	2.5	46.5
Li	0.03	0.7	0.06	1.6	-	-	0.03	0.7
Cu	0.05	1.5	0.1	3.0	0.15	5.3	0.05	1.5
Au	0.05	5.7	0.1	15.7	0.07	22.5	0.05	5.7
Zn	0.005	0.41	0.01	1.10	0.025	1.63	0.005	0.41
Fe	0.05	3.4	0.1	0.6	-	-	0.05	3.4
Mo	0.6	17.9	2.0	95.5	0.4	10.5	0.2	6.3
Al	undetectable at 3500 ppm		0.016 abs for 3510 ppm		0.5	37	0.5	37
Si	300	-	undetectable at 500 ppm		2	114	2	114

molybdenum) the highest sensitivity was obtained with an intermediate ratio of air to nitrous-oxide.

(e) The analytical graphs for some elements (e.g. lithium and calcium) were found to be far more linear with the mixed support gas flame. This factor extends the useful analytical range.

(f) The mixed flame thus appears to have the advantages of both the acetylene/air and acetylene/nitrous-oxide flames plus the added advantage of higher sensitivity.

3.3.4 Interferences

Although sensitivity is an important factor in any analytical technique, freedom from interference effects may be of more importance to the practicing analyst. Considerable attention has been directed towards the elimination of interferences, the most common means employed being the addition of a releasing or an inhibiting agent. It has been shown however, that certain interferences can also be reduced or eliminated by the use of the correct flame (Amos and Willis, 1966).

It was hoped that some of the interferences commonly encountered in the acetylene/air and acetylene/nitrous-oxide flames would be eliminated in the intermediate temperature propane-butane/nitrous-oxide flame. Many interference studies were made to test this. In addition certain types of interferences were investigated using the acetylene/nitrous-oxide + air flame.

The results given in this section are general and certain types of interference, encountered more specifically in silicate analysis, will be dealt with more fully in later chapters.

The same nebulizer was used throughout as Willis (1967) has shown that many interference effects depend on the droplet size and position in the flame where absorbance is measured and interference encountered.

Solutions used for the interference studies were prepared by adding various concentrations of the interfering element to standard solutions of

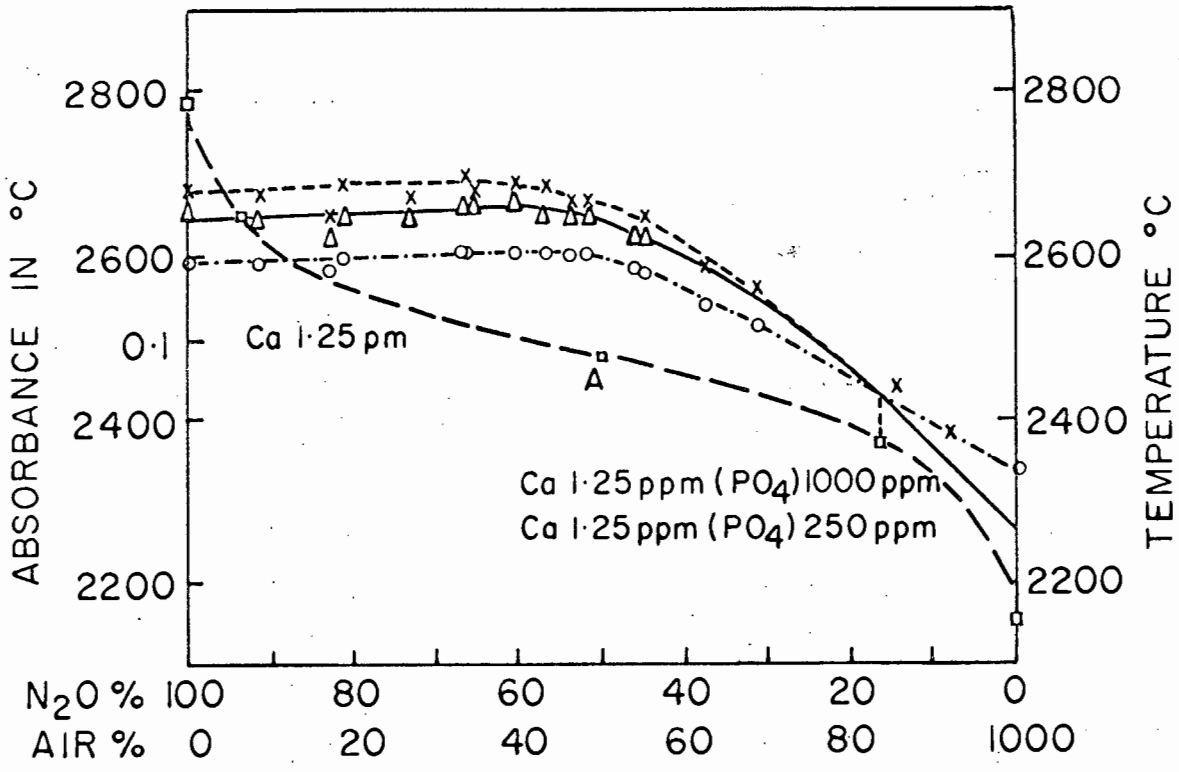


FIG. 3–8.

Effect of Changing Ratios N_2O : Air on 3 Solutions of Calcium, with Phosphorous, Temperature Curve shows Crossover Temperature 2360°C

TABLE 3.7

Comparison of Interferences in the Acetylene/Nitrous-Oxide, Propane-Butane/Nitrous-Oxide and Acetylene/Air Flames

in Fig. 3.7 was obtained.

(b) Iron on Lithium and Strontium

No reports could be traced in the literature that iron interferes with lithium or strontium in emission or absorption. Tests have shown however, that significant iron absorption interference may be present at high iron concentrations. This is shown in Fig. 3.9. It is seen that the interference is almost completely overcome with the use of the propane-butane/nitrous-oxide flame. The mixed support gas flame also overcomes this interference at a relatively high temperature.

3.3.5 Discussion on Flames

The development of a flame which has optimum atomic absorption properties for general as well as geochemical analysis is not easy, as a compromise must be achieved between the different parameters viz:

(a) A temperature, sufficiently high for proper atomization of the metallic elements in sample solutions, which includes the dissociation of chemical bonds.

(b) A temperature low enough to avoid excessive ionization of the analytical element. High ionization usually results in ionization interference by other elements or radicals with low ionization potentials.

(c) The optimum chemical environment. This extends the lifetime of an atomic species by preventing reactions with other elements or radicals, thus increasing sensitivity and reducing interference. Although atoms of an analytical element are extremely diluted in a flame plasma, the kinetics of reaction take place at very high rates. It has been suggested by Amos and Thomas (1965) that the reducing atmosphere which prevails in a fuel-rich acetylene/nitrous-oxide flame is due to the presence of incandescent free carbon in a premixed acetylene/oxygen flame. In the acetylene nitrous-oxide flame, however, it is possible that radicals such as CN, NH, H and CO may be more reactive to promote

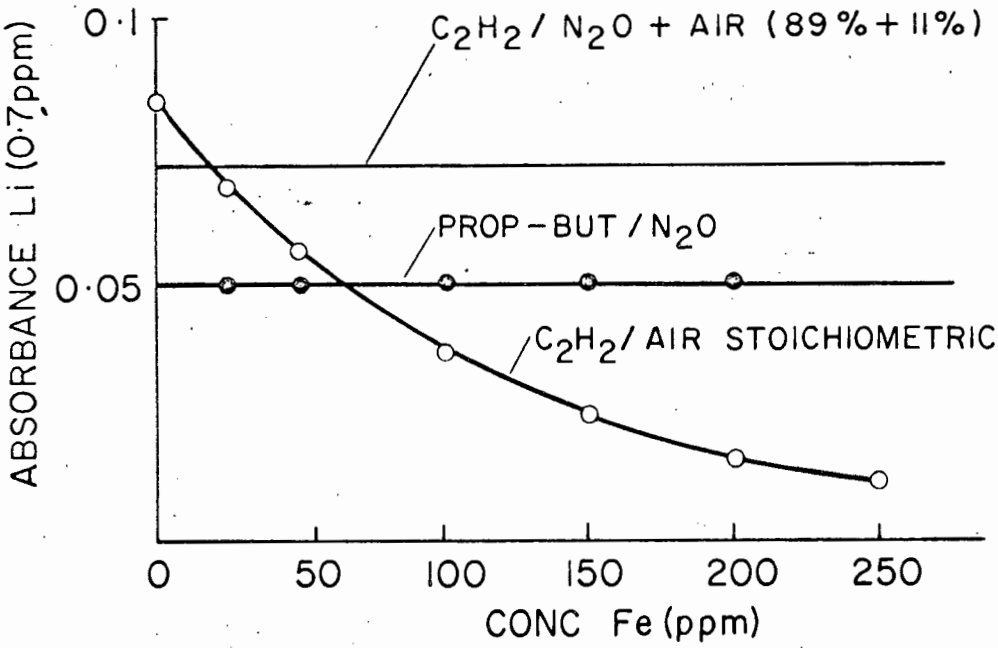


FIG. 3-9.

Interference of Iron on Lithium in Various Flames.

less oxidizing conditions.

In the propane-butane/nitrous-oxide flame, the concentration of reducing species is considerably lower. The suggested reaction for the 60% propane-40% butane reaction with nitrous-oxide is:

$$2C_4H_{10} + 13O_2 \longrightarrow 8CO_2 + 10H_2O$$

$$3C_3H_8 + 15O_2 \longrightarrow 9CO_2 + 12H_2O$$

$$56N_2O \longrightarrow 56N_2 + 28O_2$$

While this formula may describe the complete reaction, there is little doubt that the intermediate processes are complex. However, the conditions are considerably less reducing and this is the reason why refractory elements such as aluminium and silicon cannot be determined with this flame.

The investigation has shown that the propane-butane/nitrous-oxide flame meets the requirements of (a) and (b), but fails for (c), especially for those elements which form refractory oxides. This flame has specific application potential for analyses where sensitivity is less important than freedom from interference.

The acetylene/air flame meets the requirements of (b) and (c) but many elements are known to suffer from interference difficulties caused by improper atomization of the primary salts or reaction products in the flame.

The mixed support gas flame viz. the acetylene/nitrous-oxide+air complies with all the requirements listed. By changing the ratio of nitrous-oxide to air, the temperature may be changed between 2150°C and 2793°C. The variation of the chemical environment by changing the ratio of the support gases as well as the amount of fuel gas is a further advantage.

For application in geochemistry, it is preferable to use a flame which will give higher precision and freedom from interference, rather than ultimate sensitivity. (This aspect will be discussed more fully under the determination of sodium and potassium.) For this reason it is recommended that the mixed support gas flame be used with the burner designed for the

acetylene/nitrous-oxide flame.

3.4 BURNERS

In general, the burners designed by manufacturers for atomic absorption spectrometers are safe and efficient. In some cases, however, improvements for specific problems are necessary. Examples of improvements which have been made in burner design are:

(a) With the Perkin Elmer 303 spectrometer, it was found that when the standard slot burner was used, zinc absorption readings were unstable. It was found that the optical system used caused the light from the cathode to converge and diverge strongly to the point of focus in the flame and that much of the light did not pass through the flame. As the refractive index of the hot gases is high at the wavelength of zinc (2138Å), the slightest flame fluctuations caused the transmitted light intensity to change. Consequently, a special broad flame burner was designed to fit the Perkin Elmer. (See Fig. 3.10.)

This burner can be used with either acetylene/air of propane-butane/nitrous-oxide gases. The wide flame fully utilizes the full width of the light beam so that fluctuations of readings at short wavelengths are reduced significantly and sensitivity is also increased for several elements. This burner has been discussed at some length in a publication (Butler, 1962) so details will not be given here.

(b) Atomic absorption follows the Beer-Lambert law of absorption. It was seen in equation (2), Chapter 2.2.2, that the absorption coefficient is dependent on the path length of the absorbing medium.

A convenient means of reducing absorption is to shorten the flame length. When a wide concentration range in samples is encountered, it is very convenient to be able to desensitize the analytical method to enable concentrations outside the analytical range to be determined. This is done quite easily on a Techtron spectrometer, but not as easily

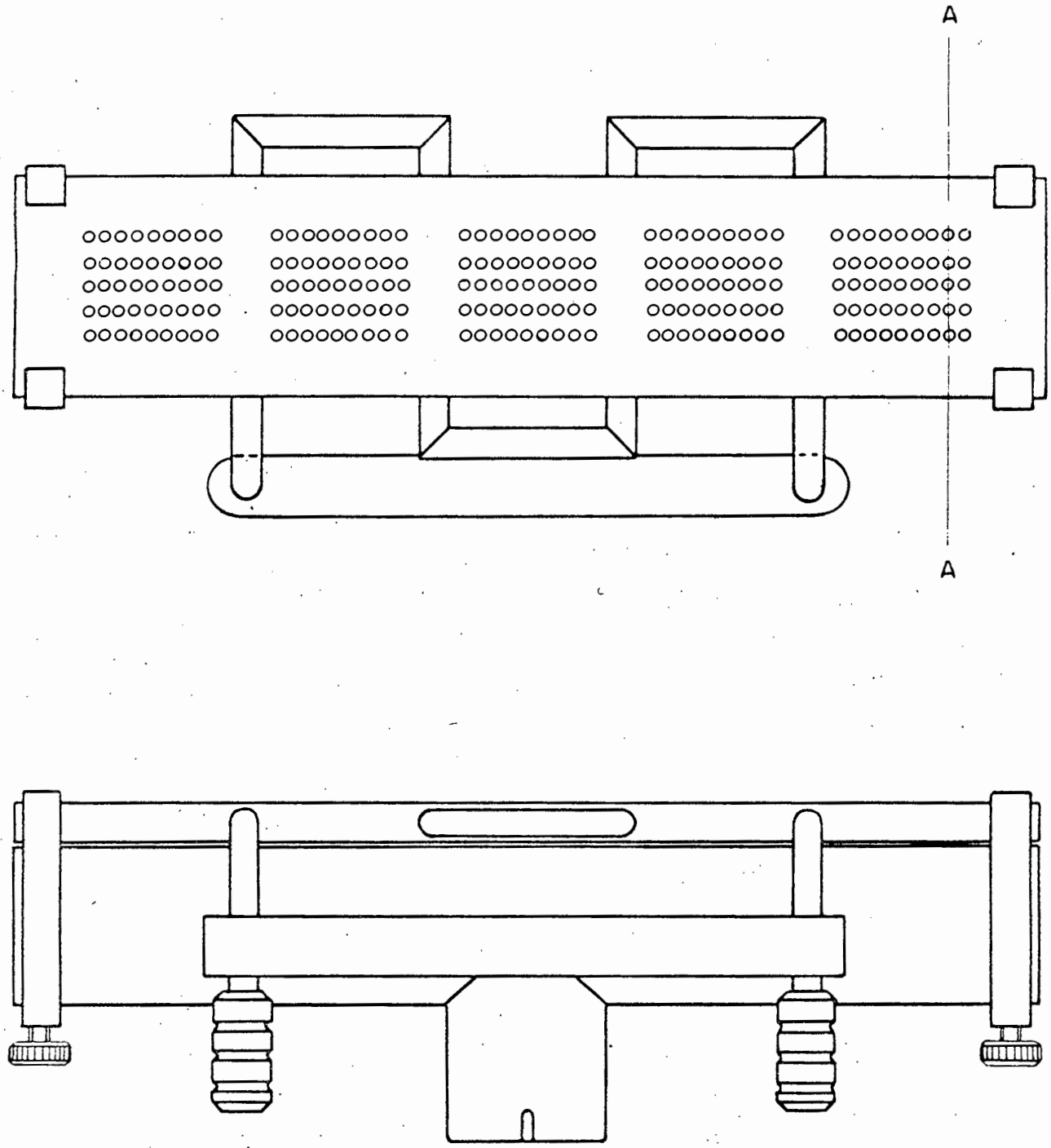


FIG. 3-10

Diagram of Broad Flame Burner.

on the Perkin Elmer.

The angle of rotation, which will define the absorption path-length is not reproducible normally. This necessitates a new run of standards to re-calibrate for a sample outside the analytical range.. A special rotating burner was designed to facilitate reproducible rotation speedily. The burner body is made of aluminium, lined with Teflon (Poly-tetrafluoroethylene). It accepts a standard Techtron burner head, but the head can be rotated about a vertical axis by means of an electric motor. A relatively large disc which rotates with the burner head about the burner axis has adjustable cams on the disc perifery. When the motor is running the burner head rotates until one of the cams touches a small micro-switch. The motor stops, but the inertia of the disc is sufficient to carry the cam beyond the micro-switch. The result is that the burner may be rotated to any pre-selected angle simply by touching the start switch. It has been found that the burner angle is reproducible to within $1/100^{o}$. This means that a set of curves can be drawn for various angular settings to cover a wider concentration range. If, during a run, a solution is found to be above the limit of one range, the burner motor switch is touched and the burner turns to the required angle. Because of the high precision of setting, no further standards need be measured at this new angle. The burner is rotated to its original setting after the sample has been measured.

A photograph of the burner is seen in Plate 2.

In Fig. 3.11 is shown how the absorption reading for a copper standard changes with burner angle. This rotatable burner is not always used in the most precise analysis of geological material, but has extended the scope of the atomic absorption method, especially for the routine analysis of a large number of widely varying samples. It is of particular use for the experiments which are being conducted on the simultaneous determination of several

PLATE 2.

The Rotating Burner.

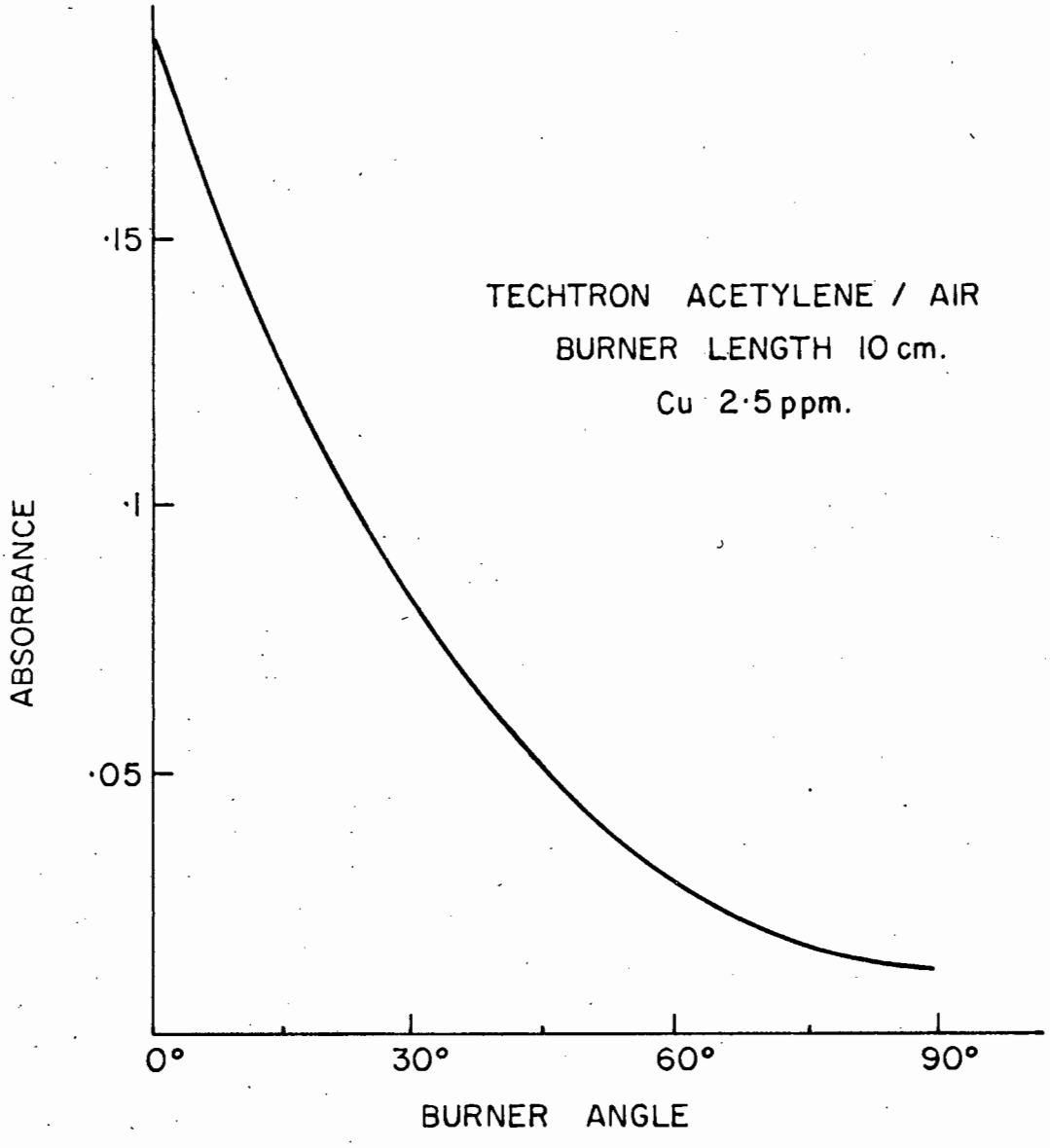


FIG. 3-11.

Change of Absorbance with Burner Angle.

elements by atomic absorption spectrometry.

This rotating burner cannot be used on a Perkin Elmer 303 spectrometer because of the limited space. Consequently a number of burner heads with shorter slots was constructed. By using these shorter burners the analytical range can be changed in a similar way.

Many different types of burners have been used for atomic absorption spectrometry. Total consumption burners which are well suited for flame emission spectroscopy are not generally suitable for atomic absorption because of their short path length. In addition, the large distribution of droplet sizes often introduces interference effects which may not be present with premixed laminar flow burners.

CHAPTER 4

PRECISION AND ACCURACY

4.1 GENERAL

With any analytical technique there are three factors of importance, viz:

(a) Systematic error or bias;

(b) precision or ability to make measurements close together;

(c) accuracy or closeness of a result to the "true" value.

In some cases the first and the third must be considered together. If the "true" value is known (e.g. with synthetic samples to which a precalculated concentration of an element has been added), the bias can be judged. However, in geochemical analysis, accuracy is generally judged by comparing a result with results of other methods of analysis, the reliable mean of which is given as the "accepted value" (Stevens et al, 1960).

The closeness whereby a mean of results can come to an accepted value is of importance, but of equal importance is the scatter or precision about this mean. It is by these factors that a method of analysis is judged. The contributory phenomena in atomic absorption spectrometry to these, are discussed.

4.2 PRECISION

There are several factors which contribute towards poor precision, both in the instrumental components and in the analytical method. These have been studied in order to assess the method for trace element determinations as well as for the determination of elements present in higher concentrations in silicate samples.

Fluctuations in the various components of atomic absorption apparatus each contribute towards the precision of measurement. In general, fluctuations may be classified as short and long term.

(a) Short-term fluctuations of five seconds and less are easily seen as oscillations of the indicator needle. Their amplitude has an influence

on the limit of detection. These may be reduced quite easily by introducing a time constant in the electrical measuring circuit, which will dampen their amplitude. Where the amplitude is continuously varying, however, the introduction of a time constant may well introduce the errors associated with long term fluctuations. These fluctuations are generally far more dangerous in analytical work. The human eye has a remarkable ability to integrate visually between limits, although bias may be introduced. With a certain amount of experience, however, it is often more satisfactory to integrate visually rather than electrically. In Fig. 4.1 is shown a diagram of how errors may be accentuated by excess electrical integration. Spurious spikes which usually result in rapid fluctuations of absorbance are easily discarded visually. These fluctuations are faster than the time constant of the circuit and may be additive, usually resulting in a signal higher than that obtained visually with a small time constant meter.

(b) Long-term fluctuations, longer than five seconds, often cause errors in an analysis as they are not easily noticed. When fluctuations are not continuous, but occur sporadically during the course of measurements, significant errors may occur. This is illustrated by the following example: For an analysis, standard solutions are sprayed and the absorbance values recorded. While the samples are being sprayed, a disturbance occurs causing a change in both the slope and the position of the calibration graph. The only practical means for detecting this type of drift is to spray a standard, which falls near the upper limit of the analytical range, at regular intervals.

4.2.1 Causes of fluctuations

(a) Supply fluctuations: Voltage fluctuations affect the stability of the lamp supply and the measuring set. The use of a good voltage stabilizer is advisable.

Air and gas pressure fluctuations influence the combustion conditions as well as the nebulizing rate. Pressure regulator valves will reduce these fluctuations. A large reservoir tank should be on the air compressor to even out pump fluctuations. An efficient filter is also necessary between the compression and the nebulizer to eliminate dust, oil and water. These impurities may cause blockage of the nebulizer or cause severe contamination in the flame. The acetylene gas pressure should not be allowed to drop too low as droplets of acetone from the cylinder may result in unusual combustion (Shepherd and Johnson, 1966).

(b) The hollow-cathode lamp: When a lamp has been used for some time, a good deal of the cathodic material may have sputtered away. This results in a decrease of the carrier gas pressure (clean-up). Excessive sputtering may even cause sporadic short-circuiting of the discharge inside the lamp. The cathode element itself may be damaged or the emitting area sputtered completely away.

There may also be a slow leak of atmospheric gas into the lamp, which will cause the pressure inside the lamp, and the background, to increase. If the anode is made of a "gettering" material, reversal of the lamp current may reduce this.

In general, the only remedy for overcoming errors caused by the lamp, is to recondition it, or when this is not possible, to replace it.

(c) Flame fluctuations: Any change in the combustion characteristics may result in a change of absorption, especially for elements where the absorbing region and chemical environment are important, e.g. lithium and aluminium. It is imperative that proper metering devices are used and that constant supply pressures are assured.

When fuel-rich flames are used, soft flames result. These flames can be affected easily by air movement around the flame, causing fluctuations in absorption. The absorbance and thus the refractive index of the flame

is higher at shorter wavelengths, so that elements with their resonance lines in the short-wavelength regions are affected more than those in the longer wavelength regions. Table 4.1 shows the coefficients of variation measured for five elements, which have resonant wavelengths in different regions of the spectrum. The measurements were made with solutions giving the same absorbance (0.1 A), with the same flame (acetylene/air). An extractor fan near the apparatus was running to introduce air turbulence in the room. Measurements were made with a digital measuring device to eliminate personal bias and an integration period of four seconds was used. The coefficients of variations were calculated from the absorbance values.

It is seen that the variation is greatest for zinc 2138Å where the flame fluctuations will have the greatest effect, because of the high absorbance of the flame gases at that region.

It is best to use as "stiff" a flame as possible to reduce flame fluctuations.

Fluctuations caused by the nebulizer may be classified with flame fluctuations. Chief causes of change in the rate of nebulization are blockage of the capillary tube, air capillary (already dealt with) and corrosion. Care should be exercised, especially with silicate samples, that all mineral particles have been dissolved. With certain types of samples, e.g. certain chondrites, carbon or other non acid-soluble particles remain in suspension. In these cases it is advisable to filter the solutions before spraying. Strong acids in the final solution should be avoided. In particular aqua regia or nitric acid are known to attack stainless steel capillaries. Some pneumatic nebulizers have rhodium capillaries which resist attack, but both the Techtron and the Perkin Elmer spectrometers use stainless steel nebulizers of the E.E.L. design. These are prone to acid attack. Fluctuations caused by the flame are

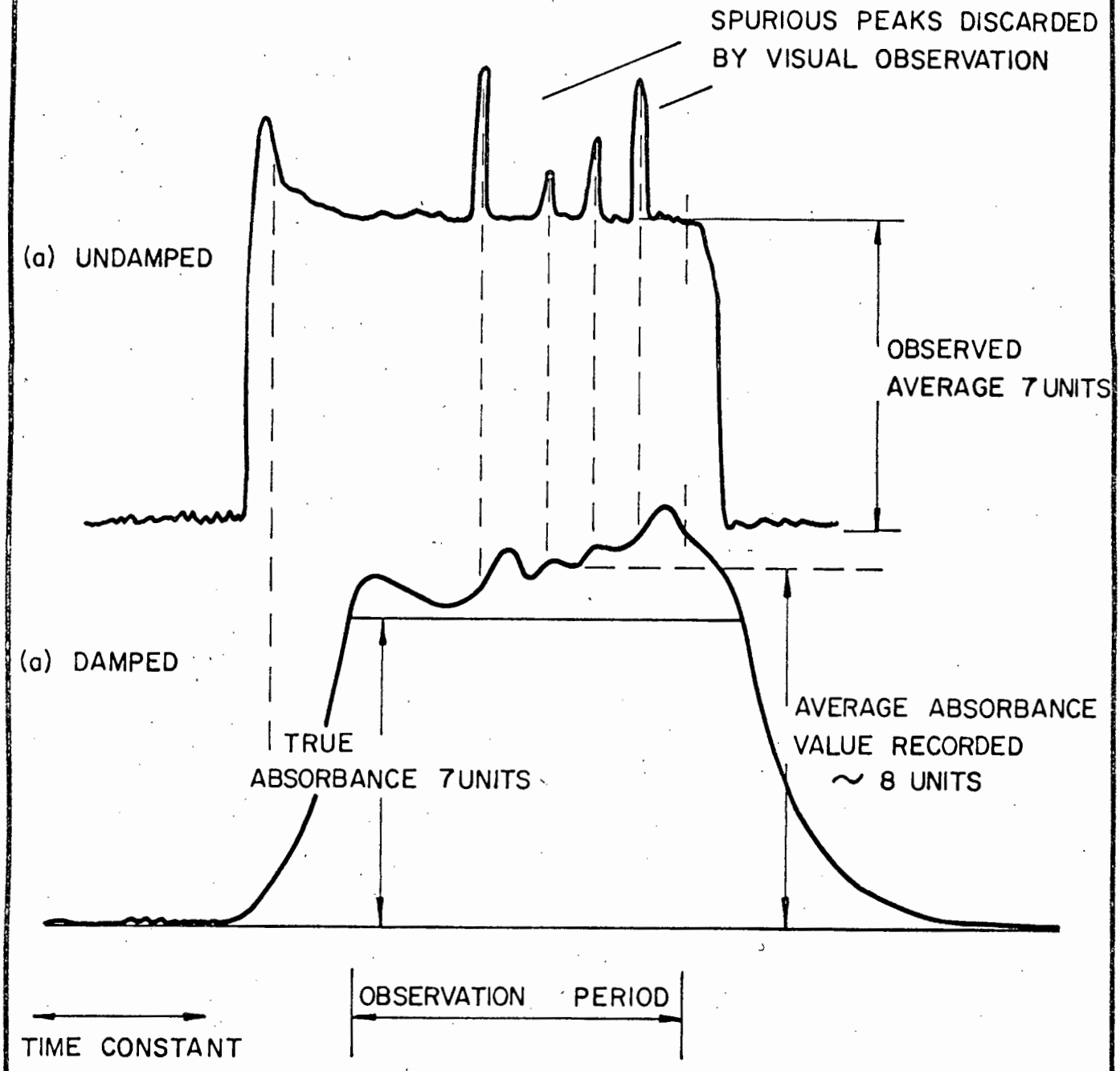


FIG. 4·1.

How excess Electrical Damping can cause Erronous Readings.

of the order of 2%, depending on the conditions and the element.

(d) Spectrometer fluctuations: If the monochromator is temperature sensitive, it may cause the spectral line to drift off the slit. This usually takes place slowly, and is not easily detected. The wavelength adjustment should be checked from time to time. The Perkin Elmer spectrometer was found to be more sensitive to temperature drift than the Techtron. This difficulty can be minimized by using a wider slit to make the wavelength setting less sensitive.

A "noisy" photomultiplier can cause significant fluctuations when the supply voltage is relatively high. An increase in voltage may become necessary when a very narrow slit is used or when the lamp intensity is low, e.g. for chromium or nickel a narrow slit is necessary for maximum sensitivity. With a potassium hollow cathode lamp as source, the reflectance of the grating at the potassium wavelength is poor for the Techtron. On the Perkin Elmer a luminous flame can cause over-saturation of the photomultiplier and amplifier. For work with this flame a very narrow slit should be used or severe fluctuations will result. Overall fluctuations of the spectrometer and source are usually less than 0.5%.

(e) Analytical fluctuations: As solutions must be made of solid samples, all the errors usually encountered with wet chemical techniques are found in atomic absorption. These include weighing errors, volumetric errors, sample inhomogeneity and incomplete dissolution or sample loss.

4.2.2 Statistics

Weir and Kobluk (1967) and Meddings and Kaiser (1967) have compared precisions obtained by atomic absorption methods with chemical methods and have shown that volumetric errors are small. Precision for atomic absorption is poorer than for "precise" chemical methods but better than for rapid chemical methods.

The calculation of precision for atomic absorption results may be done in several ways. In this thesis the standard deviation S is calculated

As many separate weighings as was practically possible were made and separate solutions prepared of each. These solutions were each analysed a number of times (usually a minimum of 3), the mean taken as one determination, and the precision calculated on the different determinations. No analysis of variance was made on the large bulk of analyses.

Laubscher (1968) has applied the one-way random model of analysis of variance to show the relationship which exists between the number of samples and the number of determinations on each sample. The theory is applied where a specific confidence limit is required. There is a significant improvement in the confidence interval as the number of samples is increased from 2 to 4, but replicate determinations do not give much improvement.

As will be seen in later sections, precision of observations obtained on a single solution of most elements is between 0.5 and 3% coefficient of variation. 15 or more observations are usually made. Variation between solutions, however, as a result of sampling, contamination, and chemical errors may be higher.

4.3 ACCURACY

Analytical results can never be more accurate than they are precise, but precise results give no indication of accuracy.

The accuracy of atomic absorption methods is very much dependent on the element to be determined, its concentration, and the concentration of other elements present in the sample. In general, atomic absorption results are accurate because of the relative lack of interferences. In cases where interferences are known not to exist, it is possible to use accurately prepared aqueous standards.

For the determination of some elements, notably the alkaline earths in complex samples, the concentration of non-analytical elements may be high, and many interferences found. In these cases, either synthetic standards or pre-analyzed standards with composition similar to the samples, are used.

Interferences have already been discussed in Section 3.3.5, but will be treated more generally in this section. Interference effects are the main limitations of the atomic absorption method, especially in its application to geochemistry.

If in a flame, X atoms of an analytical element reach the stage of being atomized,

then X^o are in the ground state and available for absorption,

and X' are in excited or ionized states and thus not available for absorption,

i.e. $X = X^o + X'$

4.3.1 Physical Interference includes temperature variation in the flame. This could be caused by the spraying of combustible solvents. Temperature effects are more noticeable in hot flames where appreciably more atoms are in excited or ionic states. A change in temperature changes the state of equilibrium, and results in a change of the ratio $\frac{X^o}{X'}$.

When the hollow cathode lamps radiate the lines of more than one element and the lines are not resolved by the spectrometer, some interferences may exist, e.g. for caesium determinations an argon filled lamp should preferably not be used as the argon 8521.44 Å line is not resolved from the caesium 8521.10 Å line.

4.3.2 Chemical and Ionization Interference

Depression or enhancement of the absorption signal may result if one or more foreign elements, I, or oxygen or some other radical take part in the reaction, causing

(a) depression:

$X^o + X' + I \rightarrow XI + X'$ or XI

or $X^o + X' + IO \rightarrow XO + I$

(b) enhancement:

$X^o + X' + I \rightarrow X^o + X' + I' + e \rightarrow X^o + I'$

or $X + XO + I \rightarrow X^o + IO$

4.3.3 Methods for Overcoming Interferences

(a) The use of a flame which prevents the interfering element from upsetting the equilibrium, or

(b) the addition of a suppressing agent.

If a suppressing agent, S, is added for overcoming depression, the reaction may be:

$$X^o + X' + I + S \longrightarrow X^o + X' + IS$$

or $X^o + X' + I + S \longrightarrow XI + S \longrightarrow X + IS$

or $X^o + X' + IO + S \longrightarrow XO + I + S \longrightarrow X + ISO$

and for overcoming enhancement interference the reaction may be:

$$X^o + X' + I + S \longrightarrow X^o + X' + I + S' + e \longrightarrow X^o + I + S'$$

(S having a low ionization potential and being added to both standards and samples),

or $X + XO + I + S \longrightarrow X + XO + IS$

Common suppressing agents are: Strontium chloride;
Lanthanum chloride;
E D T A;
Rubidium chloride;
Caesium chloride;
sometimes Potassium chloride

Table 4.2 shows how the addition of lanthanum suppresses the effect of aluminium on magnesium in various flames.

(c) The use of the technique of additions.

Known concentrations of the analytical element are added to separate aliquots of the sample solution. The absorbance is measured for each addition as well as for the sample to which only water has been added. The concentration of the element in the sample may be determined graphically by plotting absorbance against added concentration and reading the concentration value where the graph cuts the negative concentration axis.

In applying the additions method, it has been found that results are not

always as accurate or precise as desired. The reasons for this are that extrapolation of a graph is always difficult, especially if the graph is not linear. In many cases where interference effects exist the analytical graph may curve appreciably and thus make extrapolation very difficult.

A useful means of establishing whether interference exists in a sample is to plot the additions graph on the same paper as the plot of aqueous standards. If the two graphs are parallel, interference effects are absent.

TABLE 4.2

Suppression of Aluminium Interference on Magnesium

Magnesium Concentration 1 ppm				
Concentration (ppm)		Absorbance		
La	Al	C_2H_2/air	C_2H_2/N_2O	Prop.-but./N_2O
0	0	.660	.148	.305
0	2.5	.650	.150	.305
0	25	.590	.148	.303
0	50	.570	.152	.300
0	100	.530	.149	.285
0	250	.470	.144	.265
2	0	.660	.151	.305
2	2.5	.650	.151	.304
2	25	.590	.151	.305
2	50	.580	.151	.300
2	100	.570	.147	.285
2	250	.490	.142	.265
20	0	.660	.156	.305
20	2.5	.660	.156	.305
20	25	.640	.156	.305
20	50	.600	.156	.300
20	100	.570	.156	.285
20	250	.530	.151	.275
200	0	.660	.156	.305
200	2.5	.660	.156	.305
200	25	.660	.157	.305
200	50	.660	.160	.305
200	100	.660	.156	.305
200	250	.590	.156	.305
2000	0	.660	.167	.305
2000	2.5	.660	.167	.305
2000	25	.660	.167	.305
2000	50	.660	.167	.305
2000	100	.660	.167	.305
2000	250	.660	.167	.305

CHAPTER 5

SAMPLE PREPARATION AND STANDARDS

5.1 SILICATE POWDER DISSOLUTION

In the application of atomic absorption techniques to the analysis of solid geological material, rapid and efficient dissolution procedures are required.

The dissolution of silicates has received considerable attention from analysts applying classical chemical techniques, and remains important for many modern instrumental methods, e.g. spectrophotometry. Most of the successful dissolution techniques are applicable for atomic absorption purposes.

During this investigation, several different methods of dissolution were explored. Although particle size of the sample plays an important role in the dissolution of silicates, this effect was not studied in detail. All samples were received already crushed and ground to less than 120 mesh. Crushing techniques were not studied and will thus not be discussed in this thesis.

Bearing in mind the limitations of the atomic absorption techniques and the analytical objectives, the dissolution methods should:

(a) Be rapid to save time;

(b) allow complete dissolution of all sample matter;

(c) assure homogeneity of the sample throughout the final solution;

(d) be stable to enable storage;

(e) be economical of re-agents and laboratory ware;

(f) should not introduce contaminants.

In addition, where trace elements are to be detected in the ppm range, relatively concentrated solutions should be possible.

The dissolution methods should also allow as many elements as possible to be determined in one solution or simple dilutions thereof.

5.1.1 Acid Dissolution

Hydrofluoric acid has long been recognized as a decomposing agent for silicate rocks. The hydrofluoric acid reacts with silicon to form tetrafluorosilicate which become gaseous at less than 50°C, and is easily driven off.

Hillebrand (1919) preferred fusion methods for his classical scheme of analysis. His reason for this was that fluorides interfered with the precipitation of the mixed oxide group of elements.

It is common practice to add an oxidizing acid with the hydrofluoric acid when digesting silicates. A two-fold benefit is obtained. The oxidizing acid oxidizes cations to a higher ionic state. In this form the minerals are dissolved more readily in weak acids. A strong acid will also replace a weaker acid radical from its salt, e.g. a fluoride plus sulphuric acid forms a sulphate and hydrofluoric acid. The hydrofluoric acid is then evaporated away. If the process of adding sulphuric acid and evaporating to dryness is repeated twice, the fluorides will almost all be converted to sulphates (Selch, 1915).

Hydrofluoric acid digestion has several advantages for the dissolution of rocks for atomic absorption analysis:

(a) The sample size is reduced by driving off the silicon and a more concentrated solution of rock may be obtained. In addition no dilution of the rock in a flux occurs. This is of particular use for trace element determinations.

(b) Solutions are stable. Silicon often forms gels or causes deposits in solutions made from fusions.

(c) The procedure is simple and digestion can take place overnight.

Disadvantages of acid digestion are:

(a) Several minerals do not dissolve rapidly. Hoop (1964) showed that when a standard hydrofluoric-sulphuric acid dissolution method was used, rutile, zircon, and alurite, kyanite, corundum, graphite, gold and pyrite remain almost unattacked. Other minerals are attacked very

slowly.

(b) Some salts may precipitate and remain insoluble. Hoop mentioned barium sulphate and also strontium and lead sulphate. However, chlorides and nitrates are generally soluble.

(c) Some acid combinations destroy platinum-ware, e.g. hydrofluoric and nitric acids will attack platinum. With PTFE or teflon crucibles this difficulty may be obviated.

(d) The chance of contamination is greater with acid dissolution than with fusion.

(e) Acid dissolution is time consuming, especially where several evaporations must be made.

Hydrofluoric acid may be used alone (Langmyhr and Kringstad, but it is usual to use it in combination with sulphuric, nitric, perchloric or hydrochloric acids or mixtures of these.

In order to test the most suitable acid dissolution method for atomic absorption, some tests were conducted on a metamorphosed [illegible] sample which was known to contain minerals difficult to dissolve. This left a considerable residue when treated with hydrofluoric acid. Spectrographic examination of this residue showed the presence of calcium, magnesium and lithium indicating the presence of garnet. Examination of the various types of acid dissolution might thus give an indication of the nature of the dissolution for this rock. In addition to this the dissolution and residue was carefully observed.

The acids used, volumes, treatments, and results are listed in Table 5.1.

The procedure used was to weigh out 0.1g of the powder into a crucible and dampen it with water. The oxidising acid was then added in which the hydrofluoric acid was added. The mixture was heated at 70°C and more strongly after the reaction had ceased. When dry it was heated strongly until it had stopped fuming. This was repeated. The residue was dissolved finally in 2N hydrochloric

test this against mine

up to final volume.

TABLE 5.1

Test of Efficiency of Acid Dissolution

Sample: Metamorphosed eclogite EK43

Weight: 500 mg (Less than 120 mesh)

HF Vol.	Acid	Vol.	Number of treatments	Vol. HCl	Final Vol.	Li detn.	Av.
10 ml	H_2SO_4	3 ml	2	20 ml	50 ml	5.9, 5.2, 6.1	5.7
10 ml	HNO_3	5 ml	2	20 ml	50 ml	3.0, 5.6, 4.9	4.5
10 ml	$HClO_4$	5 ml	2	20 ml	50 ml	7.0, 7.2, 7.1	7.1
10 ml	"	"	1 plus 1 BOMB treatment of residue	25 ml	50 ml	7.4, 7.4, 7.4	7.4

Notes

1. The sulphuric acid treatment was the slowest and left the most residue (white powder).
2. All acids were metered with plastic medical disposable syringes. Their very low cost accuracy and freedom from interference make them well suited for this work.
3. Teflon beakers were used for the nitric acid test. The method suggested by Belt (1967) was used. Iron formed a heavy brown precipitate with this method. In subsequent tests with other samples, it was found that lower iron samples formed a brown solution which did not precipitate. Heating of teflon beakers had to be done by infra-red lamps as well as on a hot plate. The hot plate alone heated only the base and the evaporated acid condensed on the cool walls of the beaker. Solutions evaporated more slowly with teflon beakers or crucibles.

4. Perchloric acid gave the clearest solution and least residue. (Care was always taken that perchloric acid did not come into contact with organic materials and did not get hot.) An extractor fan of 100 cubic ft./min. was used to remove fumes.

The results of these tests and experience over several years, have shown the perchloric acid digestion method to be the more suitable. Langmyhr and Sveen (1965) have shown that most minerals dissolve with this acid combination. Minerals which dissolve slowly are beryl, kyanite, topaz, staurolite, ûrote. pyrrhotite, and chalcopyrite. Garnet, zircons and others are also known to dissolve slowly (Ito, 1962). However, these may be dissolved quite easily with high pressure methods.

It is essential that all the material is taken up as low readings may result if even a small portion of a mineral remains undissolved, e.g. garnet contains calcium, magnesium, iron, chromium, nickle, cobalt and lithium.

5.1.2 High Pressure Techniques

Some ultrabasic rocks, notably eclogites and kimberlites, defied complete dissolution with hydrofluoric and perchloric acid, even after many treatments. Further grinding of the sample to less than 300 mesh improved the dissolution rate but it was felt that the greater chance of contamination and the longer time taken for grinding did not make this advisable. The use of high pressure and temperature techniques was therefore explored.

Ito (1962) decomposed a large number of refractory minerals using a Teflon lined and sealed steel chamber or "bomb", which could be heated to 240°C. Very high pressures (above 300 p.s.i.) could not be achieved because of the tendency of Teflon to deform and leak at high temperatures and pressures.

The Morey type bomb described by May and Rowe (1965) appeared more attractive as pressures of 6000 p.s.i. and temperatures of 450°C can be used. It is claimed by them that most refractory minerals are decomposed within 4 to 6 hours at 375-425°C.

A platinum lined bomb was accordingly built with dimensions slightly

larger than that of May and Rowe. By increasing the volume of the platinum crucible from 3.5 to 5.0 ml and scaling other components up accordingly, the same safety factor was assured, but larger sample weights of up to 200 mg could be used. It was planned to subject the whole sample to high pressure treatment. As concentrated solutions are required, 200 mg was considered a minimum quantity.

A diagram of the bomb is shown in Fig. 5.1. The platinum crucible (1) is formed inside a nichrome holder (2) from 0.016" platinum sheet.

As suppliers of Hastaloy, used for the base (3) could not supply the metal of desired dimensions, a different nickel alloy, Nimonic 90, was substituted. Although the composition of this alloy is different from that of Hastaloy C, the expansion coefficient is the same (i.e. 12.7×10^{-6}).

No details of the other materials used could be obtained from the publication or private correspondence, so these were selected by virtue of their properties of strength. Details are given in Fig. 5.1.

It was found that a proper seal could not be maintained at temperatures above 200°C and pressures above 100 bars (1500 p.s.i.). The reasons could be either a fault in design, or a mismatching of expansion coefficients. The latter reason would result in the plunger 5 expanding at a slower rate than the nut 6, thus causing the pressure on the crucible cap to be reduced.

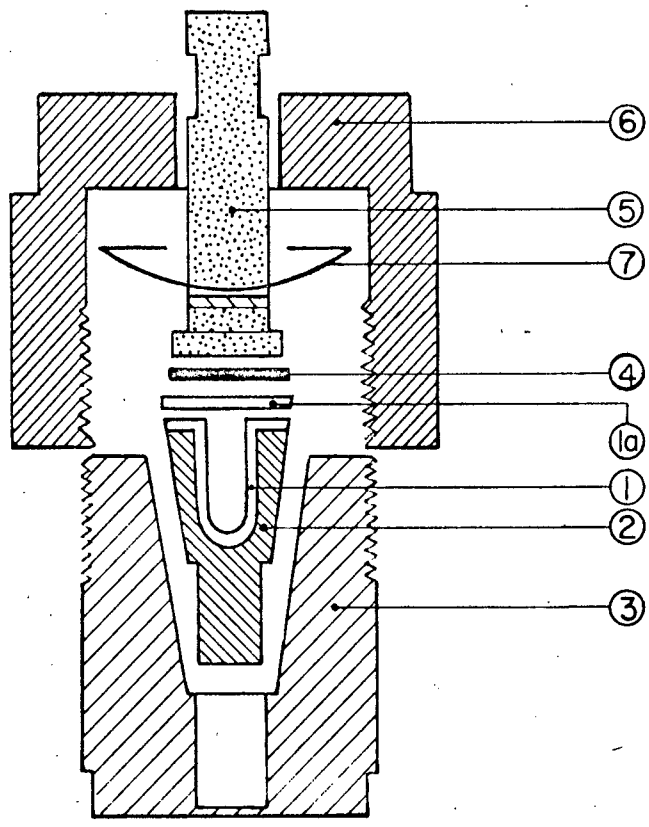
Two methods for overcoming this have been applied:

(a) Inserting a powerful disc-spring or Bellvile washer 7, between the plunger shoulder and the inner face of the nut. The pressure which can be exerted on the crucible face is calculated as follows:

If the length of the spanner is 5 ft and the force exerted manually 200 lb,

then the moment $M = 5 \times 200$ lb-ft

$$\text{force on crucible} = \frac{\text{Moment M}}{\text{area of crucible} \times \text{Tan (angle of thread)}}$$



1 1a. PLATINUM 16 GAUGE

2 NICHROME EN 23

3 NIMONIC 90

4 COPPER ANNEALED

5 STAINLESS STEEL NO 304

6 HIGH TENSILE STEEL 4140

7 DISC SPRING OR BELLEVILLE WASHER

FIG. 5·1.

Diagram of Platinum-lined "Bomb" for the Dissolution of Silicates

$$= \frac{1000}{(9.82 \times 10^{-2}) \times \frac{1}{25}}$$

$$= \frac{25 \times 10000}{9.82}$$

$$\doteq 26{,}000 \text{ p.s.i.}$$

This figure is well in excess of the maximum pressure of 6000 p.s.i. required in the bomb. If a temperature of 200°C is not exceeded the elastic properties of the steel washer are retained. This method offers a safety measure in that the pressure is released if for some reason it should exceed the safety test value of 30,000 p.s.i.

(b) Inserting a spacer washer of a metal with a higher expansion rate than that of the nut between the plunger and the nut. As the bomb heats up the more rapid expansion of the spacer ensures a continual high pressure on the crucible face. The metal used for these washers is duraluminium.

In both cases an annealed copper washer 4 is placed between the steel plunger and the platinum lid. This washer will deform slightly to maintain uniform contact of the platinum cap with the crucible lip.

To prevent the cap and crucible from welding together, both surfaces are coated with a thin, uniform layer of Aquadag, a graphic compound in solution. The pressures in the bomb at specific volumes and temperatures are determined from tables by Holzer and Kennedy (1958).

A special vertical tubular muffle-furnace with a ni-chrome wire element was designed to be used with the bomb. A chain and counterbalance enable the hot furnace to be lowered and raised with ease. The furnace, counterweight, dismantled bomb, temperature meter and the Chromel-Alumel thermocouple "cold joint" (in ice in the "Thermos" flask), are seen in Plate 3. Cooling of the bomb, after removal, was expedited by a jet of cold compressed air.

PLATE 3.

The Platinum-Lined High-pressure "Bomb" (lower centre) with the Vertical Furnace (left), Counterweight (upper right), Temperature Meter (centre), and Chromel-Alumel Cold Joint (in flask).

Although the bomb is seldom used for normal silicate rocks, it is very useful when analyzing rocks that contain minerals which defy dissolution. The most suitable procedure found when dissolving unknown rocks was to apply the normal hydrofluoric-perchloric acid technique. If undissolved material remained, the hydrochloric acid dissolved sample was carefully removed with a pipette and the residue transferred to the bomb. 2 ml of hydrofluoric acid were added and the bomb left overnight in the furnace at 300°C. On cooling the residue was usually dissolved. The solution was transferred to a platinum dish and heated to dryness and taken up in the normal way with hydrochloric acid. Most rocks, other than ultramafic types presumed to come from the upper mantle, dissolved completely with the normal hydrofluoric-perchloric acid method.

The bomb has obvious advantages, but in its present form it does not lend itself to rapid analysis. The steel nut and "Nimonic 90" base corrode easily, thus providing a source of contamination. When the bomb was first made it was envisaged that the whole sample would be dissolved in the bomb, hence its large volume. As a result of the dissolution procedure adopted here, however, very small amounts of residue are treated in the bomb and it could therefore be considerably smaller. For these reasons a new type of bomb is being designed.

5.1.3 Fusion Techniques

Many fusion techniques are available to break down silicates and enable their dissolution. Some of the better known fluxes described by Russel (1967) as fusing agents are:

Sodium carbonate,

sodium carbonate and sodium borate,

sodium peroxide and sodium hydroxide,

sodium fluoride (and bifluoride)

lithium fluoride and boric acid,

lithium metaborate,

lithium tetraborate,

potassium bifluoride.

Of these the sodium carbonate fusion appears to have found the widest application in wet chemical techniques. The lithium tetraborate technique has been used extensively for the preparation of silicate samples for X-ray fluorescence analysis.

The lithium metaborate solution technique described by Suhr and Ingamels (1966) and Suhr (1967) has the advantage that the melt is readily dissolved in nitric acid and thus provides a rapid method for dissolving rocks. Although it was developed for preparing solutions for emission spectrochemical analysis, this technique is well suited for atomic absorption analysis.

The method used is as follows:

200 mg powdered sample are mixed with 1 g of lithium metaborate in a graphite crucible and fused for 15 minutes in a furnace at 1100°C. In the meanwhile 200 ml of a 3% nitric acid solution have been placed in a Teflon or polypropylene beaker on a magnetic stirrer. The melt in the graphite crucible is removed from the furnace, swirled around to gather uncoalesced beads and poured directly into the nitric acid solution. The solution is stirred without further heating and the melt rapidly dissolves. The solution is made up to the required volume.

The fusion can also be carried out in platinum or 95% platinum-5% gold alloy crucibles. It should be remembered however, that iron, particularly ferrous iron, has a strong affinity for platinum (Russell, 1967). Iron results can be low as a result of this and platinum corrosion may result.

The fusion method results in a greater eventual dilution (flux to sample ratio 4:1) and is therefore better suited for the determination of elements at higher concentrations.

The high concentration of lithium precludes the determination of this element. As lithium salts are seldom found without other alkali metals as contaminants, it is advisable to test each new batch of chemicals and to run

blanks to detect contamination for sodium and potassium. When the alkali metals are present as traces in the unknown, fusion techniques are not recommended.

The scheme which has been adopted for the dissolution of rock samples for various types of analysis is given in Fig. 5.2. Table 5.2 gives convenient weights and volumes for the dissolution scheme suggested.

Graphite crucibles of high purity are practically more suitable. They may be re-used often and as many as 50 fusions have been made in one crucible. Similar to the platinum-gold crucibles, they do not "wet" and are thus easily cleaned. In addition when platinum-gold crucibles are used, they are more difficult to handle and to remove the "last drop" of the melt. However, the more oxidizing conditions with the metal crucible promotes the dissolution of refractory compounds, e.g. chromites (Suhr, 1967).

TABLE 5.2

Weights and Volumes used for Dissolution

A. Fusion

Method	Wt. of Sample	Wt. of Flux	Vol. 3% HNO_3	Final Vol.	Soln. Factor
F - 1	200 mg	800 mg	100 ml	100 ml	.2% (500x)
F - 2	100 mg	400 mg	100 ml	500 ml	0.02%(5000)
F - 3	10 ml of F-2 diluted to 50 ml			50 ml	0.004%(25,000)

B. Acid Dissolution

Method	Wt. of Sample	Acid Vol. $HClO_4$	Acid Vol. HF	Vol. 2NHCl	Final Vol.	Soln. Factor
A - 1	500 mg	5	10	20	50	1% (100x)
A - 2	500 mg	5 (or dilute A-1 4x)	10	20	200	0.25% (400x)
A - 3	500 mg	5	10	20	25	2% (50x)

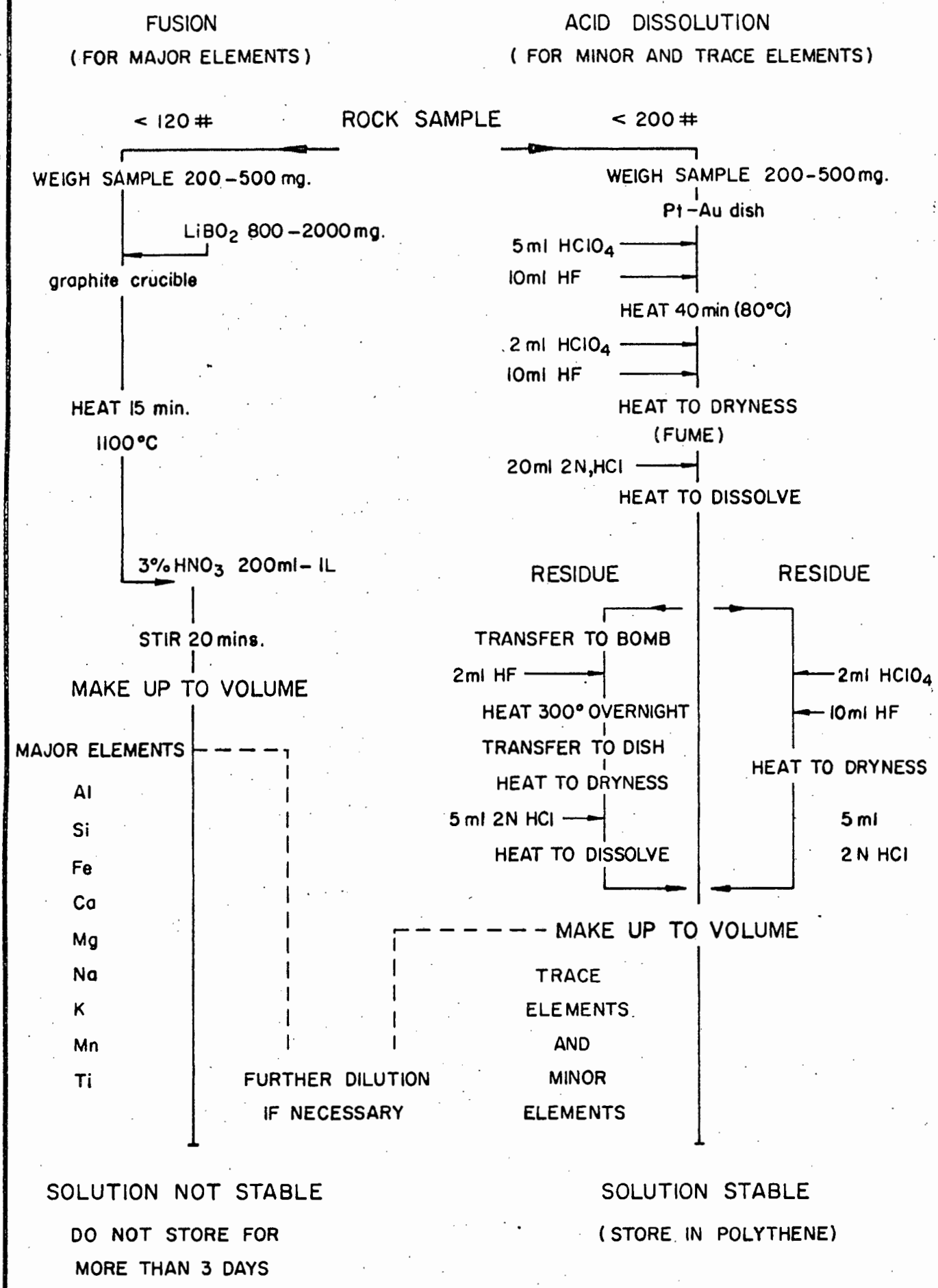


FIG. 5·2.

General Procedure for Dissolution of Silicate Rocks for Analysis by Atomic Absorption Spectroscopy.

5.2 STANDARDS

The accuracy of results is essentially dependent on the standards used for relating absorbance to concentration. It has been mentioned (Section 4.2) that various types of standards may be used, including natural standards.

One of the advantages of atomic absorption is that many elements may be determined, using simple aqueous standards. However, it should be realized that if care is not exercised in the preparation of these standards, significant errors may result.

It is good practice to use the pure metal of the element wherever possible for the preparation of the stock solution. In cases where metals are not available, stable salts, without water of crystallization are satisfactory. If some doubt exists about the metal content in the reagent it is preferable to have the solutions standardized chemically or as a last measure, to compare standards prepared from various salts.

Fresh reagents should be used, as reagents may change with time. An example of this change was found when certain calcium values, based on standards prepared from "specpure" calcium oxide were repeatedly lower than the chemical values. Eventually, it was discovered that the reagent used was old and a portion of the oxide had changed to the carbonate. Firing the chemical in an oven at 1200°C reconverted all the calcium to the oxide and further results were correct.

Stock solutions of convenient concentrations are prepared and stored in narrow-necked polyethylene bottles. When standard solutions are required, these stock solutions are diluted 10 or 20 times. Further standards are made by diluting the solution 1:1 with double distilled water.

It is convenient to have stock concentrations of 640 ppm, or multiples thereof. On dilution, standards of 64, 32, 16, 8, 4, 2, 1 are obtained. These values are more satisfactory for the plotting of the analytical graph, as concentrations with decimals (e.g. 1.25 ppm) require estimation of the point on the linear graph paper. It is very useful to prepare intermediate standards in the higher concentration ranges, e.g. 64, 48, 32, 24, when the

interval is too large for the accurate estimation of the graph (if it is not linear).

When standards are prepared from the pure metal, fresh filings, drillings or turnings should be used because they dissolve more rapidly because of their larger surface area. Metals which oxidize or form hydroxides rapidly often present difficulty, e.g. lithium. In these cases the turnings may be weighed in a beaker filled with argon or the metal converted to a salt of known metal content. During the course of the determination of lithium and lithium isotope ratios, only lithium metal isotopes were available. Standards were prepared by converting the metal and metal hydroxide to the chloride form, and standardizing these solutions (see later). Only in this way could accurate standards be prepared.

Most standard dissolutions are made in hydrochloric acid as most chlorides are soluble and give little or no interference in the flame. As little acid as possible is used. If acid concentrations are to be matched with samples, this is done at a later stage. Other acids are used for those elements which have insoluble chlorides (e.g. silver) and those which do not dissolve in hydrochloric acid (e.g. gold).

Table 5.3 gives the source of standards for the various elements and suggested methods of preparation.

Silicon standards were prepared from silicon dioxide which had been heated to 600°C to drive off adsorbed water vapour. Dissolution was then carried out using the lithium metaborate fusion technique. This meant that lithium and boron were present in these solutions, but as the samples were treated in the same way, this was no obstacle.

5.3 CONTAMINATION

Due to the high sensitivity of the atomic absorption method for most elements, scrupulous care must be exercised to prevent samples and standards from being contaminated with the elements to be determined. Contamination dangers exist mainly in the sample and standard preparation steps.

5.3.1 Sources of Contamination

(a) Instrumental

It is possible for contaminants to be introduced into the flame through burner (Gidley, 1961) and nebulizer corrosion. With most commercial apparatus, however, stainless steel parts are used which give little, if any, contamination difficulty. Contamination can be introduced from deposits inside the burner too (Butler, 1962). Although generally seen as a "memory" effect when blank solutions are sprayed, the high acid content of sample solutions may cause the deposits to dissolve rapidly and cause erroneous readings.

Contamination may also be introduced through the gas and air supplies (already discussed in Section 4.1.1(a)).

Regular cleaning of the burner and care with the acid content of solutions will prevent these causes of contamination. Cleaning of the burner slot is especially important when the acetylene/nitrous-oxide burner is used.

(b) Water contamination

Distilled water is used for all dilution of samples and standards. Before using singly distilled water, tests were conducted to determine the nature and concentration of impurities. This was done by concentrating the water 100 times, by evaporation, and spraying the concentrate. Elements determined were:

copper - 0.01 - 0.05 ppm

sodium - 0.005 - 0.1 ppm

lead - 0.001 - 0.005 ppm

The level of these elements did not remain constant and depended on the length of time that the water remained in the tin-coated copper container.

All water used for standards was therefore doubly distilled or

de-ionized through a mixed bed de-ionizer. The doubly distilled water was found more convenient, as a larger volume could be produced daily.

(c) Acid contamination

All reagents and acids used in the investigations were at least of "analar" grade purity. Unfortunately, some difficulty was experienced in obtaining supplies of guaranteed purity hydrofluoric and perchloric acids. Over the period of four years several makes of acids were used. Certain makes were found to contain significant amounts of lead and zinc.

When a new acid was used, it was analyzed to determine the level of metallic impurities.

Qualitative spectrographic tests were also made on the purest grades. The procedure similar to that suggested by Edge (1960) was followed: 10 ml volumes of acid were evaporated in platinum dishes to about 1-2 ml. The acid was then transferred to ultra high purity graphite cup electrodes and slowly heated until dry. The sample electrodes were dried with blank electrodes and the spectra examined for the sensitive lines of various metals.

The results are shown in Table 5.4.

Although methods exist for the purification of hydrofluoric, perchloric and hydrochloric acids, the methods are most tedious. It was therefore preferred to test for the level of contamination by running blank solutions and correcting for the specific elements.

(d) Atmospheric contamination

Particles of dust and other matter in the air are a serious source of contamination. In the small laboratory used for sample preparation, several other laboratory activities are carried out, including part of the preparation of samples for X-ray fluorescence spectroscopy. Lithium and sodium dust was therefore often found to be present in the

laboratory.

A special filter was fitted into the side of the fume cupboard. When the extractor fan was on and the door closed, all the air entering the fume cupboard passed through the filter. 99% of all particles larger than 5 micron and 70% of all particles larger than 1 micron are removed from the air. After the introduction of this filter and the building of special perspex baffles to prevent dust from falling back into the fume cupboard from the overhead cover and pipes, very little further difficulty from contamination from this source was experienced.

Plate 4 shows the filter in position in the side of the fume cupboard. In the foreground are two of the disposable plastic syringes.

(e) Laboratoryware contamination

For an extended period zinc results on silicate rock solutions were obviously contaminated. The contamination was erratic and difficult to trace. After useful suggestions by Orren (1967) tests were made on the polyethylene 100 ml bottles used for storage of the prepared solutions. It was found that some bottles had considerable quantities of zinc. Orren has suggested that this is as a result of zinc stearate being used in the manufacture of these bottles. All bottles were therefore rinsed with hot concentrated hydrochloric acid before usage, but in spite of this zinc contamination was encountered. When zinc was to be determined therefore, the solutions were metered into pyrex volumetric flasks, and then part of the solutions transferred to polyethylene bottles. Zinc was determined on a small amount retained in the glass volumetric flask.

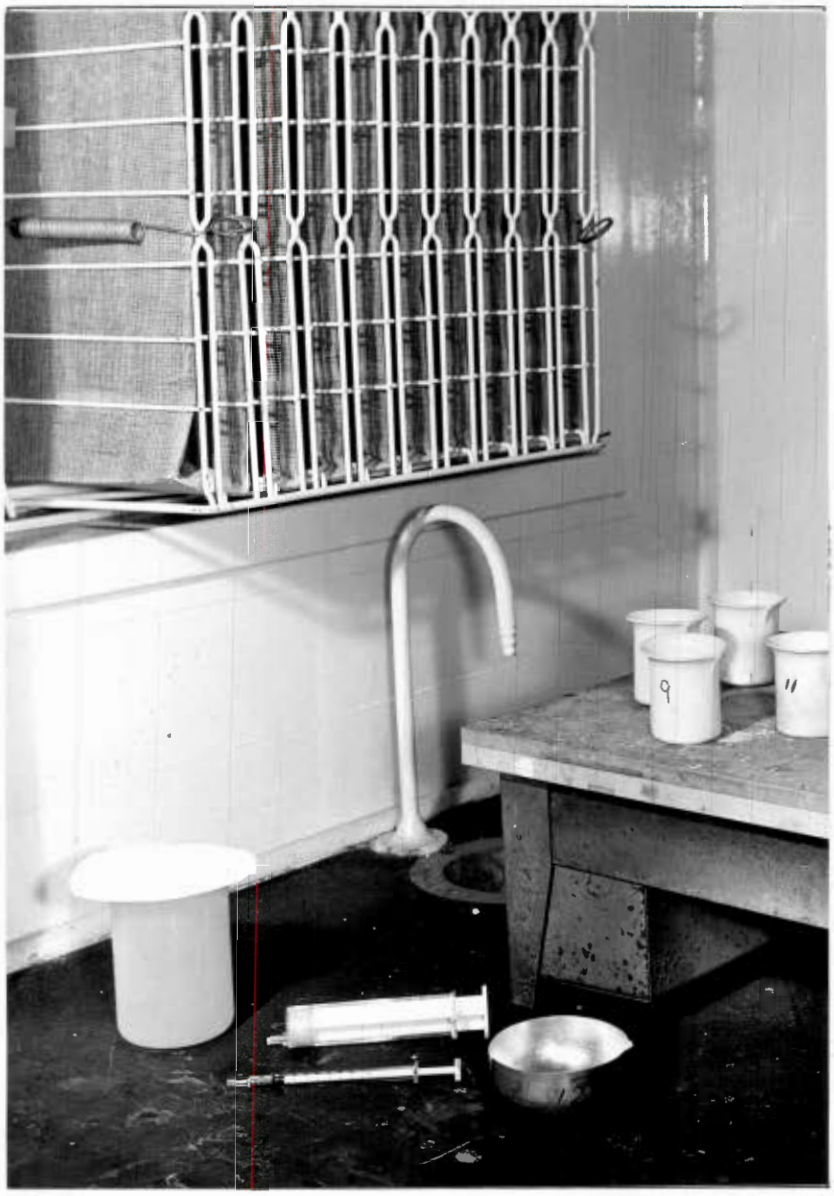


PLATE 4.

The Fume Cupboard Filter.

TABLE 5.4

Qualitative Examination of Acids and Singly Distilled Water

	HF	H_2O	HCl	$HClO_4$
Mg				
2795.53	I	I	III	III
2802.70	-	-	III	III
2852.13	-	-	III	III
Ca				
3933.67	II	II	I	III
4226.73	I	II	-	II
3968.47	I	I	-	I
Cu				
3247.5	II	II	II	-
3273.96	I	I	I	-
Al				
3092.7	-	-	I	-
Mn				
2794.77	I	-	-	-
2798.2	I	-	-	-
Na				
5890	II	-	I	I
3302	-	-	-	-

Note: I indicates lines very weak, barely visible

II indicates lines distinct

III indicates lines strong

IV indicates lines very strong, i.e. more than trace

TABLE 5.3

Preparation of Standards

Element	Stock	Procedure	Resultant compound	Grams stock per litre	Stock value ppm
Group IA					
Li	Li_2CO_3	Dry in oven at 110°C; dissolve in dilute HCl*	LiCL	1.656	640
	Li metal	Dissolve in excess HCl; evaporate to dryness; weigh out chloride; standardize	LiCL	3.910 (chloride)	640
Na	NaCl	Dissolve in freshly distilled water and stored in polyethylene containers	NaCl	1.627	640
K	KCl	Dissolve in distilled water, after drying at 110°C	KCl	1.2210	640
	KNO_3	- do -	KNO_3	1.655	640
Rb	RbU	Dissolve in water. Standardization is recommended: Pipette 25 ml to Pt dish, add 1 drop H_2SO_4, evaporate to dryness, and heat to constant weight	RbU	.9055	640
Group IIA					
Mg	Mg	Dissolve metal in minimum amount appropriate acid*	$MgCl_2$ (if HCl)	0.640	640
Ca	$CaCO_3$	Dry at 110°C; dissolve in minimum amount HCl dil. (As CaO, strength is 1,400 ppm)	$CaCl_2$	1.598	640
Sr	$SrCO_3$	Dissolve 1.6848g $SrCO_3$ in 300 ml water plus 2 ml conc. HCl* and dilute to vol.	$SrCl_2$	1.078	640
Ba	$BaCl_2$	Dissolve 1.523 g anhydrous $BaCl_2$ dried at 250°C for 2 hr, dilute to volume	$BaCl_2$	.9747	640
	$BaCO_3$	Dry at 110°C; dissolve in dilute HCl*	$BaCl_2$	.9196	640
Group VIB					
Cr	$K_2Cr_2O_7$	Dissolve in water, dilute to volume	K_2Cr_2O	1.4611	640
	Cr metal	Dissolve in HCl, or dil. H_2SO_4*	$CrCl_2$	0.640	640
Mo	$(NH_4)_6Mo_7O_{24}$, $4H_2O$	Dissolve in water and add few drops ammonia soln. to make alkaline and standardize by gravimetric method	$(NH_4)_6Mo_7O_{24}$	1.1777	640

* Use as little acid as possible

TABLE 5.3 CONTINUED

Element	Stock	Procedure	Resultant compound	Grams stock per litre	Stock value ppm
Group VIIB					
Mn	MnO_2	Dissolve in conc. HCl*	$MnCl_2$	1.013	640
Group VIII					
Fe	Fe	Dissolve fresh iron fillings (or pure iron wire) in 11 ml 6NHCl and dilute to volume	$FeCl_2$	0.640	640
Co	Co	Dissolve fresh turnings in 6NHCl* and dilute to volume	$CoCl_2$	0.640	640
Ni	Ni	Dissolve fresh turnings in minimum amount nitric acid and dilute to vol.	$Ni(NO_3)_2$	0.640	640
Pd	Pd	Dissolve fresh metal filings in aqua regia*	$PdCl_2$ & $Pd(NO_3)_2$	0.640	640
Pt	Pt	- do -	PtU_2 & $Pt(NO_3)_2$	0.640	640
Group IB					
Cu	$CuSO_4,5H_2O$	Dissolve fresh crystals in water	$CuSO_4$	2.523	640
	Cu	Dissolve fresh fillings in dilute HNO_3* plus a few drops HCl	$Cu(NO_3)_2$	0.640	640
Ag	$AgNO_3$	Dissolve in freshly distilled water	$AgNO_3$	1.007	640
	Ag	Dissolve fresh turnings in conc. HNO_3*	AgNO3	0.640	640
Au	Au	Dissolve metal in aqua regia*	$AuCl_2$ & $Au(NO_3)_2$	0.640	640
Group IIB					
Zn	Zn	Dissolve metal in dil. HCl*	$ZnCl_2$	0.640	640
Cd	Cd	- do -	$CdCl_2$	0.640	640
Group IIIA					
Al	Al	Dissolve Al wire freshly prepared turnings or filings in minimum amount HCl	$AlCl_3$	0.640	640

*Use as little acid as possible

TABLE 5.3 CONTINUED

Element	Stock	Procedure	Resultant compound	Grams stock per litre	Stock value ppm
Group VIIB					
Mn	MnO_2	Dissolve in conc. HCl*	$MnCl_2$	1.013	640
Group VIII					
Fe	Fe	Dissolve fresh iron fillings (or pure iron wire) in 11 ml 6NHCl and dilute to volume	$FeCl_2$	0.640	640
Co	Co	Dissolve fresh turnings in 6NHCl* and dilute to volume	$CoCl_2$	0.640	640
Ni	Ni	Dissolve fresh turnings in minimum amount nitric acid and dilute to vol.	$Ni(NO_3)_2$	0.640	640
Pd	Pd	Dissolve fresh metal filings in aqua regia*	$PdCl_2$ & $Pd(NO_3)_2$	0.640	640
Pt	Pt	- do -	PtU_2 & $Pt(NO_3)_2$	0.640	640
Group IB					
Cu	$CuSO_4,5H_2O$	Dissolve fresh crystals in water	$CuSO_4$	2.523	640
	Cu	Dissolve fresh fillings in dilute HNO_3* plus a few drops HCl	$Cu(NO_3)_2$	0.640	640
Ag	$AgNO_3$	Dissolve in freshly distilled water	$AgNO_3$	1.007	640
	Ag	Dissolve fresh turnings in conc. HNO_3*	$AgNO_3$	0.640	640
Au	Au	Dissolve metal in aqua regia*	$AuCl_2$ & $Au(NO_3)_2$	0.640	640
Group IIB					
Zn	Zn	Dissolve metal in dil. HCl*	$ZnCl_2$	0.640	640
Cd	Cd	- do -	$CdCl_2$	0.640	640
Group IIIA					
Al	Al	Dissolve Al wire freshly prepared turnings or filings in minimum amount HCl	$AlCl_3$	0.640	640

*Use as little acid as possible

TABLE 5.3 CONTINUED

Element	Stock	Procedure	Resultant compound	Grams stock per litre	Stock value ppm
Group VIIB					
Mn	MnO_2	Dissolve in conc. HCl*	$MnCl_2$	1.013	640
Group VIII					
Fe	Fe	Dissolve fresh iron fillings (or pure iron wire) in 11 ml 6NHCl and dilute to volume	$FeCl_2$	0.640	640
Co	Co	Dissolve fresh turnings in 6NHCl* and dilute to volume	$CoCl_2$	0.640	640
Ni	Ni	Dissolve fresh turnings in minimum amount nitric acid and dilute to vol.	$Ni(NO_3)_2$	0.640	640
Pd	Pd	Dissolve fresh metal filings in aqua regia*	$PdCl_2$ & $Pd(NO_3)_2$	0.640	640
Pt	Pt	- do -	PtU_2 & $Pt(NO_3)_2$	0.640	640
Group IB					
Cu	$CuSO_4,5H_2O$	Dissolve fresh crystals in water	$CuSO_4$	2.523	640
	Cu	Dissolve fresh fillings in dilute HNO_3* plus a few drops HCl	$Cu(NO_3)_2$	0.640	640
Ag	$AgNO_3$	Dissolve in freshly distilled water	$AgNO_3$	1.007	640
	Ag	Dissolve fresh turnings in conc. HNO_3*	$AgNO_3$	0.640	640
Au	Au	Dissolve metal in aqua regia*	$AuCl_2$ & $Au(NO_3)_2$	0.640	640
Group IIB					
Zn	Zn	Dissolve metal in dil. HCl*	$ZnCl_2$	0.640	640
Cd	Cd	- do -	$CdCl_2$	0.640	640
Group IIIA					
Al	Al	Dissolve Al wire freshly prepared turnings or filings in minimum amount HCl	$AlCl_3$	0.640	640

*Use as little acid as possible

Element	Stock	Procedure	Resultant compound	Grams stock per litre	Stock value ppm
Group IVA					
Si	SiO_2	Dry fresh SiO_2 at 500°C. Fuse SiO_2 and 400 mg lithium metaborate at 1100°C for 15 min. Pour melt into 200 ml 3% HNO_3* and dilute to volume 250 ml	-	0.400m	184 ppm
Pb	$Pb(NO_3)_2$	Dissolve 1.598 g $Pb(NO_3)_2$ which has been dried at 110°C in freshly distilled water	$Pb(NO_3)_2$	1.023	640
	Pb	Dissolve freshly filed metal filings in dilute HNO_3	$Pb(NO_3)_2$	0.640	640

* Use as little acid as possible

PART III. ANALYTICAL APPLICATIONS

CHAPTER 6

LITHIUM

6.1 INTRODUCTION

Lithium has been the subject of considerable study in the field of geochemistry. The preliminary work of Goldschmidt and Peters (1933) who outlined the geochemical rules governing the behaviour of lithium, has been followed by many papers, notably those of Strock (1936), Wager and Mitchell (1943), and more recently by Horstman (1956) and the review by Heier and Adams (1964).

Like the other alkalis, lithium is a lithophile element, but because the radius of Li^+ is smaller than the radius of the other alkali metal cations (see Table 6.1) its geochemical behaviour is unlike that of the other alkalis. In spite of charge similarities it will not substitute for sodium and potassium in minerals of these elements. It tends to be associated with magnesium and iron because of the similarity of ionic radii, i.e. Mg^{2+} 0.66Å, Fe^{2+} 0.74Å. On the other hand, because of charge differences, several magnesium-iron minerals (e.g. olivine) do not readily accept lithium into their structure. In these minerals, and consequently in rocks largely composed of these and similar minerals, concentrations of lithium as low as 1 ppm or less are found.

TABLE 6.1

Relative Abundances of the Alkali Metals

Element	Ionic radius Å	Crystal average (1)	Granite G-1 (1)	Diabase W-1 (1)	Ultrabasic (2)	Shales (1)	Sandstone (1)
Li	0.68	20	24	12	0.X*	66	15
Na	0.97	28,000	24,600	15,400	4,200	9,600	3,300
K	1.33	25,900	45,100	5,300	40	26,600	10,700
Rb	1.47	90	220	22	0.2	140	60
Cs	1.67	3	1.5	1.1	0.X*	5	0.X*

(1) Mason (1966)
(2) Turekian and Wedepohl (1961)

* 0.X indicates an order of magnitude

However, lithium does form its own minerals, e.g. lepidolite, petalite and spodumene, in which several percent of lithium may be present. Host minerals to lithium are mainly micas, e.g. biotite in granites may have several hundred ppm. The average crystal abundance of 20 ppm (Taylor, 1964) is low. The granite, G-1 and diabase W-1 have values of 24 and 12 ppm respectively.

Higher concentrations are present in sedimentary rocks, mainly because lithium rich minerals, notably biotite, do not weather easily (Goldich, 1938) and, whereas the absolute amount of other alkalis present in rocks is reduced by weathering, lithium shows no such trend (Butler, 1953, 1954).

Some average abundances are shown in Table 6.1 together with other data on lithium.

Sensitive, precise and accurate methods of analysis are required because

(a) lithium has low abundances in most rocks, and

(b) its transport from one rock type to another is indicated by very small concentration differences (Strock, 1936).

The D.C. arc emission method is usually used for the determination of lithium (Ahrens and Taylor, 1961). Strock (1936) used cathodic layer excitation and the Li 6707 line, and was able to achieve a detection limit of 1.0 ppm. A detection limit of 0.1 ppm was claimed by Taylor and Heier (1958) when determining lithium in alkali feldspars. The limitation of these methods is that the precision obtained, using the D.C. arc and photographic recording, is seldom better than a relative deviation of 5-10%.

Because of its low atomic number, lithium is not determined by X-ray fluorescence methods. Although sensitive by emission flame spectroscopy in pure aqueous solutions it is subject to line reversal and interference by other alkali and alkaline earth elements in the flame, and relatively complicated chemical procedures must be used to eliminate these (Horstman, 1956). Lithium may, however, be determined with comparative ease by atomic absorption spectrometry using the strongly absorbent 6708Å line. This technique has been employed by

Angino and Billings (1966) for the determination of lithium in seawater, by Fishman and Downs (1966), for its determination in lake water, and Price and Ragland (1966) for lithium determination in quartz. The methods described indicated good precision and sensitivity, but no mention was made of the best flame conditions and no interference effects were reported.

For the purpose of determining lithium in various types of silicate rocks, a critical study was made of the best flame conditions and the interferences likely to be encountered.

6.2 EXPERIMENTAL

6.2.1 Flame Studies

Several different types of flame were tested. Bowman (1967) used a town gas/air flame, while instrument handbooks appear to differ considerably with regard to the recommended flame for lithium.

Fig. 6.1 shows absorbance profiles for lithium in three different flames, under different burning conditions. It is seen that maximum absorbance is found at the base of a highly oxidizing or fuel-lean acetylene/air flame. The explanation for this may be the strong tendency for lithium to form hydroxides,

i.e. $Li + H_2O \rightarrow LiOH + H$

or $Li + OH \rightarrow LiOH$

The exact mechanism by which lithium is released and recombined with OH radicals is not clear, but is obviously dependent on:

(a) The temperature of the flame which causes lithium hydroxide to dissociate;

(b) the concentration of free OH radicals in the flame.

In the primary zone of a highly oxidizing acetylene/air flame, the temperature is high and the OH concentration low.

As the acetylene content of the acetylene/air flame is increased, the combustion reaction results in a higher concentration of OH radicals (Mavrodineanu and Boiteaux, 1965). The LiOH compound is relatively stable and the reverse reaction is unlikely to occur higher up in the flame because of

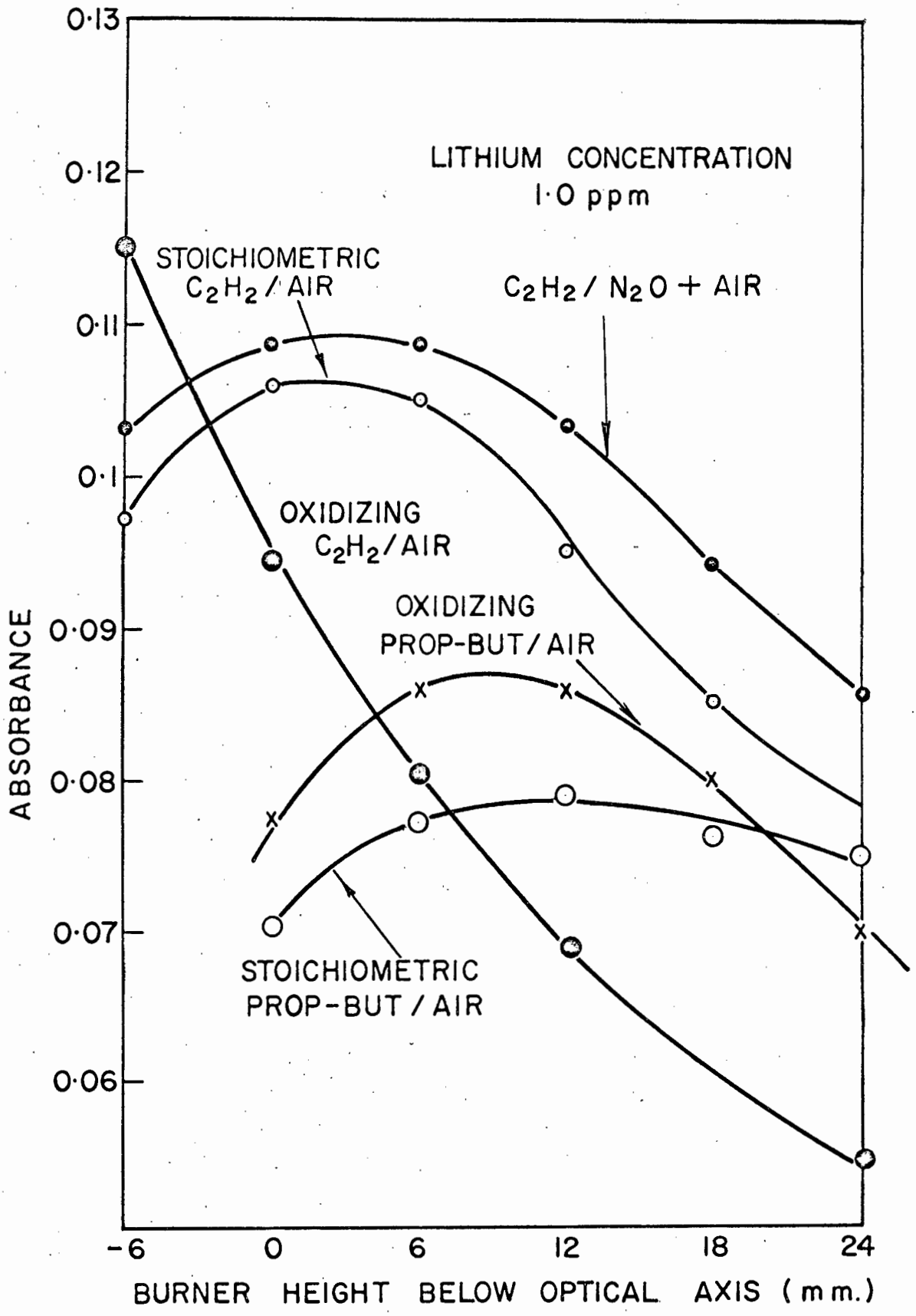


FIG. 6·1.

Absorbance for Lithium in various Flames.

higher OH content.

This explanation also holds for the propane-butane flames. In the high temperature propane-butane/nitrous-oxide flame, the concentration of free OH is high, even in the primary zone. Lower sensitivity for lithium results. Similarly the low temperature and higher concentration of OH in the propane-butane/air flame results in an even lower sensitivity.

In the acetylene/nitrous-oxide flame, the temperature is high (2795°C) so that the lithium hydroxide is dissociated, but the lithium neutral atom population is also depleted through excitation and ionization of the atoms. Interference tests, described later, confirm this.

The best flame for maximum sensitivity is thus a highly oxidizing (fuel-lean) acetylene/air flame with the light beam passing through as much of the primary combustion zone as possible

Many experiments were carried out to determine the best conditions when hotter flames (i.e. the acetylene/nitrous-oxide + air) were used. Iron interference could be removed and reasonable sensitivity obtained on lithium-iron solutions in a flame with 91% nitrous-oxide and 9% air (temperature about 2640°C).

These results are quite unlike those obtained for the other alkali metals, where cooler flames (2000°C) are more sensitive. The best overall conditions for lithium determination are given in Table 6.2.

TABLE 6.2

Most suitable conditions for the determination of Lithium

Condition	
Flame*	C_2H_2/air. Highly oxidizing (fuel lean)
Burner	10 cm laminar flow C_2H_2/air burner
Slit	100 micron (4Å bandpass)
Lamp current	5 mA. (Currents above 10 mA result in sensitivity decrease as well as a decrease in light intensity through self reversal)

* Note: The burner is adjusted without the flame burning so that it cuts off 10% of the hollow cathode lamp light.

6.2.2 Interferences

A careful study was made of the elements present in most igneous rocks which would interfere with the absorbance of lithium.

Fig. 6.2 shows the effect of sodium and potassium. With these two elements about a 10% enhancement is found for the acetylene/air flame above 100 ppm. The hotter acetylene/nitrous-oxide + air flame causes considerably more enhancement. A saturation point is reached for sodium at 80 ppm, but for potassium enhancement continues to 400 ppm and beyond.

In Fig. 6.3 is seen the effects of magnesium, calcium and aluminium. Slight depression occurs in the acetylene/air flame. In the acetylene/nitrous-oxide flame continued enhancement is seen for the three elements.

Fig. 3.9 (Section 3) shows the significant depression which was caused by iron at high concentrations in the acetylene/air flame and how this could be eliminated by using a hotter flame. The iron interference is again shown in Fig. 6.4 with the acetylene/air flame burning under optimum conditions (Curve A), and under fuel-rich conditions (Curve B). It should be noted that these tests were made with pure iron solutions containing only lithium.

When interference tests were made with mixtures of the interfering elements, it was found that iron, in the presence of more than 100 ppm sodium, had virtually no effect of lithium absorbance in the lean acetylene/air flame. (Fig. 6.4, Curve C). 50 ppm sodium were not enough to suppress this interference completely (Curve D). In the hot flame, however, severe enhancement of lithium absorption occurred.

These results indicate that if lithium is to be determined in silicate material where both iron and sodium are present, especially where iron is present above 3% (in the solid), it is necessary for lithium standards to contain 100-200 ppm sodium. The mixed support gas flame may be used for the determination of lithium in silicate samples, but was not often used for rock analyses mainly because satisfactory results were obtained with the standard acetylene/air flame and sodium doped standards.

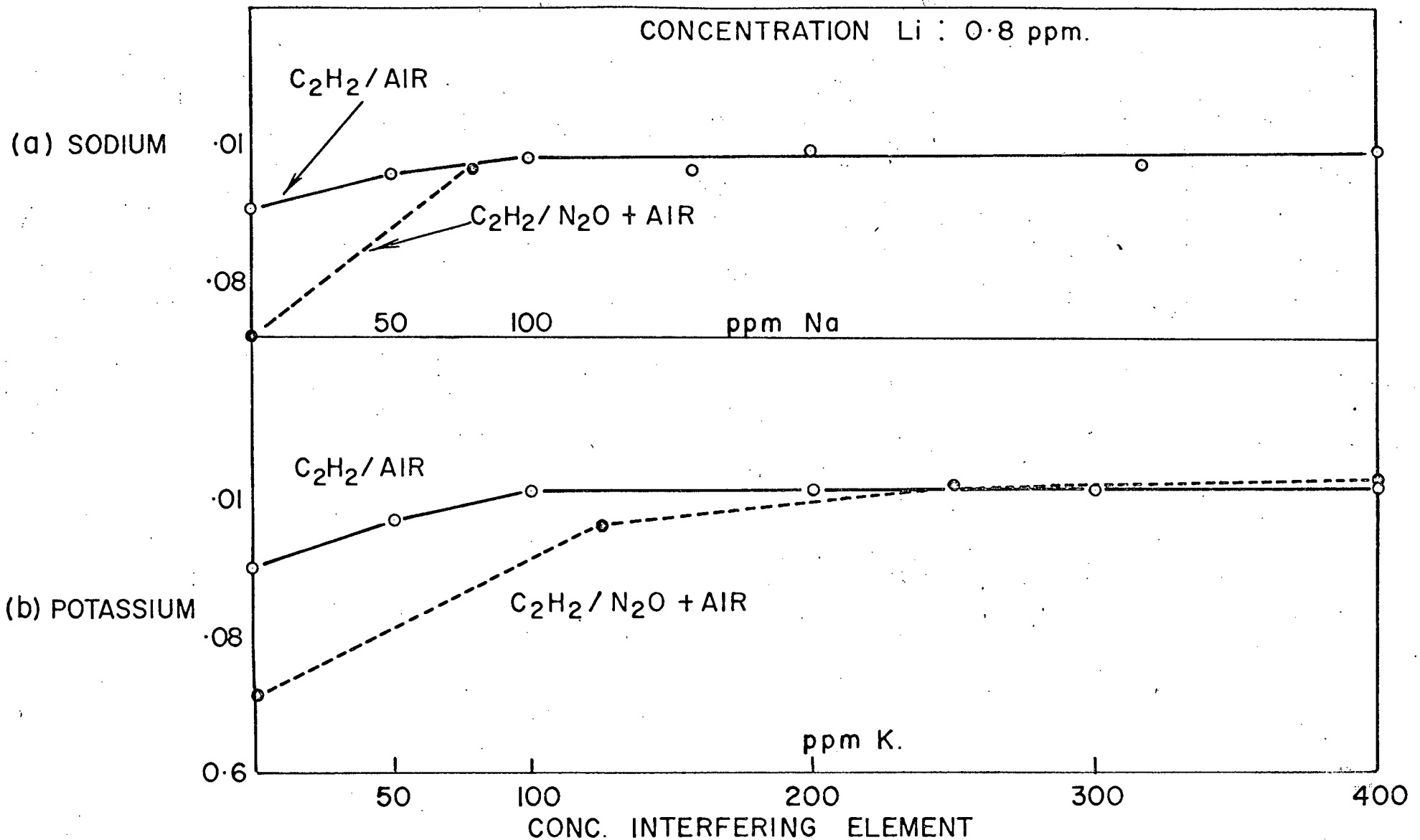


FIG. 6·2

Effect of Sodium and Potassium on Lithium Absorbance.

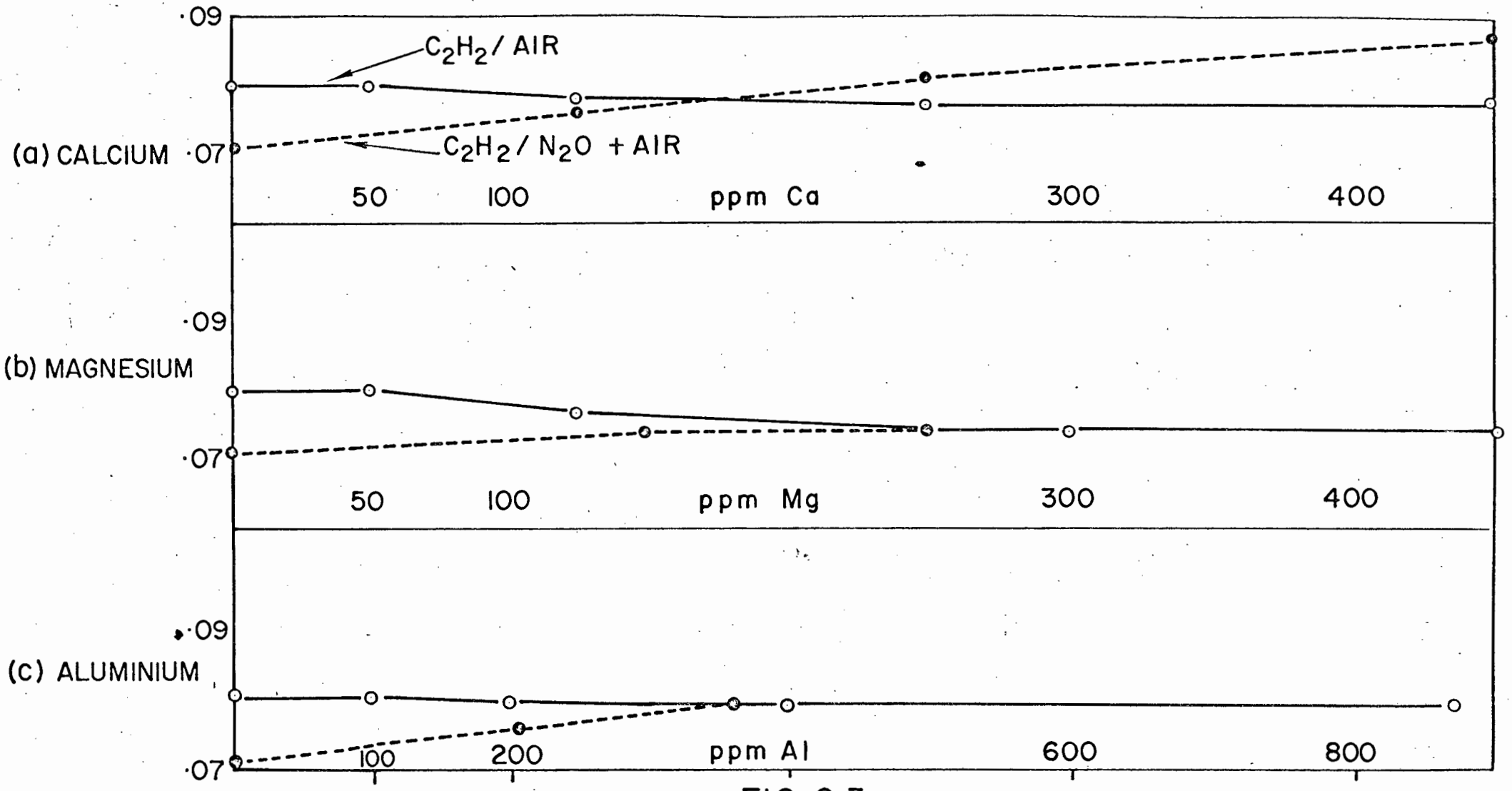


FIG. 6·3.

Effect of Magnesium, Calcium, and Aluminium on Lithium Absorbance.

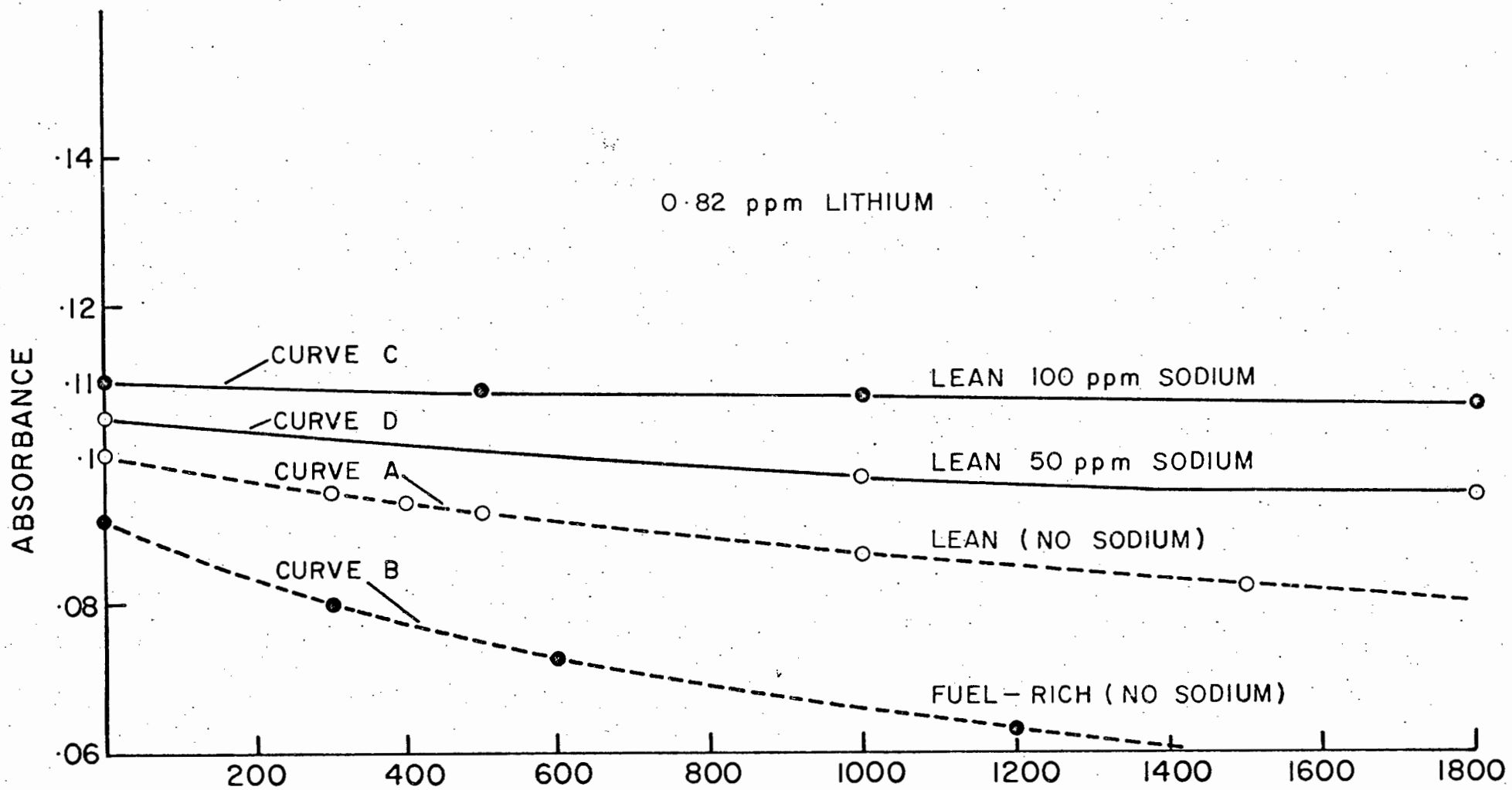


FIG. 6·4.

Interference of Iron on Lithium with and without Sodium present.

It is suggested that the iron interference in the sodium free solutions is caused by the formation of stable lithium ferrite. The hot flame dissociates this compound. When sodium is present, a preferential reaction of the iron with sodium takes place thus releasing lithium,

i.e. $Li_2Fe_2O_4 + 2Na \rightarrow Na_2Fe_2O_4 + 2Li$

The enhancement of lithium in the hot flame is caused by ionization suppression.

6.2.3 Analysis

(a) Sample dissolution. Fusion techniques were found to be unsatisfactory for lithium and other trace element determinations. Lithium fusion salts are obviously excluded, and the other alkali fusion salts could not be obtained in bulk in pure enough form. In addition, the flux dilution caused too much loss of sensitivity, especially for those rocks where lithium values were below 20 ppm. The most satisfactory dissolution method found was Technique A-1 (Table 5.2).

(b) The limit of detection for lithium in solution was found to be 0.02 ppm (0.005A), although a value of 0.04 ppm (0.01A) was considered the lowest practical determination limit. With a 1% solution, concentrations of 4 ppm in rocks could be determined. In cases where concentrations lower than this were encountered, stronger solutions (2% or 5%) were made, thus extending the limit to 0.8 ppm in the solid.

A nearly linear analytical graph was obtained up to an absorbance of 0.8A (4 ppm) after which the graph curved slightly. Absorbance reading of up to 1.0 could be taken, but if concentrations of lithium were so high, it was preferred to dilute the sample or to turn the burner.

(c) Precision. Repeated measurements were made on single solutions. The coefficients of variation were calculated and are shown in Table 6.3(a).

Several dissolutions were made of a Karroo dolerite and lithium determined in the separate solutions by the author and a colleague.

The results are given in Table 6.3(b). It is seen that the precision obtained on the aqueous solutions and on the rock sample solutions is satisfactory.

TABLE 6.3

Precision Tests

(a) Aqueous solutions of LiCl (optimum conditions)

Spectrometer	Concentration (ppm)	Number of determinations	Coeff. of Var.* %
PE 303	0.05	25	3.0
	0.25	25	1.2
	2.5	25	1.4
Techtron	0.05	25	3.6
	0.25	25	1.0
	2.5	25	0.9

(b) Separate dissolutions of rock powder

Rock: Karroo Dolerite D/S 95

HF : $HClO_4$ 1% solution (0.5 g to 50 ml)

	Mean Conc. (ppm)	No. of determinations (P.E. 303)	Coeff. of Var.* %
Author:	34.7	8	1.4
Colleague:	34.7	8	2.2

Note: These tests were made to test the precision of dissolution and determination only. Standards were aqueous and were not accurately prepared. Later results yielded different values for this sample. (See Table 6.4).

* Coefficients of variation were calculated as indicated in Chapter 4. One separate value read off the concentration graph was considered a "determination" for (a) and the average of 3 separate observations taken as a determination for (b).

(d) Accuracy. The tests for accuracy were made by analyzing powdered international rock standards. The results of these analyses are given in Table 6.4(a).

Results for lithium on several other types of rocks are given in Table 6.4(b). Only some comparative values are available but the atomic absorption values are listed for record purposes.

The results in Table 6.4(a) appear to be acceptable, although the value for G-1 is a little low. Considerable difficulty was experienced in obtaining accurate lithium standard solutions. When dried lithium chloride was used, low analytical values resulted. Standards prepared from lithium carbonate gave higher values, but it was not until lithium standards were prepared from lithium metal that fully reliable values were obtained. This was done by dissolving lithium metal in water. The hydroxide content was then determined by titration with standardized hydrochloric acid and the lithium content calculated. The same procedure was used for the preparation of lithium 6 and lithium 7 standards.

Further results were obtained for G-1 and W-1 using synthetic rock powders as the base for standards and adding lithium. The results obtained were very similar to those indicated in Table 6.4(a) and are shown in Table 6.4(c).

6.2.4 Discussion

The abundance data of Turekian and Wedepohl listed in Table 6.1, shows the relative lack of data on the lithium content of ultrabasic rocks. The level of less than 1 ppm is indicated. For the ultramafic rocks provided by J. Gurney, the lowest lithium determined is 2.8 ppm.

The atomic absorption method is sensitive down to less than 1 ppm of lithium in rocks, and this method may well enable new data to be obtained on lithium abundances in ultrabasic rocks.

TABLE 6.4

Results of Lithium Determinations

(a) Comparison with International Standards

Standard		Accepted value		Atomic absorption	No. of determinations*
		ppm	Ref.		
Granite	G-1	24	(1)	23.2	6
Diabase	W-1	12	(1)	12.1	8
Granite	G-2	30 - 75	(2)	36.5	6
Granodiorite	GSP-1	30 - 44	(2)	32.0	6
Andesite	AGV-1	8 - 15	(2)	12.4	6
Peridotite	PCC-1	<2	(2)	<2	6
Basalt	BCR-1	12 - 20	(2)(3)	14.4	6
Tonalite	T-1			14.0	6
Granite	GH	29 - 60	(3)	42.5	4

*A determination is considered as the average of results on a particular solution. Where 6 determinations are indicated, 6 separate sample aliquots were dissolved.

(b) Analyses of samples*

Sample	Value determined by other workers (3)	Method	Atomic Absorption	No. of determinations
ET3/169	2.2	Emission	4.4	6
ET3/270	2.3		4.4	6
5087	4.1		5.9	8
DS 95	28.3		29.0	16
7228	4.1		4.9	6
NOR-1	20.0		22.8	4
NOR-2			59.6	4
RV 374			8.0	4
KRV 7			10.2	6
KRV 13			20.0	4
RV 377			11.0	2
KDB 10			4.8	4
KDB 12			5.1	4
Bult 8			2.8	2
Bult 11			3.0	2
Bult 16			3.6	2
AA 5			2.8	6
Ash 1			6.7	4
EK 43			7.8	8
Tan 503			4.2	4

TABLE 6.4 (continued)

(c) International standards by method of addition

Standard	Accepted value		Atomic absorption	No. of determinations*
	ppm	Ref		
Granite G-1	24	(1)	22.1	4
Diabase W-1	12	(1)	11.5	4

(1) Fleischer (1965)

(2) Flanagan (1966)

(3) Erlank (1967)

*For reference to the origin of these samples see Appendix II

6.3 LITHIUM ISOTOPES

6.3.1 Introduction

The relatively large difference in atomic mass for the two isotopes of lithium makes it possible for them to be separated in nature. This separation may take place through natural ion exchange processes leading to an enrichment of one or other of the isotopes (Taylor and Urey, 1938) in minerals or rocks. This fractionation is of considerable interest geochemically, but has not received very much attention (Heier and Adams, 1964). The reason for this could well be the highly sophisticated instrumentation usually required for isotope abundance measurements.

Mass spectrometric techniques are usually employed for the determination of isotopic ratios of lithium (Gillieson and Thorne, 1955; Shima and Honda, 1966). Emission spectrographic techniques have also been used (Brody and Tomkins, 1958) but a high resolution spectrograph or interferometer is needed to separate the doublet. The position is complicated by the overlapping of the isotope components, and doubtful assumptions must be made regarding the relative intensities of the doublet.

In his original publication Walsh (1955) suggested the possibility of conducting isotopic determinations by atomic absorption spectrometry. This is only possible if the isotopic shift of the resonance lines is greater than the absorption line width. Absorption line-widths have been calculated to be of the order 0.03 Å (Section 2.2.5). Only elements at either end of the periodic table have isotopic separations large enough to enable the atomic absorption method to be applied for the determination of relative isotope concentrations.

0.15Å separates the wavelengths of the two lithium isotopes ^6Li and ^7Li. While this shift is adequate to resolve the absorption lines, the position is complicated by the doublet nature of the lithium resonance line 6707.8. The transitions $2s^2S_{\frac{1}{2}} - 2p^2P^o_{\frac{1}{2}}$ and $2s^2S_{\frac{1}{2}} - 2p^2P_{\frac{3}{2}}$, typical of the alkali metal spectra, have a wavelength separation of only 0.15Å in the case of lithium. (With sodium it is much larger - 5.96Å). This causes the main component of the lithium 6 line to be superimposed on the weaker component of the lithium 7 line, the wavelength difference being very nearly that of the isotopic shift. Plate 5(a) shows a photograph of the doublet for lithium 6, lithium 7 and normal lithium*. The shift is clearly seen. These spectra were recorded on a 2 meter R.S.V. spectrograph using a grating with 1200 lines/mm in the second order and having a theoretical resolution of 460,800. This instrument also has a direct-reading adapter which enables the spectra to be scanned with a photomultiplier and slit. The tracing in Plate 5(b), taken photo-electrically on the same spectrograph, shows the doublet structure of lithium 7.

Because of this overlapping of the two isotope lines, the atomic absorption measurement of the separate isotopes is complicated. If a lithium 6 lamp is used and a solution containing only lithium 6 is nebulized into the flame, normal absorbance will be recorded. If a solution of only lithium 7 is

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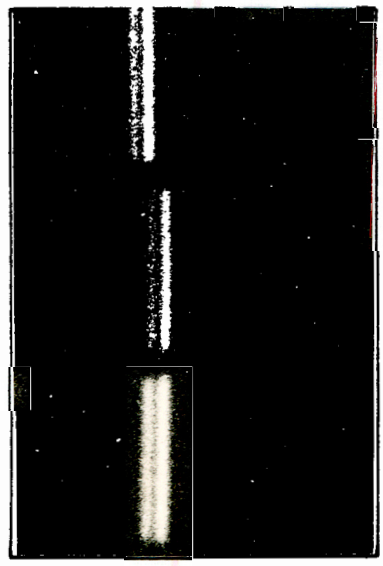
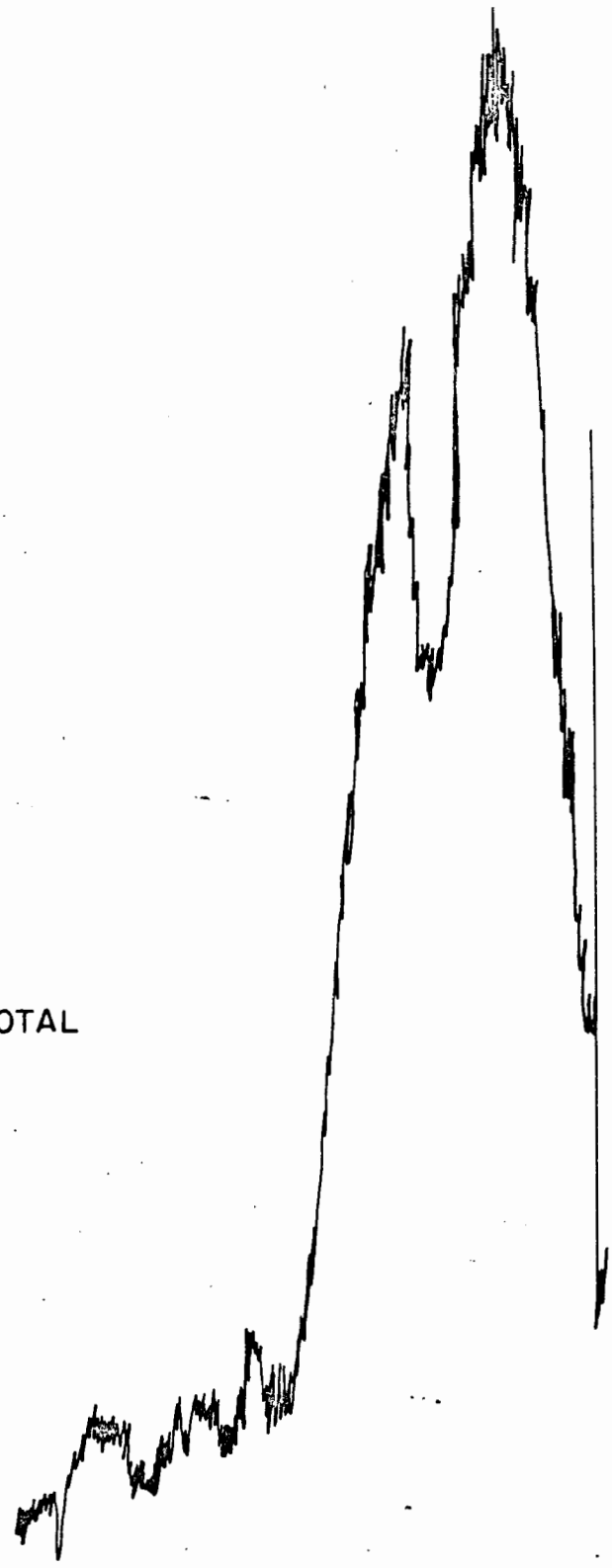
* The intensity of the weaker component of the lithium 6 is of course very weak in the total lithium exposure. If the exposure is increased, the component is seen, but the other lines are then overexposed.



(a)

SHORTER λ



(b)

RECORDING OF THE DOUBLET COMPONENT OF Li^7

PLATE 5.

Spectral Line Shifts of Lithium Isotopes.

is sprayed, however, some absorbance will also be recorded, because of the line component overlap. This is illustrated in Fig. 6.5 where the separate components of the isotope doublets and their relative positions in emission are shown. With the lithium 6 lamp in position and lithium 7 solutions being nebulized (Fig. 6.5(b)), the right leg of the emission line is partly absorbed by the left leg of the lithium 7 absorption line. This means that if a simple spectrometer is used to record line intensity some decrease will be indicated although no lithium 6 is present. (The shaded area is "seen" by the spectrometer.)

In a similar way, Fig. 6.5(c) shows the conditions when a lithium 7 lamp is in position and lithium 6 solution is nebulized.

In order to overcome this difficulty, Zaidel and Korennoi (1961) used only a lithium 6 hollow cathode lamp as source. They measured the absorbance in a flame for a series of standards with ratios of lithium 6 to lithium 7 varying between 2 and 45%. A graph of lithium 6 absorbance was plotted against this ratio. Manning and Slavin (1962) used a flame as a source. When solutions of lithium 6 and lithium 7 were sprayed into this flame, absorbance could be measured in a normal atomic absorption flame. Sensitivity was about half of that from a hollow cathode lamp. Absorbance ratios of lithium 6 to lithium 7 were plotted for a wide range, 0-100%, but no analyses were done. A de-mountable Schüler-Golnow hollow-cathode lamp was used by Goleb and Yokoyuma (1964) as a means for producing an atomic cloud. Lithium samples were dried in the cathode of this lamp. Sputtering of the material in the cathode enabled both lithium 6 and lithium 7 absorbances to be measured. Goleb plotted the absorbance ratios against the isotope ratios and obtained a straight line. He determined the natural lithium abundance in lithium hydroxide.

6.3.2 Experimental

Three lithium hollow cathode lamps were made. One contained lithium 6, one lithium 7 and one natural lithium. The metallic isotopes were purchased from the Oak Ridge National Laboratory and were stated to be 98% pure. Unfortunately,

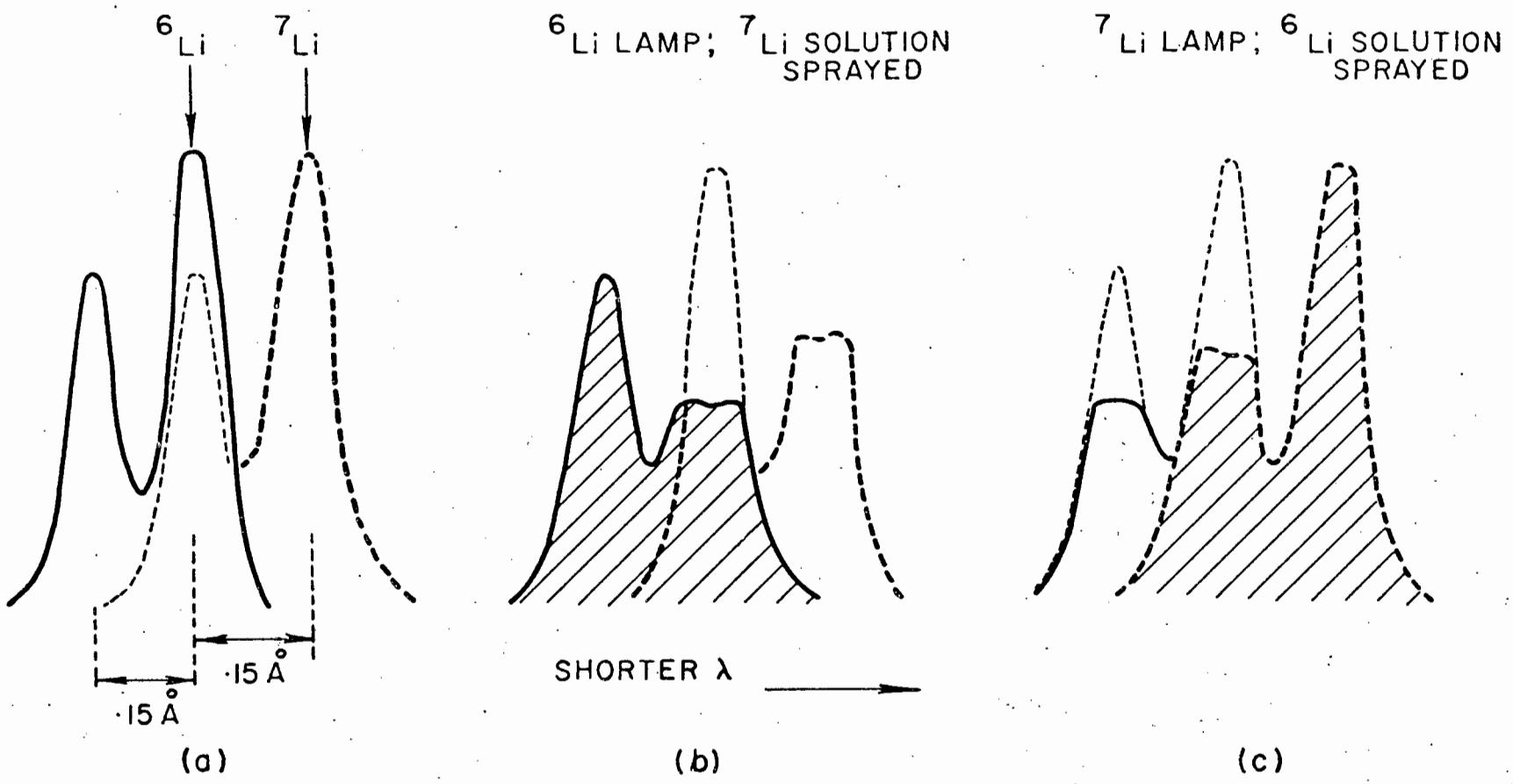


FIG. 6·5.

Diagram Showing,

(a) The Doublet Structure of the two Lithium Isotopes Superimposed

(b) ^{6}Li Light partly absorbed by ^{7}Li Atoms

(c) ^{7}Li Light partly absorbed by ^{6}Li Atoms (Note $\Sigma\,^7Li > \Sigma\,^6Li$)

concentration scale. The lithium 6 abundance was then read from the absorbance ratio:concentration graph.

TABLE 6.5

Standards preparation scheme for the determination of lithium 6 to lithium 7 isotope ratios

Sol. No.	Li Conc.	$^{6}Li/^{7}Li$	Solution
A 1	8 ppm	1 : 19	5 ml of 8 ppm ^{6}Li - 95 ml 8 ppm ^{7}Li
A 2	"	2 : 18	10 ml " " " " - 90 ml " " "
A 3	"	4 : 16	20 ml " " " " - 80 ml " " "
A 4	"	6 : 14	30 ml " " " " - 70 ml " " "
A 5	"	8 : 12	40 ml " " " " - 60 ml " " "
A 6	"	10 : 10	50 ml " " " " - 50 ml " " "
B 1	4 ppm	1 : 19	Dilute A 1 1 : 1 with water
B 2	"	2 : 18	" A 2 1 : 1 " "
B 3	"	4 : 16	" A 3 1 : 1 " "
B 4	"	6 : 14	" A 4 1 : 1 " "
B 5	"	8 : 12	" A 5 1 : 1 " "
B 6	"	10 : 10	" A 6 1 : 1 " "
C 1	2 ppm	1 : 19	Dilute B 1 1 : 1 with water
C 2	"	2 : 18	" B 2 1 : 1 " "
C 3	"	4 : 16	" B 3 1 : 1 " "
C 4	"	6 : 14	" B 4 1 : 1 " "
C 5	"	8 : 12	" B 5 1 : 1 " "
C 6	"	10 : 10	" B 6 1 : 1 " "
D series	1 ppm	As C	Diluting C 1 : 1 with water
E series	0.5 ppm	As D	Diluting D 1 : 1 with water

Fig. 6.6 shows typical calibration graphs. Absorbance ratios of lithium 6/lithium 7 are plotted against the lithium 6/lithium 7 concentrations.

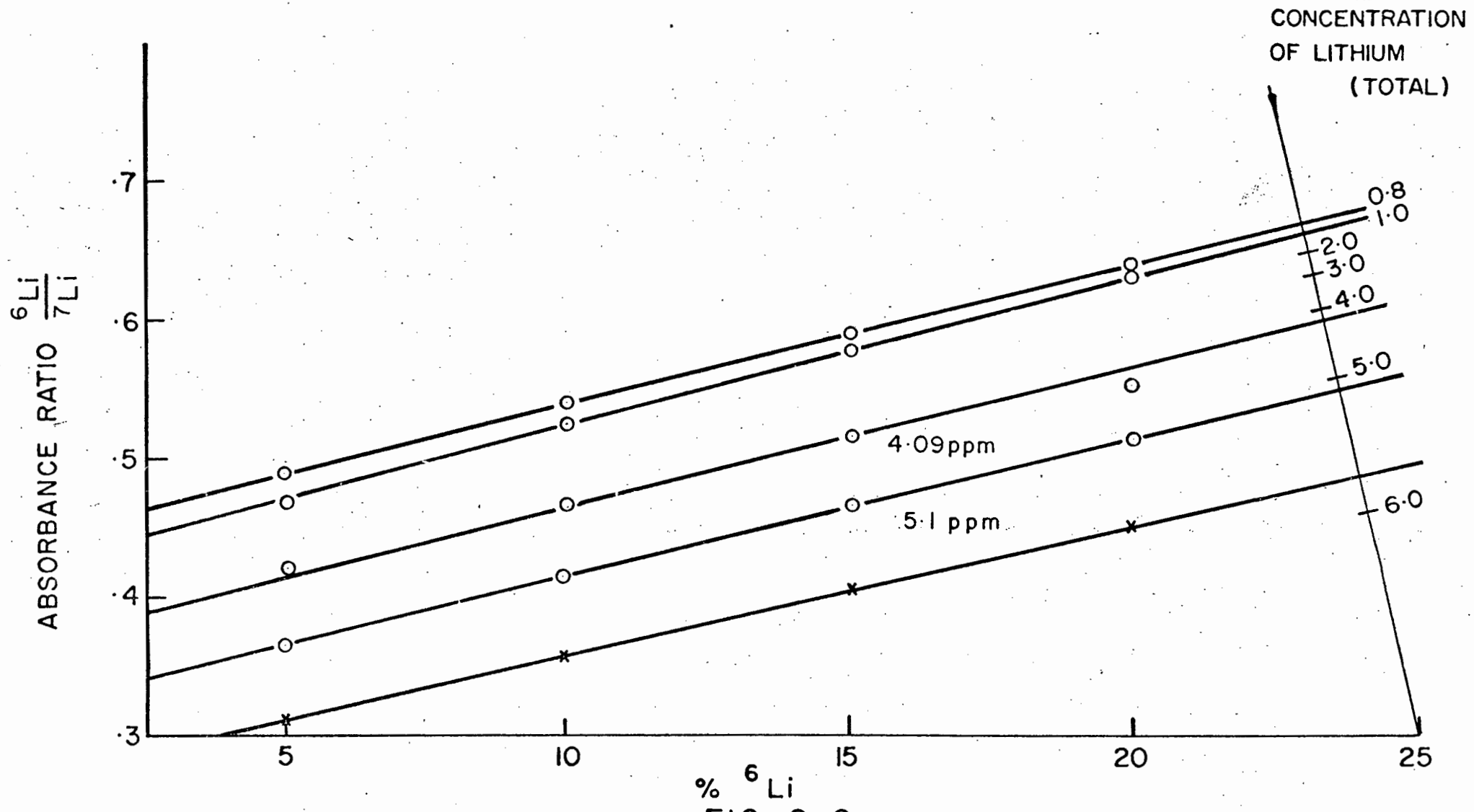


FIG. 6·6.

Calibration Curves of Absorbance Ratios for $\frac{^6Li}{^7Li}$, showing the difference between various Concentrations of Total Lithium.

Because interferences are mutual to both isotopes, no undue care was taken to prevent interference. However, care was exercised to ensure that the flame conditions and lamp conditions remained identical when measuring lithium 6 and lithium 7 solutions. It is essential that the absorption coefficient remains the same for both sets of readings.

6.3.3 Analyses

A number of measurements was made on the two international standards G-1 and W-1 for which the isotope ratios are known. The results, together with a number of results on shale samples are shown in Table 6.6.

TABLE 6.6

$^{7}Li:^{6}Li$ for a number of samples determined by atomic absorption spectrometry

Sample	% Li	Average	Accepted
G - 1	7.7, 6.4, 7.6, 10.4	8.0	8.22
W - 1	9.3, 7.0, 9.6, 7.3	8.3	8.21
19a	6.1, 6.1, 6.0, 5.6	6.0	
32a	5.1, 4.7, 4.8	4.9	
40a	6.1, 6.8, 8.2		
60a	5.6, 5.9, 7.5	6.3	
63a	6.6, 6.6, 5.9, 6.4	6.4	
G - 2	8.4, 8.0, 8.8	8.4	

It should be noted that precision of measurement is not good because of the fluctuations in the lithium 6 lamp. If a good lamp is used, there is no reason why precision of measurement should not be within 5%, provided the lithium concentration is not too low.

6.3.4 Conclusion

From the measurements made it appears that atomic absorption offers a rapid

and inexpensive method for measuring lithium isotope ratios. Because of the relatively flat graph obtained in Fig. 6.6, it is better suited for determining wide ratio differences. The natural abundance ratio is of the order 12.1 ($^{7}Li:^{6}Li$) but geological deviations from this value may be appreciable (Heier and Adams, 1964). In order to achieve the highest accuracy to establish small deviations, the utmost care must be taken to obtain precise readings. Maximum sensitivity is required to obtain as steep an absorption ratio:concentration graph as possible. At this stage it appears that the accuracy of atomic absorption isotope determination is less than that of the mass spectrometer. However, it can be compared in accuracy with spectrographic methods and is probably more precise than these (Brody and Tomkins, 1958).

Its simplicity makes it a most attractive method, and this may enable the geochemist to study the fractionation of lithium 6 and lithium 7 in various types of igneous rocks and minerals. Because of this a simple lithium isotope analyser which makes use of atomic absorption methods has been designed and is described in Appendix 1.

CHAPTER 7

SODIUM, POTASSIUM, RUBIDIUM AND CAESIUM

7.1 INTRODUCTION

The individual treatment of lithium in this thesis has been necessitated by its somewhat different behaviour in the flame as well as its geochemical characteristics. However, the remaining alkali metals, sodium, potassium, rubidium and caesium have similar atomic absorption and flame properties and the studies made of these elements are accordingly presented together in this chapter.

Sodium and potassium are considered to be major constituents in most geological matter. They occur relatively abundantly in large numbers of silicate minerals typically associated with igneous rocks, as well as in a large variety of dissolved or soluble salts in seawater and deposits. Sodium, with an ionic radius of 0.68Å is not as closely associated with potassium (radius 1.33Å) as with calcium (radius 0.99Å) in many silicate minerals of igneous rocks as would be expected (Day, 1963). In general, the concentration of sodium remains fairly uniform in common igneous rocks (excluding ultramafic varieties) whereas the concentration of potassium may vary considerably, e.g. potassium, levels may be as low as 0.1% in basalts and as high as 6% in granites. Sodium concentrations are usually of the order of 1-2% (Heier and Adams, 1964).

In sedimentary materials such as clays, etc., sodium concentrations are usually low because of the high solubility of sodium salts. When sodium is present it is usually due to minute grains of albite ($NaAlSi_3O_8$). Potassium, however, is less easily hydrated and because of its larger ionic radius is absorbed onto colloids. Potassium feldspars tend to be more resistant to weathering than sodium, so that in sedimentary deposits and soils, potassium concentrations are relatively high.

Rubidium has much lower abundances than potassium - potassium/rubidium ratios are generally of the order 200-1000. Caesium is even less

abundant and the ratio potassium/caesium generally varies from 2000-20,000.

The lowest concentrations of all the alkali metals are found in iron and magnesium rich minerals and rocks such as pyroxene (pyroxenite), olivine (dunite) and other ultramafic varieties.

While sodium and potassium form a large number of minerals, apart from the rare caesium mineral pollucite, $(Cs,Na)AlSi_2O_6.nH_2O$, the heavy alkali metals form no minerals of their own. Their large ionic radii (Table 6.1) cause them to be substituted quite easily for potassium in potassium minerals. It is therefore in potassium minerals such as feldspar, mica or lepidolite, that rubidium and caesium levels are high.

Table 6.1 in Chapter 6 gives abundance data together with the ionic radii of the alkali metals.

The geochemistry of the alkalis has been thoroughly reviewed by Heier and Adams (1964) and the need for their accurate determination stressed.

The determination of the common alkali metals by gravimetric techniques (Lawrence-Smith, 1871) as well as by the Groves (1935) method is time-consuming. Instrumental methods based on physical characteristics of atoms have largely superceded chemical methods in the determination of the alkalis. Methods such as X-ray fluorescence (for sodium, potassium and rubidium), neutron activation (for all the alkalis), isotope dilution and mass spectrometry (for potassium, rubidium and caesium) and gamma-ray spectrometry (for potassium) are precise and accurate, although sometimes expensive and time-consuming. They have been used especially for radiometric age determinations (potassium-rubidium method). Spectrometric methods are also employed, D.C. arcs or flames being used as sources. The use of the arc for alkali metal determination is adequately reviewed by Ahrens and Taylor (1961). Flame photometric techniques have also been used for many years for these elements and remain popular (Gilbert, 1961). However, they are liable to present difficulties in certain instances. Russell (1966) has pointed out that when simple filter flame photometers such as the E E L are used, iron and manganese radiation may lead to falsely high readings for sodium. This situation is aggravated when

hotter acetylene/air, acetylene/oxygen or hydrogen/oxygen flames are used. In addition other types of radiative interference such as that from calcium (Rubeska et al, 1963) may affect flame emission results, especially for sodium and potassium.

The atomic absorption technique has been applied with considerable success to the determination of sodium and potassium in all spheres of analyses. David (1960) has concluded that in soil and plant analysis, atomic absorption spectroscopy results are at least as accurate and precise as emission techniques. Accurate results for the determination of sodium and potassium in rocks by atomic absorption have been reported by Billings (1963), Trent and Slavin (1964), and Belt (1967). Various methods of sample preparation were used, and the results were similar regardless of whether fusion or acid dissolution techniques were used. Acid dissolution (hydrofluoric and sulphuric or perchloric) appears to be more popular for alkali metal determinations, probably because of the difficulty in obtaining fusion salts free of sodium.

While sodium and potassium are major elements in most rocks, they do occur as minor elements and traces in certain minerals and ultramafic rocks (e.g. pyroxene and plagioclase). In addition, their concentrations are low in chondrites. In order to extend atomic absorption techniques to these lower concentrations, as well as to the determination of rubidium and caesium, for which ultimate sensitivity is required, a study was made of the most suitable flames, as well as of the interferences likely to be encountered in them. Dissolution techniques were also studied to determine which were the most suitable for the determination of the alkalis, not only in low concentrations but also when sodium and potassium are present as major constituents.

7.2 EXPERIMENTAL

7.2.1 Flame Studies

Earlier publications (Gatehouse and Willis, 1961) listed a relatively cool flame (town gas/air) as the most suitable for the determination of the alkalis. The low excitation and ionization potentials of the alkalis (Table 7.1) result

in the ground state being depleted rapidly as the flame temperature increases, so that high temperature flames, such as the acetylene/nitrous-oxide generally are not suitable for alkali metal determination by atomic absorption.

TABLE 7.1

Excitation and Ionization Potentials of the Alkalis

Element	Ionization Pot.	Resonance Lines Wavelength Å	Excitation Pot.
Lithium	5.40	6708	1.84 e v
Sodium	5.14 e.v.	5890	2.10 e v
		5896	2.09 e v
		3303	3.74 e v
Potassium	4.34 e v	7699	1.60 e v
		7665	1.61 e v
		4044	3.05 e v
Rubidium	4.17 e v	7948	1.55 e v
		7800	1.58 e v
Caesium	3.89 e v	8949	1.38 e v
		8521	1.45 e v

From Ahrens and Taylor (1961)

A broad-flame burner was designed for both the Perkin-Elmer and the Techtron spectrometers to allow propane-butane gas to be burnt with air (Butler, 1966). Improved sensitivity was obtained with this relatively cool flame (1960°C) when compared with a standard acetylene/air flame (2150°C). This is shown in Table 7.2. The reasons for the improvement in sensitivity are not only the lower temperature but also the fuller utilization of the light from the hollow cathode lamp. The broad flame also prevented entrained air from reaching the inner regions of the flame, thus giving a large, cool, interconal zone. The flame from this burner was "softer" than the acetylene/air flame so that it was more prone to atmospheric air movement. The flame temperature is of the order of 1900°C.

TABLE 7.2

Concentrations of Alkali Metals required to give 0.004 Absorbance with the Broad Flame (Propane-Butane /Air and the Normal Flame Acetylene/Air)

Element	Concentration ppm	
	Prop.-but. (broad-flame)	acetylene/air
Na	0.007	0.05
K	0.01	0.2
Rb	0.03	0.2
Cs	0.08	0.7

In the analysis of rocks for sodium and potassium high sensitivity is seldom required. The standard acetylene/air burner is, therefore, more suitable than the broad flame burner because interference effects are reduced with the hotter flame (next section) and also because much better precision is obtained when the stiffer acetylene/air burner (slot type) is turned side-on to the light from the lamp. A greater analytical range can thus be covered.

When rubidium and caesium are to be determined in rock solutions, the hotter acetylene/air flame is preferred because of its greater freedom from interference. Unfortunately, sensitivity is much reduced. If the cool flame is used, however, the higher sensitivity enables addition techniques to be applied.

The most suitable flame conditions for maximum sensitivity as well as freedom from interference, for the determination of sodium, potassium, rubidium and caesium, are given in Table 7.3.

7.2.2 Interferences

Interference studies were made using both propane-butane/air and acetylene/air flames. Various concentrations of the elements aluminium, iron, calcium, magnesium and alkalis, sodium and potassium which are the major elements found

TABLE 7.3

Most suitable conditions for the determination of sodium, potassium, rubidium and ceasium

Note: As the flame conditions are not critical, no data on gas flow are given

(a) Maximum Sensitivity

	Sodium	Potassium	Rubidium	Caesium
Burner	Broad-flame	Broad-flame	Broad-flame	Broad-flame
Fuel Gas	Prop.-but.	Prop.-but.	Prop.-but.	Prop.-but.
Support Gas	Air 30 psi	Air 30 psi	Air 30 psi	Air 30 psi
Wavelength	5890	7665	7800	8521
Analytical range (ppm)	0.01 - 6.0	0.03 - 6.0	0.1 - 10.0	0.15 - 10.0

(b) Maximum Freedom from Interference

	Sodium	Potassium	Rubidium	Caesium
Burner	Slot	Slot	Slot	Slot
Fuel Gas	C_2H_2	C_2H_2	C_2H_2	C_2H_2
Support Gas	Air 25 psi	Air 25 psi	Air 25 psi	Air 25 psi
Wavelength	5890 3303	7665 4044	7800*	8521*
Analytical range (ppm)	0.1-6.0 10-500	0.1-6.0 20-1000	0.3 - 20.0	0.5 - 20

*Add excess strontium to overcome enhancement by Sodium and Potassium

in rocks, were added to a fixed concentration of the analytical element.

(a) Sodium. Fig. 7.1 shows the effect of the interfering elements on sodium in the acetylene/air flame. Potassium causes slight enhancement, but generally the interferences are negligible. The slight depression by iron and aluminium tends to cancel the potassium enhancement.

Note: The same absorbance scale is used for all the figures.

Fig. 7.2 shows the effect of the same elements in the propane-butane flame. Iron, aluminium and magnesium depress absorbance severely. Calcium and potassium also cause depression, but to a lesser degree. (Where the graph goes off the page, the absorbance readings are given.)

This evidence, as well as that obtained when analyses were carried out, indicated that while the cooler flame gives higher sensitivity, the acetylene/air flame is preferred for sodium analyses because of its freedom from interference effects.

(b) Potassium. Fig. 7.3 shows interference on potassium in the acetylene/air flame. Sodium causes enhancement, a result reported by Willis (1960), while aluminium and iron cause slight depression. Magnesium has no effect, while calcium enhances potassium above 500 ppm.

The effects of interfering elements on potassium in the cooler flame are shown in Fig. 7.4. No enhancements occur, but all the elements depress potassium absorbance. Depression by aluminium, iron and magnesium is severe. Both sodium and calcium cause some depression.

The overall effect in the cool propane-butane/air flame of the elements present in rock solutions is one of significant depression, a result which precludes the use of aqueous or simple standards if this flame is to be used.

The enhancement caused by sodium in the acetylene/air flame necessitates the use of potassium standards with an excess of sodium to match the enhancement effects.

A useful means for overcoming enhancing interferences is to add

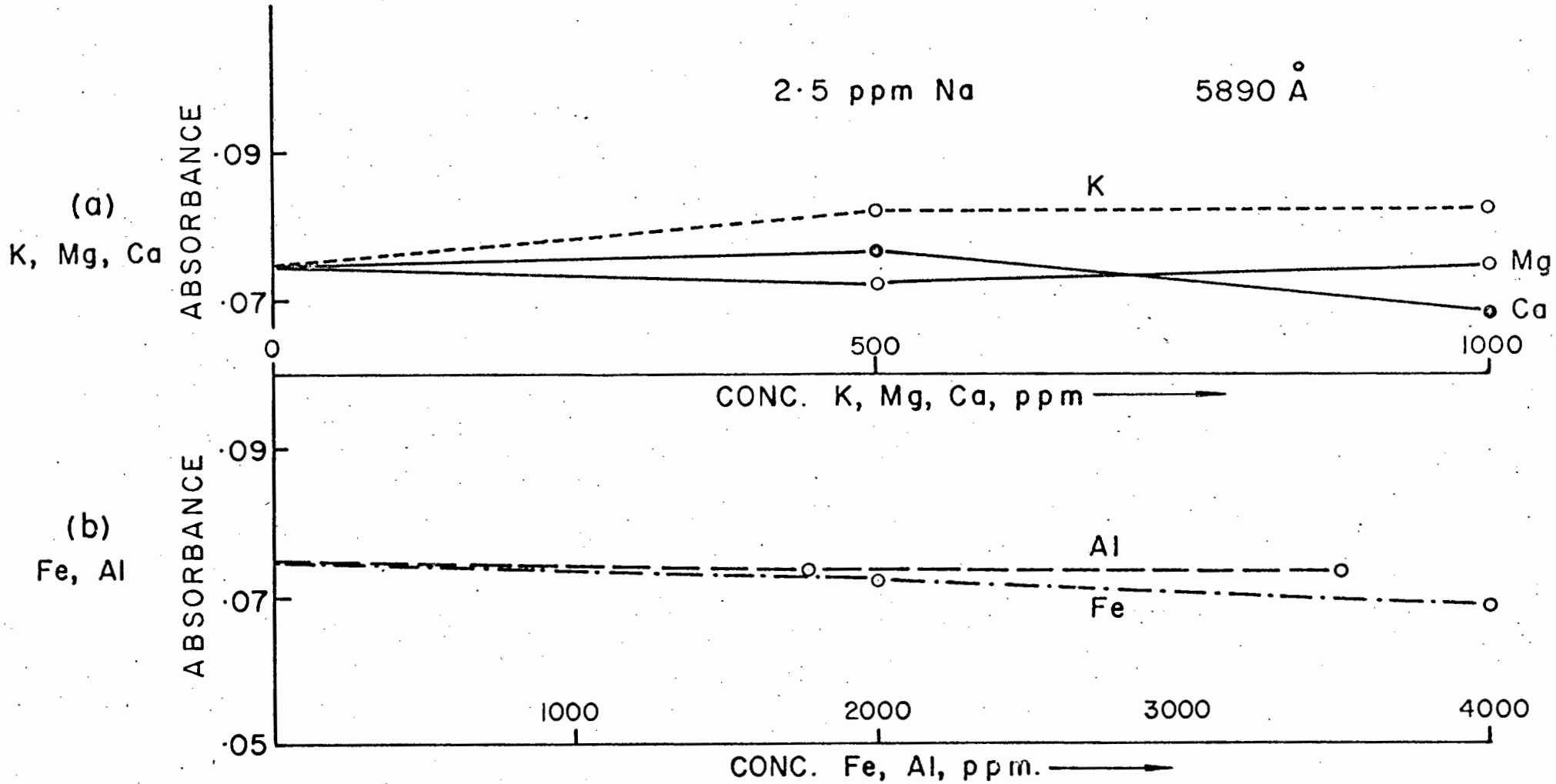


FIG. 7·1.

Interference on Sodium in C_2H_2/Air Flame.

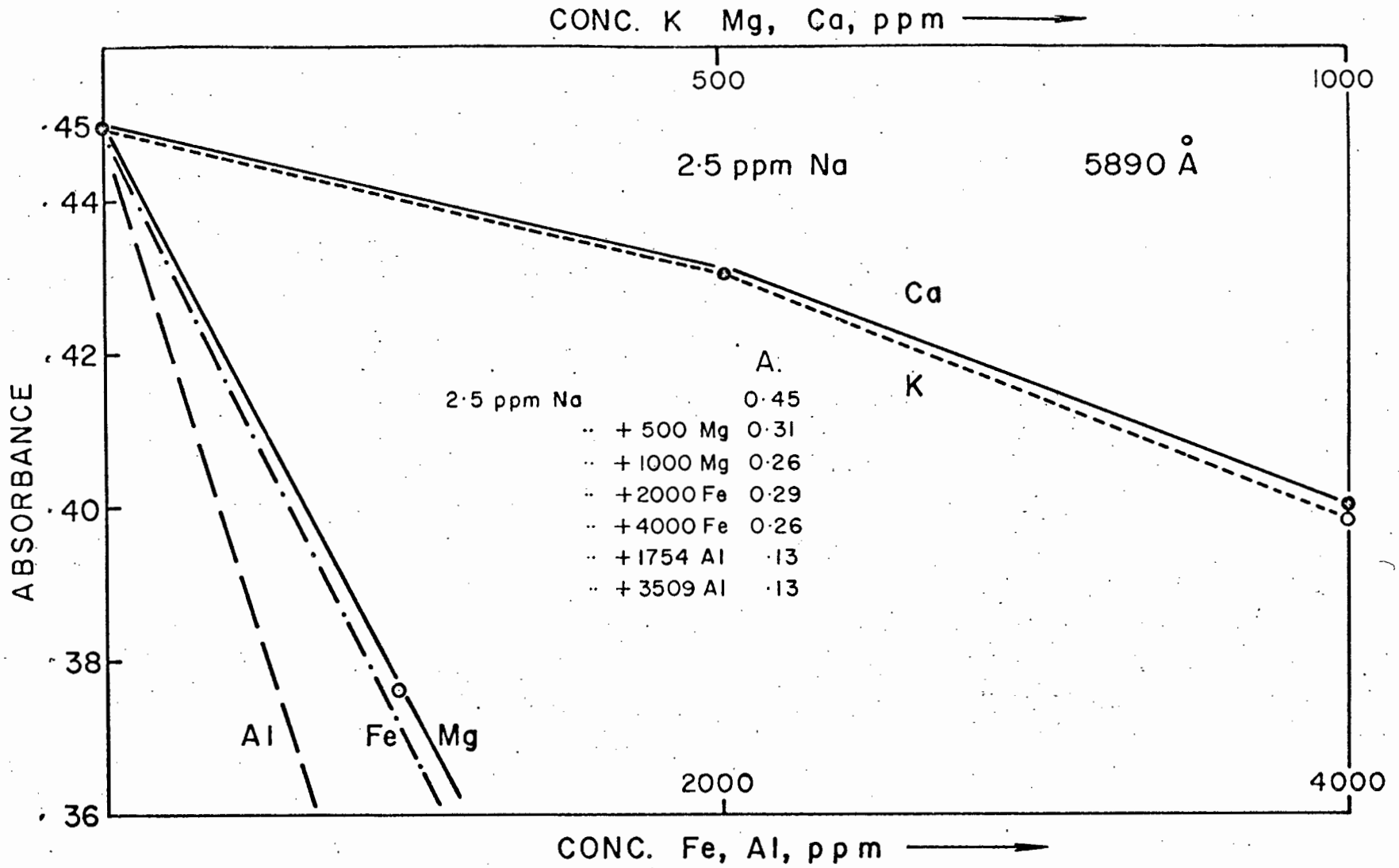


FIG. 7·2.

Interference on Sodium in Prop.—But./Air Flame.

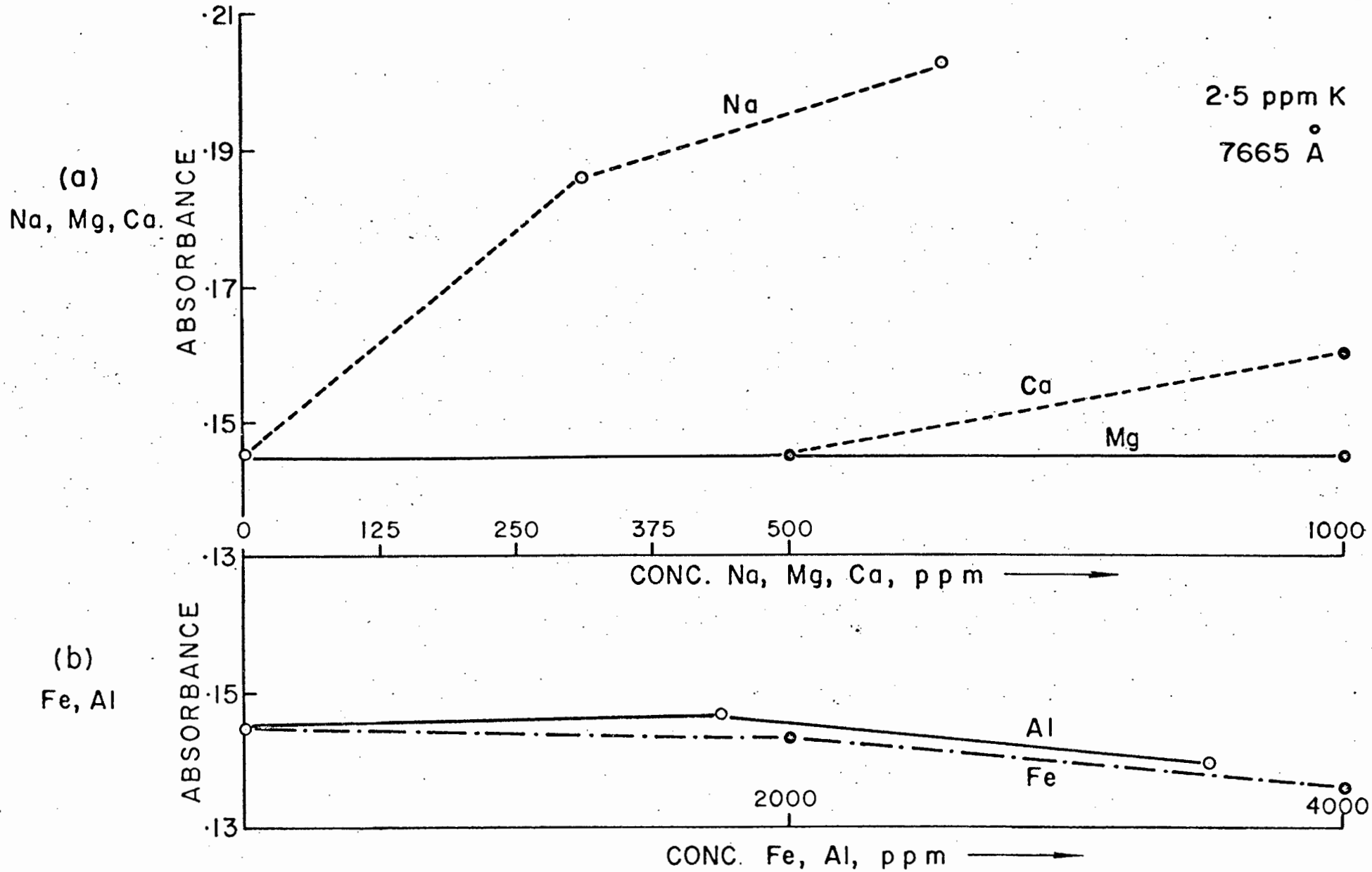


FIG. 7·3.

Interference on Potassium in C_2H_2/Air Flame.

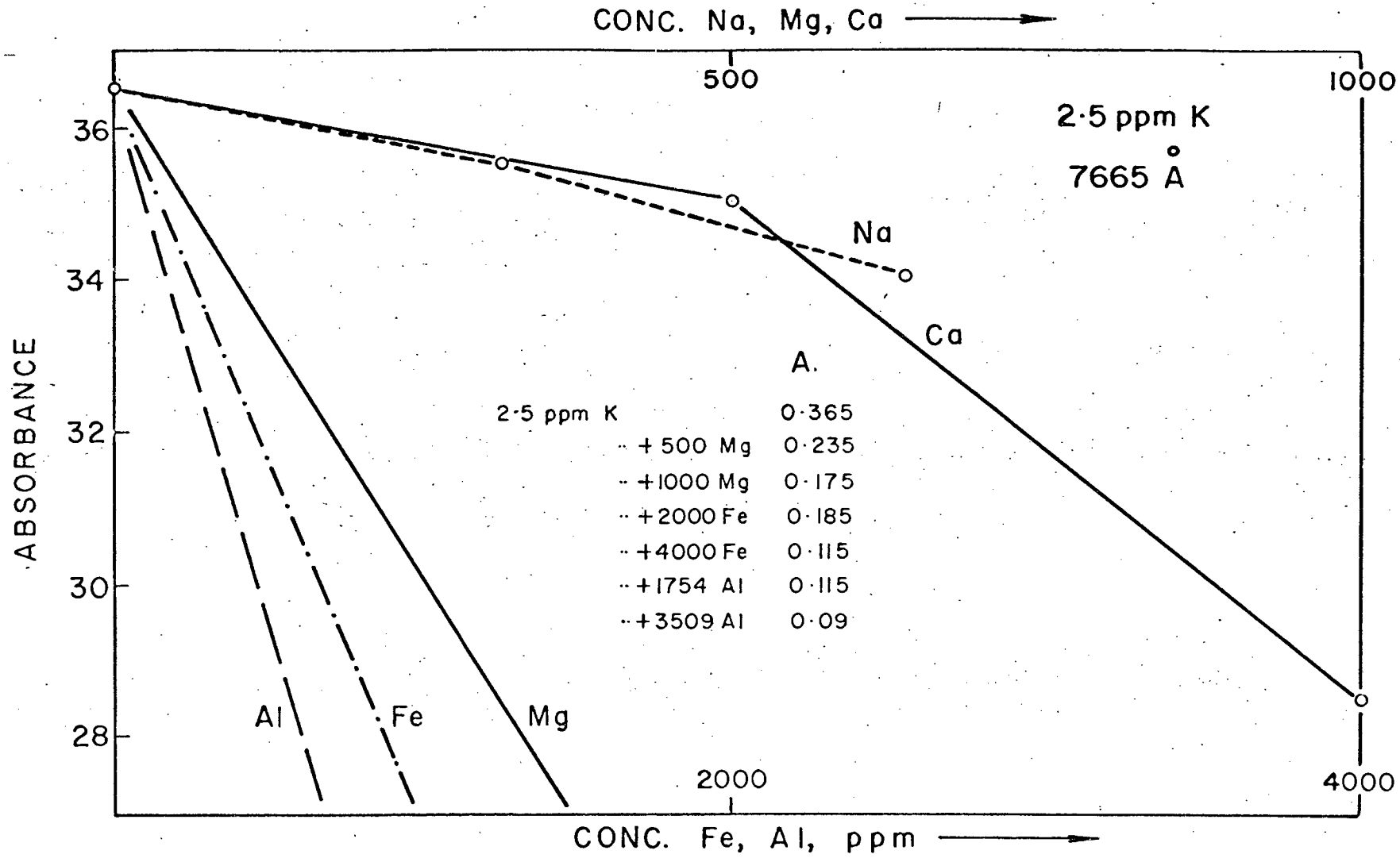


FIG. 7·4.

Interference on Potassium in Prop – But / Air Flame

an excess of an element with a low ionization potential such as strontium to both standards and sample, similar to the technique described by Butler and Brink (1963).

However, when the concentrations of sodium and potassium are high, a far more elegant technique is that suggested by Belt (1966). The potassium 4044Å and sodium 3303Å lines are used, and although they are many times less sensitive in the acetylene/air flame, absorption is affected far less by the interfering elements. This result is shown in Fig. 7.5 for both sodium and potassium. When these lines were used for analyses, results were far more reproducible and closer to accepted values, and samples did not have to be diluted excessively to bring them into the analytical range.

It should be noted that the hollow cathode lamps must be run at higher currents to provide sufficient intensity of these higher excitation energy lines. For the same reason, sensitivity with the acetylene/air flame is greater for these lines than with the propane-butane flame.

(c) Rubidium. Similar interference tests were conducted for rubidium. These are shown in Fig. 7.6 (acetylene/air) and Fig. 7.7 (propane-butane/air). As is expected, the effect of sodium and potassium is enhancement in the hotter flame. Enhancement by potassium is more severe, because of the higher degree of rubidium ionization at the temperature of the acetylene/air flame. The lower temperature flame tests (Fig. 7.7) showed that potassium, sodium and calcium had no effect on rubidium, but that aluminium and iron depressed absorption. It should be noted that with the lower temperature flame the absorbance reading for rubidium was 2.5 times greater than with the acetylene/air flame.

The choice of the best flame is difficult and depends essentially on the concentration of rubidium in the sample. The most interference free conditions are obtained with the acetylene/air flame. The addition

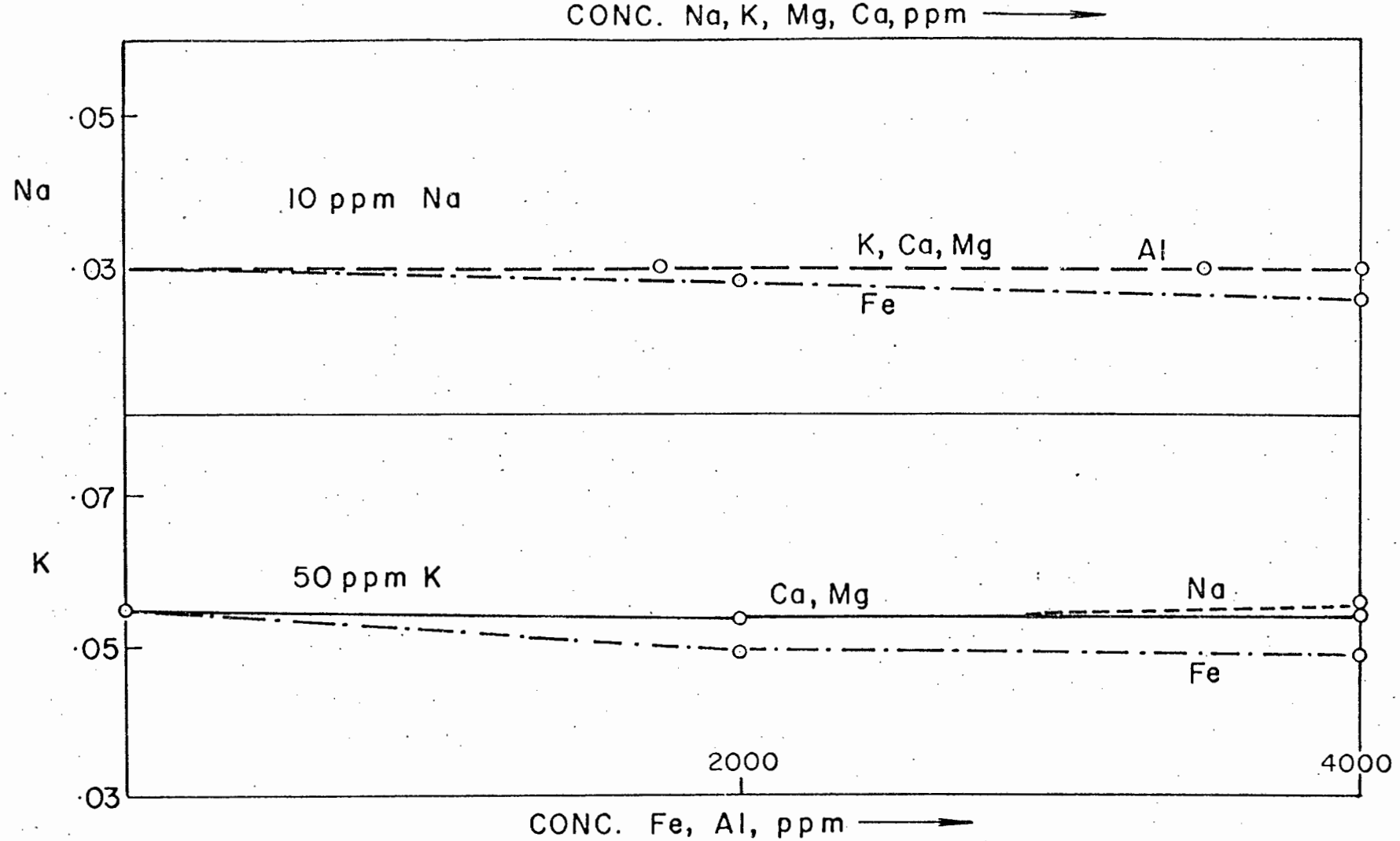


FIG. 7·5.

Interference on Sodium and Potassium using Na 3303 and K 4044 C_2H_2/Air Flame.

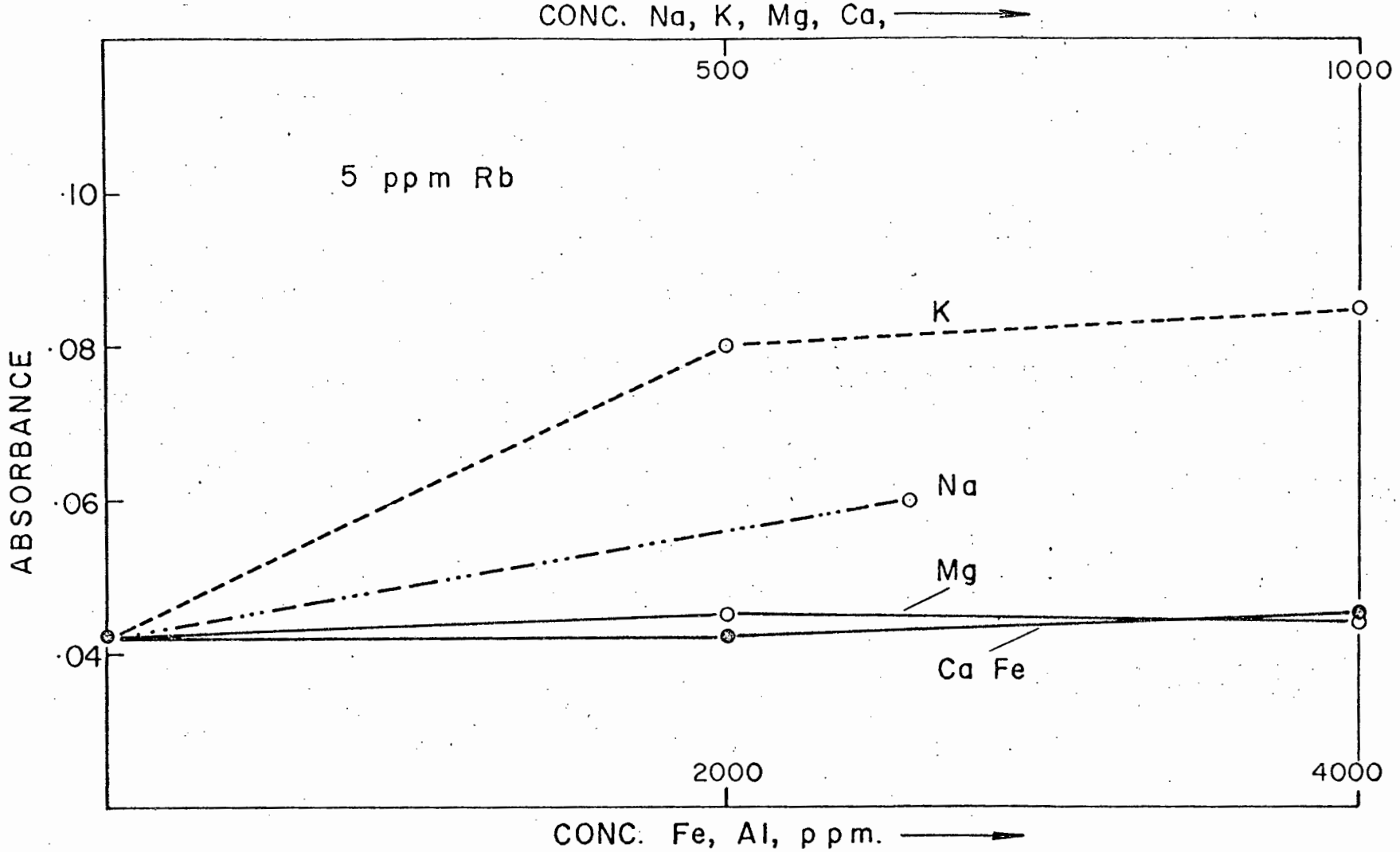


FIG. 7·6.

Interference on Rubidium C_2H_2 / Air Flame

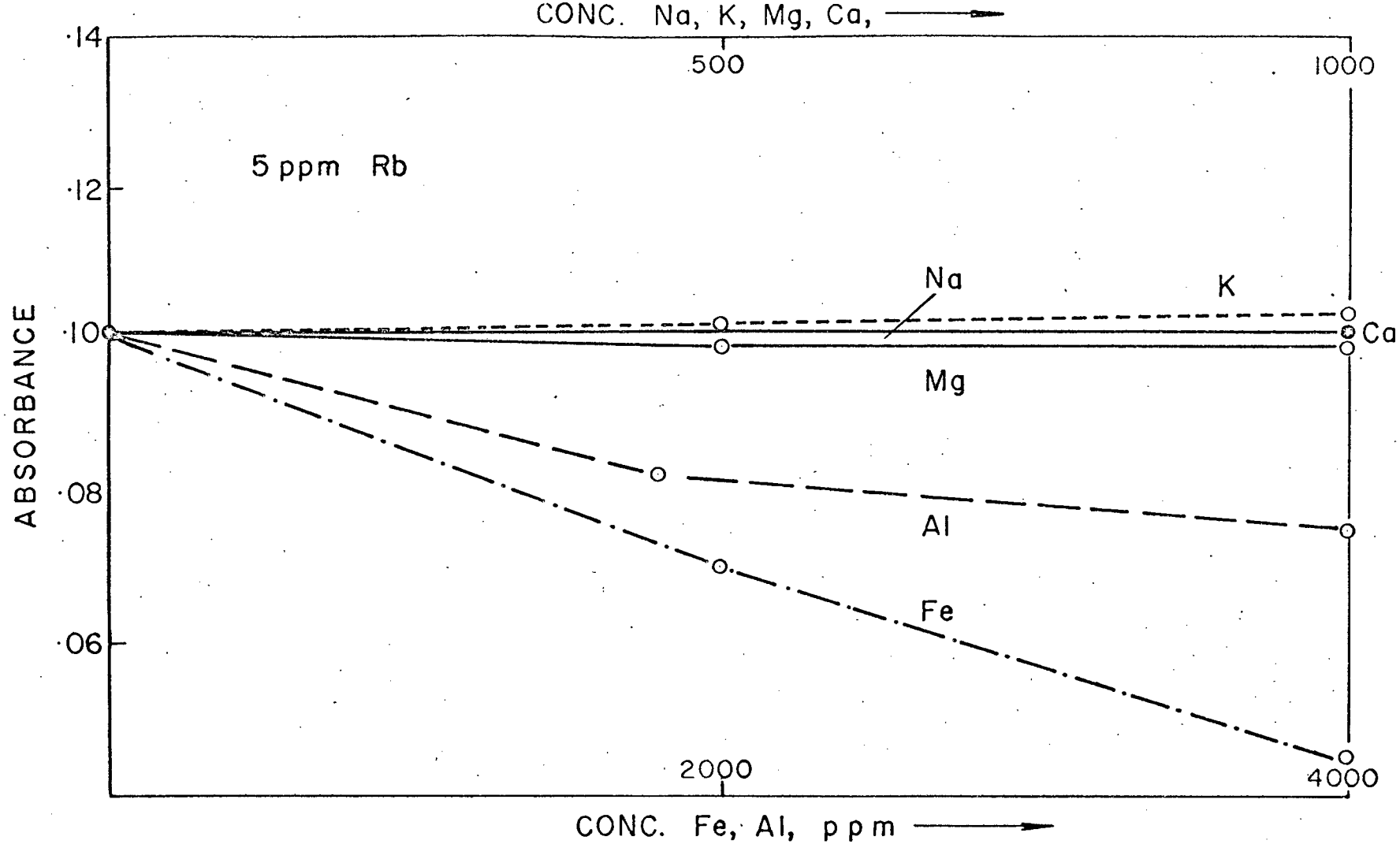


FIG. 7·7.

Interference on Rubidium Prop.–But./Air Flame

of 2000-5000 ppm strontium (or potassium) to the sample and standards effectively overcomes enhancement by other elements. An alternate method which was used with success was the use of synthetic standards containing the same concentrations of iron and aluminium with the propane-butane flame. The method of additions may also be used with this flame.

(d) Caesium. The same tests were conducted for caesium and the results are shown graphically in Figs. 7.8 and 7.9 for acetylene/air and propane-butane/air respectively. In Fig. 7.8 it is seen that potassium enhances, that sodium enhances less and that calcium, aluminium, magnesium and iron have little effect on caesium in the hotter flame. In the cooler flame (Fig. 7.9) it is seen that no enhancement occurs, but that all the elements cause varying degrees of depression. In view of the better sensitivity and the very low concentrations of caesium usually encountered in common rocks, the cooler propane-butane/air flame appears to be more suitable for the determination of caesium. For normal rocks, separation and concentration techniques are required as the abundance of caesium is usually too low to determine directly. The separation of the alkalis is complex and has been the subject of considerable investigation (Toerien, 1967); Strelow et al, 1968).

7.2.3 Analyses

(a) Sample dissolution. Many rocks were analysed for sodium and potassium at various concentration levels. Both fusion and acid dissolution techniques were applied (F-1 or F-2 and A-2: Table 5.2) and found to be equally successful. The lithium metaborate fusion was far more rapid but some earlier results were not as close to the accepted values as would have been preferred. On investigation it was found that lithium had quite a significant influence on both sodium and potassium absorbance, when using the sodium 5890 and 3303 as well as the potassium 7800 and 4044 lines. This effect is shown in Fig. 7.10. By exercising care in

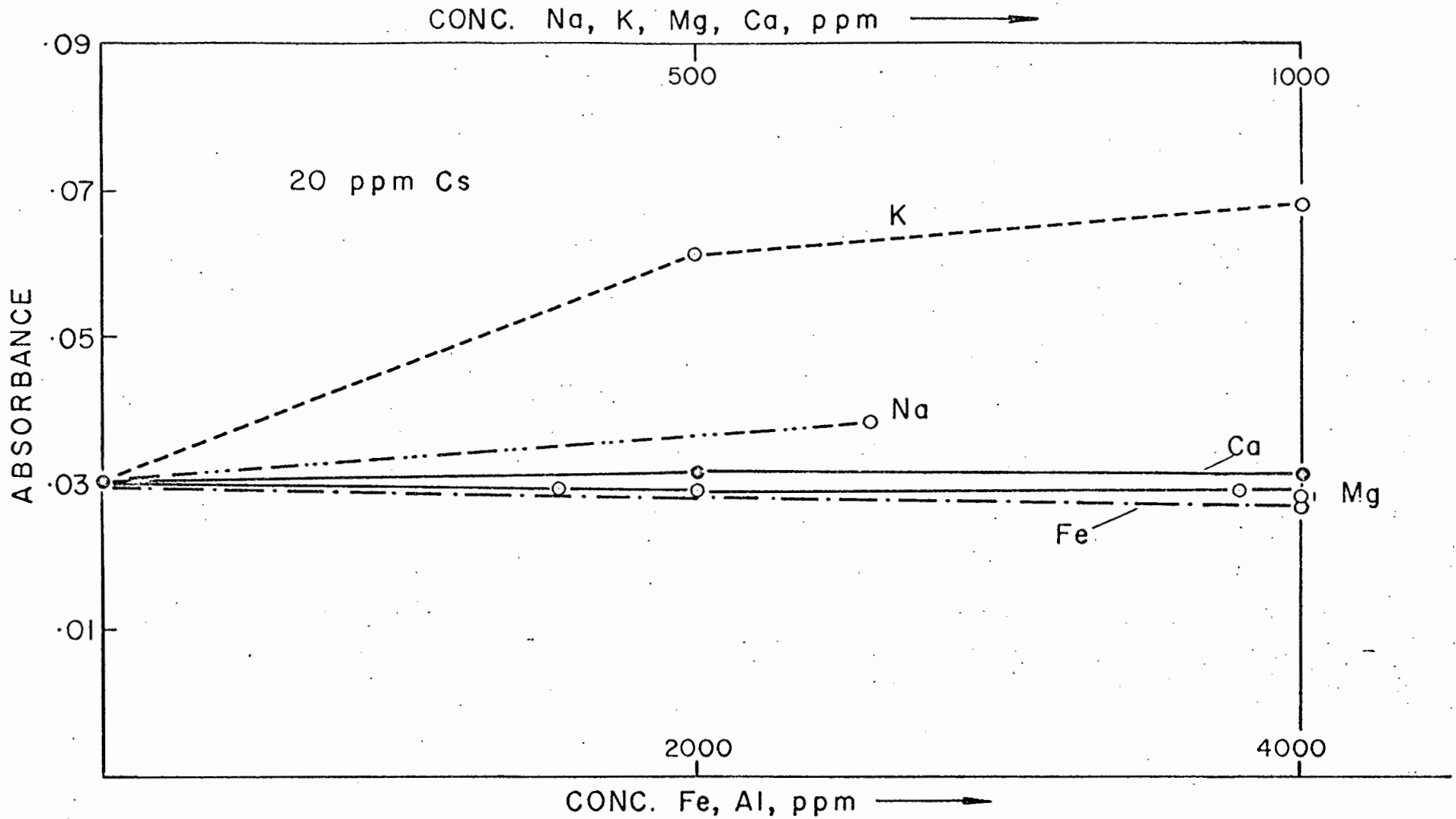


FIG. 7·8.

Interference on Caesium $C_2 H_2$ / Air Flame

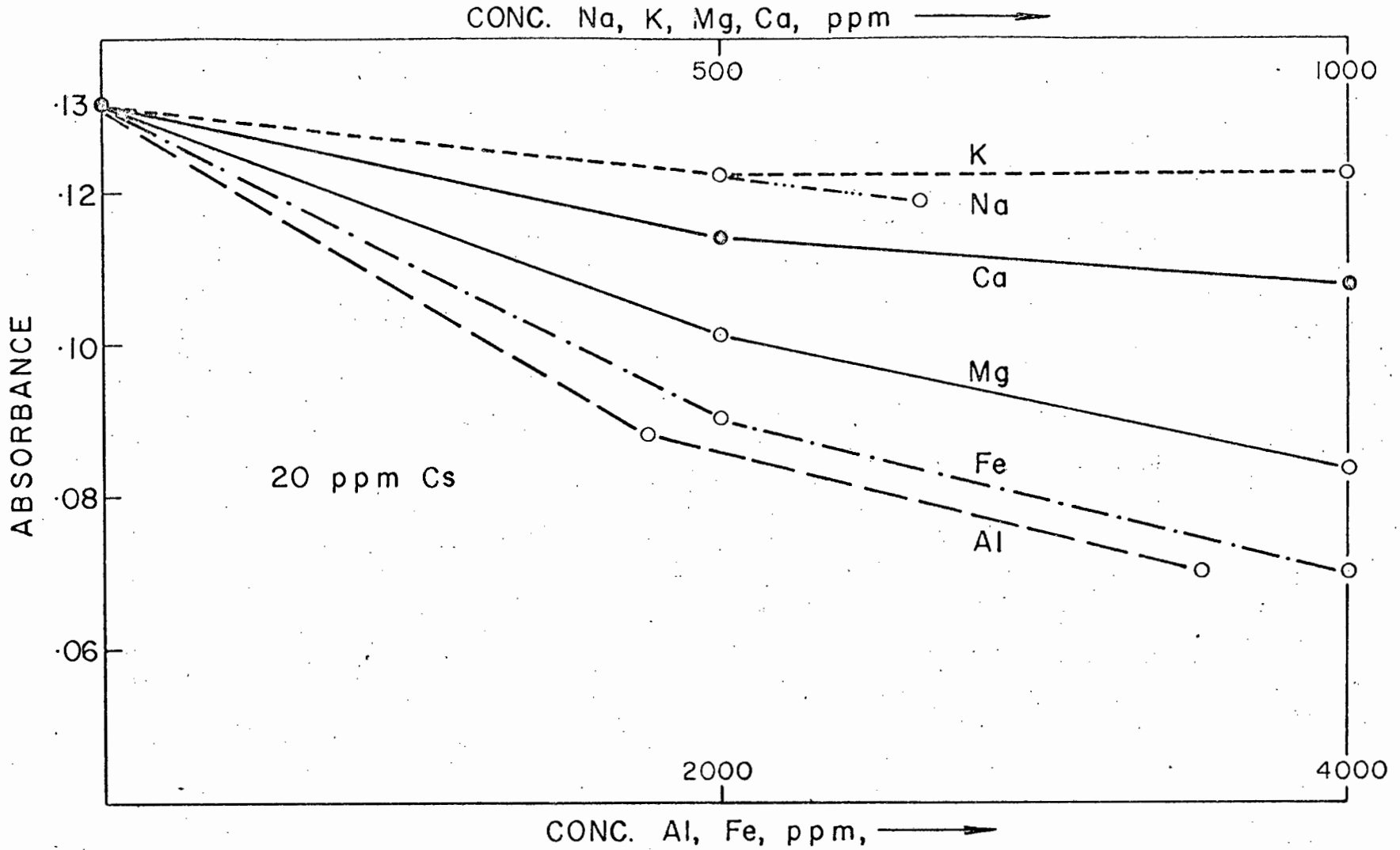


FIG. 7·9.

Interference on Caesium Prop.–But. / Air Flame

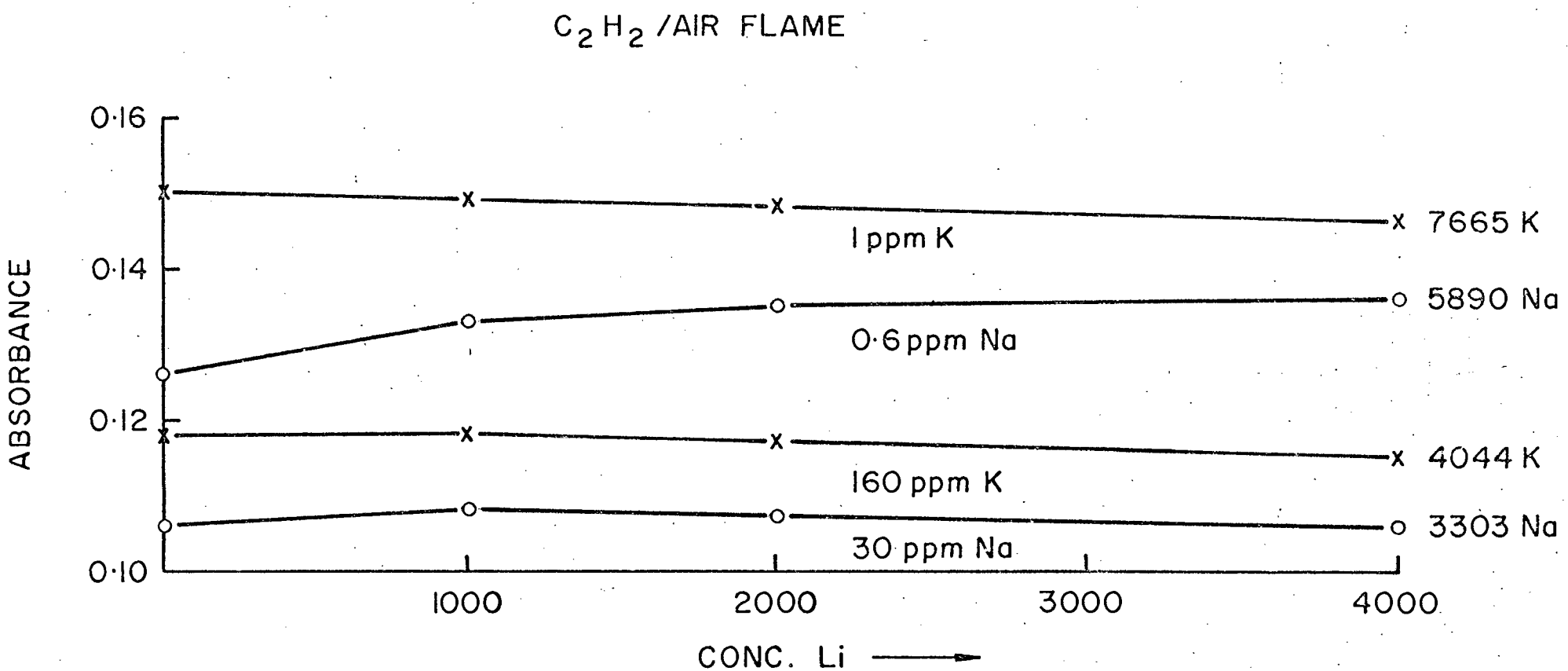


FIG. 7·10

Influence of Lithium (as metaborate) on Sodium and Potassium Absorbance with the 5890 and 3303 Na, and 7665 and 4044 K lines.

the weighing of the lithium metaborate and matching standard lithium concentrations with samples, this difficulty was overcome and accurate results obtained.

Acid dissolutions were more time-consuming and did not always provide accurate and precise results. Considerable care had to be taken with acid dissolution to prevent sodium contamination. As most reagents contain this element, duplicate or triplicate analyses were always made and triplicate blank solutions were treated in the same way as the samples.

For the determination of rubidium and caesium the highest concentrations were required and the technique of acid dissolution A-3 in Table 5.2 was used.

(b) Limit of detection. The limits of detection on aqueous solutions were given in Table 7.2. When analysing rock samples, it was found advisable to set the limit of determination at least three to five times higher than this value. The preferable determination limits for the most suitable flames are given in Table 7.3.

(c) Precision. Repeated measurements were made on aqueous and rock solutions and the results are given in Table 7.4. It should be noted that the precision of measurement taken with the burner at an angle is better than shown in this table. The precision measurements for caesium were made on rock solutions with caesium added, as the natural concentration in the rock was too low for detection.

The precision measurements were made under optimum conditions as listed in Table 7.3(a). It is seen that for aqueous solutions the precision for all the elements is acceptable. For the rock dissolutions however it is seen that the value for sodium is unusually high. The reason for this is the difficulty which was experienced with contamination. For those precision tests no blanks were run, and as mentioned in Section 5.3.1 difficulty was experienced with hydrochloric and hydrofluoric acid. The poor precision is thus almost certainly due to

TABLE 7.4

Precision measurements made on the alkali metals

(a) Aqueous Standards (acetylene/air flame)

Element	Concentration in solution (ppm)	Number of determinations	Coeff. of Var. %
Sodium	0.1	15	1.7
	1.0		1.0
	5.0		0.9
Potassium	0.1	15	2.2
	1.0		1.6
	5.0		1.5
Rubidium	1.0	15	2.1
	10.0		2.0
Caesium	1.0	15	3.5
	10.0		2.3

(b) Rock solutions Granodiorite GSP-1

HF : $HClO_4$ dissolution

Element	Line	Concentration in solution	Mean conc. detn.	Number of detns.	Coeff. of var. %
Sodium	5890	.01%	1.90%	9	6.16
Potassium	7665	.01%	4.38%	8	2.21
Rubidium	7800	1%	675 ppm	8	2.81
Caesium*	8521	1%	1100 ppm	8	7.0

* Caesium added to each solution as natural concentration too low for determination.

contamination.

(d) Accuracy. Accuracy was tested by comparing results with those obtained by other methods and also analysing international standards. Results are shown in Table 7.5 for the international standards and in 7.6 for other samples of rocks, some of upper mantle origin. Sodium and potassium were determined on most of the samples and rubidium on some international standards. Caesium could not be determined directly by the atomic absorption method on these rocks.

It is seen that the accuracy obtained for the international standards is good. The results obtained with lithium metaborate fusion and the use of the Na 3303 and K 4044 lines are particularly satisfactory. These conditions have been shown to be virtually interference free and the results confirm this. There is little doubt that this is the method to be recommended for the determination of sodium and potassium in normal rocks.

The accuracy for rubidium also appears acceptable although not as satisfactory as for sodium and potassium.

7.2.4 Discussion

Atomic absorption appears to be satisfactory for determining the alkali metals lithium, sodium, potassium and rubidium in rocks. Precision appears to be satisfactory and provided due care is taken with sodium to prevent contamination, low values (down to about 10 ppm) of these elements may be estimated. For the estimation of caesium in rocks by atomic absorption chemical concentration and extraction are necessary, as the abundances are too low and interference effects too severe for direct determination.

When considering the results presented in Table 7.5 and 7.6 it is seen that accuracy for sodium and potassium is acceptable at higher values. At low values of potassium (and sodium) however, large differences occur for some samples, notably ET3/169 and ET3/270 (Table 7.6). These discrepancies may be due to the fact that they were done in the early stages of the project.

TABLE 7.5

Comparison of Results for Sodium, Potassium, and Rubidium on International Standards

Standard	Sodium %				Potassium %				Rubidium ppm		
	Accepted	Ref.	5890	3303*	Accepted	Ref.	7665	4044*	Accepted	Ref.	7800**
Granite G-1	2.45	1	2.38	2.44	4.59	1	4.54	4.55	220	1	209
Diabase W-1	1.60	1	1.55	1.59	0.52	1	0.52	0.51	22	1	19
Granite G-2	3.06	2	2.97	3.00	3.70	2	3.43	3.60	174	7	160
Granodiorite GSP-1	2.08	2	1.88	2.05	4.56	2	4.43	4.60	254	8	245
Andesite AGV-1	3.14	2	2.99	3.12	2.32	2	2.37	2.32	65	8	61
Basalt BCR-1	2.45	2	<2.27	2.51	1.40	2	1.46	1.41	48	8	43
Dunite DTS-1	0.03	2	<0.02	<0.1	0.0009	6	<0.03	<0.2	< 1	8	< 10
Peridotite PCC-1	0.014	2	<0.02	<0.1	0.0012	6	<0.03	⩽0.2	< 1	8	< 10
Tonalite T-1	3.20	3	3.11	-	1.02	3	0.99				
Syenite S-1	2.50	4	2.56		2.01	4	1.95				
Granite GR	2.82	5	2.60		3.74	5	3.65				
Granite GA	2.65	5	2.45		3.35	5	3.01				
Granite GH	2.84	5	2.49		3.97	5	3.77				

(1) Fleischer (1965) (combined methods)
(2) Flanagan (1966) " "
(3) Ingamells (1963) (chemical)
(4) Webber (1961) (combined methods)
(5) Roubault et al (1966) (combined methods)
(6) Morgan and Heier (1966) (neutron activation)
(7) Doe et al (1968) (isotope dilution)
(8) Erlank (1968) (X-ray fluorescence; in close agreement with Gordon et al (1965) (gamma-ray detect. neutr. act. results)

*Na 3303 and K 4044 lines used with sample fusion
**Rubidium results obtained with 500 ppm Cs added to solutions and C_2 H_2/air flame

TABLE 7.6

Comparison of Results for Sodium and Potassium on Rock Samples

Sample*	Rock Type	Sodium (5890Å)			Potassium (7665Å)		
		Other values	Ref.	AA	Other values	Ref.	AA
ET3/169	Pyroxenite	0.56	1	0.63	0.034	6	0.12
ET3/270	Pyroxenite	0.10	1	0.15	0.012	6	0.06
M-19A	Hornfels	1.70	1	1.60	-		2.92
M-41	Hornfels	1.94	1	1.90	1.95	1	1.71
5087	Norite	1.75	1	1.75	0.17	6	0.18
NORI/PLAG	Plagioclase min. separated from norite	4.22	1	4.10	0.26	1	0.24
D/S 95	Karroo dolerite	1.65	1	1.75	0.60	1	0.53
Bult 8	Peridotite			0.15	0.16	2	0.15
Bult 11	"			0.22	0.06	2	0.07
KDB 10	Kimberlite			0.22	0.49	2	0.41
KDB 12	"			0.17	0.42	2	0.35
J-3	Serpentinite	0.03 0.027	3 4	0.026	0.015 0.025	5 4	0.0098
135	Peridotite	1.21 1.24	3 4	1.20	0.67 0.53	5 4	0.65
J-6	Tremolite Actinolite Schist.	2.40 2.67	3 4	2.64	0.25 0.33	5 4	0.29

*See Appendix II for source of samples

(1) Erlank (1968) (X-ray and flame emission)
(2) Gurney (1968) (X-ray)
(3) Kellerman (1966) (Flame emission)
(4) Steel (1966) (Flame emission)
(5) Strasheim and Brandt (1967) (X-ray)
(6) Erlank et al (1968) (Various)

CHAPTER 8

MAGNESIUM AND CALCIUM

8.1 INTRODUCTION

The alkaline earth elements, magnesium and calcium, are known for the difficulties which are experienced with their determination by flame spectrometry. Their ability to form stable refractory compounds with other species results in severe interferences from other elements or radicals which may be present in the sample matrix.

Particular difficulty is experienced in the flame spectrometric determination of these alkaline earth elements in rocks where the matrix composition can vary over wide ranges of concentrations.

Geochemically, magnesium and calcium are considered important elements and are included in most rock analyses. Their determination is of importance for rock classification as well as for geochemical studies of minerals and rocks.

The magnesium and calcium content of rocks may vary over wide concentrations, e.g. the magnesium content of rocks of igneous origin may be as high as 20%, and as low as a few hundred ppm. Calcium concentrations can be low (less than 0.1%) in magnesium rich rocks such as dunites, but in gabbros, basalts and anorthesites, concentrations may rise to levels of 10% or more.

Abundance data place magnesium as fourth highest in concentration in the earth as a whole at 20% (Mason, 1966). This high figure is due to the large mass of the earth's mantle, estimated to consist largely of ferromagnesium silicates. For crustal rocks, however, calcium is generally found to be more abundant. Table 8.1 lists the average abundances in various types of silicate materials.

Magnesium and calcium form a large number of minerals, in most of which both elements are bonded to oxygen; a few halides are known.

Magnesium is usually associated with divalent iron, because of the similarity in their ionic radii Mg^{2+} 0.66Å and Fe^{2+} 0.74Å. Ultramafic rocks

are composed largely of ferro-magnesium minerals; typical examples are olivine, pyroxine, hornblende, etc. Ordinary basic rocks such as gabbros and basalts also contain magnesium silicates.

TABLE 8.1

Abundances of Magnesium and Calcium

(percent Magnesium and Calcium)

Element	Ionic Radius Å	Crustal Av.(1)	Granite G-1(1)	Diabase W-1(1)	Ultra-basic(2)	Shales (1)	Sand-stones (1)
Magnesium	0.66	2.09	.24	3,99	20.4	1.50	.70
Calcium	0.99	3.63	.99	7.83	2.5	2.20	3.91

(1) Mason, 1966

(2) Turekian and Wedepohl, 1961

Calcium tends to be concentrated in the basic and intermediate types of igneous rocks. Ca^{2+} is associated with magnesium and ferrous iron, e.g. in pyroxine and amphibole minerals typical of gabbro, basalts, dolerites, etc. Because of the similarity of the calcium $^{2+}$ ionic radius (0.99Å) with those of several other elements, e.g. sodium^{+} (0.97Å), manganese^{2+} (0.91Å, strontium^{2+} (1.12Å), these elements may often replace calcium in a mineral or vice versa. In addition, calcium minerals may act as hosts for rarer cations (Goldschmidt, 1954).

Magnesium and calcium minerals are susceptible to decomposition by weathering and are thus present in relatively high concentrations in sedimentary rocks. In residual sediments (sandstone) the concentrations of magnesium and calcium are low, but in carbonates (dolomite) they are high.

Many methods exist for the estimation of magnesium and calcium concentrations. Classical chemical methods (Hillebrand and Lundell, 1953) are time-consuming and not always reliable when concentrations are low. Emission spectrographic techniques have been used with success (Kvalheim, 1947; Ahrens and Taylor, 1967). However, precision obtained with the D.C. arc and

photographic recording is seldom high enough to be acceptable.

Spark-solution (Suhr and Ingamells, 1966), spark-powder (Govindaraju, 1963), and spark-tape machine (Daniellson, 1959) methods have largely superceded the D.C. arc for major element determinations. X-ray fluoresce-nce methods are also successful although some difficulty is sometimes experienced with low concentrations of magnesium because of the low counting rate of this relatively light element.

A rapid and accurate method, which is suitable for the estimation of magnesium and calcium at low as well as higher concentrations is obviously an advantage.

The atomic absorption method is used for magnesium and calcium determinations in a wide variety of materials, such as plant materials, blood plasmas, fertilizers, etc. Several applications to the geochemical field have been published (Billings and Adams, 1964; Trent and Slavin, 1964; Belt, 1967) etc. It was reported that interferences from aluminium were serious but could be overcome by the addition of releasing agents. In all cases, the acetylene/air flame was used. Nesbitt (1966) used an acetylene/N_2O flame but added no releasing agent.

During the course of work for this thesis it was evident that the atomic absorption method could be applied with success to the determination of magnesium and calcium especially at low concentrations. It was felt, however, that a careful investigation of all the possible interferences and the use of various flames to overcome them was justified. Part of the flame studies have already been mentioned in Chapter 3. While special flames were studied, this chapter is limited to the use of "normal" flames used in standard atomic absorption apparatus.

8.2 EXPERIMENTAL

8.2.1 Flame studies

Many of the interference effects reported in the literature can be coupled

with the types of flames and gases used for emission or atomic absorption spectrometry.

As both magnesium and calcium form refractory oxides, the chemical state of the flame is important. Calcium absorbance depends markedly on the type of fuel gas used and also on its content in the flame, e.g. the propane-butane/air flame gives very poor absorption for calcium (see Fig. 3.7). Calcium absorbance in the acetylene/air flame will be at a maximum with a fuel-rich (highly luminous) flame. Magnesium is not as critical as calcium, and an acetylene/air flame burning under stoichiometric or slightly lean conditions is preferred for maximum absorbance.

While absorbance sensitivity is dependent on chemical environment, interference from other elements and radicals appears to be dependent on both temperature and environment (Willis, 1968).

In the literature it is reported that calcium is prone not only to interferences from other metallic species such as aluminium, but also from sulphates and phosphates (Alkemade and Jeunken, 1957; Menzies, 1960). Interferences depend on the flame used and also on the type of burner, e.g. Galle and Angino (1967) reported interference on calcium by nitrate when using a hydrogen/air total-consumption burner, an effect not reported by anyone else. Butler and Brink (1962) found interference from magnesium, potassium and sodium in the propane/air flame, but little interference from these elements in the acetylene/air flame when strontium was added.

While the acetylene/air flame gives lower sensitivity for calcium, interference from aluminium, silicon, iron and phosphorus is evident, even at relatively low concentration ratios, i.e. $\frac{Ca}{P}$, $\frac{Ca}{Al} \sim \frac{1}{10}$ (David, 1959; Willis, 1960; Sprague, 1963). The interference is depressive and almost certainly a result of the formation of a calcium + interfering ion complex with the possibility that oxygen plays an active role.

Magnesium is subject to similar interference from these elements but to a lesser degree.

The types of reaction likely to take place have been discussed at length by Alkamade and Voorhuis (1958) and Firman (1965). The interference from aluminium, phosphorus and silicon may be eliminated by the addition of a releasing agent, i.e. an agent which forms a preferential reaction with the interfering species, e.g. without a releasing agent the reaction may have the form:

$$Ca + PO_4 \longrightarrow CaO + PO_3$$

or $$Ca + PO_4 \longrightarrow CaPO_4 \quad \text{(refractory)}$$

With a releasing agent, e.g. La or Sr

$$Ca + \overset{Sr}{La} + PO_4 \longrightarrow \overset{Sr}{Ca} + LaO + PO_3$$

$$\text{or} \longrightarrow \overset{Sr}{Ca} + LaPO_4$$

The most common releasing or suppressing agents used are lanthanum or strontium chloride. Other types of releasing agents are ammonium chloride (Allan, 1958), lanthanum + E D T A (ethylene ditetra-acetic acid) (Adams and Passmore, 1966). The mechanism whereby these agents work may not be the same as suggested for lanthanum and strontium. They do, however, inhibit the formation of refractory calcium-oxide or calcium+interfering species+ oxygen compounds.

In a high temperature flame these compounds are known to break down. Fuwa et al (1959) used a high temperature cyanogen-oxygen flame to show this.

8.2.2 Interference Tests

Tests were carried out to determine the effects of the other major elements on magnesium and calcium absorbance. Silicon interference was not tested as this element is easily obviated (Chapter 5). Both acetylene/air and acetylene/nitrous-oxide flames were used. Interference effects for both magnesium and calcium appeared similar for similar ratios of interfering element to analytical element. Interference studies were consequently limited to one concentration of magnesium (1 ppm) and calcium (5 ppm).

Calcium absorbance depended markedly on the region of the flame through which the light passed and on the fuel flow. In general, conditions were set to give maximum absorbance, but conditions were not always reproduced and optimized accurately.

The interference on magnesium is shown in Fig. 8.1. It is seen that for calcium and iron a sharp enhancement is found in the air/acetylene flame up to a concentration of 100 ppm, after which absorbance is constant. The alkali metals cause no interference. In the acetylene/nitrous-oxide flame, interferences are considerably less, but absorbance is much lower. It should be noted that the absorbance scales used are different from those used in the figures of Chapter 7.

In Fig. 8.2 are shown the interference effects of other matrix elements on calcium. Iron causes enhancement sharply up to 50 ppm after which depression occurs.

Both sodium and potassium cause enhancement. The effect is less with the higher temperature flame.

By far the most serious effect is produced by aluminium which is shown in Fig. 8.3. Severe depression of both magnesium and calcium is seen even at relatively low concentrations of aluminium. While the effect is reduced when using the acetylene/nitrous-oxide flame, it is not overcome completely at higher aluminium concentrations. The reaction which takes place is obviously the formation of a highly stable calcium or magnesium aluminate.

The slightest change in the concentration of any of the matrix elements will cause serious errors in any analysis, if aqueous standards are used. Even if synthetic or natural rock standards are used, the composition would have to match the samples very closely if accurate results are to be obtained.

The addition of a releasing agent has been known to enable these interferences to be overcome. Trent and Slavin (1964) suggest a concentration of 1% lanthanum to be added to all solutions to be analysed for calcium in an

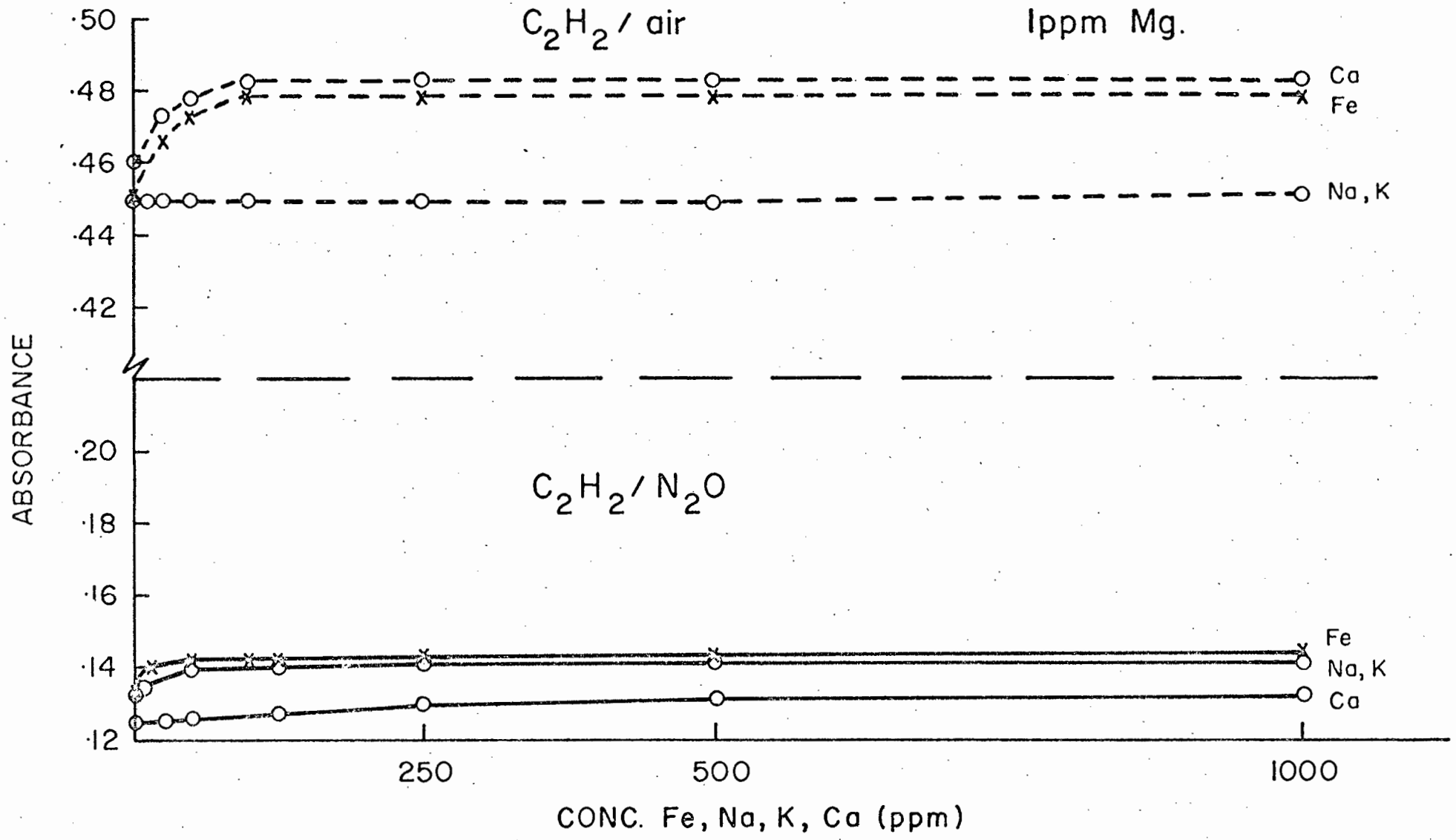


FIG. 8·1

Interference on Magnesium for C_2H_2 / air and C_2H_2 / N_2O Flames.

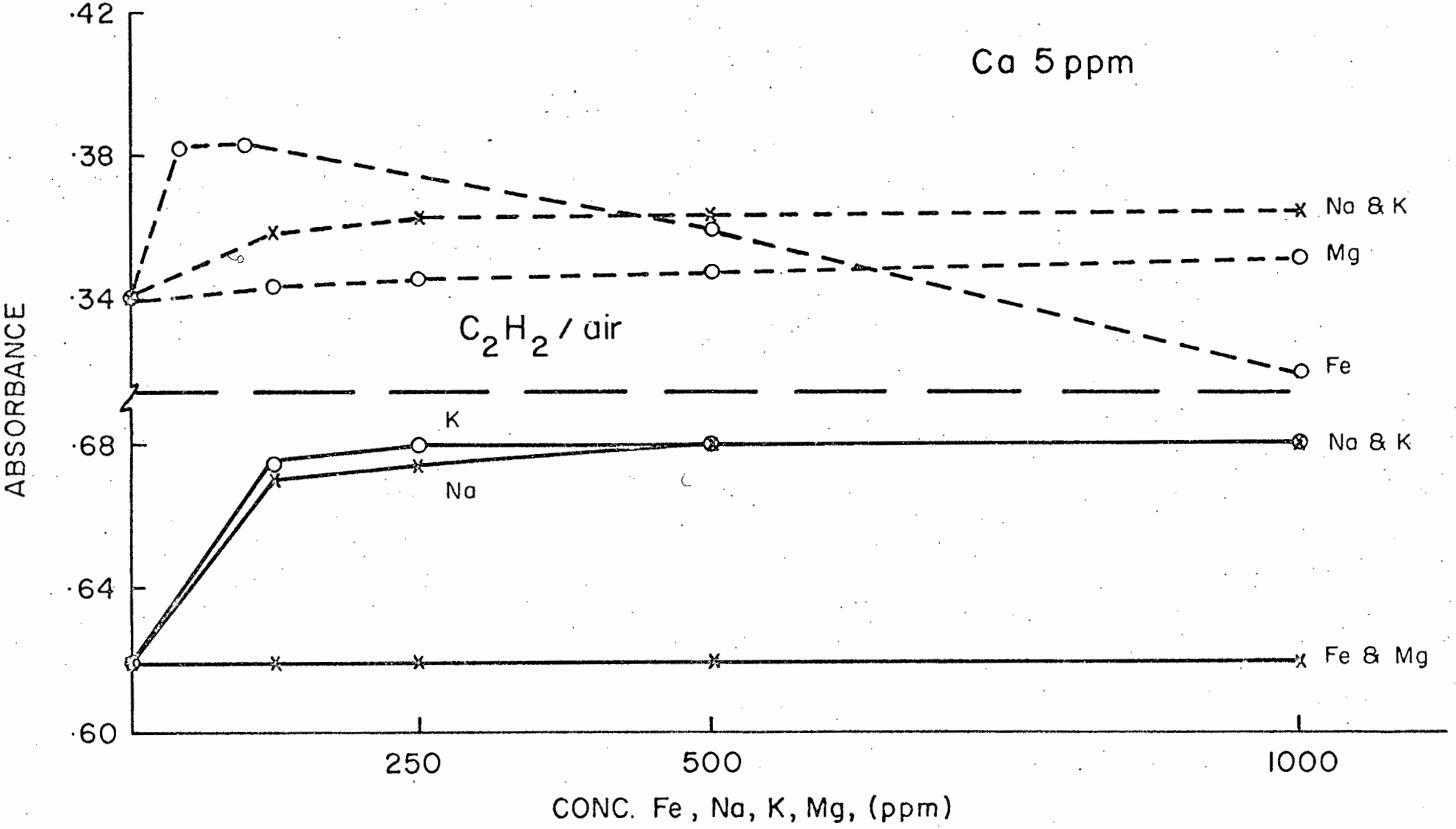


FIG. 8·2

Interference on Caicium for C_2H_2 / air and C_2H_2/N_2O Flames.

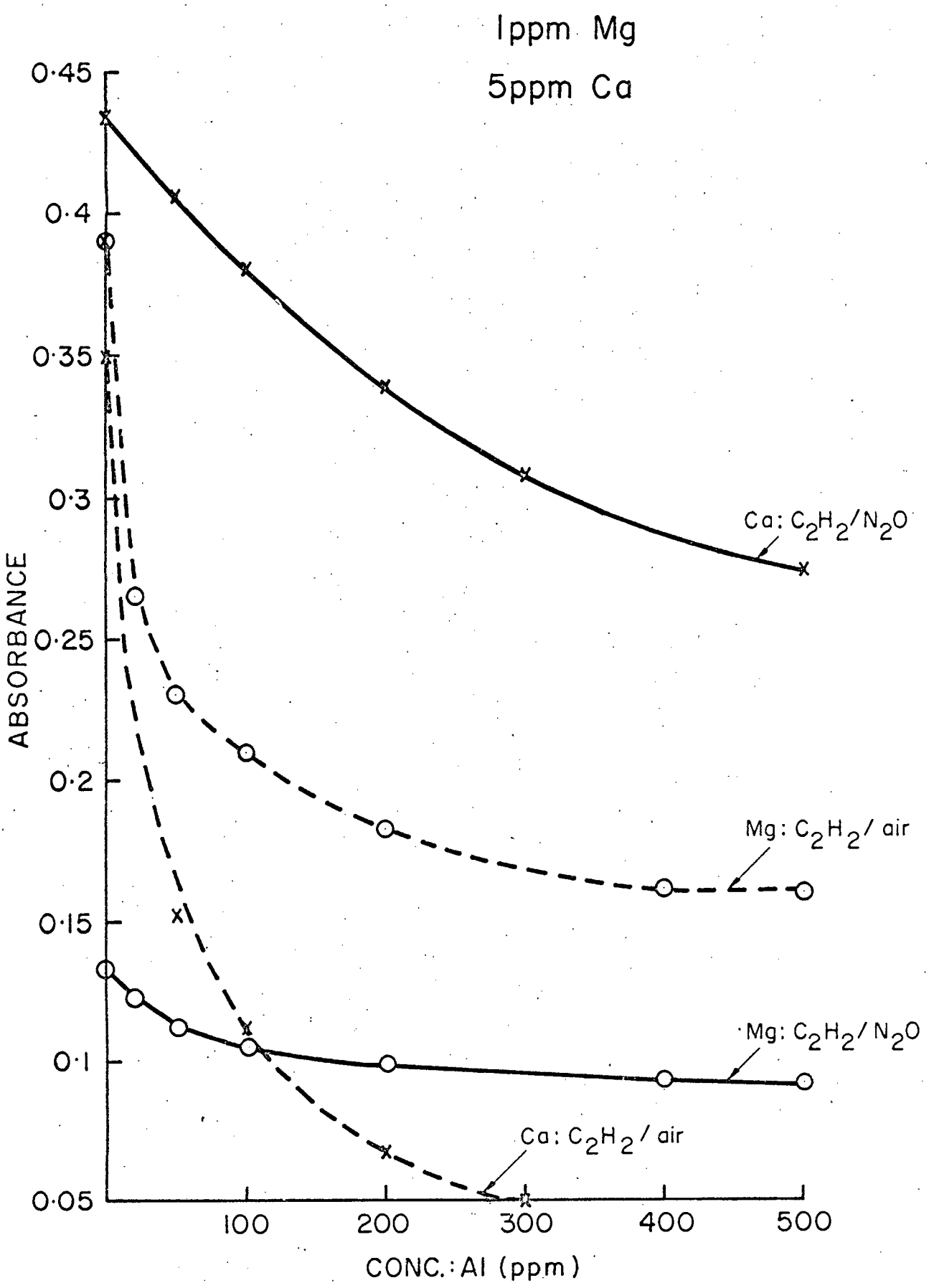


FIG. 8·3

Aluminium Interference on Magnesium and Calcium for C_2H_2 / air and C_2H_2/N_2O Flames

acetylene/air flame. Tests were conducted in both flames for various concentrations of lanthanum, and are shown in Figs. 8.4. for magnesium and 8.5 for calcium.

In Fig. 8.4 it is seen that with a ratio of 400:1 (Al:Mg), 200 ppm lanthanum are required to overcome depression. In the acetylene/nitrous-oxide flame, however, much less lanthanum is necessary. Magnesium absorbance is reduced for the nitrous-oxide flame.

In Fig. 8.5 the aluminium interference is seen to be far more severe. In the acetylene/air flame, 2000 ppm lanthanum are required to tolerate an aluminium to calcium ratio of 200:5. With the acetylene/nitrous-oxide flame, however, the lanthanum is seen to be approximately 10 times more effective so that at the same ratio of aluminium to calcium (200:5) 200 ppm lanthanum suppresses interference. At 1000 ppm lanthanum, all interferences disappear. It is seen, too, that the lanthanum enhances calcium absorbance significantly.

Fig. 8.6 shows the effects of iron, sodium, potassium, magnesium and calcium with 1000 ppm lanthanum added for both acetylene/air and acetylene/nitrous-oxide flames. It is seen that virtually no interference exists.

The results of these tests lead to the conclusion that the addition of lanthanum and the use of the nitrous-oxide flame is imperative if interference effects are to be overcome. When aluminium:magnesium and aluminium:calcium ratios are relatively small (10:1), as little as 200 ppm lanthanum would suffice. However, if these ratios become larger, it is recommended that 1000 ppm lanthanum be added.

The most suitable conditions for the determination of magnesium and calcium in rocks are summarized in Table 8.2.

8.3 ANALYSES

8.3.1 Dissolution

A number of international standards was analysed for magnesium and calcium. The dissolution methods used included acid digestion as well as lithium metaborate fusion. Results obtained with the different dissolution methods

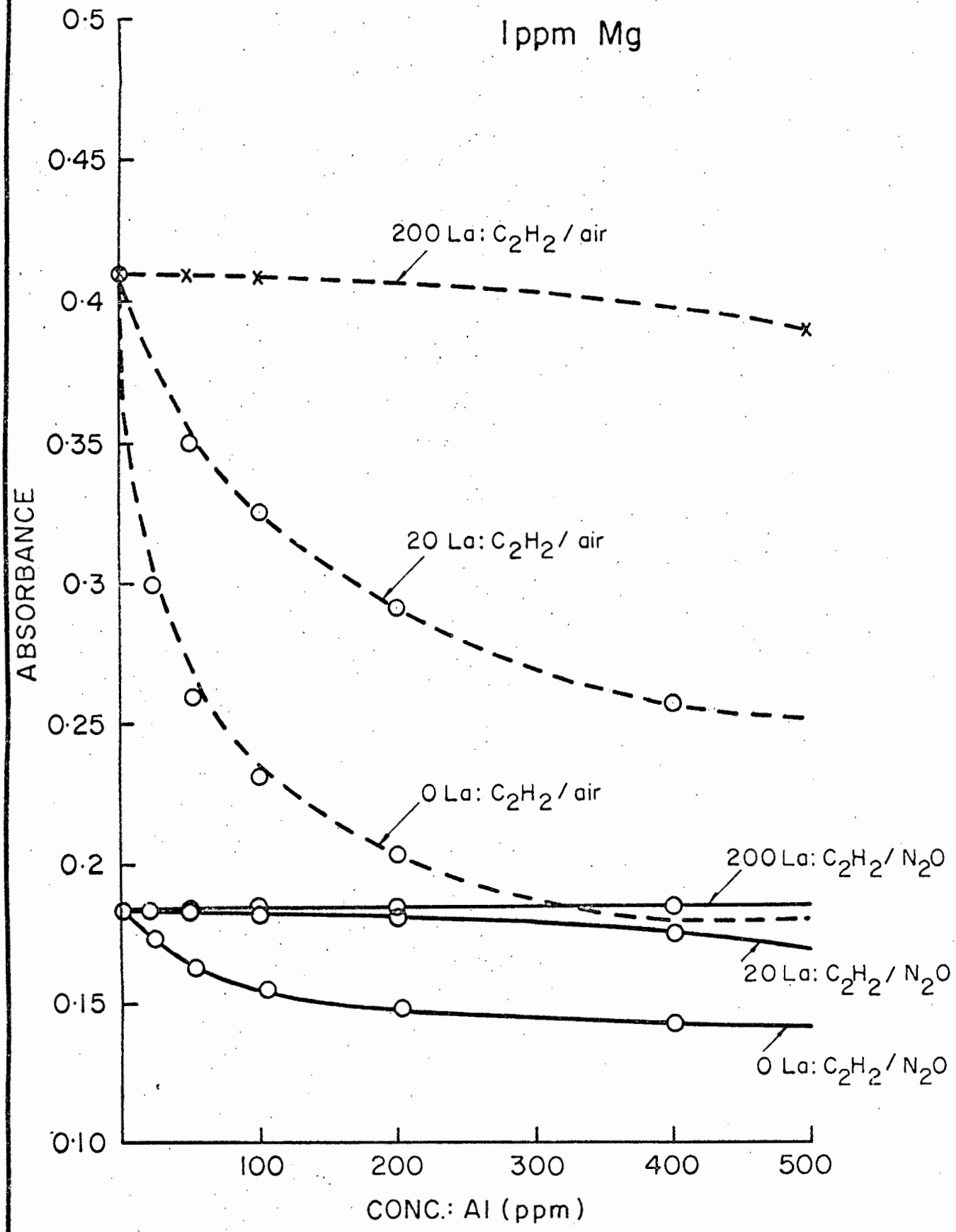


FIG.8·4

Aluminium Interference on Magnesium for C_2H_2/air and C_2H_2/N_2O Flames with Lanthanum added.

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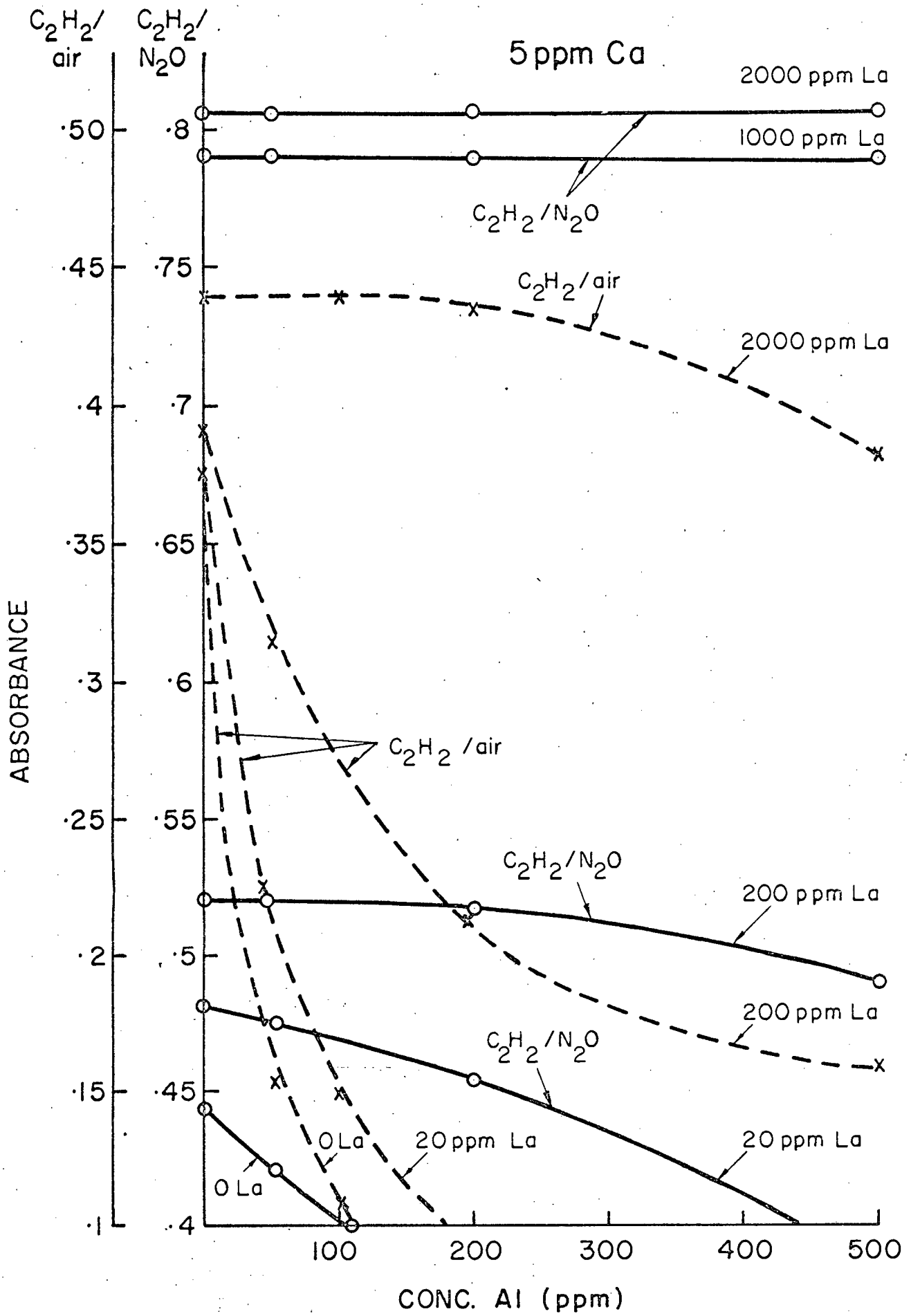

FIG. 8·5

Influence of Aluminium on Calcium for C_2H_2/air and C_2H_2/N_2O Flames with Lanthanum added

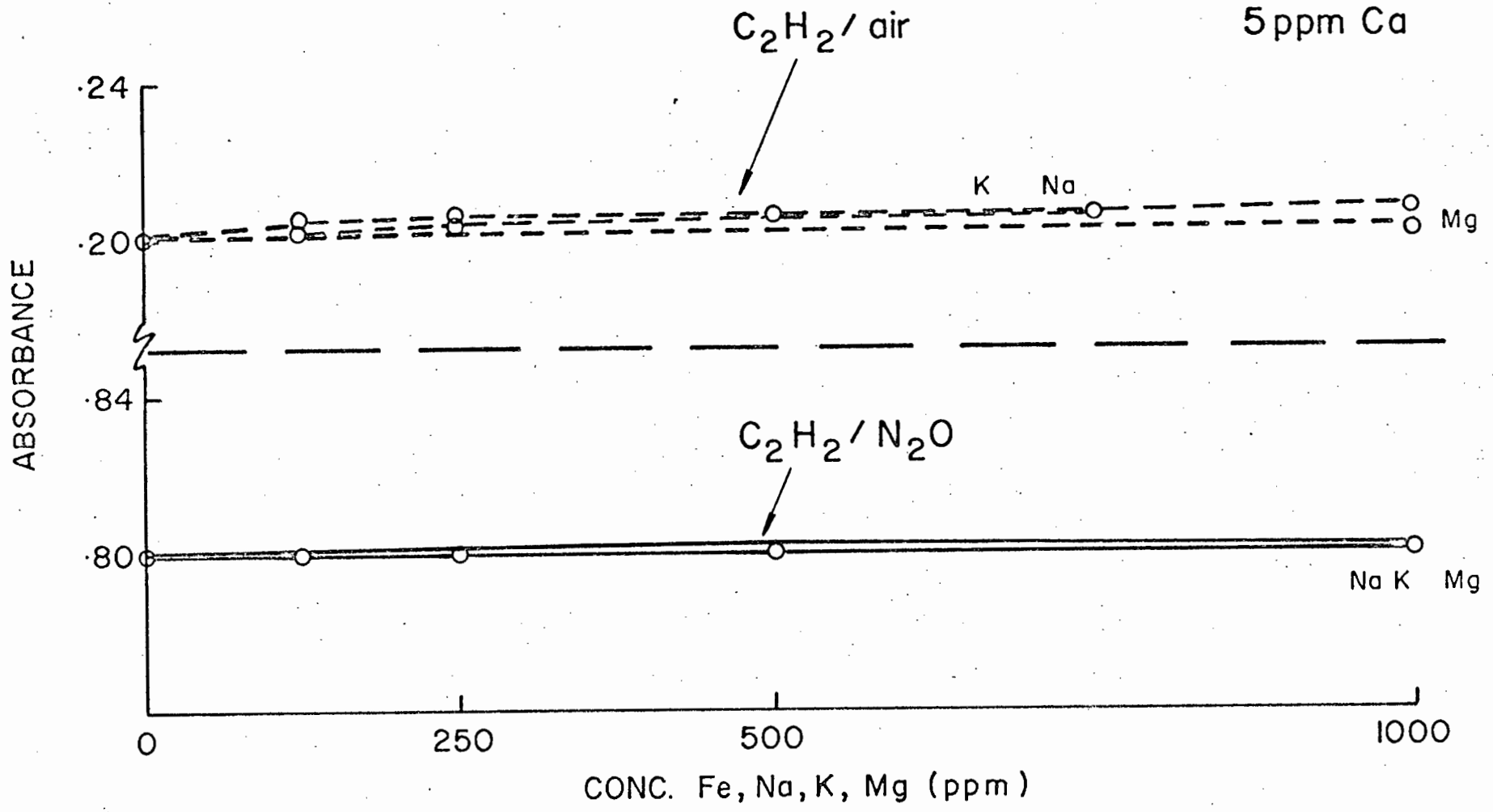

FIG. 8·6

Interference on Calcium for C_2H_2/air and C_2H_2/N_2O Flames (with 1000 ppm Lanthanum added to solutions.)

TABLE 8.2

Conditions for the determination of magnesium and calcium in silicate rocks

	Magnesium		Calcium	
Wavelength	2852 Å		4227 Å	
Lamp	Hollow cathode 5-10 mA		Hollow cathode 5-10 mA	
Slit	50 or 100 micron (2 - 4Å band-pass)		50 micron (2 Å band-pass)	
Flame	Max. sensitivity C_2H_2/air	Max. freedom from interference C_2H_2/N_2O	Normal condition C_2H_2/air	Max. freedom from interference C_2H_2/N_2O
Burner	10 cm slot	5 cm slot add 200-1000 ppm La	10 cm slot	5 cm slot add 1000 ppm La
Flame-setting	Lean or stoichiometric	Slightly fuel-rich (short red feather)	Fuel-rich luminous	Fuel-rich bright red feather
Support pressure	25 p s i	25 p s i	25 p s i	25 p s i
Burner height (below opt. axis)	5 mm	10 mm	10mm	12 mm (light passes above red feather)
Analytical range (in solution)	.02 - 5.0 ppm	.2 - 20 ppm	.1 - 20 ppm	.03 - 15 ppm
Detection limit (conc. for .004A)	.005 ppm	0.04 ppm	.03 ppm	.01 ppm

With burner at full length and conditions set for maximum absorbance

were essentially similar, provided the required amount of lanthanum was added. This result indicates that interference from silicon, which is retained during the fusion dissolution, is also effectively overcome by the added lanthanum. The fusion methods, F1 or F2, which are more rapid are more suitable for rapid analyses. Lanthanum oxide can be premixed with the flux. The lanthanum oxide assists in the oxidation process required to break down the silicates.

When added to the solution after acid digestion, lanthanum oxide is first dissolved in hydrochloric acid and then added at the required dilution.

Sample and standard concentrations were made to fall well within the linear region of absorbance. Because of the difference in absorbance sensitivities for calcium and magnesium, the solution was diluted to suit the calcium analytical graph. Magnesium was determined on the same solution and except when concentrations were low, the burner was turned side on to reduce absorbance to the linear range.

8.3.2 Limit of Detection

The limits of detection for both elements under the most sensitive conditions are given in Table 8.2.

8.3.3 Precision

The precision of the atomic absorption method for the determination of magnesium and calcium was tested. Precision tests are shown in Table 8.3.

The statistical tests made on a rock sample indicate that the precision obtained for calcium and magnesium is similar to that obtained for other elements. Magnesium results were generally more reproducible, probably because of the stiffer, more oxidizing flame, and the less critical dependence on flame conditions. The precision of the determination on the rock standards would have been better but for one of the dissolutions which showed low magnesium and calcium values.

The better precision for calcium in the nitrous-oxide flame may

TABLE 8.3

Precision measurements made on magnesium and calcium

(a) Aqueous solutions

Element	Flame	Conc. in solution ppm	Number of determinations	Coeff. of Var. %
Magnesium	C_2H_2/air	0.5	17	1.10
		2.0	17	0.93
	C_2H_2/N_2O	0.5	17	1.41
		2.0	17	1.2
Calcium	C_2H_2/air	1.0	17	2.10
		10.0	17	1.71
	C_2H_2/N_2O	1.0	17	1.67
		10.0	17	1.50

(b) Rock solutions* - Granite : GH
HF : $HClO_4$ dissolution

Element	Flame	Conc. in solution ppm	Number of determinations	Coeff. of Var. %
Magnesium	C_2H_2/air	2.1	7	1.92
	C_2H_2/N_2O	2.1	7	2.09
Calcium	C_2H_2/air	13.3	7	3.98
	C_2H_2/N_2O	13.3	7	2.89

*Note: (i) 1000 ppm lanthanum added to solutions.

(ii) Each determination is a separate dissolution of the sample.

be attributed to the stiffer, broader flame. The fuel-rich acetylene flame, necessary for maximum absorbance, gives noticeably more fluctuations. If the conditions were not set for maximum absorbance, precision with the acetylene/air flame would improve.

8.3.4 Accuracy

The U.S. Geological Survey standards and three of the French rock standards were analysed for magnesium and calcium. The results are shown in Table 8.4.

A considerable spread is reported in the literature for lower values of magnesium and calcium. The atomic absorption values fall well within this spread.

Except for a few examples, atomic absorption magnesium values are slightly lower than the accepted values. Belt (1967) and Nesbitt (1966) reported results which were also lower than the accepted value. The "accepted" value for the granite GH is strongly influenced by two unusually high chemical values (Roubault et al, 1966). If these are ignored and the more reliable values accepted (as was done by Nesbitt), the atomic absorption figures agree remarkably well.

Calcium results also appear to be close to the accepted values.

8.3.5 Discussion

The accuracy obtained with the atomic absorption method appears to be acceptable. While the precision may not be quite as good as X-ray fluorescence and colorimetric methods, it is similar to that obtained by emission spark methods (Suhr and Ingamells, 1966; Govindaraju, 1963). This fact together with the fact that the precision is maintained to very low concentrations of magnesium and calcium in rocks, makes the method attractive for geochemists. The low determination levels of 1 ppm for magnesium and 10 ppm for calcium enable these elements to be determined in minerals with very low abundances.

The interference effects seen in the various flames lead to some interesting speculation into the nature of the processes taking place. The lower sensitivity for magnesium in the acetylene/nitrous-oxide flame is

TABLE 8.4

Analysis of international rock standards for magnesium and calcium

Standard	Magnesium Oxide %				Calcium Oxide %		
	Ref.	Accepted	AA	No. of Detn.	Accepted	AA	No. of Detn.
Granite G-1	1	0.41 0.35	0.40	4	1.36	1.32	4
Diabase W-1	1	6.62 6.52	6.50	4	10.92	10.86	4
Granite G-2	2	0.75	0.78	3	1.95	1.91	3
Granodiorite (GSP-1)	2	0.97	0.95	2	2.06	1.97	2
Andesite (AGV-1)	2	1.50	1.46	2			
Basalt BCR-1	2	3.47	3.30	2			
Dunite DTS-1					0.03-000	0.026	2
Peridotite (PCC-1)					0.40	0.39	2
Granite GR	3	2.41 2.40	2.37	2	2.50	2.50	2
Granite GA	3	0.95 0.97	0.93	2	2.48	2.50	2
Granite GH	3	(0.03)* 0.07	0.025	7	0.68	0.41	7

References:

1. Fleischer (1965)
2. Flanagan (1967)
3. Roubault et al (1966)

*There is considerable spread in the results and the recommended value for Mg is generally not accepted. The value of 0.03% is usually quoted (Nesbitt, 1966).

explained by the more reducing conditions and the higher temperatures (2750°C) in this flame.

Higher temperatures also explain the decrease of interference for both elements. The addition of lanthanum stabilizes the flame by ionization and the saturation of the flame with electrons. It also reacts preferentially with molecule-forming foreign species.

The enhancement of both calcium and magnesium absorbance by iron at low concentrations (Figs. 8.1 and 8.2) is less easily explained. Ionization cannot be the cause, as sodium, which is more easily ionized, does not show the same result. It is suggested that iron reacts with calcium either before entering the flame or shortly after entering the primary zone to form a calcium ferrite. This reduces the number of atoms reacting with oxygen. When the calcium ferrite reaches the high temperature interconal zone it dissociates, but as this region of the flame is highly reducing, the calcium atoms do not combine with oxygen and are thus available for atomic absorption.
An enhancement results.

This theory is partially substantiated by tests made under various flame conditions. In strongly fuel-rich flames, the enhancement is reduced, while in an oxidizing flame the enhancement peak is more pronounced.

CHAPTER 9

COPPER AND ZINC

9.1 INTRODUCTION

Copper and zinc are two elements for which the atomic absorption method is ideally suited. Not only is sensitivity high, but both elements are known to be relatively free from interference effects (Strasheim et al, 1960; Farrar, 1965; Billings, 1967). The method has been used for the determination of both elements in a wide variety of materials, including geological samples (Bowditch et al, 1966; Slavin, 1965).

Both copper and zinc are classified as trace elements in rocks. It is not surprising that the high sensitivity of atomic absorption spectrometry has been useful for the determination of these elements in geological and agricultural materials.

Copper and zinc are elements of considerable geochemical interest for academic and economic reasons, e.g. copper is used extensively as an electrical conductor and consequently current market prices are high. It is in the field of geochemical prospecting that the atomic absorption determination of copper and zinc has probably been applied most extensively (Bowditch et al, 1966; Sampey, 1967).

Copper has a relatively low terrestrial abundance. Acidic rocks tend to have lower concentrations than the more basic rocks but even at higher concentrations, the copper values in common rocks seldom exceed 200 ppm. Table 9.1 lists the average abundance data for both copper and zinc. In spite of the low abundance figures, the availability of the group 1B elements (copper, silver and gold) as well as zinc, is high, mainly because they are found in concentrated sporadic deposits.

The geochemistry of copper is well known (Goldschmidt, 1954) and is characterized by the highly chalcophilic nature of the element. As such, it occurs mainly in the form of sulphides and does not contribute

significantly to rock-forming silicate minerals. Oxy- and halide salts also occur, but these are generally found in oxidized zones of copper deposits. More than 150 minerals of copper, including the raw metal, exist. Copper is associated with iron and sulphur in magmatic deposits. Chalcopyrite ($CuFeS_2$) is probably the most common mineral of copper, but bornite (Cu_5FeS_4) is often found in large quantities.

TABLE 9.1

Abundances of Copper and Zinc

(Concentrations in ppm)

Element	Ionic Radius Å	Crustal Average[1]	Granite G-1 [1]	Diabase W-1 [1]	Ultra-mafic[2]	Shales[1]	Sand-stones[1]
Copper	0.96	55	13	110	10	45	very low
Zinc	0.74	70	45	82	50	95	16

1. Mason (1966)
2. Turekian and Wedepohl (1961)

Zinc is a metal which is found in both lithophile and chalcophile associations in the upper lithosphere, but in magmas it tends to be concentrated in the sulphide phases. Having an ionic radius of 0.74Å it can enter the lattices of Fe^{2+} (0.74Å), Mg^{2+} (0.66Å) minerals, and is consequently widely distributed in most rock types as a trace element. Zinc concentrations are generally lower in acid type rocks and higher in basic and intermediate igneous rocks. In feldspars the zinc concentrations are extremely low (0.1 - 1.0 ppm). Zinc minerals in turn seem to have an unusual capacity for capturing other metals, e.g. sphalerite (ZnS) is known to harbour the guest elements copper, cadmium, mercury, gallium, indium, germanium, iron, manganese and cobalt (Goldschmidt, 1954). It is known that in many zinc deposits, lead and even copper are found (Day, 1963).

Copper and zinc salts are generally highly soluble in water or weak acids, and their minerals are prone to weathering. Argillaceous sediments thus

TABLE 9.2

Conditions for the determination of copper and zinc in silicate rocks

	Copper		Zinc	
Wavelength	3247 Å		2138 Å	
Lamp	Hollow cathode 5-10 mA		Hollow cathode 5-10 mA	
Slit	50 or 100 micron (2-4 Å)		200 micron (8Å)	
Flame	(a) Max. sensitivity prop.-but./air	(b) Max. freedom from interference C_2H_2/air	(a) Max. sensitivity prop.but./air	(b) Max. freedom from interference C_2H_2/air
Burner	Broadflame	10 cm slot	Broadflame	10 cm slot
Flame setting	stoichiometric	stoichiometric	stoichiometric (slightly rich)	slightly fuel rich
Support pressure	30 psi	25 psi	30 psi	25 psi
Burner height	8 mm	4 mm	8 mm	10 mm
Analytical range (ppm)	0.02 - 4.0	0.05 - 10.0	0.01 - 2.0	0.05 - 4.0
Detection limit (ppm)	0.005	0.1	0.001	0.01

cooler propane-butane/air flame (1950°C) than in the acetylene/air flame (2150°C). (See also Chapter 2, Table 2.1; the population of neutral atoms is decreased with a change in temperature.)

The broad-flame burner was used for the lower temperature flame. Both elements gave stable absorbance readings in this flame. When the slot burner, supplied for the propane-butane/air flame by the manufacturers, was used, severe fluctuations occurred for zinc. Flame conditions were not critical and absorbance did not change significantly for a change in burning conditions.

9.2.2 Interference Tests

The effect of the major elements present in rocks was tested on zinc and copper. Both propane-butane/air and acetylene/air flames were used under conditions which gave the highest sensitivity.

The results of the interference studies are indicated graphically. Fig. 9.1 shows the effects of the major elements on copper with the propane-butane flame, and Fig. 9.2 shows the effects with the higher temperature acetylene/air flame. It it seen that some depression results for both elements at higher concentrations of the interfering element in the propane-butane/air flame. A slight enhancement by calcium, magnesium and sodium is seen.

Fig. 9.3 shows the effect of other elements on zinc with the lower temperature flame. Slight depression by magnesium is shown. Other elements have a slight depressive effect too.

Fig. 9.4 shows that interference for all elements is virtually eliminated with the acetylene/air flame. Magnesium (as the chloride) causes a slight depression.

The light scatter effect reported by Billings (1965) was noticed and found to be more severe in the cooler flame. In the acetylene/air flame slight corrections were made to correct for this. As a self-built zinc-copper lamp was used for most analyses, a non-resonant copper line at 2179 Å was used

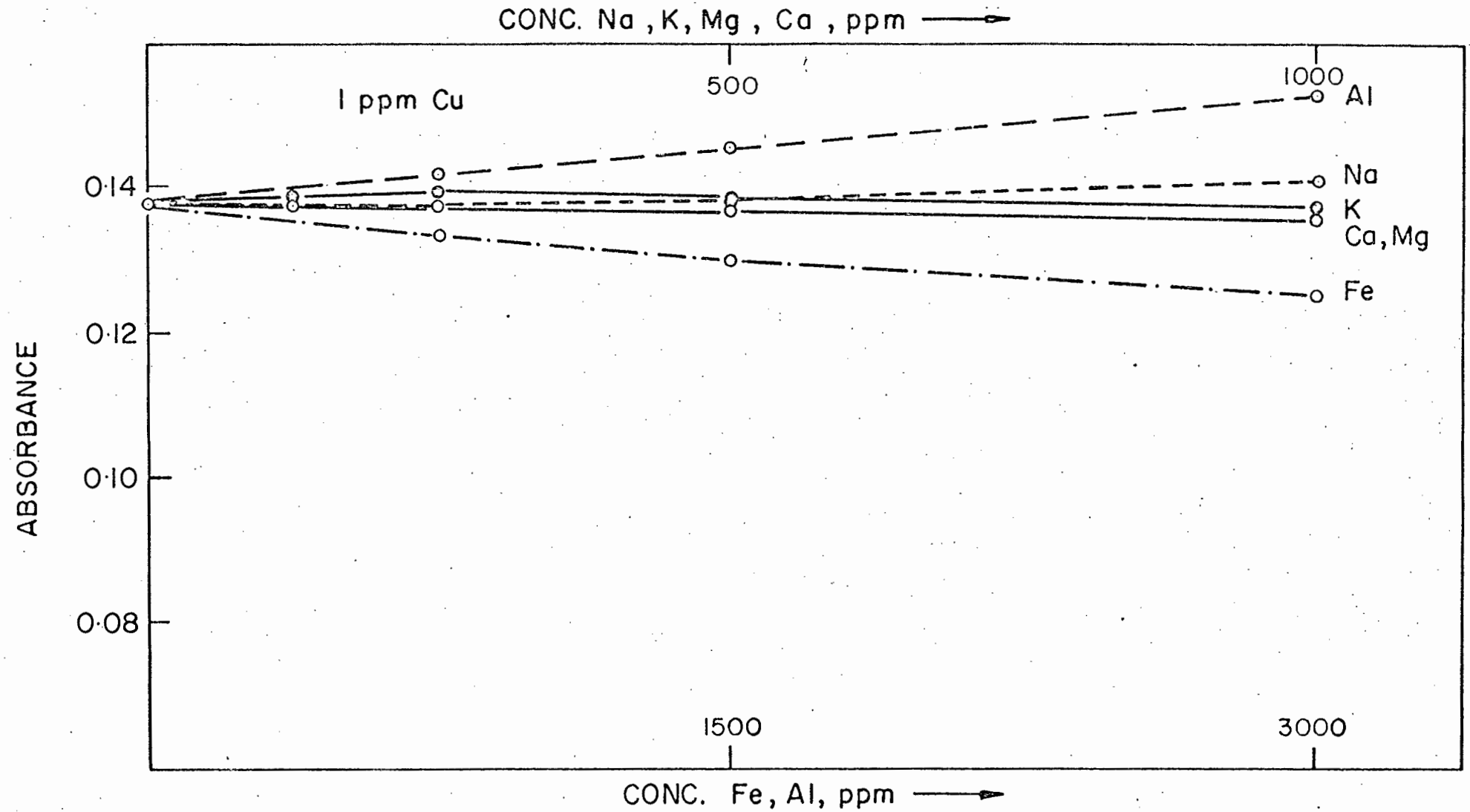

FIG. 9·1

Interference on Copper. Prop.–But. / Air Flame

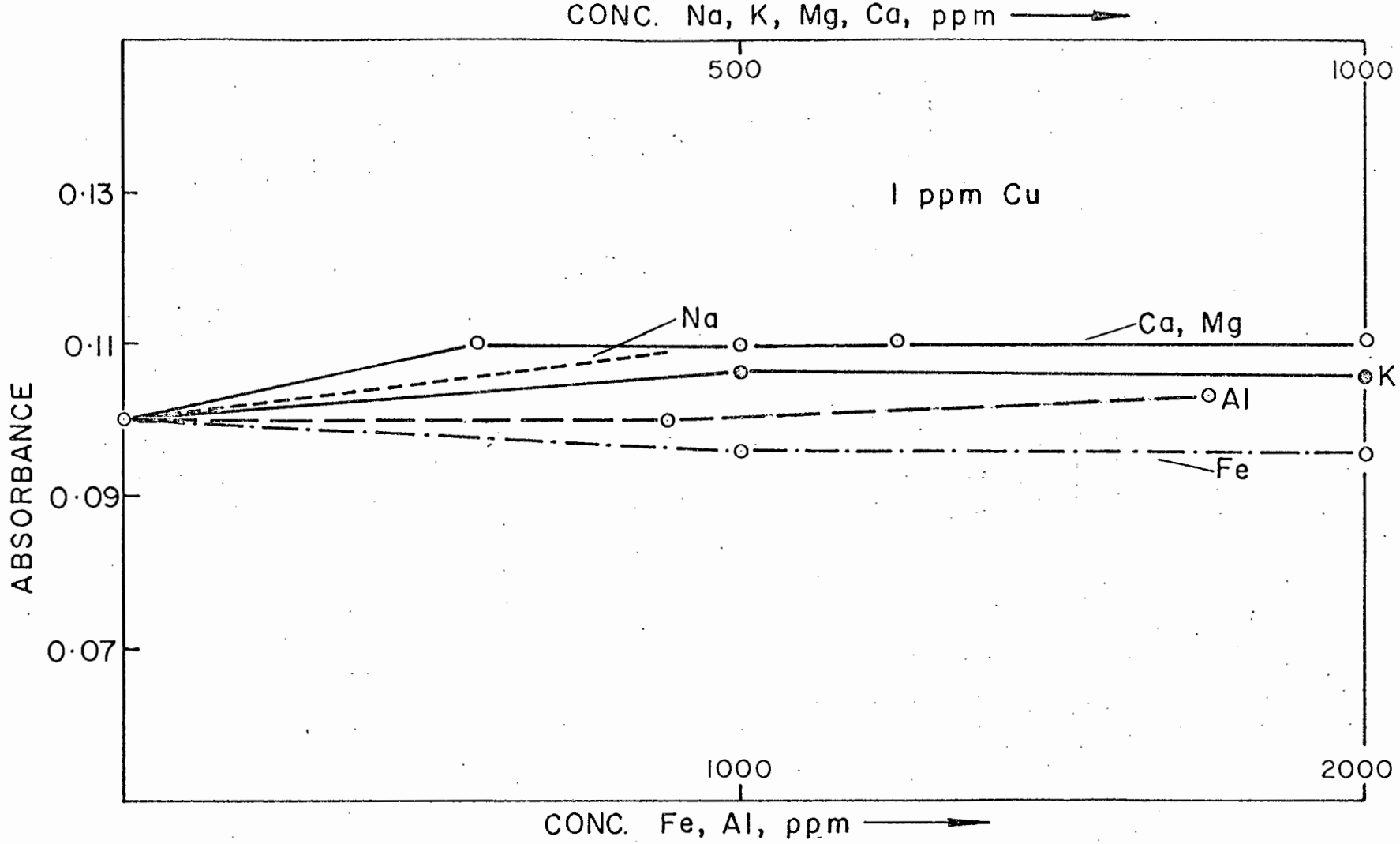

FIG. 9·2

Interference on Copper C_2H_2 / Air Flame.

PG4-1529

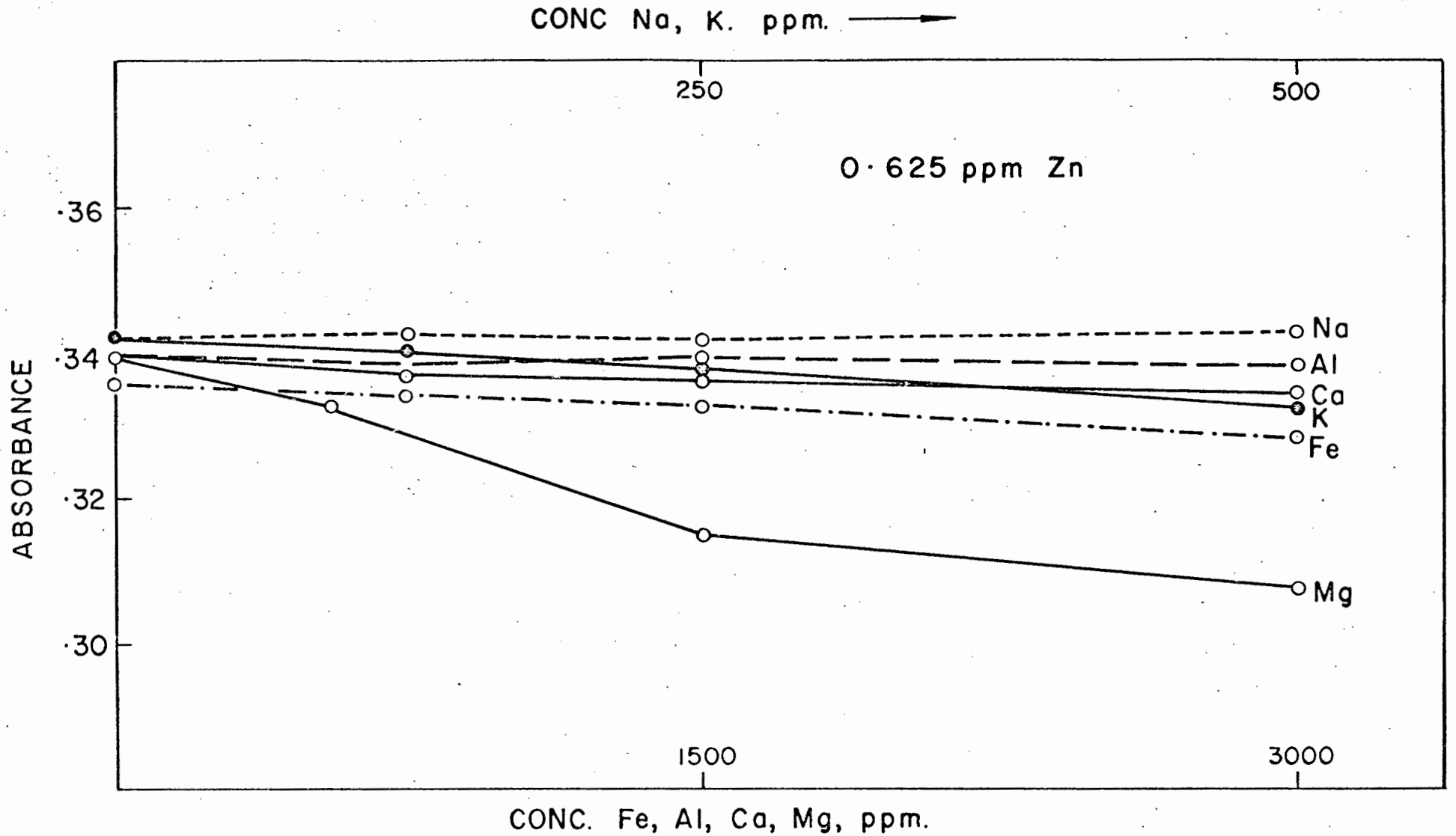

FIG. 9·3

Interference on Zinc Prop. – But./Air Flame

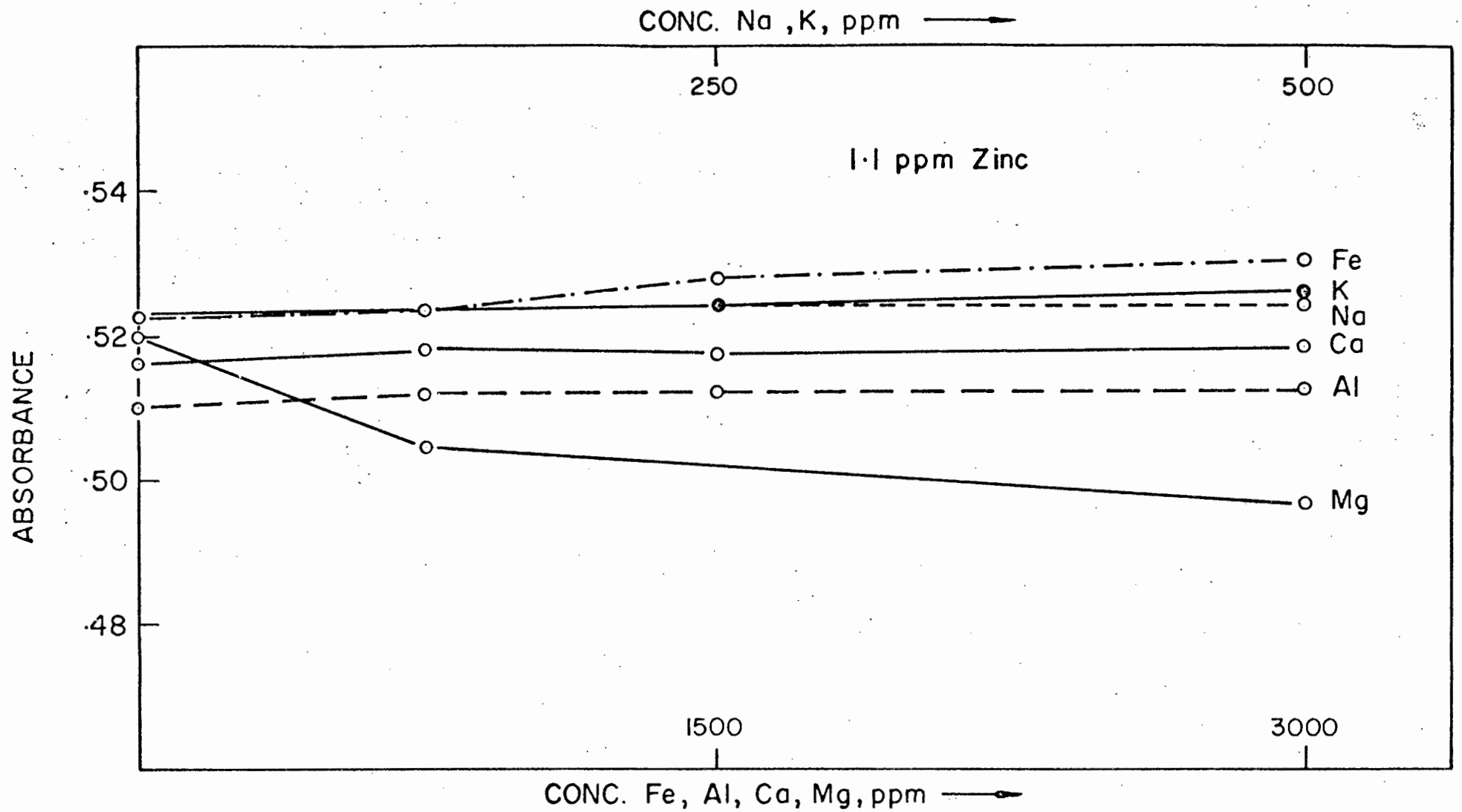

FIG. 9·4

Interference on Zinc. C_2H_2 / air Flame

for this purpose.

As a result of these tests it was decided to use only the acetylene/air flame for analytical work. Although sensitivity is lower, especially for zinc, results are far more reliable. This result confirms the work of Bowditch et al, 1966, who also prefer the acetylene/air flame for zinc determinations.

9.3 ANALYSES

9.3.1 Dissolution

The highest sensitivity is required for the determination of copper and zinc in rocks. For this reason and also because it is desirable that silicon be removed, the hydrofluoric acid method A-1 (or A-3) is recommended. This dissolution method was used for all estimations of copper and zinc reported in this thesis.

The great difficulty experienced with zinc analyses should again be stressed here. Results obtained were extremely haphazard until the contamination from the polythene bottles was pointed out. (See Chapter 5.3.)

When zinc was to be determined in a rock, only part of the solution was transferred to a polythene bottle from the volumetric flask. The portion left was used for the zinc determinations.

It is only in cases where all the silicates are to be dissolved that hydrofluoric-perchloric acids need to be used. When rapid dissolution is required, other acids can be used. Slavin (1965) described a method whereby an hydrochloric-nitric acid mixture is used and then sulphuric acid added. Farrar (1965) described the use of sodium hyposulphate followed by fusion. Certain minerals and elemental copper are dissolved more easily by weak nitric acid. This characteristic is used by prospecting geochemists to obtain an indication of the mineral type (Sampey, 1968).

9.3.2 Detection Limit

The detection limit for copper and zinc in both flames is given in Table 9.2.

These figures refer to aqueous solutions.

TABLE 9.3

Precision measurements for copper and zinc

(a) Aqueous Solutions

Element	Flame	Conc. in solution ppm	Number of determinations	Coeff. of Var. %
Copper	Prop.but./air	0.63	12	0.92
		2.5	12	1.11
	C_2H_2/air	0.63	12	1.60
		2.5	12	1.85
Zinc	Prop.but./air	0.5	12	2.25
		2.0	12	2.13
	C_2H_2/air	0.5	12	1.10
		2.0	12	0.98

(b) Rock Solutions Granodiorite - GSP-1
HF - $HClO_4$ dissolution 1%

Element	Flame	Conc. in solution ppm	Number of determinations	Coeff. of Var. %
Copper	C_2H_2/air	0.35	10	3.7
Zinc	C_2H_2/air	0.95	10	8.6

9.3.3 Precision

The precision with which determinations can be made was tested by measuring absorbance for aqueous copper and zinc aqueous solutions in both the acetylene/air and propane-butane/air flames. The results of these tests are shown in Table 9.3(a).

It is seen that the precision with the propane-butane flame is poorer than with the acetylene/air flame for copper and more so for zinc. Precisions in the acetylene/air flame are much better. This can be attributed

to the higher burning velocity and consequent "stiffness". It was shown in Section 4 (Table 4.1) that because of the change of refractive index flame movement will influence the Zn 2138 more strongly than the Cu 3247 line.

Several dissolutions of a rock powder sample were made and zinc and copper determined. The results for the acetylene/air flame are shown in Table 9.3(b).

In spite of careful precautions taken in the metering of acids, precision for zinc is far from satisfactory. The relatively high blank values obtained indicate the presence of zinc in the acids or solution and it is thought that this may be the cause of poorer precision. The precision obtained for copper is more satisfactory.

9.3.4 Accuracy

Various international standard rocks were dissolved and analysed for copper and zinc. Results are shown in Table 9.4(a).

Some samples analysed by other workers were also analysed and the results are shown in Table 9.4(b). Results shown without comparative figures are included for record purposes.

In order to check results and also to obtain higher sensitivity, an extraction method was applied to determine copper in some standard rock solutions.

The well known ammonium pyrolidine dithiocarbonate (A P D C) technique of Malissa and Schaffman (1955) was used. The method is as follows:

20 ml of the rock solution (which has a 5N concentration of hydrochloric acid) are thoroughly mixed with 4 ml of a 1% A P D C solution to complex the copper.

5 ml of iso-butyl methyl ketone (M I B K) are added and the sample is shaken for 2 minutes to dissolve the copper complex in the ketone. After standing to allow the two phases to separate, the ketone is sprayed into the acetylene/air flame.

Standards with various copper concentrations should be treated in the same way as the samples.

TABLE 9.4 (a)

Analysis of international rock standards for copper and zinc

Standard	Copper (ppm)				Zinc (ppm)			
	Accepted value	Ref.	Atomic Absorption		Accepted value	Ref.	Atomic Absorption	
			Value	No. of detns.			Value	No. of detns.
Granite G-1	13	1			45	1		
Diabase W-1	110	1	112	4	82	1	82	2
	116	2			83	2		
Granite G-2	9 - 14	3	13	4		3	76	4
	6.7	2			77	2		
Granodiorite GSP-1	34 - 60	3	33.5	8		1		
	33	2			108	2	114	4
Andesite AGV-1	55 - 100	3	54	4		1	98	4
	52	2			87	2		
Basalt BCR-1	21 - 35	3	15	4		1	128	4
	13	2			115	2		
Dunite DTS-1	3 - 9	3	8	4		1	55	4
	6.1	2			61	2		
Peridotite PCC-1	5 - 16	3	10	4		1	48	4
	9.0	2			42	2		
Granite GA	10 - 16.6	4	13	6				
					33 - 94	4	63	3
Granite GH	9 - 15	4	13	6	60 - 97	4	83	6
Granite GR	270 - 440	4			(56)	4	58	6
Basalt BR	65 - 74	4	68	4	80 - 175	4	166	6

1. Fleischer (1965)
2. Brunfelt et al (1967)
3. Flanagan (1966)
4. Raubault et al (1966)

TABLE 9.4 (b)

Analysis of samples for copper and zinc

(Concentrations in ppm)

Sample	Rock Type	Copper	No. of Detns.	Other values	Ref.	Zinc	No. of Detns.	Other values	Ref.
ET3/169	Pyroxenite	28	4			79	4		
ET3/270	"	26	4			61	4		
5087	Norite	6	2			50	4		
D/S 95	Karroo dolerite	152	2			107	4		
7228	Pyroxinite	5	3			50	4		
NOR-1	Norite	220	2			9			
NOR-2	"	(450) 344*	4			(52)* 11	2		
RV 374	Eclogite	155	2	1		53	2		1
KRV 7	Eclogite	47	2	1		75	4		1
KRV 13	Kimberlite	24	2	1		45	4	36	1
RV 3	"	187	2	1		40	4	32	1
KDB 10	"	(55)* 44	2	1		56	2	54	1
KDB 12	"	(53)* 44	2	1		56	2	55	1
BULT 8	Peridotite	(12)* 4	2	1		30	4	30	1
BULT 11	"	3	2	1		30	3	28	1
BULT 16	"	2	2	1		32	4	34	1
AA 5	"	2	2	1		29	4	31	1
ASH 1	Melilite basalt	86	2	1		110	4	104	1
EK 43	Eclogite	24.2	8	1		(95)**		78	1
TAN 503	"	28	4	1		37		31	1

See Appendix II for locality of samples

1. Gurney (1968)

*Two sets of dissolutions gave considerably different results. Both values are given.

**Severe difficulties experienced with EK 43 dissolution. Result is that obtained from "bomb" dissolutions.

An enhancement of sensitivity was obtained when the organic solvent was sprayed. This and the concentration factor of 4 enabled copper as low as 0.1 ppm in rocks to be determined. A higher concentration factor can easily be obtained with this method. Certain rock standards were analysed in this way and the results are shown in Table 9.5. It is seen that results are similar to those obtained with the direct aspiration of the aqueous solution. For very low concentrations, the extraction procedure is thus recommended. Unfortunately no analysed samples with very low copper concentrations were available to enable the technique to be tested to its limit.

9.3.5 Discussion

When the relatively low concentration levels in rocks are considered, the accuracy for both copper and zinc is acceptable. Blank solutions must be prepared at the same time that the samples are dissolved because reagent solutions may be contaminated with zinc. The lowest concentration which may be determined is limited by the amount of zinc impurity in the reagents used. Values lower than the blank concentration cannot be determined. In these tests the blank content was of the order of 0.01 ppm (in solution). The poorer precision obtained for zinc (because of contamination) suggests that samples should be analysed in triplicate, at least, if reliable results are to be obtained.

TABLE 9.5

Analysis of international standards for copper using E D T A and M I B K extraction

Sample	Accepted	Ref.	Atomic Absorption (extract.)	No. of detns.
Granodiorite	34 - 60	1	34	4
GSP - 1	33	2		
Andesite	55 - 100	1	63	4
AGV - 1	52	2		
Basalt	21 - 35	1	27	4
BCR - 1	13	2		
Dunite	3 - 9	1	4.0	4
DTS - 1	6.1	2		
Peridotite	5 - 16	1	8.0	4
PCC - 1	9.0	2		

1. Flanagan (1966) (various)
2. Brunfelt et al (1967) (atomic absorption)

CHAPTER 10

MOLYBDENUM

10.1 INTRODUCTION

The determination of molybdenum is of interest for several reasons:

(a) Because of its relatively low abundance in nature and the difficulties which are associated with its determination, there is much to be learnt about its geochemical behaviour.

(b) Molybdenum ores are of importance in the steel industry and demand high prices; the deposits are few and far between; the U.S.A. apparently produces nearly 30% of world molybdenum. It is consequently a metal much sought after.

(c) Molybdenum is an essential trace element for plant metabolism, and thus often determined in plant materials, soil extracts and natural waters.

(d) Molybdenum-disulphide is one of the best known dry lubricants. It is used especially in high temperature aircraft jet engines.

Molybdenum has low natural abundances and its determination is not easy by instrumental methods. Ahrens and Taylor (1961) note that normal concentrations border on the spectrochemical detection limit (about 1 ppm). Chemical enrichment methods are normally used for estimating lower concentrations in soils and plants (Mitchell and Scott, 1957).

Other methods which have been used for the determination of molybdenum are neutron activation (Towell et al, 1965) and mass spectrometry (Taylor, 1965).

Table 10.1 lists abundance data for molybdenum. It should be noted that G-1 shows an abnormally high concentration of molybdenum.

Molybdenum and tungsten are closely related crystallo-chemically because of their similar atomic and ionic radii.

However, molybdenum usually occurs as the sulphide MoS_2, while tungsten is usually found in combination with oxygen. The most common mineral of

molybdenum is molybdenite MoS_2, occurring mainly in granites, syenites, and their pegmatites. Small amounts of molybdenum may also occur in basic gabroid magmas such as norite.

TABLE 10.1

Abundances of Molybdenum
(ppm)

Ionic radius	Crustal average	Granite G-1 (1)	Diabase W-1 (1)	Ultra basic (2)	Shales (1)	Sandstone (1)
Mo^{6+} 0.62Å	1.5	7.0	0.05	0.3	2.6	0.2

(1) Mason (1966)

(2) Turekian and Wedepohl (1961)

The behaviour of molybdenum during weathering processes is not well known, but it appears to dissolve under some conditions and may be accummulated in oxidate sediments, particularly those containing manganese. However, the concentration of molybdenum in natural waters is very low, 0.01 ppm in sea water, so highly sensitive methods must be used for its determination.

David (1961) made a comprehensive study of the factors influencing the determination of molybdenum by atomic absorption spectroscopy and achieved a detection limit of the order of 0.5 ppm in aqueous solutions. A fuel rich, acetylene/air flame was used. This detection limit is not low enough for the determination of molybdenum in most silicate rocks, soils or natural water. Moreover, there are elements present in these samples which David found interfered with molybdenum absorption.

Butler and Mathews (1966) used liquid-liquid extraction techniques to determine molybdenum in natural waters, plant materials and the rocks G-1 and W-1. This method has been found to be highly satisfactory. It is described in this chapter with slight modifications and new results are given.

10.2 EXPERIMENTAL

10.2.1 Flame Studies

David stressed the importance of using only a small region of the atomic absorption flame. This can be done by placing apertures at the lenses, but with the optical arrangement on the Techtron this results in a considerable loss of light. It was found that a similar effect could be obtained when a smaller image of the cathode was formed by moving the hollow cathode lamp and the first lens further from the flame. In this way the region of maximum absorbance in the acetylene/air flame could be isolated.

The relative sensitivity, when using an acetylene/air flame under extreme fuel-rich conditions and the acetylene/nitrous-oxide flame, were found to be similar. Maximum absorbance occurred in the "black-cone" of the nitrous-oxide flame, which was also required to burn under fuel-rich conditions. Measurements with the nitrous-oxide flame were far noisier, however, and the acetylene/air flame was preferred, especially for spraying organic solvents.

Table 10.2 lists the most suitable conditions for the determination of molybdenum.

TABLE 10.2

Conditions for the determination of molybdenum in aqueous solutions

Wavelength	3133 Å	
Lamp	Hollow cathode 15 - 20 mA	
Slit	50 micron (2Å bandpass)	
Flame	C_2H_2/air	C_2H_2/N_2O
Burner	Slot 10 cm	Slot 5 cm
Settings	V. fuel rich (luminous)	Fuel rich (luminous at tip of red feather)
Burner below optical axis	10 - 15 mm	15 - 25 mm
Determination range (aqueous)	1.0 - 100 ppm	1.0 - 100 ppm
Detection limit (0.004 absorbance)	0.5 ppm	0.3 ppm

10.2.2 Interference Studies

Severe depression of molybdenum absorbance was found by iron in aqueous solutions in an acetylene/air flame. This interference was not as strong in the acetylene/nitrous-oxide flame, but was still too severe to enable the determination of molybdenum at the concentrations occurring in rocks without the removal of the interfering species.

Interference effects on the extraction method developed, are given in Section 10.2.4(c).

10.2.3 Sample Dissolution

Both fusion techniques and acid digestion were used. The fusion method used was in addition to that described in Chapter 4. A sodium hydroxide and sodium peroxide mixture was used (1.5 g : 2.0 g respectively) with a 0.5 g sample in platinum at 470°C (for 30 minutes). Platinum corrosion from iron was obviated by first leaching the sample with hydrochloric acid and then filtering. The residue was fused and the filtrate was recombined with it. The lithium metaborate fusion method also worked well and was used on several occasions.

The results obtained from acid digestion were slightly lower than from fusion methods. These are shown in Table 10.3. Both methods gave nearly 100% recovery on rock solutions to which molybdenum had been added. In view of the greater concentration factor possible with acid digestion and the consequent lower limit of detection, acid dissolution of rock samples was preferred. For the analysis of ultramafic rocks, however, where the molybdenum might be included in the crystal lattices of acid-defying minerals, the fusion methods would be preferred. Solutions were made to give 5-10% (weight of solid (gm) per 100 ml) solutions.

10.2.4 Extraction

It was obvious that some form of extraction method would have to be used to eliminate interfering ions and concentrate molybdenum to a determinable level. Liquid-liquid techniques are more satisfactory for atomic absorption

purposes because of the ease with which certain organic solvents burn in the flame.

TABLE 10.3

Comparison of results using acid digestion and fusion of rock powder

		Mo determined on G-1 ppm
1. Acid digestion	:	10.7
2. Fusion (Na_2O + NaOH)	:	13.0
3. Fusion ($LiBO_2$)	:	12.1

Malissa and Schöffmann (1955) have reported the chelating of many heavy metals, including molybdenum, by ammonium pyrollidine dithiocarbamate (APDC). This extraction technique was, however, found to be unsuitable for samples with high iron content, because of the preferential extraction of this element.

Mitchell and Scott (1947) reported the use of 8-hydroxyquinoline as a complexing agent for molybdenum and other metals with subsequent determination by emission spectroscopy. With certain modifications this method was found to be more suitable for silicate materials where iron concentrations are high. Willis (1962), Allan (1961), and Robinson (1960) have shown that considerable enhancement in sensitivity may be achieved by spraying an organic solvent containing the analytical element, into the flame. Combinations of these methods, viz. liquid-liquid organic extraction with subsequent determination of molybdenum in the organic phase, have satisfactorily been used for the determination of molybdenum.

(a) Method. Methyl isobutyl ketone (MIBK) has a relatively high solubility in water (1.8g/100 ml) which is not desirable if a high concentration factor is required. Amyl methyl ketone is less soluble in water (0.5 g/100 ml) and separates more easily from the aqueous phase because of its lower density). This solvent burns well in the acetylene/

air flame and was consequently used as the solvent for dissolving the molybdenum chelate.

The extraction technique is as follows:

The pH of the solutions (standards and samples) is adjusted to 1.0 after adding 25 ml of a 4% 8-hydroxyquinoline solution. The solution is then thoroughly mixed. The amyl methyl ketone is then added to give a concentration factor of 10 to 20. The mixture is shaken for 4 minutes and the two phases allowed to separate. (A special separating flask was designed to enable the organic phase to be sprayed without running off the aqueous phase. This flask has a narrow opening and a broad opening. The organic phase accumulates in the narrow neck when the flask is turned upside down. Fig. 10.1 shows a diagram of the flask.) Aqueous standards with known concentrations of molybdenum are treated in the same way as the samples. The spectrometer should be zeroed with pure ketone.

(b) Extraction efficiency. The effect of pH on the extraction of molybdenum from various solutions was tested. Tests on aqueous solutions indicated that 99% extraction is obtained at a pH of 2.0. Fig. 10.2 shows the extraction curve for 8-hydroxyquinoline. Unfortunately, when rock solutions were tested at this pH, it was found that a heavy dark precipitate formed. Spectrographic examination showed this to be mainly iron, which had precipitated in the presence of excess 8-hydroxyquinoline. When a pH value of 1.0 was used, the extraction was only 92% efficient, but the precipitate did not form. As sensitivity can easily be increased by using a higher concentration factor, the less efficient extraction is not serious. It is important, however, to adjust the pH accurately.

In cases where the fusion method was used and the silicon content of the sample was high, an emulsion sometimes formed when the samples were heated to drive off excess liquid. Although the addition of

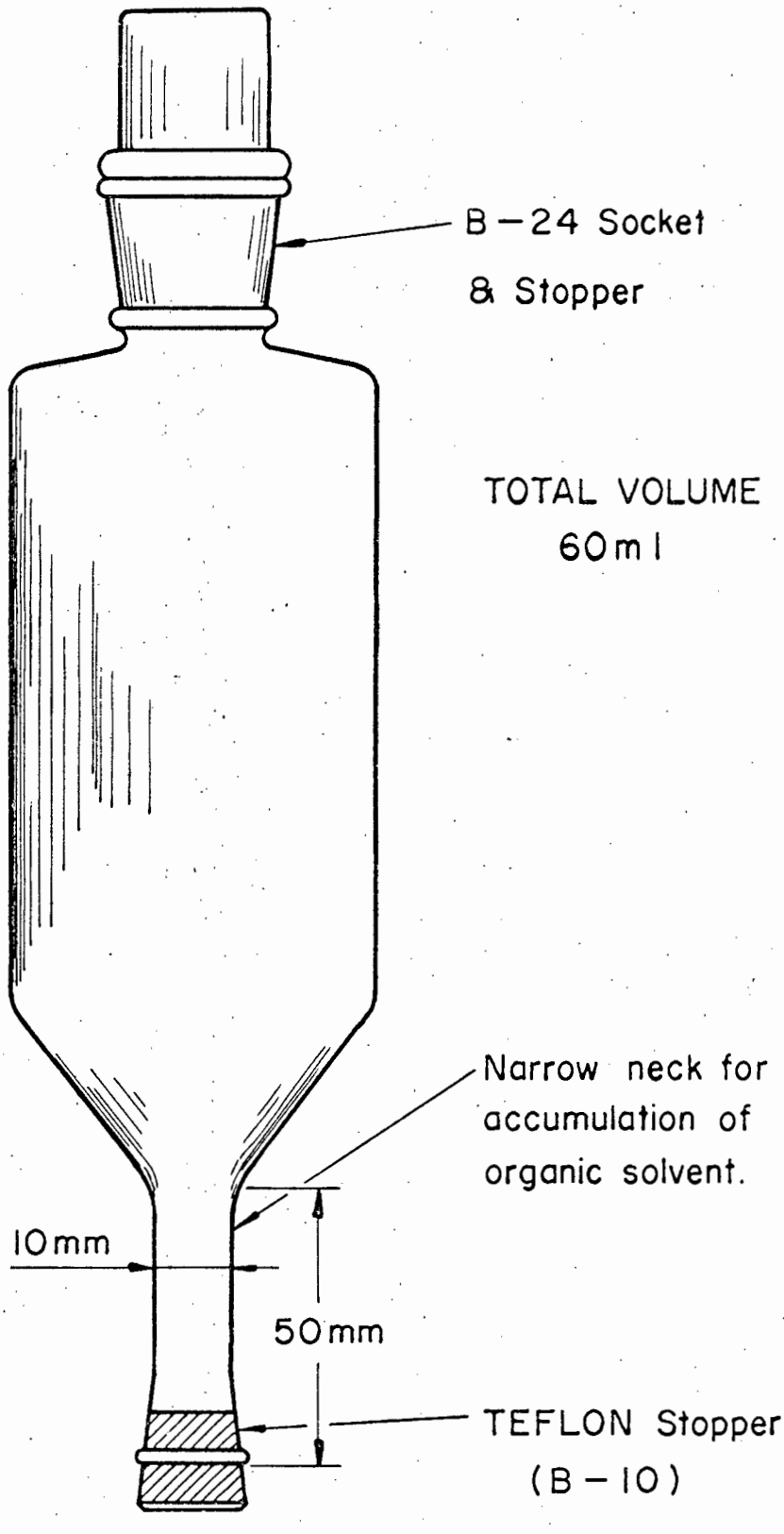

FIG. 10:1

Special Shaking Flask for separating Organic and Aqueous Phases.

PG4-1531

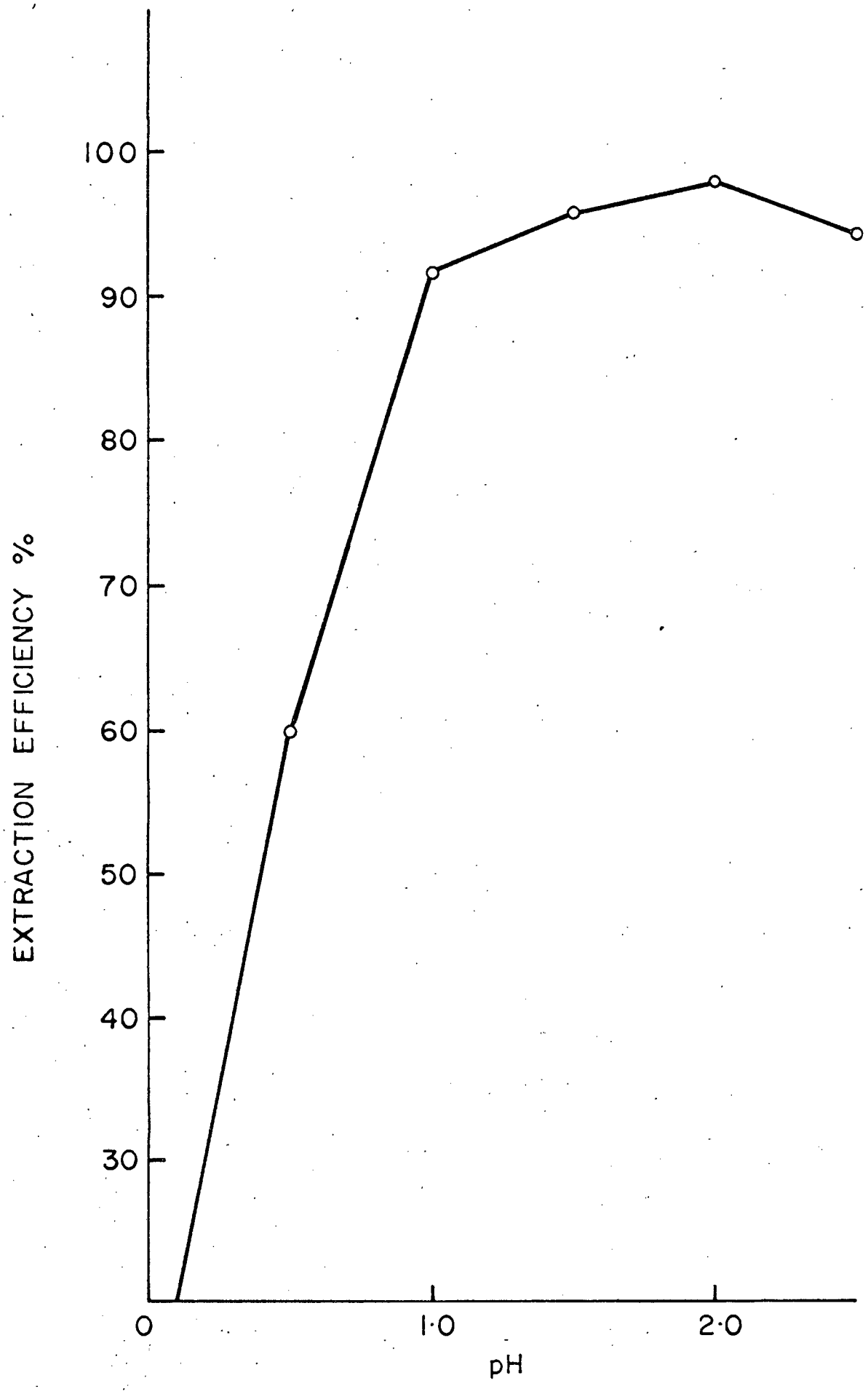

FIG. 10·2

Extraction Efficiency of Molybdenum

hydrofluoric acid eliminated this, it was found more simple to work so that sample solutions did not require concentration, but only dilution to bring them to volume.

Recovery tests were carried out on two samples. These are shown in Table 10.4. Analyses of aqueous standards carried out by colorimetric chemical methods showed close agreement. These are shown in Table 10.5.

(c) Interference tests. The influence of major elements on the efficiency of extraction and determination was tested. Fig. 10.3 shows that no interference is evident at the concentrations normally found in rocks.

TABLE 10.4

Recovery Tests

Sample	Mo present (ppm)	Mo added (ppm)	Mo recovered (ppm)	Recovery %
Sulphide ore	4.0	2.0	5.8	98
	4.0	4.0	8.0	100
	4.0	10.0	13.9	99

TABLE 10.5

Comparison of results with chemical values

(Values in ppm)

Sample	A A value	Colorimetry
1	0.010	0.011
2	0.048	0.052
3	0.091	0.091

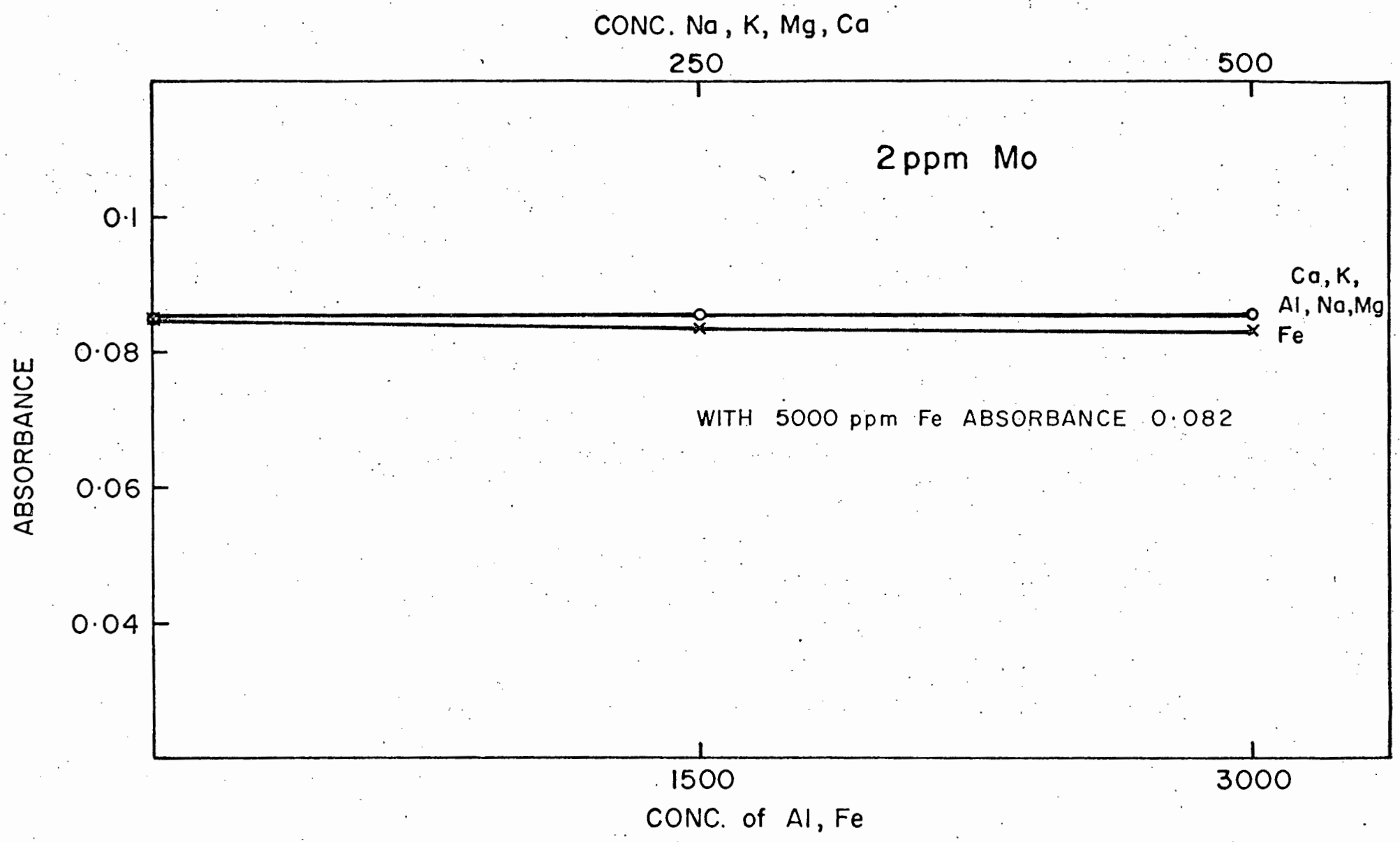

FIG.10·3

Interference on Molybdenum.

PG4-1532

10.3 ANALYSES

10.3.1 Detection Limit

The limit of detection in aqueous solutions is given in Table 10.2. The limit of detection for the organic extraction depends on the concentration factor. Working from 5% solids in solutions and using a 20x factor a limit of detection of about 0.1 ppm of molybdenum in the solid, is realized.

10.3.2 Precision

Several series of precision tests were carried out on aqueous standards, on aqueous standard extractions, and on rock samples. Results are shown in Table 10.6 (a), (b), and (c) respectively. It is seen that the precision is generally good. The precision obtained for the extractions is surprisingly good when all the chemical steps are taken into account.

TABLE 10.6

Precision Tests

(a) Aqueous Solutions

Sample	Concentration (ppm)	No. of determinations	Coeff. of Var.%
1	1.0	15	3.5
2	2.0	15	1.8
3	10.0	15	1.6

(b) Aqueous Solutions Extracted

Sample	Concentration (ppm)	Conc. in Ketone (ppm)	No. of Determinations	Coeff. of Var. %
1	0.01	0.1	5	5.1
2	0.05	0.5	5	3.3
3	1.0	1.0	5	2.1

TABLE 10.6 (Continued)

(c) Rock Standards

Sample	Mean Conc.	Conc. in Ketone	No. of Determinations	Coeff. of Var. %
Granite	12.6	6.3	8	4.0
Sulphide ore	4.0	2.0	8	8.1
Andesite	2.05	1.03	8	5.1

10.3.3 Analysis of Samples

Table 10.7 shows the results obtained for the analysis of several rock standards. The value for G-1 is higher than the accepted value, while that for W-1 is lower than the accepted value. No reliable comparative values are available for the newer series of standards from the U.S. Geological Survey.

TABLE 10.7

Analysis of Rocks

Sample	Accepted value	Ref.	Value obtained	No. of determinations
Granite G-1	7.0 (14.0)(4)	(1)	10.7 (12.6)*	8 (8)
Diabase W-1	0.5	(1)	0.2	8
Sulphide ore	10.0	(2)	4.0	8
Granite G-2	< 2.0	(3)	2.0	2
Granodiorite GSP-1	< 2.0	(3)	0.6	2
Andesite AGV-1	4.0	(3)	2.1	8
Basalt BCR-1	9, 6, 6	(3)	2.0	2
Dunite DTS-1	< 2.0	(3)	0.2	2
Peridotite PCC-1	< 2.0	(3)	2.8	2

*Value obtained from fusion

(1) Fleischer (1965) (various)
(2) Webber (1961) "
(3) Flanagan (1966) "
(4) Stevens et al (1960) (chemical value)

10.3.4 Discussion

The results for G-1 and W-1 do not differ radically from the latest accepted values. Comparison with a value of 14 ppm published previously (Stevens et al, 1960) is better. Recovery tests indicate that recovery of molybdenum is good and that if values are too low this is probably due to minerals such as zircon, which contain molybdenum not dissolving.

CHAPTER 11

IRON AND MANGANESE

11.1 INTRODUCTION

Iron and manganese are important elements in rocks and minerals. Both elements are usually included in whole rock analyses, and the highest accuracy and precision are required in their determination.

Although chemical methods are recognized for the determination of these elements, rapid instrumental methods such as X-ray fluorescence and emission spectrometry have become accepted. For low concentrations, emission techniques may be more accurate than chemical methods (Ahrens and Taylor, 1961).

Iron and manganese may be determined by atomic absorption spectrometry, and sensitivity is good for both elements. Interference effects are reported to be low (Allan, 1959; David, 1962). It was decided to include these elements in this study as the atomic absorption method could be useful as an independent method especially for the determination of low concentrations.

The geochemistry of iron and manganese is complex and is thoroughly discussed by Goldschmidt (1954) and Rankama and Sahama (1950).

Iron is a major element and may exist in a variety of forms, viz: Free metallic iron, primary oxides in several valency states, sulphide minerals, primary silicate minerals and secondary compounds of iron. Instrumental methods usually determine total iron and separate tests must be made to distinguish ferrous and ferric iron.

Manganese is considered a strong lithophile element, but has some chalcophile tendencies. The ionic radius of the Mn^{3+} ion (0.70Å) is similar to that of Fe^{2+} (0.74Å) and the two elements are often found together in crystal lattices. As other elements such as calcium and magnesium have similar ionic radii (0.99Å and 0.66Å respectively), iron and manganese are associated with a wide variety of rocks and minerals; iron either as a major or minor element and manganese as a minor or trace element.

Manganese is related to iron and follows its manner of occurrence in nature. Concentrations are highest in ultramafic rocks and lowest in acidic rocks. Table 11.1 shows the abundances. The ratio MnO:FeO in igneous rocks is remarkably stable. (Rankama and Sahama, 1950).

TABLE 11.1

Abundances of iron and manganese

(Concentration in % iron and manganese)

Element	Ionic Radius Å	Crustal Average (1)	Granite G-1 (1)	Diabase W-1 (1)	Ultra-mafic (2)	Shales (1)	Sand-stone (1)
Iron	Fe^{2+} 0.74 Fe^{3+} 0.64	5.0	1.37	7.76	9.43	4.72	0.98
Manganese	Mn^{2+} 0.91 Mn^{3+} 0.70 Mn^{4+} 0.52 Mn^{7+} 0.46	0.095	0.023	1.32	0.162	0.085	0.00X*

(1) Mason (1966)

(2) Turekian and Wedepohl (1961)

*X denotes an order of magnitude

Iron and manganese have been determined by atomic absorption spectrometry in many types of materials, including geological matter such as sea water (Fabricand et al, 1962), fresh water (Butler and Brink, 1963) and silicate rocks (Trent and Slavin, 1964b; Billings, 1965a; Bowditch et al, 1966; Belt, 1967). These workers have shown that the estimation of iron and manganese presents no difficulties and that accuracy of this method is high. The tests carried out in this study confirm this conclusion.

11.2 EXPERIMENTAL

11.2.1 Flame Studies

The acetylene/air flame is usually recommended for maximum sensitivity for

iron while a lower temperature flame gives highest sensitivity for manganese. Tests show that a slightly fuel rich acetylene/air flame gives the best absorbance signal for iron. Although manganese absorbance is higher in the propane-butane/air flame, interference from iron was noted. As the sensitivity in the acetylene/air flame is satisfactory, and interference is considerably reduced, this flame was used. Table 11.2 gives the sensitivities obtained for iron and manganese under the most suitable conditions.

TABLE 11.2

Conditions for the determination of iron and manganese in rocks

Condition	Iron		Manganese	
		Sens. factor		Sens. factor
Wavelength Å	2483.3	1	2795	1
	2522.8	0.5	4030.8	0.1
	3020.6	0.2		
	3719.9	0.1		
	3589.9	0.05		
Lamp	Hollow cathode 10 mA		Hollow cathode 10 mA	
Slit	25 micron (1 A Band-pass)		50 micron (2 A Band-pass)	
Flame	C_2H_2/air		C_2H_2/air (for max. freedom for interference)	prop.but./air (for max. sensitivity
Support pressure	25 p s i		25 p s i	30 p s i
Burner height	10 mm		15 mm	25 mm
Analytical range (ppm)	0.2 - 25		0.1 - 10	0.05 - 5
Detection limit (ppm)	0.1		0.05	0.02

Sensitivity factor indicates the approximate amount that other lines are less sensitive than the most sensitive line.

Analytical range and detection limit are given for the most sensitive line.

11.2.2 Interferences

Interference studies of the major elements in rocks on iron and manganese were made. For iron, only the acetylene/air flame was used, but for manganese, both the acetylene/air and the propane-butane/air flames were tested. The results of the tests are shown in Figs. 11.1 for iron and 11.2 and 11.3 for manganese.

Interference on iron is mostly enhancement and is small. A fuel rich flame shows less enhancement and gives a higher absorbance signal.

In Fig. 11.2 it is seen that iron causes a depression of manganese absorbance in the propane-butane/air flame which disappears in the acetylene/air flame. The interference effect is dependent on the flame region, and the best position for maximum absorbance and minimum interference is just above the primary reaction zone. Above this, both aluminium and iron cause depression which increases with flame height. It has been reported that silicon interferes with manganese (Platte and Marcy, 1965). When analyses were made on international rock standards using fusion techniques, very little depression of manganese absorbance was noted. Lanthanum, which was present in the solutions, probably eliminated this interference.

11.3 ANALYSES

11.3.1 Dissolution

Both fusion and acid digestion have been found suitable for the determination of iron and manganese. For basic rocks where concentrations are high, considerable dilution is necessary for iron, but for acid rocks, a dilution factor of 100 or 1000 usually suffices. For fusion of ultramafic rocks, F-3 is suggested and acid digestion A-2 for acid rocks.

11.3.2 Detection Limit

Both determination and detection limits are listed in Table 11.2. As both iron and manganese show high sensitivity either the burner must be turned side-on or less sensitive absorption lines used. These lines are also shown

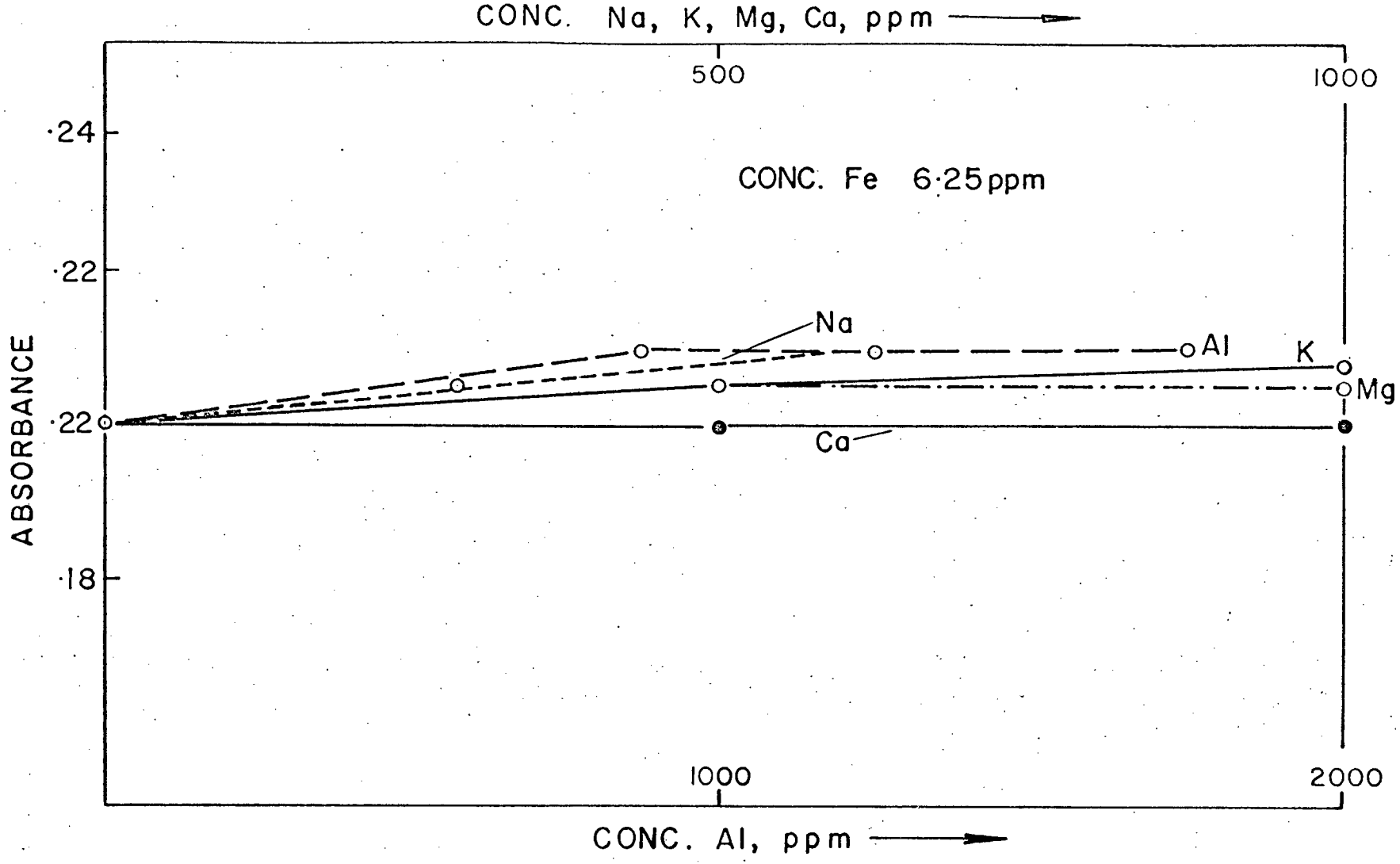

FIG. 11·1

Interference on Iron C_2H_2 / Air Flame

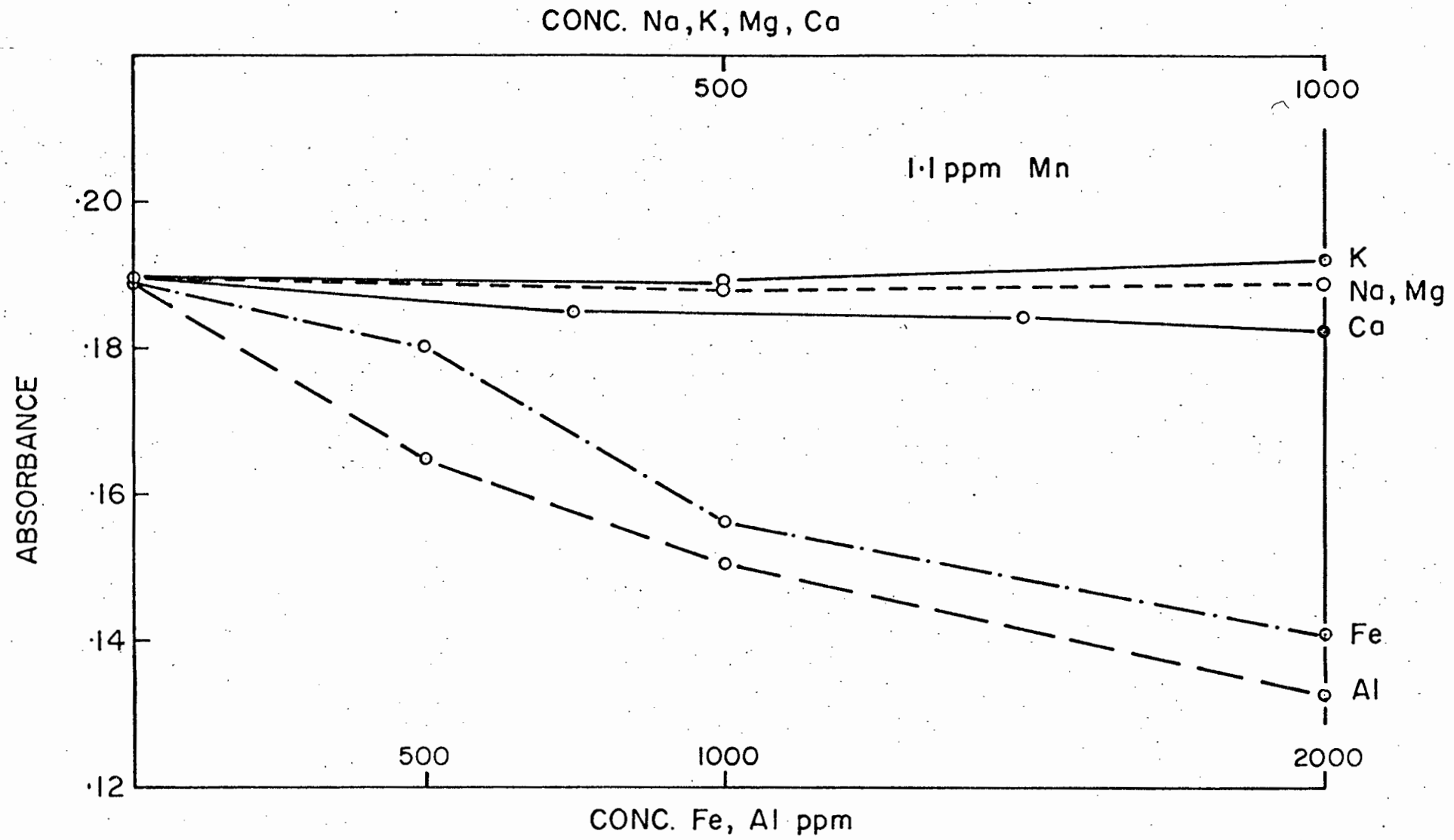

FIG. 11·2

Interference on Manganese Prop.–But. / Air Flame

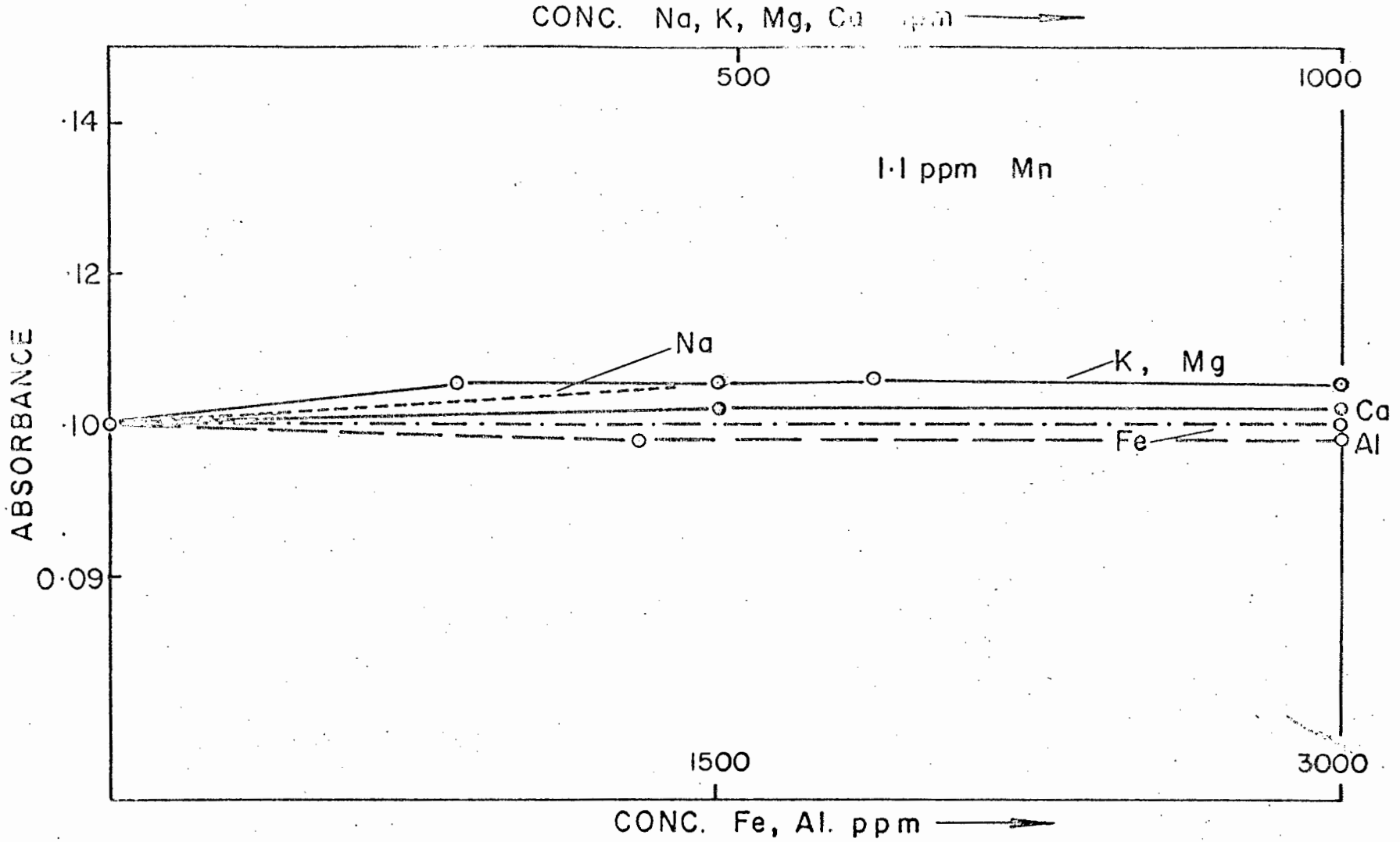

FIG. 11·3

Interference on Manganese C_2H_2/Air Flame

in Table 11.2. Because iron concentrations are normally higher than manganese, solutions are diluted to suit the manganese determinations.

11.3.3 Precision

Precision measurements on aqueous solutions and rock samples are shown in Table 11.3. The precision measurements for the burner turned side-on are seen to be better. This could account for the high precision for these elements.

11.3.4 Accuracy

International standards were analysed and the results are given in Table 11.4. These show the high accuracy of the atomic absorption method. Unfortunately, very low values of iron were not available and the method could thus not be tested at the lowest concentrations. Manganese results also compare well with accepted values.

TABLE 11.3

Precision measurements for iron and manganese

(a) Aqueous Solutions

Element	Wave-length	Flame	Concentration in Solution (ppm)	No. of determinations	Coeff. of Variation %
Iron	2483.3	C_2H_2/air	1.0	15	1.4
			5.0	15	0.9
	3719.9	C_2H_2/air	10.0	15	0.90
			50.0	15	0.93
Manganese	2795	C_2H_2/air	0.5	15	2.1
			2.5	15	1.4

(b) Rock Solutions

Granite G-H HF - $HClO_4$ dissolution (1% solutions)

Element	Wave-length	Flame	Mean concentration* (ppm)	No. of determinations	Coeff. of Variation %
Iron (total)**	2483.3	C_2H_2/air	9430	8	2.9
Manganese	2795	C_2H_2/air	402	8	2.6

*Mean concentration is the average concentration of the element, calculated to the solid.

**Iron was determined with the burner turned side on.

TABLE 11.4

Analysis of rock standards for iron and manganese

Sample	Iron (% Fe)				Manganese (ppm)			
	Accepted value	Ref.	Atomic absorption		Accepted value	Ref.	Atomic absorption	
			Value	No. of detns.			Value	No. of detns.
Granite G-1	1.22	1	1.30	5	230	1	241	5
	1.34	4						
Diabase W-1	7.69	1	7.80	8	1320	1	1347	8
	7.99	4						
Granite G-2	1.82	2	1.90	4	212±14	5	250	4
Granodiorite GSP-1	2.92	2	2.96	4	264±16	5	300	2
Andesite AGV-1	4.51	2	4.69	4	640±30	5	750	2
Basalt BCR-1	7.06	2	8.91	4	1300±70	5	1200	4
Dunite DTS-1	6.01	2	5.97	2	840-1100	2	800	4
Granite GA	1.92	3	2.01	2	698	3	720	4
Granite GH	0.90	3	0.94	3	388	3	408	4
Granite GR	2.83	3	2.81	2	300-430	3	441	2

1. Fleischer (1965) (Suhr and Ingamells preferred values)
2. Flanagan (1966) (Average of Conventional Chemical Values)
3. Raubault et al (1966) (preffered mean)
4. Huffman (1965) (atomic absorption values)
5. Gordon et al (1968) (neutron activation analysis)

11.3.5 Discussion

The lack of interference and the high accuracy obtained with the atomic absorption method show it is well suited for the determination of iron and manganese. The method is useful for any scheme where independent estimations are required or where other methods fail, either through a lack of reliable pre-analysed standards or because of low sensitivity.

CHAPTER 12

ALUMINIUM

12.1 INTRODUCTION

Aluminium is the third most abundant element in the crust of the earth, coming after oxygen and silicon. The common igneous rocks, basalt (plus related varieties) and granite (plus related varieties) contain high aluminium contents, whereas the ultramafic varieties have low concentrations (<~1.0 %). It may be noted also, that the Al contents of most meteorites, including the chondrites (the commonest type) is usually low (1% or less). Table 12.1 lists abundances of aluminium in various types of rocks.

TABLE 12.1

Abundance of Aluminium

(Values in ppm)

Ionic Radius Å	Crustal[1] Average	Granite[1] G-1	Diabase[1] W-1	Ultra[2] basic	Shales[1]	Sandstone[1]
Al^{3+} 0.51	8,300	78,300	78,600	20,000	80,000	25,000

(1) Mason (1966)

(2) Turekian and Wedepohl (1961)

Aluminium may be determined by several methods, including chemical (gravimetric, colorimetric, complexometric, etc.), x-ray fluorescence, and emission spectroscopy. These methods are not always accurate when the concentrations of aluminium are low, e.g. the wide spread of results for aluminium in meteorites has long been a source of concern to geochemists and a real need has existed for accurate methods for determining this element (Ahrens, 1968).

In view of the developments in atomic absorption high temperature flames, it was decided to study the application of atomic absorption

spectrometry for the determination of aluminium in silicate rocks.

Aluminium may be considered to be representative of other refractory elements, and Bowman and Willis (1967) have shown that the atomic absorption behaviour of titanium and vanadium is similar to that of aluminium. These elements form highly stable refractory oxides and it was not until the development of the acetylene/nitrous-oxide flame that they could be determined with reasonable ease and sensitivity.

Robinson (1962) showed that if a spark was used in a flame, aluminium oxide was dissociated and gave an atomic absorption signal. Shortly after this, several workers (Chakribarti et al, 1963; Slaving and Manning, 1963) obtained absorption signals for aluminium, using acetylene/oxygen total-consumption burners. It was found that if aluminium was dissolved in an organic solvent (4-methyl-2-pentanone), sensitivity was improved. Precision was poor, however.

The real break-through in the determination of refractory elements by atomic absorption spectrometry came when Amos and Thomas (1963) used a mixture of oxygen and nitrogen pre-mixed with acetylene in a fuel-rich flame to determine aluminium. A detection limit of 1.7 ppm was obtained. It was stressed that a pre-mixed flame and the right gas combination were essential to obtain the correct chemical environment. They suggested that AlO was reduced by the free carbon in the flame.

Later work by Amos and Willis with the acetylene/nitrous-oxide flame resulted in a flame with low burning velocity and thus a safe means for determining refractory elements such as aluminium, silicon, titanium, as well as most of the rare earths by atomic absorption.

Since then, several papers have been published on the determination of aluminium. Its determination in cement together with silicon and titanium (Capacho-Delgade and Manning, 1967) has been an important development. Aluminium has been determined in soils (Laflamme, 1967). A recent publication by Van Loon (1968) describes the determination of aluminium in high silica materials by atomic absorption. In all cases good agreement with accepted

chemical results is reported.

Mallett et al (1967) reported that other elements in silicate rocks interfered so severely with aluminium that an extraction with cupferron was necessary to reduce or eliminate interferences. These authors apparently did not fully explore the use of releasing agents.

12.2 EXPERIMENTAL

12.2.1 Optimizing of Conditions

As the conditions for aluminium determination are critical, the various factors pertaining to flame settings were investigated. It was found that absorbance was strongly dependent on the amount of acetylene in the flame. When a fuel-rich flame was adjusted to be strongly luminous, aluminium absorbance was at a maximum. The region of the flame through which the light from the hollow cathode passed was also critical. Because of this, the cathode image was reduced and the detection limit was reduced below that reported in the literature (1 ppm, Amos and Willis, 1966). Addition of a releasing agent reduces the detection limit even more.

Under the fuel-rich conditions necessary for maximum absorbance, a carbon lip rapidly forms at the burner jaws. The reason for this is probably that a certain degree of turbulence exists at this point and carbon is condensed from the flame on the comparatively cool metal. As this carbon builds up, a slightly higher absorbance signal is recorded. Thomas (1968) mentioned an improvement by undercutting the jaws to give a smoother flow to the entrained air. When this was done, it did not improve matters, but the carbon deposit was more easily removed while the flame was burning with this type of burner.

Before conducting analyses, it was found necessary to allow the burner to warm up for about 15 minutes. It should be noted that a slit of less than 100 micron is desirable to prevent over-saturation of the photomultiplier from the highly luminous flame. At this slit setting, the wavelength should be checked at regular intervals to prevent drift off the line. Another point to be stressed is that there are several less sensitive lines

of aluminium which may be used for higher concentrations of aluminium. The best conditions are shown in Table 12.2.

TABLE 12.2

Conditions for the determination of aluminium

	Wavelength Å	Sensitivity Factor
Analytical lines	3092.7	1.0
	3961.5	0.78
	3082.2	0.70
	3944.0	0.50
	2373.4	0.30
	2367.1	0.25
	2575.4	0.12
Lamp	Hollow cathode 10 mA (about 20 mA on Perkin Elmer 303	
Slit	50-100 micron (2-4 Å bandpass)	
Flame	C_2H_2/N_2O	
Burner	5 cm slot burner	
Flame setting	Luminous fuel-rich	
Burner height (below optical axes)	20-25 mm adjust for max. absorbance	
	Without La	With La (1000 ppm)
Analytical range ppm	3.05-500	1.0-200
Detection limit ppm (conc. for .004 A)	0.90	0.6

12.2.2 Interference Effects and Flame Studies

The effect of various elements on aluminium absorbance was tested. Aluminium solutions were prepared by dissolving pure aluminium metal in hydrochloric acid and making up a stock solution. The effect of hydrochloric acid was tested as conflicting reports appear in the literature about its effect. Van Loon (1968) reports significant depression while Mallett et al report no effect. Only concentrations below 2 N were tested and very little effect was noted. All other elements added gave an enhancement of aluminium absorbance. The results are shown in Fig. 12.1 .

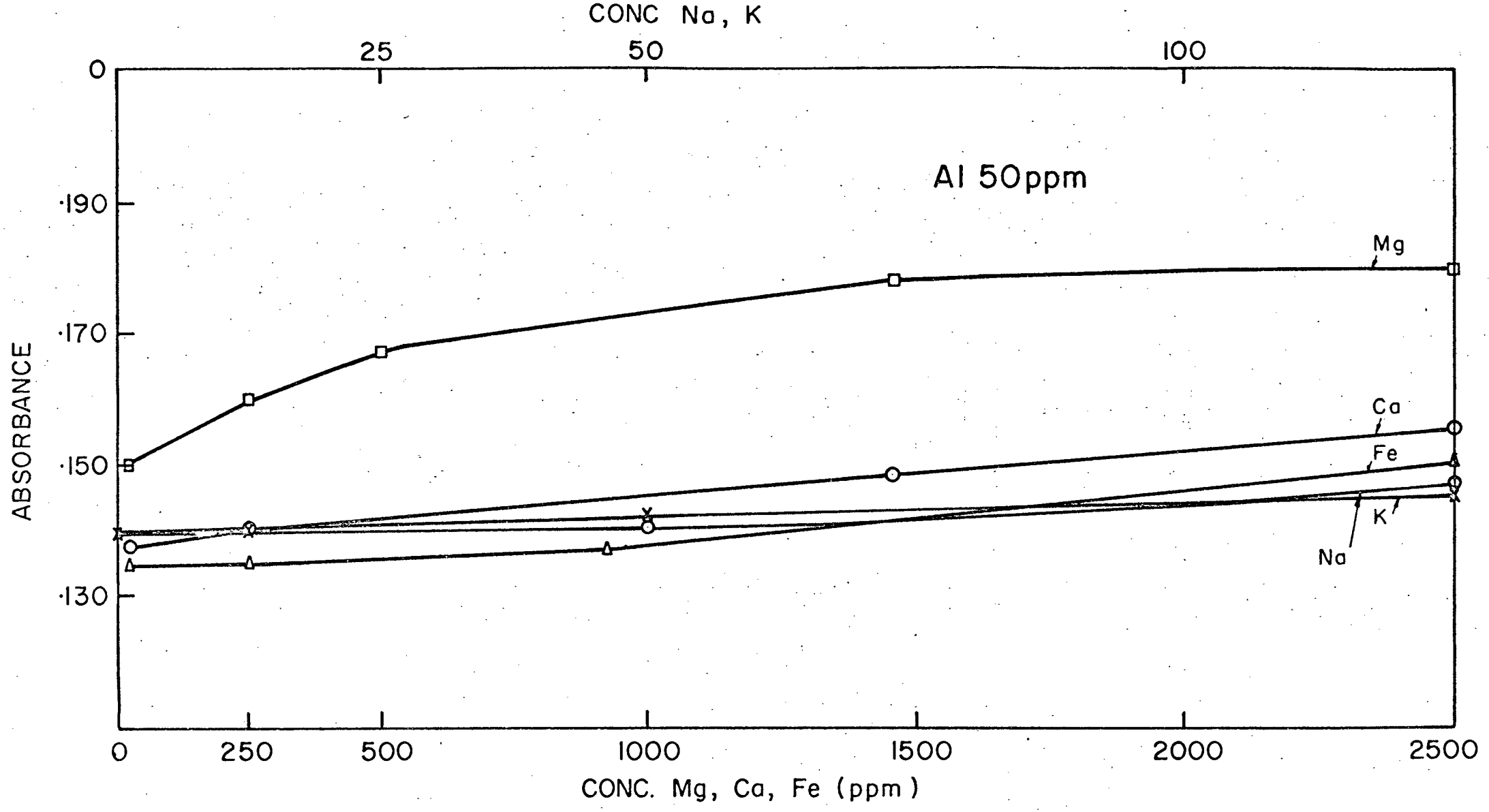

FIG. 12·1

Interference on Aluminium.

PG4-1523

It was found that the enhancement effect was not only dependent on flame type, but also position in the flame, e.g. if the flame was set to be stoichiometric, not only was absorbance less, but sodium and potassium gave a greater degree of enhancement.

Ionization of the aluminium in the relatively high temperature flame almost certainly occurs and the enhancing effect could be due to ionization suppression by the other elements. This was proved by using the mixed air + nitrous-oxide flame at various ratios, as described in Section 3.3.4. Potassium at two different concentrations, 250 and 500 ppm, was added to an aluminium solution and the absorbance measured at various ratios of the two gases. The acetylene was adjusted always to give the same type of flame, viz. slightly fuel-rich. Fig. 12.2 shows that as the nitrous-oxide content and thus the temperature increases, the enhancing effect of potassium also increases.

It is also seen that the sensitivity for aluminium increases with the nitrous-oxide content. Maximum sensitivity was obtained in the pure nitrous-oxide flame.

Experiments were conducted to determine a flame temperature where the ionization enhancement effect could be overcome, similar to the calcium-phosphorus experiment described in Section 3.3.4. Each of the enhancing elements was investigated individually and in most cases the enhancement could be overcome. Unfortunately, the gas ratios were different for each element and it was found that the gas ratio only held for one concentration of aluminium. When the aluminium concentration changed, enhancement once again appeared. The results of the test are summarized in Table 12.3. In view of this difficulty and the decrease in sensitivity with the mixed flame, the idea of using it for analytical purposes was abandoned.

The use of releasing agents was next investigated. Rubidium was used at first because of its low ionization potential (4.17 eV). It was found that rubidium enhanced aluminium absorption by approximately 20% (depending on the flame conditions). The other elements had no further effect on aluminium.

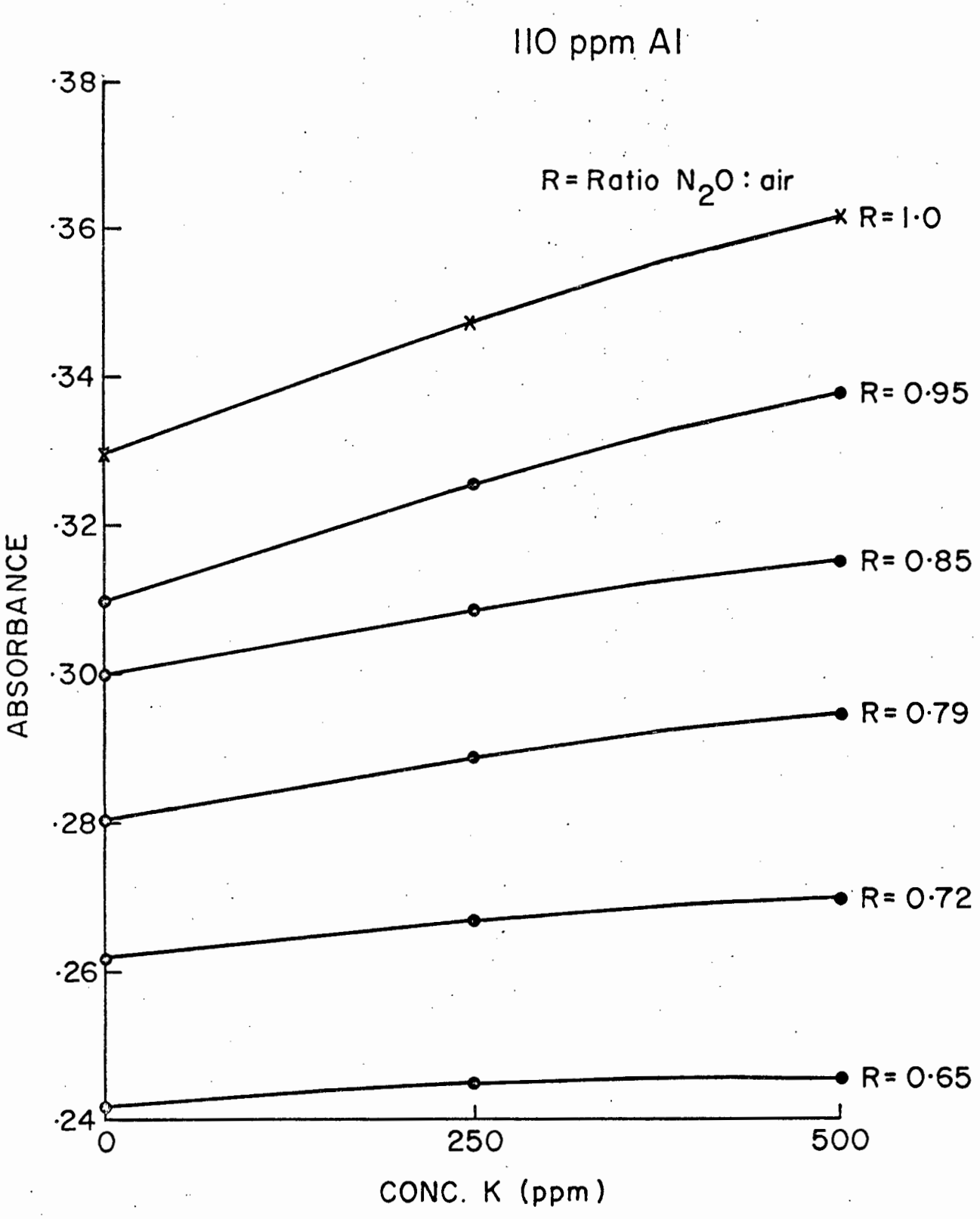

FIG. 12·2

Effect of Changing Nitrousoxide : Air Ratios on Absorbance of Aluminium and Enhance — ment by Potassium.

TABLE 12.3

Summary of tests with mixed nitrous oxide and air flame

Interfering Element	50 ppm Aluminium		Remarks
	Maximum Conc. Tested (ppm)*	N_2O: air ratio where int. eliminated	
Calcium	2500	0.73	Int. eliminated for one conc. of Al only
Magnesium	3000	0.73	Int. eliminated for one conc. of Al only
Sodium	2500	0.67	Int. plateau reached. Different for different Al concentrations
Potassium	500	0.71	Int. plateau reached. No further interference
Iron	2000	0.78	Int. eliminated for low concs. of Fe

*Lower concentrations were tested but the most pronounced effects were obtained for the maximum concentrations.

The same tests were conducted using lanthanum (ionization potential 5.6 eV) which proved useful for reducing depression and enhancement with the alkaline earths (Chapter 8). The same result as for rubidium was obtained, viz. no enhancement by foreign elements above the maximum absorbance caused by lanthanum. The results of this test are shown graphically in Fig. 12.3. Iron is seen to cause slight depression.

When the same tests were conducted with a lower temperature flame, it was found that the lanthanum did not fully suppress enhancement by the alkalis. At the lower temperature the alkali metals, potassium and sodium are more easily ionized than lanthanum, and still have an effect on aluminium.

When the acetylene/nitrous-oxide flame is used, the temperature is

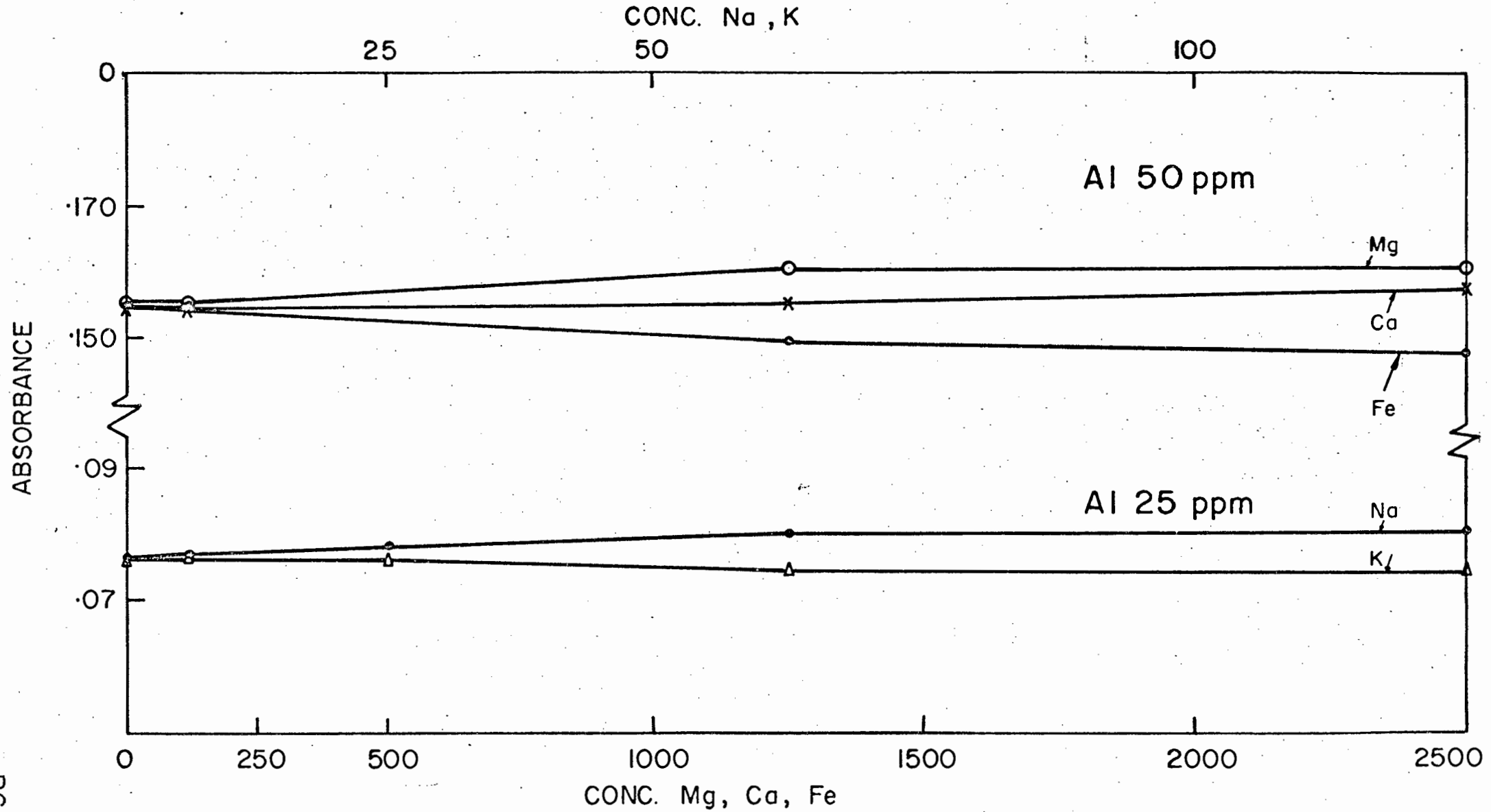

FIG. 12·3

Interference on Aluminium with 1000 ppm Lanthanum added.

PG4-1522

sufficiently high to ionize both lanthanum and the alkalis. The acetylene/nitrous-oxide flame was accordingly used and 1000 or more ppm lanthanum added to solutions. Under these conditions the detection limit was better and interference effects virtually eliminated.

12.3 ANALYSES

12.3.1 Dissolution

Because it was felt that fusion dissolution techniques would be more useful for rapid analyses, tests were made on the effect of silicon on aluminium absorbance. A melt was made of silicon dioxide in lithium metaborate. The lithium metaborate content was kept constant and various amounts added to an aluminium solution.

When these solutions were nebulized the reading did not remain constant, but decreased continuously with time. When the carbon deposit was removed, the absorption was re-established but rapidly decreased again. It appeared as if the lithium inter-acted with the carbon lip at the burner mouth, but no definite explanation is offered for this effect. When the lithium concentration was decreased, the effect was considerably reduced.

This result indicates that for very low concentrations of aluminium, the fusion technique is not recommended. For high aluminium concentrations, however, the fusion method is satisfactory. If the lithium metaborate content in the solution is below 0.1%, the effect is almost eliminated. Aluminium concentrations above about 5% can thus be determined with the fusion method.

When the interference tests for silicon were repeated with other silicon compounds, it was found that silicon had very little effect on aluminium in the presence of a releasing agent.

Dissolution methods (Table 5.2) recommended are:

For aluminium (Al) 0 - 6% : A-1, or A-2;

6% or more: F-2, or A-2 diluted.

12.3.2 Detection Limit

The limits of detection with and without a releasing agent are listed in Table 12.2. The analytical range may be extended by using less sensitive lines or using a less fuel-rich flame, but this latter course is not recommended.

12.3.3 Precision

The normal precision measurements were made and are shown in Table 12.4.

TABLE 12.4

Precision measurements for aluminium

(a) Aqueous solutions (1000 ppm La added)

Concentration (ppm)	No. of determinations	Coeff. of Variation %
12.5	15	3.8
50	15	1.6
125	15	2.16

(b) Rock solutions Granite G-H
$HF:HClO_4$ dissolution

Flame	Mean Conc. (ppm) in solution*	No. of determinations	Coeff. of Variation %
C_2H_2/N_2O (luminous)	170.5	8	3.6

*Mean concentration is the average of the values read off the absorbance: concentration graph.

Best precision was obtained when a fuel-rich flame was used. It was difficult to stabilize the reading when a slightly fuel-rich flame was used. The reason could be that the flow meter ball was off scale and that it caused a degree of turbulence to the acetylene flow. All precision measurements were accordingly made with a luminous fuel-rich flame.

12.3.4 Accuracy

Difficulty was initially experienced in obtaining accurate results. This was traced to the standards. As a test, granite G-1 was used as the standard and diluted to give various concentrations of aluminium. When the other rock solutions were read off the analytical curve obtained in this way, good agreement with the accepted values was obtained, especially for the high values. When the aqueous standards were standardized, results were far more acceptable.

Although particular attention was paid to the determination of low concentrations of aluminium, a useful method has been used for high concentrations. This method is in effect an extention of the absorbance scale at the absorbance value of the sample and was recently described in a personal communication by Thomas (1968). The procedure is as follows:

> Standards are prepared which straddle the concentrations of aluminium in the sample. The lowest of these is sprayed. It will give a high absorbance but this is backed off by adjusting the gain of the amplifier to give a reading of nearly zero on the absorbance scale. The other standards are now measured and they will cover nearly the full absorbance scale. When the sample is sprayed, it will fall within the range. It is important to have several standards as the analytical curve is usually curved.

This method was used for the higher concentrations of aluminium shown. By selecting the best conditions, the precision obtained was very much higher than with the normal method.

The results of rock analyses are given in Table 12.5.

12.3.5 Discussion

The results of this investigation suggest that atomic absorption is a suitable method for aluminium determination. The sensitivity obtained indicates that the lowest concentrations found in rocks may be determined. The high concentrations found in acid rocks may also be estimated. The precision appears to be of the same order as other methods and is probably better for low concentrations than for chemical methods.

TABLE 12.5

Analysis of international rock standards for aluminium

(Values given in Al_2O_3)

Sample	Accepted value	Ref.	Atomic absorption	
			Value	No. of determinations
Granite G-1	14.08	1	14.15	4
Diabase W-1	14.94	1	15.01	4
Granodiorite GSP-1	15.35	2	15.27	4
Peridotite PCC-1	0.77	2	0.533	4
Dunite DTS-1	0.31	2	0.133	2
Basalt BCR-1	13.7	2	14.45	4
Granite GH	12.63	3	12.88	4
Granite G-1	15.42	2	15.33	4
Granite GA	14.61	3	14.06	4

1. Fleischer (1965)
2. Flanagan (1966)
3. Roubault et al (1966)

Other instrumental methods such as X-ray fluorescence probably give better precision however.

The atomic absorption results for higher aluminium concentrations are generally satisfactory but considerable differences are evident for the lower concentrations of the peridotite PCC-1 and the dunite DTS-1. No explanation can be offered for this difference. The scatter of atomic absorption results at this low level was approximately 15%.

The ability to determine aluminium at the 1% level, is of particular interest to geochemists. There is considerable current interest in the upper mantle and its composition (White, 1968). Low concentrations of aluminium in ultramafic rocks and xenoliths, thought to originate in the upper mantle, underline the need for accurate methods. Atomic absorption spectrometry may well fulfil this need.

CHAPTER 13

CONCLUSION

13.1 GENERAL

In reviewing the results obtained for the elements discussed in this thesis, as well as for other elements which have been determined, but not mentioned here, the general conclusion reached is that atomic absorption spectrometry is an extremely useful tool for the analysis of rocks and minerals. The particular fields in the earth sciences to which it is applicable are:

(a) Whole rock analyses. The main elements in rocks which are determined in whole rock analyses are silicon, aluminium, iron, calcium, magnesium, sodium, potassium, manganese, titanium and phosphorus. With the exception of silicon, titanium and phosphorus, these elements have been discussed and it has been found that their determination presents no difficulties providing the necessary precautions are taken. Silicon has been determined, but has not been included in this dissertation because precision and accuracy are not yet acceptable. Titanium can be determined under conditions similar to aluminium. Phosphorus cannot be determined directly.

The atomic absorption method has thus provided the geochemist with a simple means for analysing rocks at low cost. The fact that pre-analysed standards of material similar in matrix to the samples are generally not required is a particularly attractive feature. It puts the method in the same category as wet chemical analysis, viz. a primary method.

(b) Trace element analysis. The very high sensitivity of the method makes it ideally suited for the determination of trace and minor elements such as copper, zinc, etc. in rocks and minerals. This fact has already been realized by many geochemists and the method is finding widespread application for geochemical prospecting. However, the academic

geochemist will find the method useful for the determination of elements, not necessarily of economic interest, e.g. lithium and lithium isotope determinations.

(c) Micro-trace element determination. The high specificity of the method enables chemical concentration techniques such as liquid-liquid extraction and ion exchange methods to be applied to the accurate estimation of elements present in low concentrations, e.g. molybdenum.

However, it is in the field of trace and minor element determinations that atomic absorption is of the greatest use to the geochemist at present. As has been shown, atomic absorption results are not always as accurate or precise as other methods for some elements, e.g. rubidium, is determined down to 1 ppm by X-ray fluorescence. In some instances, e.g. iron and manganese, many other methods exist which may equal the precision and accuracy of atomic absorption. When the various factors whereby a method of analysis is weighed, are considered, such as initial cost, analysis cost (running), convenience, precision, accuracy, sensitivity and versatility, it is concluded that atomic absorption spectrometry is indeed a technique which can be of invaluable assistance to the geochemist. It should be looked upon as complementary to other techniques and efficiently fills a gap which has long existed in analytical laboratories.

13.2 FUTURE DEVELOPMENTS

Methods for the determination of silicon should be finalized to provide the precision and accuracy required by geochemists. There is little doubt that this will be done.

The determination of the non-metals in rocks and minerals and other materials by atomic absorption remains a problem. However, the development of non-flame atomizing techniques would enable phosphorus, chlorides, fluorides, oxygen, carbon, sulphur, etc. to be determined. It is postulated that this development will take place.

Multiple element methods and instruments have already been

developed, but it is suggested that these will also be developed for whole rocks analyses by atomic absorption spectrometry.

Atomic fluorescence may well find application for rock analysis. This method has high sensitivity for many elements and has the advantage of having a wider analytical range.

Selective modulation and very simple instruments based on this technique should also appear within the next few years.

BIBLIOGRAPHY

1. Abromovich, L.Yu., Klyarfel, D.B.M. and Mastich, Yu.N. (1966) Soviet Physics - Technical Physics, 11, No. 4, p. 528.
2. Adams, P.B. (1961) Anal. Chem., 33, p. 1602.
3. Adams, P.B. (1961) Anal. Chem., 33, p. 160.
4. Adams, P.B. (1965) Scott's Standard Method of Analysis, 3.
5. Adams, P.B. and Passmore, W.O. (1966) Anal. Chem., 38, p.630.
6. Ahrens, L.H. and Taylor, S.R. (1961) "Spectrochemical Analysis". (Addison-Wesley Publ. Co. London, 2nd Ed.)
7. Ahrens, L.H. (1964) Advancement of Science, May.
8. Ahrens, L.H. (1968) Personal communication.
9. Alekseeva, U.G. and Mandelstam, S.L. (1947) Zh. Eksp. Teor. Fiz. U.S.S.R., 17, p. 759.
10. Alkemade, C.T.J. (1954) Ph.D. Thesis, Utrecht, 1954.
11. Alkemade, C.T.J. and Milatz, J.M.W. (1955) Appl. Sci. Res. B4, p. 289.
12. Alkemade, C.T.J. and Milatz, J.M.W. (1958) J. Opt. Soc. Am., 45, p. 583.
13. Alkemade, C.T.J. and Jeunken, M.E.J. (1957) Z. Anal. Chem., 158, p. 401.
14. Alkemade, C.T.J. and Voorhuis, M.H. (1958) Spectrochim. Acta, 12, p. 394.
15. Allan, J.E. (1959) Spectrochim. Acta, 10, p. 800.
16. Allan, J.E. (1961a) Analyst, 86, p. 530.
17. Allan, J.E. (1961b) Spectrochim. Acta, 17, p. 459.
18. Allan, J.E. (1962a) Spectrochim. Acta, 18, p. 259.
19. Allan, J.E. (1962b) Spectrochim. Acta, 18, p. 605.
20. Amiel, S. and Welwort, Y. (1962) Israel At. Energy Comm. Report, IA, p. 690.
21. Amos, M.D. and Thomas, P.F. (1965) Anal. Chem. Acta, 32, p. 139.
22. Andrew, T.R. and Nichols, P.N.R. (1965) Analyst, 90, p. 161.
23. Amos, M.D. and Willis, J.B. (1966) Spectrochim. Acta, 22, p. 1325.
24. Angino, E.E. and Billings, G.K. (1966) Geochim et Cosmochim. Acta, 30, p. 153.
25. Angino, E.E. (1967) Kans. Geol. Survey Bull., 187, I.
26. Angino, E.E. and Billings, G.K. (1967) Atomic Absorption Spectrometry in Geology (Elsevier Publ. Co., N.Y.)
27. Angot, J. (1959) Mikrochim. Acta, p. 346.

28. Ball, T.K. and Filby, R.H. (1965) Geochim. et Cosmochim. Acta, 29, p. 737.

29. Belcher, C.B. and Brooks, K.A. (1963) Anal. Chim. Acta, 29, p. 202.

30. Belt, C.B. (1964) Econ. Geol., 59, p. 240.

31. Belt, C.B. (1967) Anal. Chemistry, 39, p. 676.

32. Billings, G.K. and Adams, J.A.S. (1964) P. Elmer A.A. Newsletter, No. 23.

33. Billings, G.K. (1965a) P. Elmer A.A. Newsletter, 4, p. 312.

34. Billings, G.K. (1965b) Bull. of Can. Petroleum Geology, 13, p. 529.

35. Billings, G.K. (1965c) Atomic Absorption Newsletters, 4, p. 357.

36. Billings, G.K. (1965d) Bull. Can. Petrol Geologists, 13, p. 532.

37. Billings, G.K., Ragland, P.C. and Adams, J.A.S. (1966) Nature, 40, p. 289.

38. Biskupsky, V.S. (1965) Anal. Chim. Acta, 33, p. 333.

39. Bleekrode, R. (1967) XIII Coll. Spect. Internationale, Ottowa, Paper 138.

40. Boar, P.L. and Sullivan, J.V. (1967) Fuel, 46, p. 47.

41. Boling, E. (1965) Anal. Chem., 37, p. 482.

42. Borovik-Romanova, T.C. and Belyaev, Y.V. (1963) U.S. Dept. of Commerce, Office of Techn. Services, 63-11661.

43. Bowditch, D.C., Chalmers, A.H. and Powell, J.A. (1966) Paper presented at Geol. Soc. Australia. Tech. Memo 5/33, AMDEL, Adelaide.

44. Bowman, J.A., Sullivan, J.V. and Walsh, A. (1966) Spectrochim. Acta, 22, p. 205.

45. Bowman, J.A. (1967) Anal. Chim. Acta, 37, p. 465.

46. Bowman, J.A. (1968) Anal. Chim. Acta, 42, p. 285.

47. Bowman, J.A. (1968) Anal. Chim. Acta, 42, p. 285.

48. Bowman, J.A. and Willis, J.B. (1967) Anal. Chem., 39, p. 1210.

49. Boswell, C.R. and Brooks, R.R. (1965) Analytica Chim. Acta, 33, p. 117.

50. Brody, J;K; and Tomkins, F.S. (1958) Basic Chemistry in Nuclear Energy, 28, p. 639.

51. Brunfelt, A.O., Johansen, O. and Steinnes, E. (1967) Anal. Chim. Acta, 37, p. 172.

52. Burrell, D.C. (1965) Norsh. Geol. Tidsskrif, 45, p. 21.

53. Burrell, D.C. (1965a) P. Elmer A.A. Newsletter, 4, p. 309.

54. Burrell, D.C. (1965b) P. Elmer A.A. Newsletter, 4, p. 328.

55. Butler, L.R.P. (1962) J. S.A. Inst. Min. and Metall., 62, p. 786.

56. Butler, L.R.P. (1963) M.Sc. Thesis, University of Stellenbosch.

57. Butler, L.R.P. and Brink, D. (1963) The S.A. Industrial Chemist, July.

58. Butler, L.R.P. and Strasheim, A. (1965) Spectrochim. Acta, 21, p. 1207.

59. Butler, L.R.P. (1966) Atomic Absorption Newsletter, 5, p. 99.

60. Butler, L.R.P. and Mathews Phyllis (1966) Anal. Chim. Acta, 36, p. 319.

61. Butler, L.R.P. and Fulton, Ann (1968) J. Appl. Optics.

62. Butler, J.R. (1953) Geochim. et Cosmochim. Acta, 4, p. 157.

63. Butler, J.R. (1954) Geochim. et Cosmochim. Acta, 6, p. 268.

64. Carte, A.E. (1954) S.A. J. Sci., 51, p. 136.

65. Capacho-Delgade, L. and Manning, D.C. (1967) Analyst, 92, p. 553.

66. Chakrabarti, C.L., Lyles, G.R. and Dowling, F.B. (1963) Anal. Chim. Acta, 29, p. 489.

67. Chan, K.M. and Riley, J.P. (1966) Anal. Chim. Acta, 34, p. 337.

68. Danielsson, R., Lundgren, F. and Sunokuisk, G. (1959) Spectrochim. Acta, 126, p. 122.

69. David, D.J. (1958) Analyst, 83, p. 655.

70. David, D.J. (1959) Analyst, 84, p. 536.

71. David, D.J. (1960) Analyst, 85, p. 1012.

72. David, D.J. (1961) Analyst, 86, p. 730.

73. David, D.J. (1962) P.Elmer A.A. Newsletter, No. 9.

74. Davies, D.A., Venn, R. and Willis, J.B. (1965), Journal of Scientific Instruments, 42, p. 816.

75. Dawson, J.B. and Ellis, D.J. (1967) Spectrochim. Acta, 23A, p. 565.

76. Dawson, J.B. and Heaton, F.W. (1967) "Spectrochemical Analysis of Clinical Material" (Charles C. Thomas, Springfield, Ill. U.S.A.)

77. Day, F.H. (1963) "The Chemical Elements in Nature", Harry and Co., London.

78. Dinnin, J.I. (1960) Anal. Chem., 32, p. 1475.

79. Doe, B.R., Mitsumobu Tatsumoto, Delevaux, M.H. and Peterman, Z.E. U.S. Geol. Survey Professional Paper, 575B, p. B.170.

80. Eardley, R.P. and Clarke, H.S. (1965) Applied Spectros., 19, p. 186.

81. Easton, A.J. and Lowering, J.F. (1964) Anal. Chim. Acta, 30, p. 543.

82. Edge, R.A. (1960) Ph.D. Thesis, University of Cape Town.

83. Ellestad, R.B. and Horstman, E.L. (1955) Anal. Chem., 27, p. 1229.

84. Elwell, W.T. and Gidley, J.A.F. (1962) "Atomic Absorption Spectrophotometry", (Macmillan, New York, N.Y.)

85. Erlank, A.J. (1967). Personal communication of results for samples.

86. Erlank, A.J. (1968). Personal commentation on values for sodium.

87. Erlank, A.J., Danchin, R.U. and Fullard, C.C. (1968) Earch and Planetary Science Letters, 4, p. 22.

88. Fabricand, B.P., Sawyer, R.R., Ungar, S.G. and Adler, S. (1962) Geochim. et Cosmochim. Acta, 26, p. 1023.

89. Fabricand, B.P., Imbimbo, E.S., Brey, M.E. and Weston, J.A. (1966) J. of Geophysical Research, 71, No. 16.

90. Farrar, B. (1965) Atomic Absorption Newsletter, 4, p. 325.

91. Farrar, B. (1966) P. Elmer A.A. Newsletter, 5, p. 62.

92. Firman, R.J. (1965), Spectrochim. Acta, 21, p. 341.

93. Fixman, M. and Boughton, L. (1966) P. Elmer A.A. Newsletter, 5, p. 33.

94. Fishman, M.J. and Downs, S.C. (1966) U.S. Geol. Survey Water Supply Paper, 1540 C, p. 45.

95. Flanagan, F.J. (1966) Geochim. et Cosmochim. Acta, 31, p. 289.

96. Fleischer, M. (1965) Geochim. et Cosmochim. Acta, 29, p. 1263.

97. Fleming, H. (1967) Spectrochim. Acta, 23B, p. 207.

98. Foster, W.H. and Hume, D.H. (1959) Anal. Chem., 31, p. 2033.

99. Fuwa, K. and Vallee, B.L. (1963) Anal. Chem., 35, p. 942.

100. Fuwa, K., Thiers, R.E. and Vallee, B.L. (1959) Anal. Chem., 31, p. 1419.

101. Galle, O.K. and Angino, E.E. (1967) Bull. Kans. Geol. Surv., 185(1), p. 9.

102. Gatehouse, B.M. and Willis, J.B. (1961) Spectrochim. Acta, 17, p. 710.

103. Gaydon, A.G. and Wolfhard, H.G. (1948) Proc. Roy. Soc. London, A.194, p. 169.

104. Gaydon, A.G. and Wolfhard, H.G. (1953) "Flames - Their Structure, Radiation and Temperature". (Chapman and Hall, London).

105. Gaydon, A.G. (1957) "The Spectroscopy of Flames" (Chapman and Hall, London).

106. Gidley, J.A.F. (1961) IX Colloquium Spectroscopicum Internationale, Lyons.

107. Gidley, J.A.F. and Jones, J.T. (1961) Analyst, 86, p. 271.

108. Gilbert, P.T. Jr. (1960) Symposium on Spectroscopy, Am. Soc. Testing Materials, Spec. Tech. Publ., No. 269, p. 73.

109. Gillieson, A.H. and Thorne, R.P. (1955) Nature, 176, p. 1228.

110. Goldberg, E.D. (1961) Am. Rev. Phip. Chem., 12, p. 29.

111. Goldich, S.S. (1938) J. Geol., 46, p. 17.

112. Goldschmidt, V.M., Berman, H., Hauptmann, H. and Peters, U. (1933) Nach. Ges. Wis., Göttingen, Math-physik klasse IV, NF1.

113. Goldschmidt, V.M. (1938) Skr. Norske victahad Oslo, 1. Math-nat., p. 1937.

114. Goldschmidt, V.M. (1954) "Geochemistry" (Oxford-Clarendon Press).

115. Goleb, J.A. and Yokoyama, Y. (1964) Anal. Chim. Acta, 30, p. 213.

116. Gordon, G.E., Randle, K., Goles, G.G. Corliss, J.B., Beeson, M.H. and Oxley, S.S. (1968), Geochim. et Cosmochim. Acta, 32, p. 369.

117. Govindaraju, K. (1963) Publication GAMS, 3, p. 217.

118. Govindaraju, K. (1966) Appl. Spectr., 20, p. 302.

119. Greig, J.R. (1965) Brit. J. of Appl. Phys., 16, p. 957.

120. Griffin, W.L. and Murthy, V.R. Earth and Planetary Science Letters, 4, p. 497.

121. Groves, A.W. (1937) "Silicate Analysis" (Thomas Murly and Co., London).

122. Gurney, J. (1968) Personal communication on Zn and K values for his samples.

123. Heier, K.S. and Adams, J.A.S. (1964) Physics and Chemistry of the Earth Series, 5, p. 253.

124. Hillebrand, W.F. (1919) U.S. Geol. Surv. Bull. No. 700, p. 89.

125. Hillebrand, W.F. and Lundell, G.E.F. (1953) "Applied Inorganic Analysis" (2nd Ed., John Wiley and Sons)

126. Hollander, T. (1964) Ph.D. Thesis, University of Utrecht.

127. Holzer, W.R. and Kennedy, G.C. (1958) Amer. J. Sci., 256, p. 744.

128. Hoop, G.K. (1964) Geochim. et Cosmochim.Acta, 28, p. 405.

129. Horstman, E.L. (1956) Anal. Chem., 28, p. 1417.

130. Huffman, C. (1965) Private communication to M. Fleisher (Ref. Fleischer 1965)).

131. Huffman, C. and Meurich, J.D. (1967) Appl. Spectr., 21, p. 125.

132. Ingamells, C.O. (1962) Talanta, 9, p. 781.

133. Ingamells, C.O. and Suhr, N.H. (1963) Geochim. et Cosmochim. Acta, 27, p. 908.

134. Intonti, R. and Staichini, A. (1966) Met. Ital. 58, p. 335.

135. Ito, J. (1962) Chem. Soc. Jap. Bul. 35, p. 225.

136. Jones, A.H. (1965) Analyt. Chem., 37, p. 1761.

137. Joyner, T. and Finley, J.S. (1966) P. Elmer A.A. Newsletter, 5, p. 4.

138. Kahn, H.L. (1966) J. Chem. Ed., 43, p. A7.

139. Keats, G.H. (1965) P. Elmer A.A. Newsletter, 4, p. 319.

140. Kirchoff, G. (1861) "Researches on the solar spectrum and the spectra of the chemical elements" (Translated from Transact. of the Berlin Acad.) (Macmillan and Co., London).

141. Kellerman, S (1966) Confidential report on the analysis for the Upper Mantle Project, File S/66/1.

142. Kirkbright, G.F., Semb, A. and West, T.S. (1968) Spectroscopy Letters, 1, p. 7.

143. Kvalheim, A. (1947) J.O.S.A., 37, p. 585.

144. La Flamme, Y. (1967) P. Elmer A.A. Newsletter, 6, p. 70.

145. Lakanen, E. (1962) Ann. Agr. Fenniae, 1, p. 109.

146. Lang, W. (1964) Microchim. Acta, 5, p. 717.

147. Langmyhr and Graaff (1965) Norges Geol. Undersökeles, 230.

148. Langmyhr, F.J. and Sveen, S. (1965) Anal. Chim. Acta, 32, p. 1.

149. Langmyhr, F.J. and Kringstad, K. (1966) Anal. Chim. Acta, 35, p. 131.

150. Langmyhr, F.J. and Kringstad, K. (1966) Anal. Chim. Acta, 35, p. 127.

151. Lapp, M. and Gallagher, C.J. (1967) Paper No. 139, XIII Colloquium Spectroscopicum Internationale, Ottawa.

152. Laubscher, N. (1968) CSIR (NRIMS) Research Report.

153. Lewis, B. and Von Elbe, G. (1951) "Combustion, Flames and Explosions of Gases" (Academic Press Inc., N.Y.)

154. Lundegardh, H. (1934) "The quantitative spectral analysis of the elements" (G. Fischer (Jena)).

155. L'Vov, B.V. (1961) Spectrochim. Acta, 17, p. 761.

156. Magee, R.J. and Rahman, A.K.M. (1965) Talanta, 12, p. 409.

157. Malissa, H. and Schaffmann (1955) Mikrochim. Acta, 1. 187.

158. Mallett, R.C., Taylor, J.D., Faure, P.K., Steel, T.W. (1967) National Institute for Metallurgy Report No. 137.

159. Manning, D.C. and Slavin, W. (1962) Atomic Absorption Newsletter, No. 8.

160. Manning, D.C., Capacho-Delgado, L. (1963) Conf. on Anal. Chem and Appl. Spectr., Pittsburgh.

161. Manning, D.C. (1965) P. Elmer A.A. Newsletter, 4, p. 267.

162. Manning, D.C. and Vollmer, J. (1967) A.A. Newsletter, 6, p. 38.

163. Mansell, R.E. and Emmel, H.W. (1965) P. Elmer A.A. Newsletter, 4, p. 365.

164. Mason, B. (1966) "Principles of Geochemistry". Third Edition. (John Wiley and Sons, Inc., New York).

165. Mavrodineanu, R. and Boiteux, H. (1965) "Flame Spectroscopy" (John Wiley and Sons, Inc., New York).

166. Mavrodineanu, R. (1967) U.S. Dept. of Comm. N.B.S. Publ. 281.

167. May, I. and Rowe, J.J. (1965) Anal. Chim. Acta, 33, p. 648.

168. May, I., Rowe, J.J. and Letner, R. (1965) U.S. Geol. Survey Res. Rep. B.166.

169. Means, E.A. and Ratcliff, D. (1965) P. Elmer A.A. Newsletter, 4, p. 174.

170. Meddings, B. and Kaiser, H. (1967) P. Elmer A.A. Newsletter, 6, p. 28.

171. Menzies, A.C. (1960) Anal. Chem., 32, p. 898.

172. Mitchell, R.L. and Scott, R.O. (1947) J. Soc. Chem. Ind., 66, p. 330.

173. Mitchell, A.G. and Zemansky, M.W. (1961) "Resonance Radiation and Excited Atoms" (Cambridge Univ. Press, 1934. New Edition, London, 1961).

174. Morey, G.W. and Hesselgesser, J.M. (1952) Am. J. Sci., Bowen Vol. II, p. 343.

175. Morgan, J.W. and Heier, K.S. (1966) Earth and Planetary Sci. Letter, 1, p. 158.

176. Moroney, M.J. (1951) "Facts from Figures" (Penguin).

177. Mossotti, V.G. and Laqua, K. (1967) Spectrochimica Acta, 23B, p. 197.

178. Mulford, C.E. (1966) P. Elmer A.A. Newsletter, 5, p. 88.

179. McBride, C.H. (1965) P. Elmer A.A. Newsletter, 3, No. 11.

180. McBride, C.H. (1967) J. Ass. Off. Anal. Chemists, 50, p. 401.

181. Nesbitt, R.W. (1966) Analytical Chim. Acta, 35, p. 413.

182. Orren, M. (1967) Talk given to S.A.C.I Summer School on Atomic Absorption, Stellenbosch, October.

183. Parker, W.G. and Wolfhard, H.G.(1952) Proc. of the 4th Int. Supp. Comb., 420.

184. Parker, W.G. and Wolfhand, H.G. (1954)Proc. of the 5th Int. Supp. Comb., 420.

185. Passmore, W. and Adams, P.B. (1965) Atomic Absorption Newsletter, 4, p. 237.

186. Passmore, W. and Adams, P.B. (1966) P.Elmer Newsletter, 5, p. 77.

187. Pawluk, S. (1967) P. Elmer A.A. Newsletter, 6, No. 3.

188. Peterson, G. (1966) P. Elmer A.A. Newsletter, 5, No. 5.

189. Platte, J.A. and Marcy, P.M. (1965) P. Elmer A.A. Newsletter, 4, p. 289.

190. Price, V. and Ragland, P.C. (1966) Southeastern Geol. 7, p. 93.

191. Ramirez-Munoz (1968) "Atomic Absorption Spectroscopy (and Analysis by Atomic Absorption Flame Photometry)" (Elsevier).

192. Rankama, K. (1939) Bull. Comm. Geol. Finlande, 12, p. 6.

193. Rankama, K. and Sahama, Th. G. (1950) "Geochemistry" (Univ. of Chicago Press, London).

194. Rann, C.S. (1967) Ph.D. Thesis, Australian National University, Canberra.

195. Rann, C.S. (1968) Spectrochim. Acta, 32B, p. 245.

196. Raubault, M., de la Roche, H. and Govindaraju, K. (1966) Sciences de la Terre, 11, p. 105.

197. Rawling, B.S., Greaves, M.C. and Amos, M.D. (1960) Nature, 188, p. 137.

198. Reck, J., Sumi, K. and Weinberg, F.J. (1956) Fuel, 35, p. 364.

199. Rigg, T. and Wagenbauer, H.A. (1964) Res. Council of Can. Prelim. Report 64-1.

200. Robinson, J.W. (1960) Anal. Chim. Acta, 23, p. 479.

201. Robinson, J.W. (1962) Anal. Chim. Acta, 27, p. 465.

202. Robinson, J.W. (1966) "Atomic Absorption Spectroscopy" (Marcel Dekker, New York).

203. Rony, P.R. (1966) Rev. Sci. Instruments, 37, p. 532.

204. Roy, N. (1956) Anal. Chem., 28, p. 34.

205. Rubeska, I., Moldam, B. and Valmy, Z. (1963) Anal. Chim. Acta, 29, p. 206.

205. Rubeska, I., Moldam, B., and Valmy, Z. (1963) Anal. Chim. Acta, 29, p. 206

206. Rubeska, I. (1968) Anal. Chim. Acta, 40, p. 187.

207. Russel, B.G. (1966), The Analyse, 91, p. 511.

208. Russel, B.J., Shelton, J.P. and Walsh, A. (1957) Spectrochim. Acta, 8, p. 317.

209. Sampey, D. (1967) Personal communication (Sampey Exploration Co. Ltd., Perth, Australia).

210. Sampey, D. (1968) Personal communication (Sampey Exploration Co. Ltd., Perth, Australia).

211. Selch, E. (1915) Z. Anal. Chem., 54, p. 395.

212. Schuler, K.E. (1950) J. Chem. Phys., 18, p. 1221.

213. Shepherd, G.A. and Johnson, A.J. (1966) P. Elmer A.A. Newsletter, 5, p. 142.

214. Shima, M. and Honda, M. (1966) Geochim. J., 1, p. 27.

215. Slavin, W. and Manning, D.C. (1963) Anal. Chem., 35, p. 253.

216. Slavin, W. (1965) P. Elmer A.A. Newsletter, 4, No. 8, p. 330.

217. Slavin, W. (1965) P. Elmer A.A. Newsletter, 4, p. 243.

218. Slavin, W. (1967) P. Elmer A.A. Newsletter, 7, p. 11.

219. Slavin, W. (1968) "Atomic Absorption Spectroscopy" - in press.

220. Slavin, W. and Manning, D.C. (1963) Anal. Chem., 35, p. 253.

221. Sprague, S. (1963) Perkin Elmer A.A. Newsletter, 2, p. 43.

222. Stanton, R.E. (1966) "Rapid Methods of Trace Analysis for Geochemical Application" (Edward Arnold Ltd.)

223. Steel, T. (1966) Report on the analysis of 10 samples of rock, submitted by Mr W. Simpson. Project K14/65, No. 12A, National Institute for Metallurgy, Johannesburg.

224. Stevens, R.E. et al (1960) U.S. Geol. Survey Bull. 1113.

225. Stone, M. and Thomas, J.F. (1958) Analyst, 83, p. 691.

226. Strasheim, A., Strelow, F.W.E. and Butler, L.R.P. (1960) J. S.A. Chem. Inst., 13, p. 73.

227. Strasheim, A. and Butler, L.R.P. (1962) Appl. Spectroscopy, 16, p. 109.

228. Strasheim, A. and Brandt, M.P. (1967) Spectrochim. Acta, 23B, p. 183.

229. Strelow, F.W.E., Van Zyl, C.R. and Coetzee, E.H.J. (1968) Anal. Chem. 40, 196.

230. Strock, L.W. (1936) Nachr. Ges. Wiss. Göttingen, Math-Phys., 1, p. 171.

231. Stuber, A.M. and Goles, G.G. (1967) Geochim. et Cosmochim. Acta, 31, p. 75.

232. Suhr, N.H. and Ingamells, C.O. (1966) Anal. Chem., 38, p. 730.

233. Suhr, N.H. (1967) XIII Coll. Spectroscopicum Internationale, Ottawa.

234. Sullivan, J.V. and Walsh, A. (1965) Spectrochim. Acta, 21, p. 721.

262. Willis, J.B. (1959) Nature, 184, p. 187.

263. Willis, J.B. (1960a) Spectrochim. Acta, 16, p. 259.

264. Willis, J.B. (1960b) Spectrochim. Acta, 16, p. 551.

265. Willis, J.B. (1962) Anal. Chem., 34, p. 614.

266. Willis, J.B. (1965) Nature, 207, p. 15.

267. Willis, J.B. (1967) Spectrochim. Acta, 23A, p. 811.

268. Willis, J.B. (1968) Personal communication; also Spectrochim. Acta - in press.

269. Wilson, L. (1963) Austr. Dept. Supply Report ARL/MET, 17, p. 131.

270. Winefordner, J.D. and Vickers, T.J. (1964) Anal. Chem., 36, p. 161.

271. Wolfhard, H.G. (1939) Z. Physik., 112, p. 107.

272. Zaidel, A.N. and Korermoi, E.P. (1961) Optics and Spectroscopy, 10, p. 299.

273. Zeeman, P.B. and Butler, L.R.P. (1962) Appl. Spectr., 16, p. 120.

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APPENDIX I

A PROPOSED INSTRUMENT FOR DETERMINING THE ISOTOPIC RATIO OF LITHIUM 6 TO LITHIUM 7

An instrument has been designed and built whereby the isotopic ratio of lithium ^{6}Li : ^{7}Li may be determined speedily in solutions with high precision and accuracy. The analytical method used is similar to that described in Chapter 6.3.

A diagram of the optical arrangement is shown in Fig. A-I-1.

Two hollow cathode lamps, one with a lithium 6 and the other with lithium 7 cathode are mounted at right angles. On the optical path of the one lamp (lithium 6 in the figure) is a normal atomic absorption arrangement of a lens to focus the cathode image in the flame, and another lens to focus this image onto the cathode of a photomultiplier tube. An interference filter with a half-bandwidth transmission of 40 Å isolates the lithium resonance line at 6708 Å.

The image of the other lamp (lithium 7 in the figure) is also focussed onto a photomultiplier with a similar filter. This photomultiplier is marked A and the one behind the flame is marked B.

A sector which rotates at slightly less than 3000 r.p.m. is placed at 45° to the optical axes. This sector has the form shown in the figure. It is provided with three mirrors aluminized on both surfaces and three similar shaped openings. Both mirrors and openings are large enough not to vignette the light beams. On the perimeter of the sector are cut-away portions for the timing mechanism.

As the sector rotates and when a hole is in position, the light from the lithium 6 lamp will pass through the flame onto photomultiplier B and the light from the lithium 7 lamp will pass onto photomultiplier A. At the next instant, when the mirror is in position, the light from the lithium 6 lamp will be reflected onto photomultiplier A and the lithium 7 light will be reflected through the flame onto photomultiplier B. In this way the lithium 6 and lithium 7 light beams will be measured alternately by photomultipliers

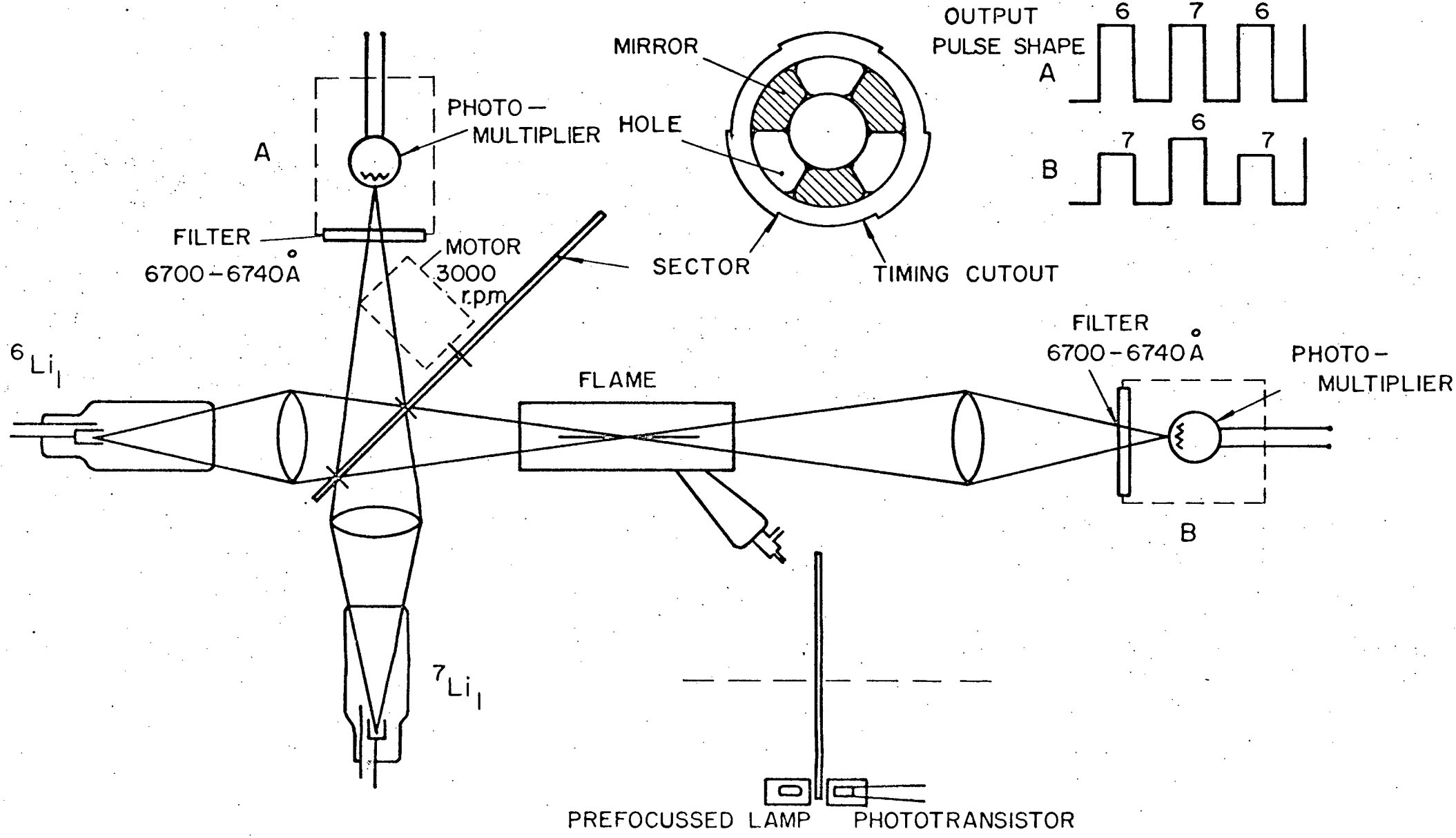

FIG. A I·1.

PG4-1513

A and B and will give signals as shown in the figure, at a frequency of approximately 285 c.p.s. The amplitude of the pulses from B will be lower than from A depending on the concentrations of lithium 6 and lithium 7 in the flame. No spectrometer is required because the absorption line-widths are smaller than the isotopic line separation.

A prefocussed torchlamp and a phototransistor provide the timing mechanism. As the disc rotates the phototransistor is periodically illuminated and this gives a signal which switches the lock-in amplifier system connected to the output of each photomultiplier. A field effect transistor switches each alternate pulse to its own integrating circuit so that four separate signals are recorded viz:

A. 1. Lithium 6 - unabsorbed

2. Lithium 7 - unabsorbed

B. 3. Lithium 6 - absorbed

4. Lithium 7 - absorbed

By forming the ratio 3:1 and 4:2 the absorption signals of each isotope are monitored with respect to their original intensity. A much more constant signal is assured by integrating all the signals for a definite period. The collector currents from each photomultiplier should be the same.

The isotopic ratios lithium 7 : lithium 6 can be calculated by forming the ratio $\frac{3}{1}/\frac{4}{2}$. This can be done electronically with relative ease. In this way the lithium isotope ratio may be obtained on a single spraying of a lithium solution, and thus provide the means, using the techniques described in Chapter 6, for rapidly estimating isotopic ratios for lithium with very high precision and accuracy.

APPENDIX II

DATA ON SAMPLES

a. Supplied by A.J. Erlank Esq., Department of Geochemistry, University of Cape Town.

1.	ET3/270	:	Bushveld pyroxenite, lower critical zone, Marikana, Western Transvaal.
2.	ET3/169	:	do.
3.	5087	:	Bushveld norite, Bon Accord Quarry, near Pretoria.
4.	DS/95	:	Karroo dolerite from dyke, Spitskopvlei area, C.P.
5.	7228	:	Great Dyke pyroxenite. West side of Great Dyke, Rhodesia.
6.	NORI - PLAG	:	Calcic plagioclase (separated from NORI rock norite) O'Okiep, C.P.
7.	NOR2 - PLAG	:	do.
8.	M - 19A	:	Malmesbury hornfels inclusion. Sea Point contact.
9.	M - 32	:	Microgranite vein, Bantry Bay, C.P.
10.	M - 34	:	Porphyritic Cape granite, Clifton, C.P.
11.	M - 36	:	Aplite vein, Kuilsrivier, C.P.
12.	M - 40	:	Malmesbury shale. Bellville Quarry, C.P.
13.	M - 41	:	Malmesbury siltstone, do.
14.	M - 60	:	Granitised Malmesbury xenolith, Bantry Bay, C.P.
15.	M - 63	:	do.
16.	M - 64	:	Malmesbury inclusion, Bantry Bay, C.P.
17.	Me - 10	:	Anorthosite; Messum igneous complex, S.W.A.
18.	Me - 11	:	Eucrite (gabbro); same locality as Me - 10.
19.	K - 1	:	Malmesbury hornfels, Kloof Quarry, Cape Town.
20.	K - 2	:	do.
21.	K - 10	:	Microgranite, Kloof Quarry, Cape Town.

b. Supplied by J. Gurney Esq., Department of Geochemistry, University of Cape Town.

1. *RV 374 : Eclogite, Robert Victor Mine, Boshoff, C.P.
2. KRV 7 : Eclogite; do.
3. KRV 13 : Kimberlite, do.
4. RV 3 : Eclogite, do.
5. *RV 377 : Eclogite, do.
6. KDB 10 : Kimberlite, de Beers Mine, Kimberley.
7. KDB 12 : do.
8. Bult 8 : Peridotite from Bultfontein Mine, Kimberley.
9. Bult 11 : do.
10. Bult 16 : do.
11. AA 5 : Peridotite, unknown source, Kimberley.
12. Ash 1 : Melilite basalt, Ashton, C.P.
13. EK 43 : Metamorphic eclogite, Norway (Eskola).
14. *Tan 503 : Eclogite from Dodoma Mine, Tanzania.

* From Williams (1932) Collection.

THE DETERMINATION OF MAGNESIUM, CALCIUM, POTASSIUM, SODIUM, COPPER AND IRON IN WATER SAMPLES BY ATOMIC ABSORPTION SPECTROSCOPY

L. R. P. Butler* and Denise Brink†

The Council for Scientific and Industrial Research is currently engaged in a chemical survey of water supplies in South Africa. The analysis of various types of water samples such as those obtained from rivers, boreholes and wells and also industrial and sewage effluents plays an important role in this survey. The metallic elements of interest are calcium, magnesium, sodium, potassium and iron which occur in widely varying concentrations, and also the trace elements copper, zinc, chromium, *etc.* The atomic absorption method of analysis seemed to be particularly suited for this problem for the following reasons:

(1) The samples must be in the form of a solution, and as the samples submitted in this project are solutions, little sample preparation is required.
(2) The method is very sensitive for a large number of elements.
(3) The analyses are speedily effected and a large number of samples can be analysed daily.
(4) Interference effects are less serious than with flame emission spectrometry and are often more easily subdued.
(5) The apparatus is relatively inexpensive and simple to use.

The atomic absorption technique has previously been applied to the analysis of biological samples, such as blood serums[1] and wine[2], but there is no record of its being used for the wide variety of water samples expected in this programme. Flame photometric techniques are used successfully for the determination of sodium and potassium in water samples, but it was decided to include these elements in the project for the purpose of comparison.

This paper describes the development of the apparatus which was built to meet the special requirements of the problem, the analytical method, and the investigation of the interferences experienced with certain elements. These interferences were overcome by the addition of strontium chloride[3].

EXPERIMENTAL

Apparatus

A Zeiss PMQ II spectrometer, operating from a Wandell and Goltermann voltage stabilizer was used to isolate and measure the analytical absorption lines. Hollow cathode lamps, manufactured in the laboratory were used as light sources for all elements except potassium and sodium, where Phillips laboratory discharge lamps were used. Silica-quartz lenses were used to pass parallel light from the source through the flame, and to refocus the image of the source on the slit of the spectrometer.

The concentrations of some of the elements in water samples vary over a wide range. One of the failings of the atomic absorption method is that it is accurate over only a relatively small range of concentration depending on the experimental conditions. The most convenient way in which the analysis range can be changed is by changing the flame path length. An alternate method[4] is to use a less sensitive absorption line, but with many elements this method is not practicable as the difference in sensitivity between the two lines is too great.

In this project the former way was chosen as being the most convenient, and a special perspex burner was designed for this purpose. This burner is shown in Fig. 1. The upper portion of the burner can be rotated through fixed angles to give varying and reproducible flame lengths without extinguishing the flame.

The burner plate was made of brass with 1 mm. holes drilled to the form shown. Transverse holes were drilled to circulate cooling water through the hottest regions of the plate. It was found that, when this burner-top was turned side-on to the light beam the 2 cm. path length was still too long and absorption readings were too high for some samples. A fishtail burner-top also shown in Fig. 1 was therefore built and was found to give a very stable flame. When this burner-top was used side-on with a 2 mm. slit width a very short absorption path was presented to the light beam. In this position the wide, stable flame completely filled the optical aperture and very steady absorption readings were obtained. Both burners can be used with either "Handigas" or acetylene, but with acetylene the fishtail burner slit-width must be reduced to 1 mm. to prevent flash-back.

Even though these burners allowed the analysis of a wider range of concentrations, the atomic absorption method is so sensitive for some elements (*e.g.* sodium) that dilutions still had to be made when these elements were present in high concentrations.

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THE DETERMINATION OF MAGNESIUM, CALCIUM, POTASSIUM, SODIUM, COPPER AND IRON IN WATER SAMPLES BY ATOMIC ABSORPTION SPECTROSCOPY

L. R. P. Butler* and Denise Brink†

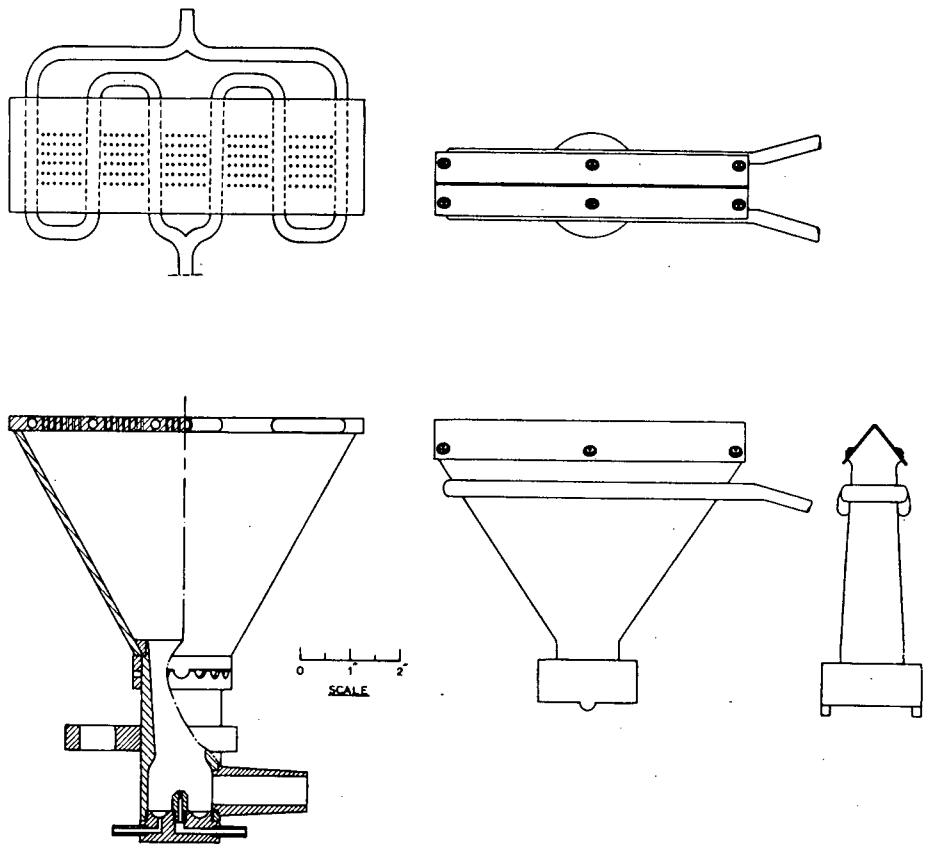

Fig. 1
Diagram of plastic burner with broad and narrow flame burner tops.

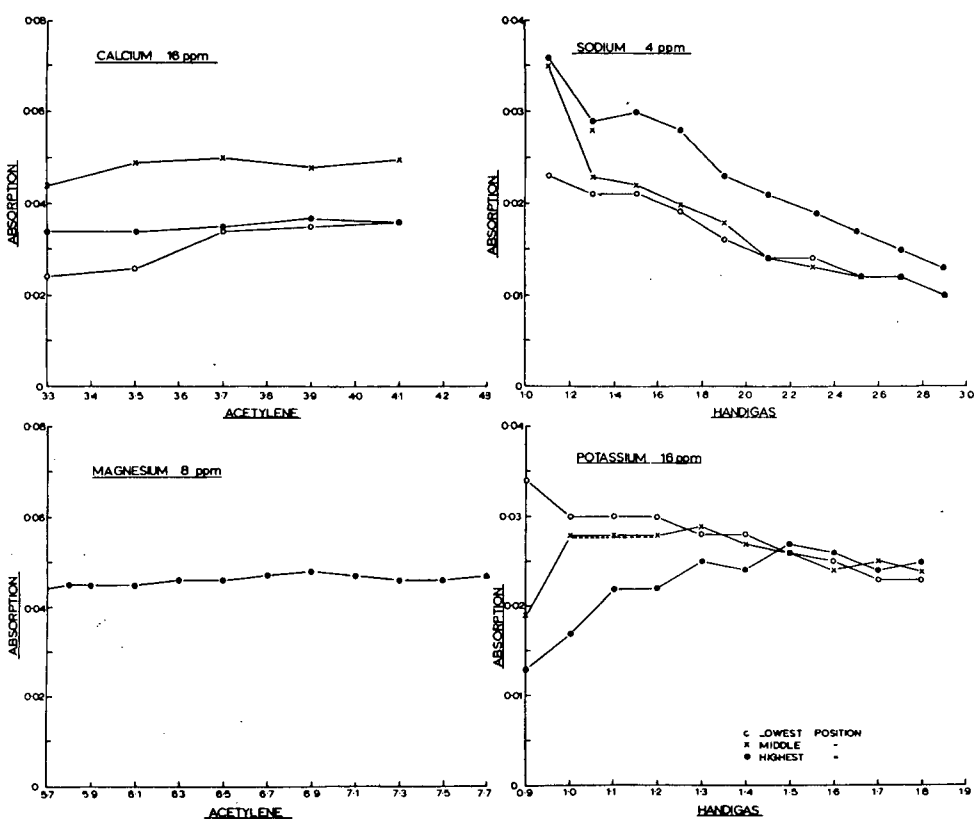

Fig. 2
Effects of gas sorts and pressures on absorption of the different analytical elements.

TABLE I
Experimental Constants

Element	*Wavelength*	*Slit*	*Lamp Current*	*Air Pressure*	*Fuel Gas*
Calcium	4227 Å	·1 mm.	20 mA	15 lb./sq. in.	Acetylene
Magnesium	2852 Å	·1 mm.	20mA	15 lb./sq. in.	Acetylene
Sodium	5890 Å	·05 mm.	discharge	15 lb./sq. in.	Handigas*
Potassium	7665 Å	·2 mm.	lamp	15 lb./sq. in.	Handigas*
Copper	3247 Å	·1 mm.	25 mA	15 lb./sq. in.	Handigas*
Iron	2483 Å	·07 mm.	30 mA	15 lb./sq. in.	Acetylene

*Propane-Butane

TABLE II
Interference Effects

Analytical element	*Interfering element*	*Concentration of interfering element p.p.m.*	*Percent change in absorption*	
			*without strontium**	*with strontium†*
CALCIUM 16 p.p.m.	Magnesium	250	+ 2·7	+ 3·5
		2500	− 14·3	− 4·0
	Sodium	250	− 1·0	0
		2500	− 82·4	+ 2·7
	Potassium	250	− 12·5	− 1·0
		2500	− 55·0	− 8·0
	Phosphate (PO_4)	10	− 20·0	0
		60	− 80·0	0
	Aluminium	30	− 30·5	0
		60	− 82·8	0
SODIUM 4 p.p.m.	Magnesium	250	− 0·68	0
		2500	− 1·0	0
	Calcium	250	+ 3·3	0
		2500	+ 5·0	0
	Potassium	250	0	0
		2500	0	0
MAGNESIUM 4 p.p.m.	No Interference			
POTASSIUM 4 p.p.m.				
COPPER				
IRON				

* These values are taken relative to an aqueous solution of the analytical element.
† These values are taken relative to a solution containing 1500 p.p.m. of strontium, and the analytical element.

TABLE III
*Coefficients of Variation**

CALCIUM		*MAGNESIUM*		*SODIUM*		*POTASSIUM*		*IRON*		*COPPER*	
conc. p.p.m.	*coeff. of var. %*	*conc. p.p.m.*	*coeff. of var. %*	*conc. p.p.m.*	*coeff. of var. %*	*conc. p.p.m.*	*coeff. of var. %*	*conc. p.p.m.*	*coeff. of var. %*	*conc. p.p.m.*	*coeff. of var. %*
1	7·4	1	2·2	1	4·8	1	3·6	1	4·3	0·5	6·1
4	7·4	4	1·6	4	1·6	4	1·6	8	0·72	2	1·4
12	1·5	12	7·4	8	3·6	8	1·4	16	0·86	8	0·98
								32	0·88	16	0·76

* Calculated on ten repeat readings.

TABLE IV
Recovery Tests

Element	*p.p.m. added*	*p.p.m. detected*	*p.p.m. recovered*
CALCIUM	0	14·2	0
	16	30·0	15·8
	32	46·5	32·3
MAGNESIUM	0	9·8	0
	8	17·6	7·8
	16	25·0	15·2
POTASSIUM	0	3·5	0
	4	7·6	4·1
	8	11·5	8·0
SODIUM	0	10·4	0
	8	18·6	8·2
COPPER	0	0·64	0
	1·0	1·63	0·99
	4·0	4·63	3·99
IRON	0	11·3	0
	4	15·4	4·1
	8	19·4	8·1
	16	27·2	15·9

A Zeiss atomizer was used to aspirate the samples and a glass spray chamber to separate the larger droplets, and to feed the fine aerosol into the burner. None of the samples were strongly acidic and no contamination difficulties were experienced.

Further experimental details are given in Table I.

Preparation of Standards

The standards were prepared by dissolving spectroscopically pure salts of the elements in as little acid as possible and making stock solutions. These stock solutions were then further diluted and strontium chloride solution added to give a range of standards containing 1,500 p.p.m. of strontium and various concentrations of the desired element.

Preparation of samples

All samples were carefully filtered to remove larger particles of organic and other matter which could block the atomizer. When the source of the sample was known it was possible to estimate in what concentration range the analytical elements occurred. River and borehole waters usually have relatively low concentrations of the analytical elements. For sodium, potassium, calcium and magnesium determinations the samples were diluted 1:1 with 3,000 p.p.m. strontium chloride solution.

TABLE V
Results of Analysis of Various Water Samples
All values in p.p.m.

SAMPLE	*CALCIUM*			*MAGNESIUM*			*SODIUM*		*POTASSIUM*	
	At. Abs.	Chem. (1)*	Chem. (2)†	At. Abs.	Chem. (1)*	Chem. (2)†	At. Abs.	Flame Photo.	At. Abs.	Flame Photo.
1. Vaal Dam I	18·4	22·4	18·1	21·6	19·6	15·4	16·0	16·5	4·7	5·7
2. Vaal Dam II	28·0	27·6	27·3	19·8	19·6	15·4	31·2	31·0	20·7	23·0
3. Sewage Pond 5	35·0	35·7	33·3	23·8	17·0	16·5	100·2	105·0	16·0	16·5
4. Sewage Pond 7	33·0	35·3	40·9	23·8	17·0	16·5	88·0	93·4	15·5	16·5

	At. Abs.	At. Abs. by Add.	At. Abs.	At. Abs. by Add.	At. Abs.	Flame Photo.	At. Abs.	Flame Photo.
5. Pienaars River I ...	9·4	9·4	6·6	6·0	15·2	17·0	1·37	1·99
6. Dam II	4·2	4·1	2·7	2·5	7·3	8·4	0·5	0·80
7. Sewage Pond	14·2	14·3	9·8	9·2	19·6	20·5	1·72	2·30

	CALCIUM		*MAGNESIUM*	
	At. Abs.	*Chem.‡*	*At. Abs.*	*Chem.‡*
8. Sewage Pond B	34·5	38·5	19·5	19·9
9. Moereletta River ...	17·6	17·6	7·5	8·8
10. Apies River	59·6	62·5	29·0	29·2
11. Moereletta + 40 p.p.m. Ca + 14·4 p.p.m. Mg.	56·0	58·0	22·0	23·0

	COPPER		*IRON*	
	At. Abs.	*At. Abs. by Add.*	*At. Abs.*	*At. Abs. by Add.*
12. HCL soil extract ...	0·63	0·64	224	226
13. Sewage Pond B	0·15	0·14	0·8	0·72

* National Chemical Research Laboratory (EDTA titration).
† National Institute for Water Research (EDTA titration).
‡ National Chemical Research Laboratory (gravimetric method and EDTA titration).

For the trace elements, such as copper and iron the samples were evaporated to reduce their volume and to concentrate the impurities. No strontium is necessary for these elements. The sewage and industrial effluents have high concentrations of impurities. These samples were diluted to the required concentration range and strontium chloride added to obtain 1500 p.p.m. strontium.

It was found that a white precipitate containing calcium and magnesium, formed with some water samples after standing. This precipitate was not always noticeable and had a very marked influence on results. After some investigation it was suggested that the precipitate was caused by a change in pH due to biological activity. For this reason, it was found advisable to add approximately 2 ml. of formaldehyde per 5 litres of water soon after the samples were taken. This prevented the precipitation and the results became much more reproducible.

Analytical procedure

Once the standards and samples had been prepared the standards were sprayed in ascending order of concentration and an analysis curve of absorption against concentration drawn. The samples were then sprayed and the absorption values converted to concentration with the analysis curve obtained from the standards. Each sample was analysed a number of times to obtain an average of values.

Interference effects

It has been reported by other workers[3] that inter-element effects are present with some elements. The interference effects most likely to occur were investigated. It was found that magnesium and calcium interfered with sodium, and magnesium, sodium, potassium, phosphates and aluminium interfered with calcium. The addition of strontium at a concentration of 1500 p.p.m. almost eliminated these effects. The results of this investigation are given in Table II. No definite reason has been obtained as to why strontium eliminates the interferences. Tests made with barium chloride showed that even though it did reduce the interferences it did not eliminate them.

RESULTS

The precision of the method was tested by analysing different concentrations of the analytical elements. The coefficients of variation were calculated on the absorption values and are shown in Table III.

It can be seen that the precision of the method is generally good. When high concentrations are to be analysed the dilutions should be made to fall in the region of higher precision.

To test the accuracy of the method recovery tests were made, and a number of samples analysed. Where possible these samples were also analysed by other methods to obtain comparative values. The results of these tests are given in Tables IV and V. The chemical values for magnesium and calcium were obtained by EDTA titration and gravimetric methods, as shown, while the sodium and potassium results were obtained by flame emission photometry. Not all the results could be verified chemically and the method of additions was used to see if any biases were present.

At first there were some differences between the atomic absorption magnesium values and the chemical magnesium values. Once the magnesium stock solutions had been standardized chemically, however, these differences disappeared.

It can be seen that the magnesium values obtained are slightly higher than the EDTA values. Willis[1], who experienced similar differences, suggested that this difference was due to the presence of proteins or organic matter which prevented magnesium in organic molecules from being determined by the EDTA titration.

The atomic absorption method was also used to analyse different extracts of a soil sample for magnesium and calcium. The EDTA procedure which is commonly used for the determination of these elements, requires that the extracts be treated in the following way to remove ammonia and iron. The ammonium chloride extract, which is made by eluting the soil with ammonium chloride solution, is taken to near dryness and then redissolved in nitric acid. The hydrochloric acid extract, obtained by shaking the soil with hydrochloric acid is treated to remove iron by precipitation. From Table VI it can be seen that there is little difference between the results of treated and untreated extracts, so that, if analysed by the atomic absorption technique the extracts do not require further treatment.

TABLE VI

Atomic Absorption Analysis of Soil Extracts

Type of Extract	*Calcium p.p.m.*	*Magnesium p.p.m.*
NH_4Cl (untreated)	77·6	33·6
NH_4Cl (treated)	69·0	34·4
HCl (untreated)	100·5	99·2
HCl (treated)	106·0	116·0

CONCLUSION

It is debatable whether the atomic absorption method offers any advantages over the flame emission method for sodium and potassium determinations where speed and convenience are concerned. It has been found, however, that the atomic absorption results are less easily affected by changes in sample composition, and gas and air pressures, and are more reproducible.

The recovery tests and comparison of results with those obtained by other methods show the method to be accurate. This together with the acceptable precision and high speed with which analyses can be made, makes the method particularly suitable for routine analyses.

ACKNOWLEDGMENTS

The authors are indebted to Mr. J. J. van Huysteen and Dr. F. W. E. Strelow for the chemical analyses and to T. J. de Wet for technical assistance. They are also indebted to Dr. A. Strasheim for helpful suggestions and to Mrs. D. B. de Villiers for help with the manuscript.

REFERENCES

1. Willis, J. B., *Spectrochim. Acta* **16**, 259 (1960).
2. Zeeman, P. B. and Butler, L. R. P., *Applied Spectroscopy* (in press).
3. David, D. J., *Analyst*, **84**, 536 (1959).
4. Gatehouse, B. M. and Willis, J. B., *Spectrochim. Acta*, **17**, 710 (1961).

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Multiple element atomic absorption analysis

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Abstract—Apparatus has been developed for doing simultaneous atomic absorption measurements. Descriptions are given of the special moveable detector direct reading head and of the methods used to bring the light from several cathodes onto the optical path. It is shown that the precision of results may be improved when absorption readings are ratioed with an internal standard or with a non-resonant monitor line. The method has been tested by analysing gold and copper-base metals. Some of the difficulties encountered are discussed.

INTRODUCTION

SINCE the introduction of atomic absorption spectroscopy as an analytical method in 1955 [1, 2], there has been a remarkable increase in the number of problems to which the method has been applied. Generally u.v. spectrometers with light dispersive systems allowing only single element determinations are used. There appear to have been only a few attempts [3, 4] to extend the method to multiple element determinations. The reasons for this appear to be: (a) the difficulty of efficiently directing the light from several elements along the optical axis of the absorbing system, (b) the inflexible commercial direct reading spectrometers, set to predetermined analytical programs, which do not allow any adjustment of the analytical program, and (c) the limited number of spectral lines available for atomic absorption measurement and the close proximity of some of them. This means that if a spectrometer designed on conventional lines is to be used, a high dispersion would be required, making it an expensive proposition.

In order to do multiple element atomic absorption measurements and to investigate the interesting possibilities which this offers, a versatile, movable detector, direct reading attachment was built to fit a Hilger medium quartz spectrograph. Methods for passing the light from several elements efficiently along the optical axis of the absorbing system were also investigated. This paper describes the apparatus and some of the experiments which were carried out to determine the advantages to be gained from multiple element atomic absorption analysis.

[1] A. WALSH, *Spectrochim. Acta* **7**, 108 (1955).
[2] B. J. RUSSELL, J. P. SHELTON and A. WALSH, *Spectrochim. Acta* **8**, 317 (1957).
[3] A. C. MENZIES, *Anal. Chem.* **32**, 898 (1960).
[4] J. L. SAUNDERSON, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (March 1962).

APPARATUS

The direct reading attachment

With a medium dispersion spectrograph the photoelectric measurement of closely adjacent spectral line intensities is often hampered by the physical dimensions of the exit slits. In Fig. 1 are shown the more sensitive absorption lines of 33 elements marked against the wavelength scale of a medium prism spectrograph. The close proximity of many lines is evident especially in the

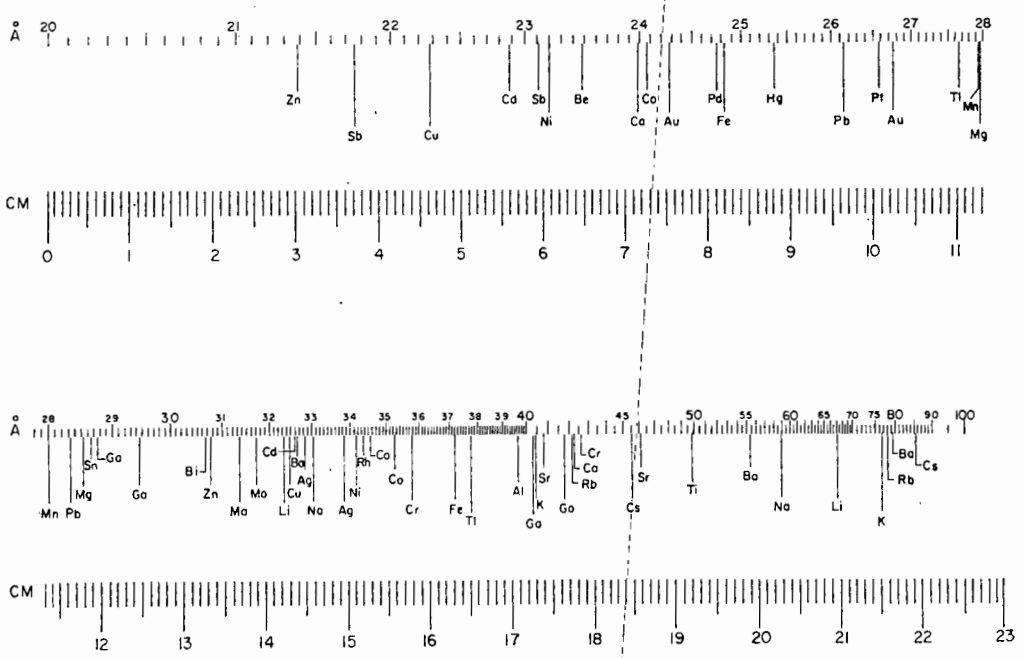

Fig. 1. The wavelength scale of a medium spectrograph with the more sensitive absorption lines of 33 elements marked.

vicinity of 3300 Å and 2850 Å. The simultaneous atomic absorption determination of several elements such as copper and silver, iron and palladium etc. would be severely hampered with conventionally designed exit slits placed side by side.

In the direct reading attachment developed, use is made of the upper–lower arrangement of exit slits shown schematically in Fig. 2a. This system allows two closely adjacent lines to be measured or if required, two simultaneous measurements to be made on the same line. Each slit is mounted on a shaped light duct attached to a movable photomultiplier housing. By shaping the ducts as shown in Fig. 2b, it is possible to bring two adjacent slits to within 4 mm of each other. The two mirrors M_1 (plane) and M_2 (concave) reflect the transmitted light to the photomultiplier cathode.

Figure 3 shows the general details of the attachment, without the scale projection system, which is attached to the front cover plate (not shown). There are four photomultiplier tube units (1) with their respective ducts and slits (2),

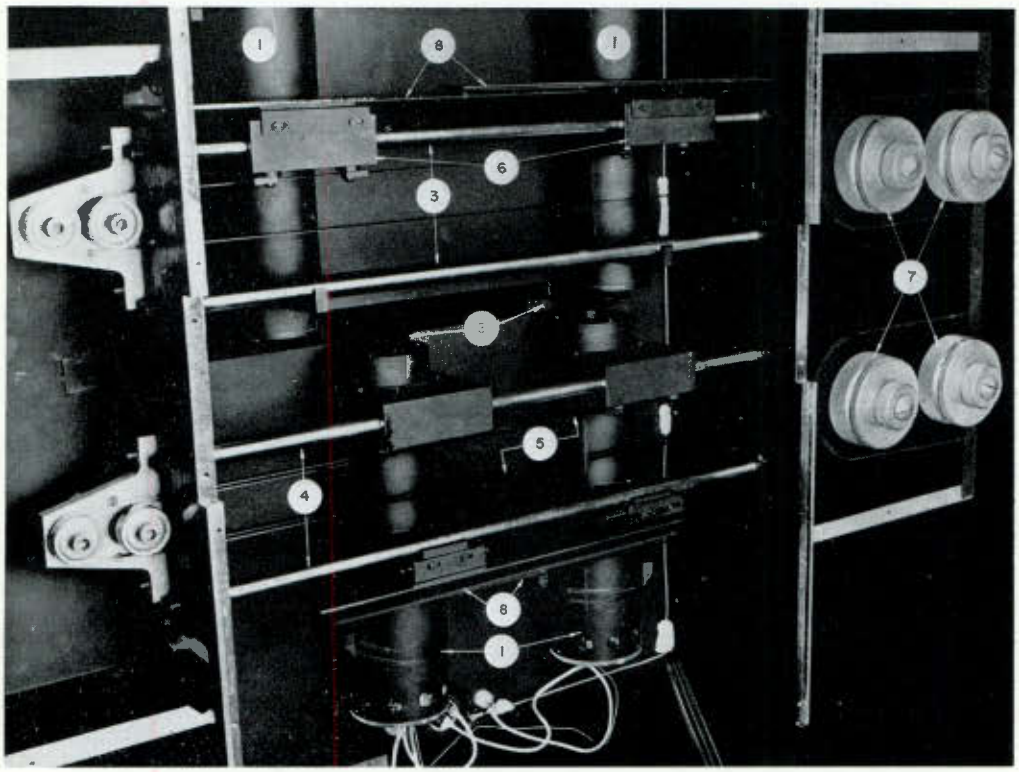

Fig. 3. Photograph of direct reading attachment without scale projection assembly. 1. Photomultiplier tube units. 2. Ducts and slits. 3. Upper guide rods. 4. Lower guide rods. 5. Steel tapes for transporting units. 6. Bearing blocks. 7. Anti-backlash gearboxes. 8. Wavelength scales.

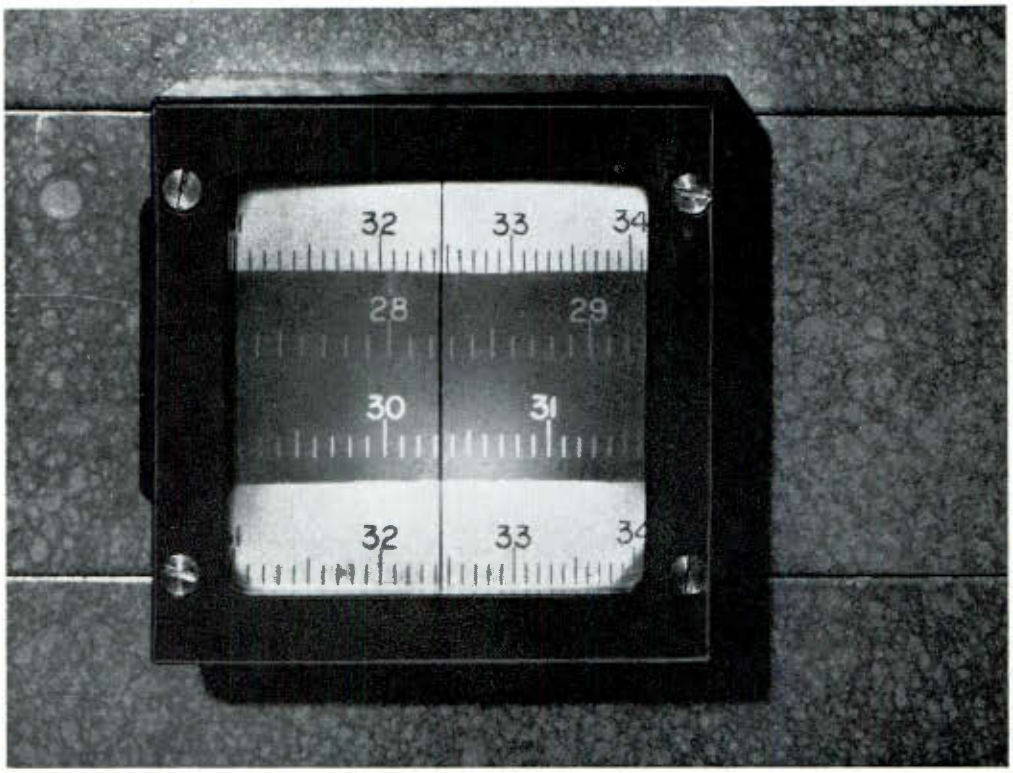

Fig. 4. Wavelength scales of each tube projected onto screen.

two moving along the upper pair of guide rods (3) and two along the lower guide rods (4). Smooth, accurate movement is achieved by means of linear ball races. The photomultiplier tube housings are remotely moved by means of steel tapes (5) attached to the bearing blocks (6), and driven from four, two-speed planetary gearboxes (7) with anti-backlash devices. The coarse 1 : 1 ratio allows the slit

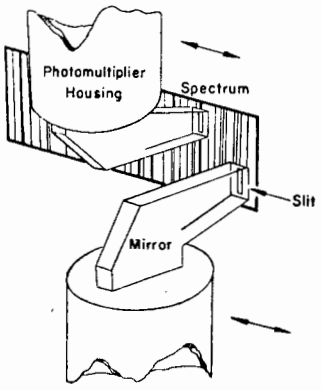

Fig. 2a. Schematic diagram of upper–lower arrangement of movable photomultiplier tube and exit slit assemblies.

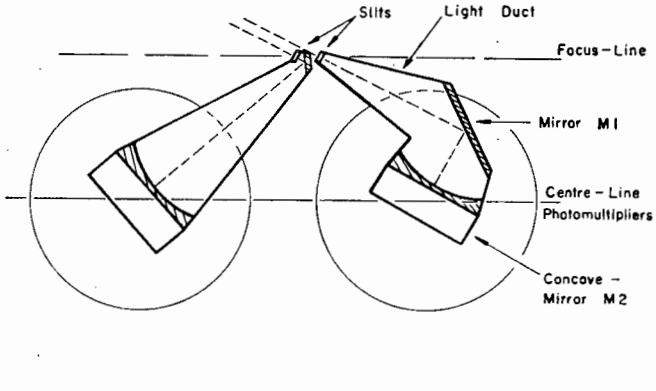

Fig. 2b. Top view of adjacent light ducts and exit slits.

and tube housing to be brought into the approximate region of the spectrum quickly, and the fine 150 : 1 ratio allows a precise profile of the spectrum line to be made. One revolution of the 6 cm adjusting knob moves the tube and slit 530 μ on the fine setting.

The positions of the exit slits with relation to the spectrum are read off a glass screen onto which images of scales (8), calibrated in wavelength units, are projected. There is a scale attached to each housing and when projected onto the screen, the scales are seen as in Fig. 4. The positions of the exit slits in relation to the spectrum may be read as accurately as with any single channel spectrometer. No difficulty has been experienced in locating a spectral line which is resolved by the spectrograph.

Prism spectrographs have inherent line curvature. Although a curved entrance slit was available to "straighten" spectral lines, it was found more convenient to retain the adjustable 18 mm long entrance slit and have 8·5 mm long, 60 μ wide exit slits. With entrance slit settings of up to 40 μ there was no loss of light as a result of curvature and there was sufficient resolution to carry out the analyses.

Electronics

E.M.I. 13-stage, end-on photomultiplier tubes were used because of their high sensitivity. The spectrograph was found to be so light strong, even when hollow

cathode lamps were used at low currents, that the high voltage supply to the photomultipliers was seldom set to exceed half the permitted maximum. A Carlsson electronic console* modified to give higher photomultiplier voltage, was used. Although no scale expansion device was used, readings taken on a large display micro-ammeter gave sufficient precision. The electronic system, being of the d.c. type, required the use of a non-modulated light source. An a.c. converter has since been built to reduce flame emission.

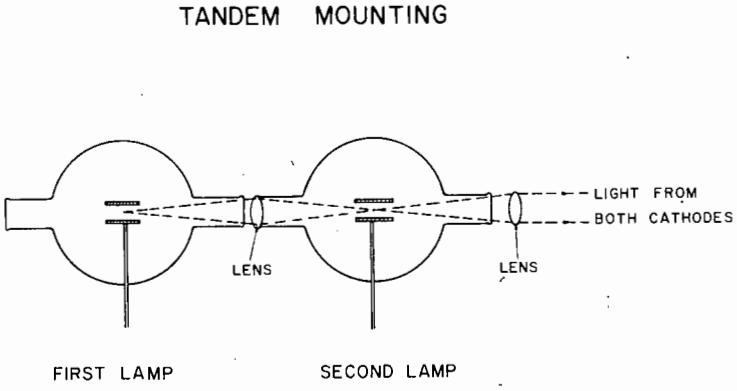

Fig. 5. Tandem mounting of hollow cathode lamps.

Hollow cathode lamps

Cathodes made from alloys of metals have been used for obtaining the radiation from several elements. However, few alloys appear to give constant emission for all the constituent elements, as one element tends to subdue the emission from the others [5].

A system of using semi-transparent mirrors placed at 45° to the optical axis has been used in this laboratory to determine potassium, sodium, calcium and magnesium in plant ash solutions. This system is limited by the appreciable loss of light and was only successful because of the high intensity radiation from sodium and potassium discharge tubes.

Another method, that of tandem mounting of lamps, has been used successfully. This requires the use of specially made lamps [6] mounted as shown in Fig. 5. By attaching a quartz lens onto the rear neck of the front lamp a slightly reduced image of the rear cathode may be formed in the front, open-ended cathode. When more than 3 lamps are used this system becomes impracticable because of light losses and alignment difficulties.

The method proposed by Massman [7] gives constant emission for a number of elements depending on their sputtering rates and melting points. This type of cathode is made up of concentric metallic rings pressed into a thin copper or

* Sold by Hilger and Watts.

[5] W. G. Jones and A. Walsh, *Spectrochim. Acta* **16**, 249 (1960).
[6] A. Strasheim and L. R. P. Butler, *Appl. Spectrosc.* **16**, 109 (1962).
[7] H. Massman, *Z. Instr.* **8**, 225 (1963).

steel sheath as shown in Fig. 6a. Emission intensities may be varied by having longer or shorter rings of the elements. As many as four elements have been used together *viz.* nickel, iron, copper and manganese, but it is usual to have only two or three rings in one cathode.

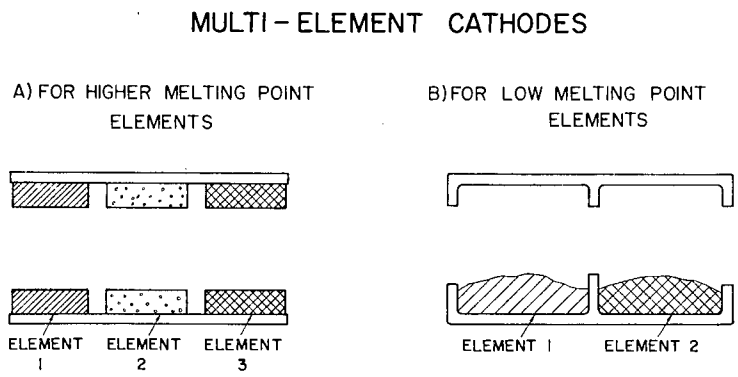

Fig. 6. Multiple element cathodes.
(a) For elements with higher melting points e.g. iron, nickel, chromium.
(b) For elements with low melting points e.g. lead, calcium, zinc.

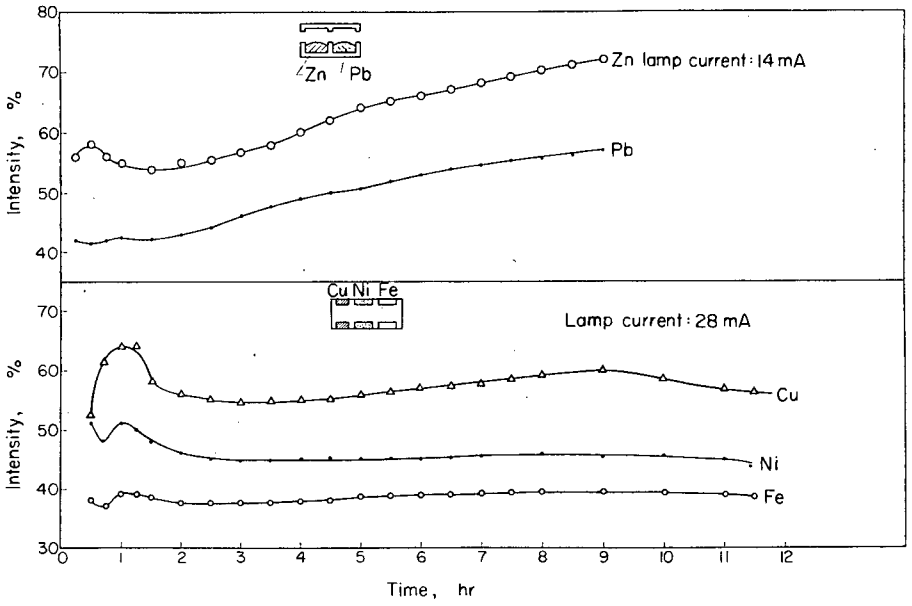

Fig. 7. Change of light intensity from multiple element cathodes with time.

When low melting point elements are required, the cathodes shown in Fig. 6b may be constructed with divisions in the sheath separating the globules of metals. Emission from metals with low melting points is more inclined to change with time than that from the solid ring cathodes as is shown in Fig. 7. These lamps are usually run so that the metals are not molten during operation.

Emission is generally more constant from multiple ring cathodes than from lamps in tandem, and this system has the added advantage that only one power supply is required. When the light from several elements of widely different characteristics is required, a combination of the two methods (lamps in tandem and ring cathodes) works satisfactorily.

Absorption equipment

All work was done with a relatively low temperature premixed propane butane/air flames. Flame lengths could be varied by rotating the water-cooled aluminium burner top in much the same way as proposed by CLINTON. [8] To reduce flame emission the system of passing parallel light through the flame was used. An EEL atomizer and a glass spray chamber were used to obtain a fine, uniform spray of the sample solutions.

EXPERIMENTAL

Integration tests

To determine optimum exposure times absorption signals were integrated for various periods of time with three different solutions of copper being sprayed

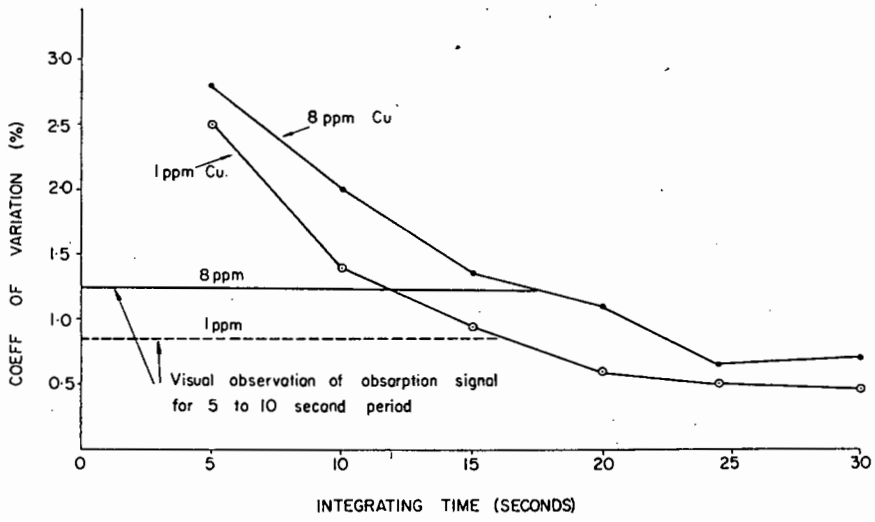

Fig. 8. Coefficient of variation for various integration times compared to coefficients of variation obtained by visual observation. (Time constant of meter: 1 sec.)

into the flame. The precisions were calculated and compared with those obtained from visual observation of absorption for the same solutions on a direct indicating meter (time constant 1 sec) for 5 to 10 sec.

The results are shown graphically in Fig. 8. The precisions obtained from visual observations are better than those obtained by integrating for periods of less than 15–20 sec. This is obviously due to the ability of the operator to disregard severe deflections. For all further parallel absorption measurements a minimum integration time of 24 sec was used.

[8] O. E. CLINTON, *Spectrochim. Acta* **16**, 985 (1960).

Improvement of precision by the use of ratios

Double beam atomic absorption spectrometers [9] have been shown to reduce lamp fluctuations and warm up time by separating the light from the hollow cathode lamp into two beams, one passing through the flame and one around it, and amplifying the difference. In this laboratory it has been found that when the lamp current is well stabilized, lamp fluctuations are not serious, but that flame and sprayer fluctuations are the greater causes of poor precision, especially when the parallel light system is used. To test whether the use of ratios improved analytical results, solutions containing gold as the internal standard and copper as the analytical element were analysed repeatedly by six different operators under conditions where the flame was fluctuating more than would normally be tolerable. The following spectral lines were measured: Cu 3247, Au 2428 (internal standard) and Au 3122 (non-resonant monitor line), a single lamp, containing a copper–gold–silver ring cathode was used. The concentration of the gold was chosen so that the absorption was of the same order as that of the copper. Three analytical curves were constructed plotting copper absorption and the ratios copper/internal standard and copper/monitor line against concentration. The standard deviations for the final analytical results are shown in Table 1. From Table 1 the following conclusions may be drawn:

Table 1. Improvement in precision by the use of ratios

Person	Copper absorption results coefficient of variation	Ratio copper line non-resonant gold line		Ratio copper line resonant gold line	
		Coefficient of variation	Improvement factor	Coefficient of variation	Improvement factor
1	15·9	6·0	2·65	9·3	1·71
2	26·4	10·6	2·49	11·2	2·36
3	13·9	7·3	1·90	4·5	3·09
4	17·5	5·6	3·13	13·6	1·28
5	14·9	7·1	2·10	10·8	1·38
6	12·2	4·5	2·71	9·6	1·27
Average improvement factor		2·5		1·85	

All readings were obtained by integrating signals for 24 sec.

(i) The higher precision obtained by certain operators with the copper absorption readings alone, reflects their more precise timing ability.

(ii) The monitor line ratios give higher precision generally than the internal standard line ratios. This indicates that the gold resonant line is susceptible to more fluctuations than the monitor (non-resonant) line. As the monitor line is only affected by changes of the refractive index of the flame, while the internal standard line is also affected by changes in the atomic gold concentration in the flame, this is to be expected.

(iii) In all cases there has been a significant improvement in precision when ratios are used for analytical purposes instead of the absolute measurements.

[9] H. L. Kahn and W. Slavin, *Appl. Optics* **2**, 931 (1963).

Multiple element analysis

The simultaneous determination of several elements was tested by analysing gold bullion and certain copper-base samples.

(i) *Gold analysis.* Samples of gold bullion were dissolved in *aqua regia*, the solutions taken to near dryness and the residue taken up in nitric acid to convert the chlorides to nitrates in order to prevent precipitation of silver chloride. Silver is usually the main impurity element in gold bullion and is present in much higher concentrations than copper. Because of this it was found expedient to use different dilutions for silver and copper determinations, and also to use two silver lines with different sensitivities. The spectrometer was set to measure the non-resonant gold line Au 4756, the copper line Cu 3247, and the two silver lines Ag 3281 and Ag 3383.

Absorptions were measured and results were calculated with and without the gold line as monitor. Both methods of calculation give similar results although the ratioed values gave a higher degree of precision. The atomic absorption values for copper and silver were added to indicate total impurities present in the gold and to enable comparison with the fire assay values as is shown in Table 2.

Table 2. Analysis of gold bullion

Sample	Atomic absorption				Fire assay Au value %
	Copper ppm	Silver ppm	Sum ppm	Difference %	
1	3384	96	3480	99·65	99·66
2	3717	163	3880	99·61	99·62
3	4015	125	4140	99·58	99·58
4	4530	160	4690	99·53	99·54
Standard deviation				±0·05	±0·012

(ii) *Copper-base analyses.* Several analysed standards and samples were dissolved in nitric acid and simultaneous determinations of lead, nickel and iron made. Because of the high sensitivity of zinc two different sample dilutions were necessary. The burner was also turned to give a path length of 1 cm for the zinc determinations. Copper could not be used as an internal standard because of its variation in concentration in the samples, but absorption measurements were ratioed with a non-resonant copper line. The spectrometer was set to measure Pb 2833, Ni 2320, Fe 2483 and Cu 2618 and for the zinc determinations, Zn 2138 and Cu 2618. Two separate hollow cathode lamps were used in tandem, the front lamp having copper, nickel, and iron rings and the rear, lead and zinc globules in a copper sheath. The results shown in Table 3 were calculated by plotting the ratios of measurements against concentrations for aqueous standards.

Discussion

The simultaneous determination of several elements by atomic absorption spectroscopy appears to be a practical possibility. The saving in time and, in

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THE DETERMINATION OF TRACE QUANTITIES OF MOLYBDENUM BY ATOMIC ABSORPTION SPECTROSCOPY

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(Received April 25th, 1966)

There has recently been an attempt to extend geochemical methods of prospecting to the analysis of water samples from boreholes, springs, and rivers. In view of the low solubility of certain elements such as molybdenum, chromium, and lead, highly sensitive methods, capable of determining concentrations as low as 0.001 p.p.m., and having sufficient accuracy to detect trends and anomalies, are required. An atomic absorption method for the determination of molybdenum in these low concentrations has been developed. Not only is the determination of this element of interest to geochemists in water and rock samples, but also to agricultural chemists in plant and soil samples.

DAVID[1] made a comprehensive study of the factors influencing the determination of molybdenum by atomic absorption spectroscopy and achieved a detection limit of the order of 0.5 p.p.m. in aqueous solutions, when a fuel-rich air–acetylene flame was used. This detection limit is not low enough for the determination of molybdenum in natural waters (0 to 0.005 p.p.m.), silicates and soils (0 to 20 p.p.m.), and plant materials (0 to 10 p.p.m.). There are, moreover, several elements present in these samples, which DAVID found interfered with molybdenum. Liquid–liquid extraction methods were investigated which simultaneously concentrate the molybdenum and eliminate most of the interfering cations. There do not appear to be any previous attempts to combine organic solvent extraction with atomic absorption spectroscopy for the determination of trace quantities of molybdenum.

MALISSA AND SCHÖFFMANN[2] have reported the chelating of many heavy metals, including molybdenum, by ammonium pyrollidine dithiocarbamate (APDC). This extraction technique was, however, found to be unsuitable for samples with high iron content, because of the preferential extraction of this element. MITCHELL AND SCOTT[3] reported the use of 8-hydroxyquinoline as a complexing agent for molybdenum and other metals with subsequent determination by emission spectroscopy. With certain modifications this method was found to be more suitable for silicate materials where iron concentrations are high. WILLIS[4], ALLAN[5,6] and ROBINSON[7] have shown that considerable enhancement in sensitivity may be achieved by spraying an organic solvent containing the analytical element, into the flame. Combinations of these methods, *viz.* liquid–liquid organic extraction with subsequent determination of molybdenum in the organic phase, have satisfactorily been used for the determination of molybdenum.

EXPERIMENTAL

Apparatus

Initially a Zeiss PMQ II spectrophotometer with self-built atomic absorption attachments was used with a flat-topped, water-cooled type of burner[8], the premixed flame and sample aerosol issuing from a number of 1.0-mm diameter holes. DAVID[1] stressed the importance of using only a small region of the air–acetylene flame. For this reason the light beam through the flame was controlled by apertures as is shown in Fig. 1. Under optimum conditions a detection limit of 2 p.p.m. could be achieved, which indicated that this type of burner was not suitable for the determination of low concentrations of molybdenum.

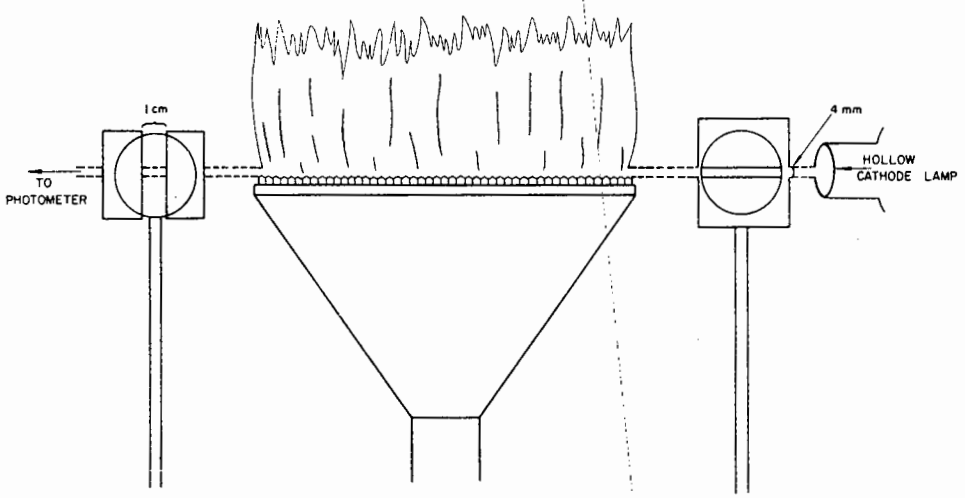

Fig. 1. Position of light beam.

TABLE I

OPTIMUM INSTRUMENTAL PARAMETERS

Spectrometer	Perkin Elmer 303.
Atomizer	EEL at 25 lb/sq. in. air pressure.
Gas	Acetylene at 10.0 on flowmeter. Supplementary air at 7.5 on flowmeter.
Burner	Slit, laminar flow type, gap 0.025 in., length 4.25 in. Height set ± 3 mm below centre of optical axis.
Wavelength	3133 Å.
Slit width	0.3 mm.
Light source	Self-built Mo hollow-cathode lamp run at 15 mA, stabilized D.C. power supply.

At this stage a Perkin Elmer 303 atomic absorption spectrometer was acquired. Optimum conditions using this instrument are shown in Table I. It has a slit-type burner and with a slightly luminous (fuel-rich) flame, a detection limit of 0.1 p.p.m. was obtained for molybdenum with aqueous standards. Figure 2 shows some of the calibration curves obtained with this instrument, using both aqueous solutions and an organic solvent. Also shown is the best curve obtainable with the flat-topped burner.

When spraying a combustible organic solvent, careful adjustment of the supple-

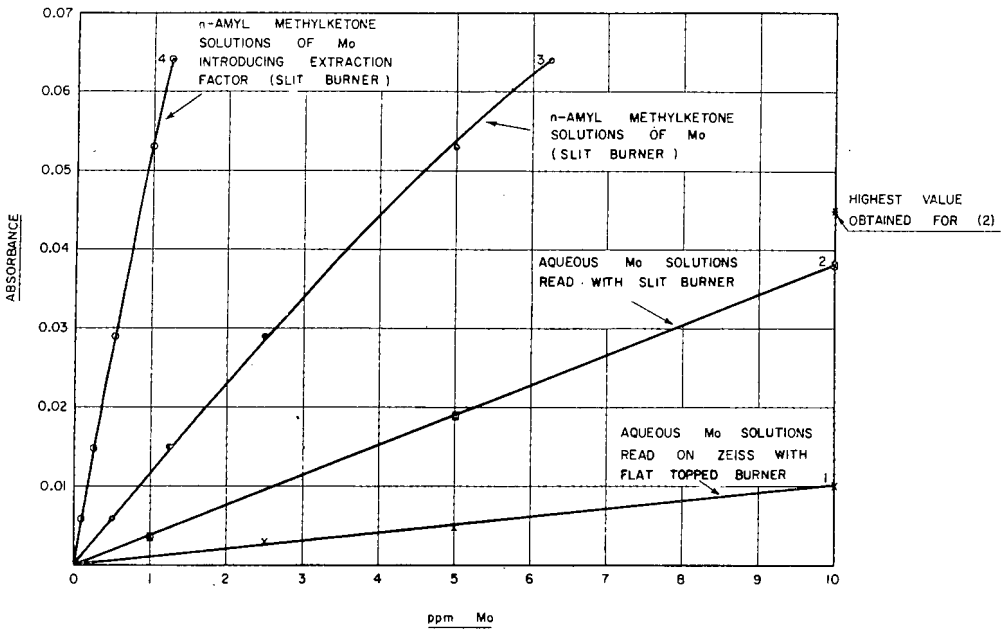

Fig. 2. Calibration graphs.

mentary air supply should be made to obtain optimum combustion. The flame tends to blow off when the ketone is not being sprayed and it is advisable to spray a blank ketone between samples.

Preparation of samples and standards

The samples and standards are prepared as follows.

Water samples. These require little preparation apart from acidifying and partial concentration by evaporation. It was found convenient to evaporate 500 ml to approximately 40 ml and then to add 2 ml of hydrochloric acid to dissolve any precipitate that formed. As iron is present in relatively small quantities in most natural water samples, it can be prevented from interfering by adding 5 ml of a 10% solution of citric acid, which complexes the iron. The pH is adjusted to 2.0 and after transferring the mixture to a separating funnel, 5 ml of a 2% solution of APDC are added. After addition of 10 ml of *n*-amyl methyl ketone, the mixture is shaken and allowed to stand for 5–10 min to allow the two phases to separate. The aqueous phase is discarded and the organic phase containing the molybdenum is transferred to a 10-ml beaker for convenient handling.

Plant samples. After drying and grinding, 5–10 g of plant material are ashed at 500°. The ash is dissolved in as little concentrated hydrochloric acid as possible and diluted to 40 ml with distilled water. It is then treated in the same way as the water samples.

Silicate samples. Finely crushed material (0.5 g of 200 mesh) is fused with 2 g of sodium peroxide and 1.5 g of sodium hydroxide at 470° for 30 min in a platinum crucible[9]. Platinum corrosion may occur if the iron content of the sample exceeds 5%.

This can be prevented by first leaching the sample with hydrochloric acid, filtering, and igniting the filter paper before fusion. The fusion product is dissolved in hydrochloric acid and recombined with the filtrate. As APDC forms preferential complexes with iron, 8-hydroxyquinoline (25 ml of a 4% solution) is added before adjusting the pH to 1.0. The procedure of ketone addition etc. follows as described above.

Standards. Standard ketone solutions are prepared by following the extraction procedure on aqueous standards containing known concentrations of molybdenum. These aqueous standards are prepared by dissolving ammonium molybdate in distilled water and making up the volume to form a stock solution (200 p.p.m. Mo) from which further dilutions are made.

Extraction procedure

Because of the deviation from reported procedures, an investigation was carried out to determine suitable pH extraction ranges and to test interference effects.

Methyl isobutyl ketone has a relatively high solubility in water (1.8 g per 100 ml), which is not desirable when the concentration factor (10 ×) is large. Amyl methyl ketone is less soluble in water (±0.5 g per 100 ml) and separates more easily from the aqueous phase because of lower density. This solvent was therefore selected as being the most suitable for extraction.

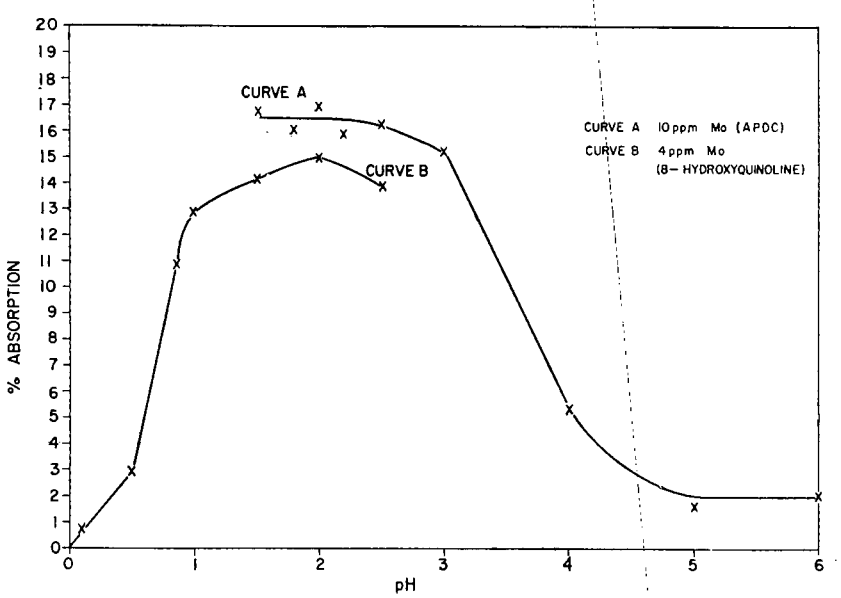

Fig. 3. Extraction efficiency graphs.

The effect of pH was tested by carrying out the extraction procedure with known standards and APDC at pH values varying from 1.5 to 6.0. Graph A in Fig. 3 shows that optimum recovery (94%) takes place between pH values of 1.5 and 2.5.

Similar tests made with 8-hydroxyquinoline (Graph B, Fig. 3) indicate that optimum extraction (99%) takes place at a pH value of 2.0. Unfortunately at this pH value a heavy precipitate forms, probably due to iron in the presence of excess

8-hydroxyquinoline. For this reason extraction is done at a pH value of 1.0, extraction efficiency being 98%.

Interference with the determination of molybdenum, by other elements likely to be present in the sample, was investigated by adding these elements at various concentration levels to known standards and extracting molybdenum using both the APDC and the 8-hydroxyquinoline procedures. The results of the investigations are shown in Tables II and III. It may be seen in Table II that with the APDC extraction,

TABLE II

THE INFLUENCE OF Cu, Zn, Pb, Na, Mg, Ca AND Fe ON THE EXTRACTION AND ABSORPTION OF MOLYBDENUM USING APDC EXTRACTION

p.p.m. Mo	*Elements added to 50 ml of aq. soln.*	*Mo absorbance after extraction*
2.0	Nil	0.090
	1.0 p.p.m. Cu	0.090
	5.0 p.p.m. Cu	0.088
2.0	Nil	0.089
	0.5 p.p.m. Zn	0.089
	1.0 p.p.m. Zn	0.088
2.0	Nil	0.089
	0.2 p.p.m. Pb	0.089
	0.5 p.p.m. Pb	0.088
2.0	Nil	0.090
	30 p.p.m. Na, 100 p.p.m. Mg, 200 p.p.m. Ca	0.086
	300 p.p.m. Na, 400 p.p.m. Mg, 800 p.p.m. Ca	0.084
2.0	Nil	0.085
	0.10 p.p.m. Fe	0.085
	0.20 p.p.m. Fe	0.082
	0.50 p.p.m. Fe	0.076
	1.0 p.p.m. Fe	0.065
	2.0 p.p.m. Fe	0.059
	5.0 p.p.m. Fe	0.042
2.0	Nil	0.089
	10 p.p.m. Fe + citric acid	0.086
	20 p.p.m. Fe + citric acid	0.086

copper, zinc, and lead have no effect; sodium, calcium, and magnesium at high concentrations depress the absorbance slightly. Iron, however, in excess of 0.2 p.p.m. depresses molybdenum absorption markedly, probably because of preferential extraction or complex formation and flame interference. The prior addition of citric acid to complex the iron and thus prevent its extraction was successful for concentrations up to 20 p.p.m. For higher concentrations of iron, 8-hydroxyquinoline was used for extraction at a pH of 1.0. Table III shows that iron, even at a concentration of 5000 p.p.m. in solution, has no effect on the extraction and determination of molybdenum. Other elements, at concentrations most likely to occur in rock samples were also tested for interference. The results are shown in Table III.

TABLE III

THE INFLUENCE OF Mg, Ca, K, Al, Cr, Mn, Ni, Co AND Fe ON THE EXTRACTION AND ABSORPTION OF MOLYBDENUM USING 8-HYDROXYQUINOLINE

p.p.m. Mo	*Elements added to 50 ml of aqueous solution*	*Mo absorbance after extraction*
2.0	Nil	0.084
	100 p.p.m. Mg, 100 p.p.m. Ca, 100 p.p.m. K	0.084
	250 p.p.m. Mg, 250 p.p.m. Ca, 250 p.p.m. K	0.084
2.0	Nil	0.084
	100 p.p.m. Al	0.084
	250 p.p.m. Al	0.084
2.0	Nil	0.084
	20 p.p.m. Cr	0.080
2.0	Nil	0.084
	20 p.p.m. Mn	0.083
	50 p.p.m. Mn	0.082
2.0	Nil	0.084
	80 p.p.m. Ni	0.084
	200 p.p.m. Ni	0.084
2.0	Nil	0.084
	20 p.p.m. Co	0.083
	50 p.p.m. Co	0.081
2.0	Nil	0.084
	2000 p.p.m. Fe	0.082
	5000 p.p.m. Fe	0.082

RESULTS

Precision tests were carried out on borehole water samples to which molybdenum had been added, and on 2 geological samples. The results are shown in Table IV.

Recovery tests and chemical analyses were used to determine the accuracy of

TABLE IV

PRECISION TESTS

Type of sample	*No. of samples analysed*	*p.p.m. Mo*	*Average absorbance*	*Coefficient of variation (%)*
Borehole water	22	0.050	0.049	1.9
Silicate rock G1	10	13.0	0.034	4.0
Sulphide ore 1	10	4.0	0.011	10.0

TABLE V

RECOVERY TESTS

Type of sample	*p.p.m. Mo present*	*p.p.m. Mo added*	*p.p.m. Mo recovered*	*Recovery (%)*
Borehole water	0.050	0.010	0.061	102
	0.050	0.025	0.075	100
	0.050	0.050	0.100	100
Sulphide ore 1	4.0	2.0	5.8	98
	4.0	4.0	8.0	100
	4.0	10.0	13.9	99

TABLE VI

COMPARISON OF RESULTS OBTAINED FOR WATER SAMPLES ANALYSED BY ATOMIC ABSORPTION SPECTROSCOPY AND COLORIMETRY

Sample	*p.p.m. Mo*	
	Atomic absorption spectroscopy	*Colorimetry*
I	0.048	0.052
II	0.091	0.091
III	0.010	0.011

TABLE VII

COMPARISON OF RESULTS OBTAINED FOR PLANT SAMPLES ANALYSED BY ATOMIC ABSORPTION SPECTROSCOPY AND OTHER METHODS

Sample	*p.p.m. Mo*		
	Atomic absorption spectroscopy	*Spectrographic*	*Chemical*
Peach leaves 4A	0.33	0.1 0.04 0.05 0.2 0.1 0.13	0.1
Beetroot leaves 4C	1.19	0.85 0.67 0.85 0.74 0.4 0.76	2.7
Lucerne 3	0.27		0.27
Lucerne 4	7.5		6.6
Lucerne 13	1.84		1.0
Lucerne 26	0.18		0.05

the method. The results of the recovery tests are given in Table V. Comparisons of atomic absorption determinations on a variety of samples with those obtained by chemical and spectrochemical methods are given in Tables VI, VII and VIII.

DISCUSSION

If due care is taken, the precision of the method is acceptable. Results obtained for plant and rock samples, however, were less precise than those obtained for water samples. It was felt that this could be explained by non-homogeneity of the sample, as comparatively small weights of material were used. Nevertheless, the precisions obtained on these samples compared favourably with those obtained by other methods.

The results of the recovery tests shown in Table V indicate that the extraction procedure is reliable.

The comparison values of plant samples given in Table VII show the atomic absorption values to be somewhat higher than those of the other methods. The large spread of values obtained by other methods makes it difficult to assess these results

TABLE VIII

COMPARISON OF RESULTS OBTAINED FOR SILICATE ROCKS ANALYSED BY ATOMIC ABSORPTION SPECTROSCOPY AND OTHER METHODS

Sample	*p.p.m. Mo*		
	Atomic absorption spectroscopy	*Spectrographic*[10]	*Chemical*[10]
G1[a]	13.0	6	14
	(±0.7)	6	6.5
		5	6.7
		4	
		11	
		10	
		4	
		9	
		7	
		6	
		7	
		9	
W1	<0.2	5	5
		<4	0.5
			0.4
			0.5
Sulphide ore 1	4.0	10	—
	(±0.6)		

[a] The latest accepted mean value for this standard is 7.0 p.p.m.

conclusively. The sensitivity of the method for plant material is of the order of 0.1 p.p.m. using the weights mentioned previously. There is little doubt that this limit of detection could be improved by increasing the initial sample weight. The detection limit of 0.1 p.p.m., however, is probably sufficient to meet the requirements of most plant chemists.

Table VIII shows the values obtained with 3 standard rock samples. It is interesting to note that relatively few values are available for molybdenum for the much analysed G1 and W1. Comparison values[10] show a marked spread, but atomic absorption values are well within the order of magnitude of values obtained by other methods.

The limit of detection for silicate samples is about 1 p.p.m. This limit could probably also be improved by the use of larger sample weights.

CONCLUSION

The methods developed appear to be satisfactory from the point of view of accuracy and precision. Although the chemical steps are time-consuming, many samples can be analysed daily. The method appears to be at least as rapid and accurate as any other method at present in use.

The authors are indebted to Mrs. D. B. DE VILLIERS for help with the manuscript.

SUMMARY

A procedure is described for the determination of trace quantities of molyb-

denum by atomic absorption spectroscopy. Molybdenum is complexed with ammonium pyrollidine dithiocarbamate or 8-hydroxyquinoline and extracted into *n*-amyl methyl ketone. Molybdenum is then determined by atomic absorption spectroscopy. Interferences have been eliminated and detection limits of 0.002 p.p.m. for water samples, 0.1 p.p.m. for samples of dried plant material, and 1 p.p.m. for silicate rock samples have been obtained.

RÉSUMÉ

Un procédé est décrit pour le dosage de traces de molybdène par spectroscopie par absorption atomique. Le molybdène est complexé au moyen de pyrollidine dithiocarbamate d'ammonium ou d'hydroxy-8-quinoléine et extrait dans la *n*-amylméthylcétone. On procède ensuite au dosage par spectroscopie par absorption atomique. Limites de détection: 0.002 p.p.m. pour eaux, 0.1 p.p.m. pour des échantillons de plantes séchées et 1 p.p.m. pour des échantillons de silicates.

ZUSAMMENFASSUNG

Es wird ein Verfahren für die Bestimmung von Spuren Molybdän mit der Flammenabsorptionsspektroskopie beschrieben. Das Molybdän wird mit Ammoniumpyrollidindithiocarbamat oder 8-Hydroxychinolin komplexiert und mit N-Amylmethylketon extrahiert. Molybdän wird dann mit der Flammenabsorptionsspektroskopie bestimmt. Störungen konnten eliminiert werden. Es wurden Nachweisgrenzen von 0.002 p.p.m. für Wasserproben, 0.1 p.p.m. in getrocknetem Pflanzenmaterial und 1 p.p.m. in Silikatgesteinen erhalten.

REFERENCES

1 D. J. DAVID, *Analyst*, 86 (1961) 730.
2 H. MALISSA AND E. SCHÖFFMANN, *Mikrochim. Acta*, 1 (1955) 187.
3 R. L. MITCHELL AND R. O. SCOTT, *J. Soc. Chem. Ind.*, 66 (1947) 330.
4 J. B. WILLIS, *Anal. Chem.*, 34 (1962) 614.
5 J. E. ALLAN, *Spectrochim. Acta*, 17 (1961) 459.
6 J. E. ALLAN, *Spectrochim. Acta*, 17 (1961) 467.
7 J. W. ROBINSON, *Anal. Chim. Acta*, 23 (1960) 479.
8 L. R. P. BUTLER, *J. S. African Inst. Mining Met.*, 62 (1962) 786.
9 M. H. JENKINS AND J. A. V. WEBB, *Analyst*, 75 (1950) 481.
10 R. E. STEVENS AND OTHERS, *Second Report on a Co-operative Investigation of the Composition of Two Silicate Rocks*, Geological Survey Bulletin 1113, U.S. Govt. Printing Office, Washington, 1960, p. 130.

A BROAD-FLAME BURNER FOR THE PERKIN-ELMER ATOMIC ABSORPTION SPECTROMETERS

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ABSTRACT

A water-cooled, flat-top burner for atomic absorption, that produces a broad flame through holes instead of slots, is described. The burner is suitable for acetylene and air or propane-butane and air. It allows the use of a softer flame without instability or danger of flash-back, and yields higher sensitivities, increased precision, and lower detection limits for several elements, including sodium, potassium, rubidium, cesium, zinc, copper, gold, silver, and manganese.

RÉSUMÉ

Description d'un brûleur refroidi a l'eau pour absorption atomique comportant un plat percé de trous au lieu de fentes à la partie supérieure et produisant une flamme large. Ce brûleur convient aux mélanges air-acetylène et air-propane-butane. Il permet l'emploi d'une flamme plus douce sans instabilité ou danger de retour de flamme, donne de meilleures sensibilités, une plus grande précision et des limites de détection plus basses pour plusieurs éléments y compris le sodium, le potassium, le rubidium, le cesium, le zinc, le cuivre, l'or, l'argent et le manganèse.

ZUSAMMENFASSUNG

Ein Brenner mit Wasserkühlung und einer flachen Oberfläche, der eine breite Flamme durch Löcher anstatt Schlitzen erzeugt, wird beschrieben. Der Brenner ist für Azetylen, Propan, oder Butan mit Luft brauchbar. Er erlaubt die Benutzung einer weicheren Flamme ohne Schwankung oder Rückschlagsgefahr, und ergibt höhere Empfindlichkeit, bessere Genauigkeit, und niedrigere Nachweisgrenzen für mehrere Elemente, darunter Natrium, Kalium, Cäsium, Zink, Kupfer, Gold, Silber, und Mangan.

INTRODUCTION

Analysts making use of atomic absorption spectroscopy are generally aware that the various elements require differing flame conditions to attain maximum sensitivity (1) or freedom from chemical interferences. For this reason several manufacturers of atomic absorption equipment offer a range of burners capable of burning various gas mixtures. Probably because of manufacturing ease and cost, slot-type burners are usually made, the slot width and burner rigidity depending on the gas mixture to be burnt. For example, the burner offered by Perkin-Elmer for acetylene and nitrous oxide is a rigid casting with thick stainless-steel jaws to prevent distortion of the narrow slot at high temperatures.

Slot burners provide relatively long, thin, laminar flames, in which the various flame zones are clearly defined and controllable. This is ideal for the determination of certain elements such as molybdenum or lithium (2), where absorption is confined to a critical zone in the flame. For some elements, notably the other alkali metals and zinc, low-temperature, low-velocity (soft) flames give higher sensitivities than do hard, high-temperature flames. However, soft flames are susceptible to even slight room air movements, and if the light beam utilizes most or all of the flame area, flame fluctuations may cause severe absorption noise and so limit sensitivity (3) and precision.

A flat-top burner capable of burning mixtures of acetylene and air or propane-butane and air has been built, which gives higher sensitivity for a number of elements and which may be exchanged quickly and easily with the conventional Perkin-Elmer burners. This burner has been used successfully for a number of years and is based on a previous design (4).

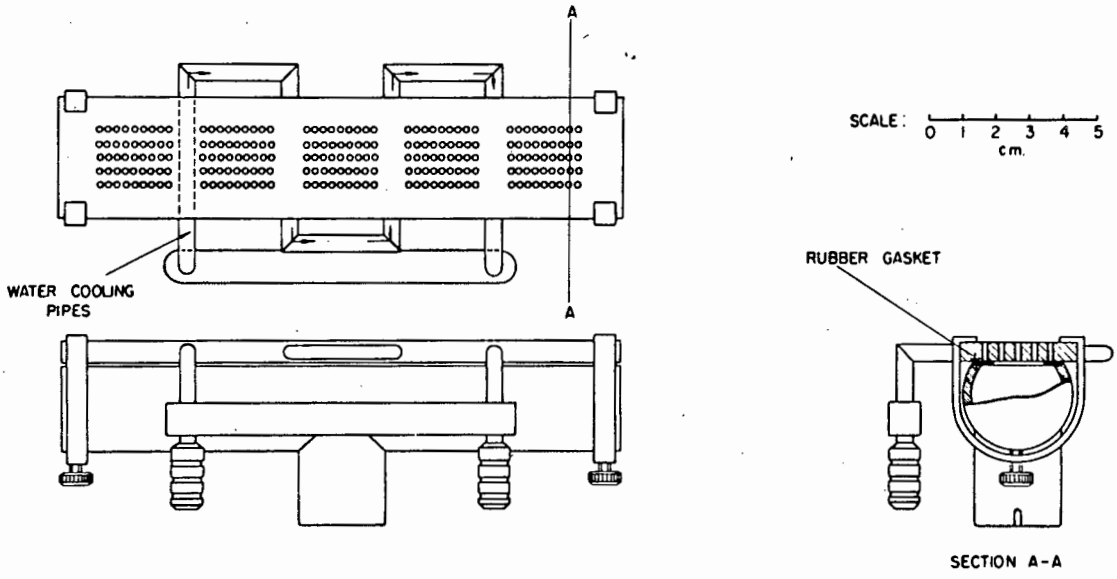

Fig. 1 – Diagram of broad-flame burner.

CONSTRUCTION

A diagram of the burner is shown in Figure 1. The burner body is made from stainless-steel tubing of the same diameter as in the conventional Perkin-Elmer burner. The burner top is a flat, 1/4-inch-thick stainless-steel plate with holes 1.1 to 1.5 mm in diameter (depending on the fuel gas used) drilled through it according to the pattern shown. Aluminum plates have also been used, but these tend to corrode when highly acidic solutions are sprayed. Holes of a larger diameter are drilled transversely between the banks of small holes, and pipes are attached by soldering or glueing to provide water cooling. This is necessary, as this type of burner becomes very hot. By adjusting the water flow through the burner so as to keep it moderately warm, little or no condensation of the aerosol will occur on the underside of the burner plate. The burner plate is held down onto the body with clamps as shown, care being taken not to obstruct the light beam across the burner top. A thin silicone or "Gayco" rubber gasket provides a seal between burner top and body.

Blow-out plugs may be provided on the ends, although this has never been found necessary. As with any burner, the normal lighting and extinguishing procedures should be followed to reduce the chances of flashback, the fuel gas always being turned on last and off first.

Although designed primarily for burning propane-butane as fuel gas, the burner works well with acetylene. However, care should be taken not to allow the flame to become too soft, as flashback may then occur. Smaller-diameter holes (about 1.1 mm) reduce the chance of this happening with acetylene.

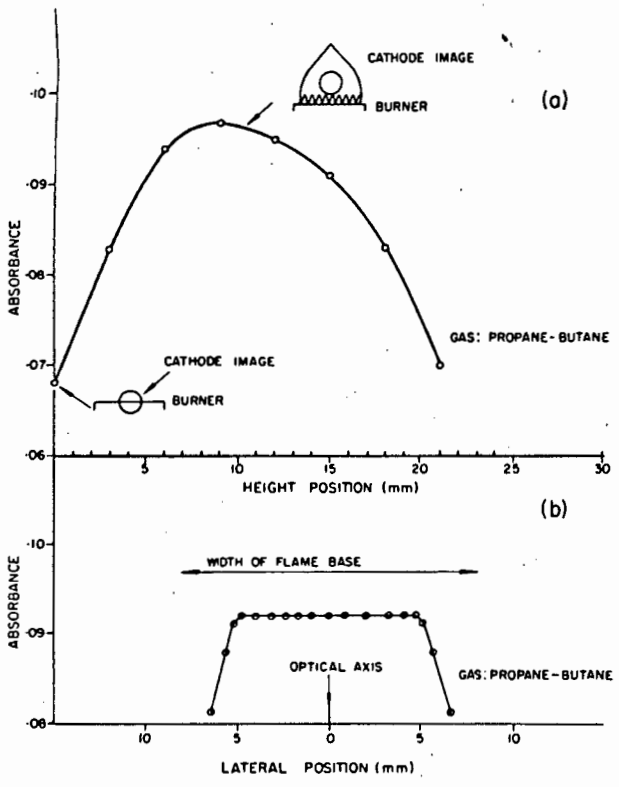

Fig. 2 – The change of absorbance for 1 ppm potassium with flame height (a) and horizontal flame position (b). Best absorbance takes place directly above the blue-green cones.

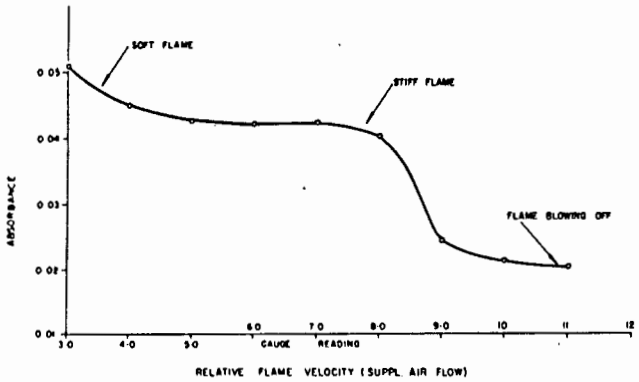

Fig. 3 – The change of potassium absorbance with air flow (taken as a measure of flame stiffness). An atomizing pressure of 30 psi was used. The supply of fuel gas was adjusted to give the same type of flame for each reading.

PERFORMANCE

The flame obtained from this burner is broad enough to more than fully utilize the full light beam, which converges to the image point near the center of the flame and then diverges again on both the Models 303 and 290. Because of this and because of the nature of the flame, vertical and horizontal positioning of the burner is not critical. Figure 2 shows the change of potassium absorbance with horizontal and vertical adjustment.

The gas and air mixture is normally adjusted so that the flame burns to give small blue-green cones about 2 mm high above each hole. The secondary combustion regions of these flames tend to flow together, particularly along the center of the burner, the effect being accentuated under fuel-rich conditions. This region down the center of the burner has a relatively uniform temperature (from thermocouple temperature measurements) and probably has a low oxygen content because of the lack of secondary entrainable air. The outer surface of the flame presents the normal flame appearance.

An important feature of this burner is that with propane-butane a very soft flame can be obtained, without the danger of flashback, which gives remarkably stable absorption readings. Figure 3 shows how the sensitivity for potassium decreases with increasing flame velocity (or "stiffness"). For these measurements, the supplementary air supplied was taken as a relative measure of flame velocity, the fuel gas being adjusted in each case to give the same type of flame (blue-green cones). The atomizing air pressure was maintained at 30 psi.

One probable reason for the increase in sensitivity is that the dwelling time for neutral atoms in the optical path is greater, and thus also the absorption probability.

SENSITIVITY

Analytical curves were drawn for a number of elements with the use of both the Perkin-Elmer standard slot acetylene-air burner and the broad-flame burner with propane-butane-air and acetylene-air. The steepness of the curves may be taken as a measure of sensitivity. Figure 4 shows that the sensitivities for potassium and zinc are better with the low-temperature propane-butane flame. Sodium, cesium, rubidium, gold, silver, and manganese behave similarly. The broad-flame burner using acetylene is also more sensitive for these elements than is the slot-type burner (with

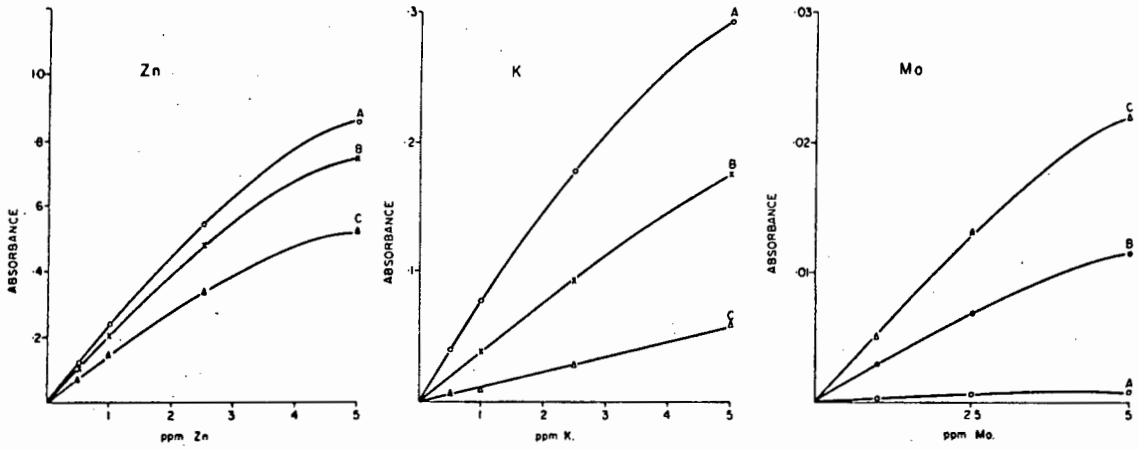

Fig. 4 – Working curves for zinc, potassium, and molybdenum with (A) the broad-flame burner and a propane-butane air mixture; (B) the broad-flame burner and an acetylene air mixture; and (C) the Perkin-Elmer slot burner and an acetylene air mixture.

acetylene). This is probably due to the more efficient utilization of the light beam, as with the three-slot Boling burner (5).

Figure 4 shows that for molybdenum, the slot burner gives far higher sensitivity, because this element has a critical region in the flame where absorption takes place (5). This would also be the case for other elements such as chromium, lithium, etc., where absorption is critically dependent on the flame region. Obviously the broad-flame burner is not suited for these elements.

Table I gives sensitivities for some elements tested with this burner. It should be noted that although these are given in the conventional way (ppm to register 1% absorption), much lower absorption can be measured because of the stability of the readings.

TABLE I

Some Sensitivities Obtained with the Broad-Flame Burner, Burning a Propane-Butane Air Mixture

Element	*ppm for 1% Absorption**
Na	0.007
K	0.011
Rb (discharge lamp)	0.03
Cs	0.2
Zn	0.01
Cu	0.005
Au	0.05
Ag	0.05
Mn	0.05

* The atomizing air pressure was set to give optimum absorption, viz. 28 psi. The best absorption for most of these elements occurred just above the primary combustion zone of the flame.

INTERFERENCES

As this burner is used mainly for the determination of the alkali metals in geological samples, the investigation of interferences has been limited to other alkalis, alkaline earths in considerably higher concentrations, iron and aluminum, and anions, using propane-butane as the fuel gas.

It was found that the enhancing effects which some alkali metals have on one another were very much reduced in the cooler propane-butane air flame. The depressing effect of calcium, and to a lesser extent magnesium, on potassium and sodium absorption was slightly greater. Interference by iron depression was also slightly greater than with the acetylene air flame.

Anions (nitrates and chlorides) had no effect on absorption, nor did aluminum.

CONCLUSION

The interference effects noted are in keeping with the findings of other workers, and it is doubtful whether burner design will have much effect on chemical interferences inherent in a flame, providing these effects are not dependent on a particular flame region. However, the burner described has enabled the determination of far lower concentrations of those elements requiring a low-temperature flame, with a greater degree of precision than is possible with conventional slot burners.

Higher absorption can be obtained for several elements when acetylene is burned as fuel in the broad-flame burner than in a slot burner. The flame from this burner is broad enough to intercept the full light beam.

Although the broad-flame burner is probably not universally as acceptable as the less expensive slot burner, it may nevertheless be of use to those analysts who are working near the detection limit in the determination of certain elements and who would appreciate more sensitivity and reading precision.

BIBLIOGRAPHY

1. B. M. Gatehouse and J. B. Willis, Spectrochim. Acta **17**, 710 (1961).
2. L. R. P. Butler and L. H. Ahrens, The Determination of Lithium in Geological Samples (to be published).
3. W. Slavin, S. Sprague, and D. C. Manning, Atomic Absorption Newsletter No. 18, Feb. 1964.
4. L. R. P. Butler, S. A. Min. and Met. **62**, 786 (1962).
5. S. Sprague and W. Slavin, Atomic Absorption Newsletter 4, 293 (1965).

Table 3. Analysis of brass

Sample	Values							
	Lead		Nickel		Iron		Zinc	
	At. abs.	Chem.	At. abs.	Chem.	At. abs.	Chem.	At. abs.	Chem.
NBS 124b	4·65	4·64	0·76	0·75	0·261	0·260	5·39	5·39
NBS 37d	0·95	0·94	0·58	0·58	0·076	0·076	26·70	26·65
BCS 183	1·85	1·83	0·041	0·040	0·072	0·070	1·88	1·86
Phosphor no. 1 Bronze	0·16	0·15	0·95	0·93	—	—	0·12	0·10
Phosphor no. 2 Bronze	0·11	0·11	0·10	0·11	—	—	0·032	0·030
60/40 Brass	0·11	0·10	0·10	0·10	0·76	0·75	37·5	37·3*

* Zinc determined by difference.

certain circumstances, the improvement of precision, would make it particularly useful in a routine or semi-routine laboratory. There are still many problems to be solved and it is more than likely that each analytical problem would have to be investigated individually.

Some of the problems which have been encountered during the investigations can be summarised as follows:

Lamps. The success of the multiple ring cathodes for the simultaneous determination of a number of elements by atomic absorption, is unfortunately hampered by the choice of metals which can be used in combination. The tandem system often requires that the relative change in intensities from separate lamps be compensated for by periodic adjustment of detector sensitivity, especially soon after switching on. The change of emission intensity from the different elements in a ring cathode is generally far less, and only small periodic adjustments to detector sensitivities are required.

Flames. Different elements often require different flame conditions for optimum absorption. This is especially the case with highly refractory elements where fuel-rich conditions are preferred. The height above the burner at which maximum absorption occurs is also often critical [10]. With the upper-lower system of exit slit mounting this was carefully investigated, but although the degree of absorption was sometimes different for upper and lower channels, it was reproducible. The channels could usually be arranged to suit the analytical conditions.

Widely differing concentrations of elements. When several elements with widely differing concentrations or absorptions are analysed, it is often difficult to arrange conditions to obviate the preparations of two or more dilutions of the sample. Less sensitive absorption lines [11] may be used where possible, but the choice is often limited. Another useful means of attenuating sensitivity is to change the

[10] D. J. David, *Analyst* **86,** 730 (1961).
[11] B. M. Gatehouse, and J. Willis, *Spectrochim. Acta* **17,** 710 (1961).

burner path length. A rather unorthodox method sometimes used to reduce sensitivity is to adjust the exit slit slightly off the peak of the spectral line. This method is, however, not generally recommended.

Spectrometer. In spite of the ability to measure four spectral lines simultaneously, it would have been convenient in some cases to measure five or six. For this reason a six tube version of the attachment has been designed.* The close proximity of the lines in the 3300 Å vicinity sometimes presented some difficulty. It was generally possible to arrange experimental conditions to suit the problem in hand.

The work on the simultaneous determination of several elements by atomic absorption is being continued and it is hoped that a further report on this work will be published in the near future.

Acknowledgement—The authors would like to record their thanks and appreciation to Mr. R. L. CARR for his efforts and ingenuity in the development of the four tube direct reading attachment, to Mr. T. J. DE WET and Mrs. E. C. FEAST for technical assistance and to Mrs. D. B. DE VILLIERS for help with the manuscript.

* Commercially available from Hilger and Watts, London.

THE DETERMINATION OF COPPER BY MEANS OF ATOMIC ABSORPTION SPECTROSCOPY*

by

A. STRASHEIM, F. W. E. STRELOW and L. R. P. BUTLER.

OPSOMMING

Die bepaling van koper in ertse, konsentrate en in ertsafal met behulp van atoomabsorpsie, word beskryf. 'n Vinnige ekstraksieprosedure om die kopererts ens. in oplossing te bring, met behulp van gemengde sure, maak die metode geskik vir produksiekontrole. Vir koperkonsentrasies wat varieer van 0·18 tot 24% is die noukeurigheid van die metode beter as 7%.

SUMMARY

The determination of copper in ores, concentrates and tailings by means of atomic absorption, is described. A rapid extraction procedure to bring the copper ores etc. into solution, using acid mixtures, allows the method to be used for production control. The accuracy of the method is better than 7% for copper concentrations varying from 0·18 to 24%.

INTRODUCTION

The use of atomic absorption spectroscopy for analytical purposes was revived by Walsh[1] and furthered by Russell, Shelton and Walsh.[2] Other authors[3,4] have since been equally successful in developing analytical methods based on this principle. Atomic absorption spectroscopy, when used for analytical purposes, has certain advantages over other methods, viz.:

(*a*) It can be used for absolute determinations.[1]

(b) It does not require standards in the same physical condition, but does require that samples and standards should be in solution.

(c) It is not affected by self reversal or self absorption.

(d) The very stable hollow cathode excitation gives good accuracy.

These advantages suggested its use as a routine method for the analysis of copper in sulphide or silicate ores. Methods have been described for the estimation of copper by emission flame-photometry,[5] but they have the inherent difficulties experienced with this type of analysis. In this paper a method is discussed for using atomic absorption spectroscopy for determining copper in solutions prepared from ores, concentrates or tailings.

EXPERIMENTAL

Apparatus. A Hilger and Watts Uvispek spectrometer together with atomic absorption attachments, was used.

The jet in the water-cooled burner was replaced by one having a 0·027 inch diameter hole to enable it to be used with Handigas fuel. It was found that if tap water was used to cool the burner, this became too cool and vapour condensed on the lower face, causing contamination and less efficient vaporisation. These difficulties were overcome by circulating water from a 5 litre reservoir through the burner top

*A paper read in Stellenbosch at the Fourteenth Annual Convention of the S.A. Chemical Institute on February 11, 1960.

by means of a Stuart-Turner centrifuge pump. During use, the temperature of the water rose to approximately 60°C and then remained constant. The burner was positioned approximately $\frac{3}{4}$ inch below the optical axis. This position was found by adjustment of the burner height to obtain maximum absorption.

The performance of the spectrometer was appreciably improved by stabilising the mains supply to the hollow cathode and Uvispek power supplies with a Wandel and Golterman voltage stabiliser.

Principle of the method. The principle of the method has been fully described by Walsh and others [1, 2, 3, 4] and will only be briefly mentioned here. The light from the cathode passes through the flame into the spectrometer which is set at the wavelength of one of the resonant lines of copper, viz. 3247Å. If now a solution containing copper is sprayed into the flame, sufficient heat is available to break up the solution into an atomic vapour. A large number of free neutral copper atoms will then be present in and around the flame mantle. These atoms absorb the characteristic radiation of copper coming from the hollow cathode lamp, and the spectrometer measures the decrease in light intensity at this resonant wavelength.

General analytical procedure. In the atomic absorption method using the Uvispek spectrometer the analytical results are based on single absorption measurements. Constancy of the apparatus is, therefore, a stringent prerequisite. New analysis curves must thus be prepared when the instrument has to be used for a new analysis or a new series of analyses and standard solutions have also regularly to be sprayed into the flame to check the instrument. Readily available material for standards, which can easily be prepared, is thus a necessity. A primary standard solution for the preparation of the analytical curves and for checking the instrument was prepared by dissolving a weighed quantity of specpure copper in warm dilute hydrochloric acid. This solution was made up to volume to give a standard stock solution containing 1000 p.p.m. of copper. Further standards were prepared by dilution from this stock solution.

The general analytical procedure was as follows: After allowing sufficient time for the instrument to warm up, a series of standards was sprayed through the flame, the different density readings recorded and the analytical curve prepared (a typical curve is illustrated in Fig. 1). The solutions containing the unknown amounts of copper were then sprayed into the flame, the density readings recorded and the unknown concentration values read from the analytical curve.

It was found unnecessary to rinse the spray chamber after each solution, as fresh solution removed contamination within a few seconds.

The operating data of the instrument are given in Table I. The settings were found by adjusting all components to optimum conditions.

TABLE I

Standard analytical conditions

Element line	Cu 3247 Å
Slit	0·20 mm
Meter sensitivity setting	6
Air pressure	20 lb/sq inch
Handigas pressure	0·75 lb/sq inch
Sample consumption	20 ml/min
Anode current of hollow cathode	40 mA

(*a*) *Factors affecting atomic absorption results.*

(i) *Influence of gas and air pressures.* The temperature of the flame is not very dependent on the air pressures applied to the atomiser (varying from 15 to 30 lb per

square inch). For air pressures above 30 lb per square inch the angle of the curve is lowered as is illustrated for a pressure of 35 lb per square inch in Fig. 2. Although 30 lb per square inch gave the steepest curve, a pressure of 20 lb per square inch was chosen as standard operating condition, because of the lower rate of sample consumption and the more reproducible results. The curves illustrated in Fig. 2 also indicate that low concentrations of copper are less affected by changes in pressure. This fact should be borne in mind when doing routine analysis. These results also suggest the use of two dilutions when determining unknown samples. In this way a check can be achieved on the results.

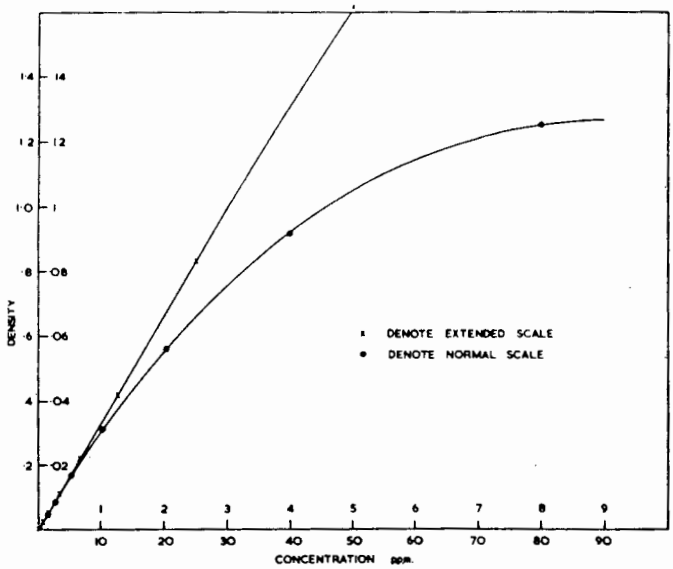

Fig. 1—Typical analytical curve

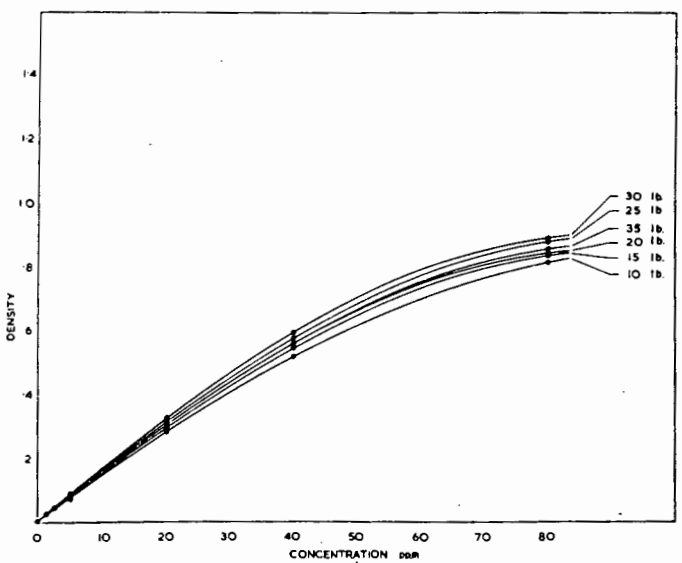

Fig. 2—Influence of air pressure on analytical curve

In contrast to flame-photometric spectroscopy[6,7] where high temperatures are now preferred, the temperature of an atomic absorption unit should only be sufficient to vaporise the sample and dissociate the molecules into neutral atoms. When the gas pressure to the burner is changed from 0·25 to 1 lb per square inch, the total variation possible, the temperature increases from 950 to 1390°C. As no difference in the evaporation or dissociation of the copper molecules could be detected with variation in gas pressure, 0·75 lb. per square inch was chosen as the standard analytical condition.

(*ii*) *Influence of anode current of hollow cathode lamp on analytical curve.* Fig. 3 shows the effect of the anode current of the hollow cathode lamp on the analytical curve. The lower the anode current, the steeper and the more linear the analytical curve becomes. A decrease in the anode current results in a decrease in the cathode temperature. Under these conditions the copper line is narrowed and more effective absorption of the copper resonant radiation can be expected, as absorption occurs in a very narrow band of wavelengths.

The line intensity of the hollow cathode lamp is unfortunately related to the anode current and the sensitivity of the spectrometer limits the use of anode currents which are too low. These findings are in agreement with those of Allan.[3]

(iii) *Influence of extraneous elements and acids.* One of the drawbacks of flame-spectroscopy is that chemical combinations occur in the solution and in the flame. This prevents the atoms from coming into the flame in a free neutral form. In order to test the influence of extraneous elements, a series of solutions was prepared containing varying concentrations of Ca, Na, Fe, K, Al and Co, the elements most likely to occur as impurities in copper ores and associated materials. The influence of acids was also tested and the results in Table II show that no influence could be detected.

(b) *Procedure for the analysis of copper ores.* The success of an analytical method when used for production control generally depends on the "lapse of time" before results become available. A rapid extraction procedure to bring the copper ores etc. into solution was thus sought. Various methods of dissolving the samples were tried. The most successful acid mixtures to dissolve a 0·5 gram sample were, in order of merit:

(i) 10 ml 40% HF + 10 ml conc. HNO_3,

(ii) 10 ml conc. H_2SO_4 + 10 ml conc. HNO_3 and

(iii) 10 ml conc. HCl + 10 ml conc. HNO_3

The general extraction procedure is as follows: The samples are weighed and transferred to platinum crucibles. After adding the HF-HNO_3 mixture, the crucibles are heated on a hot plate. The solution is then transferred to a 200 ml volumetric flask and made up to volume. This solution is filtered, the first 20-30 ml discarded and the next 20-30 ml used for the analysis. If the copper content of this solution is too high, the necessary dilutions are made.

With some flotation samples a little black carbonaceous or sulphurous matter remained undissolved after the acid treatment. The amount of copper present in this residue was found to be negligible.

To determine the optimum extraction time, three samples containing 19·6, 27·5 and 30·64% copper were digested for varying times. The copper concentrations in the extracted solutions were then determined using the atomic absorption procedure. These results are shown in Table III. From these results it is evident that:

(i) for full extraction a digestion time of about 40-60 minutes is required,

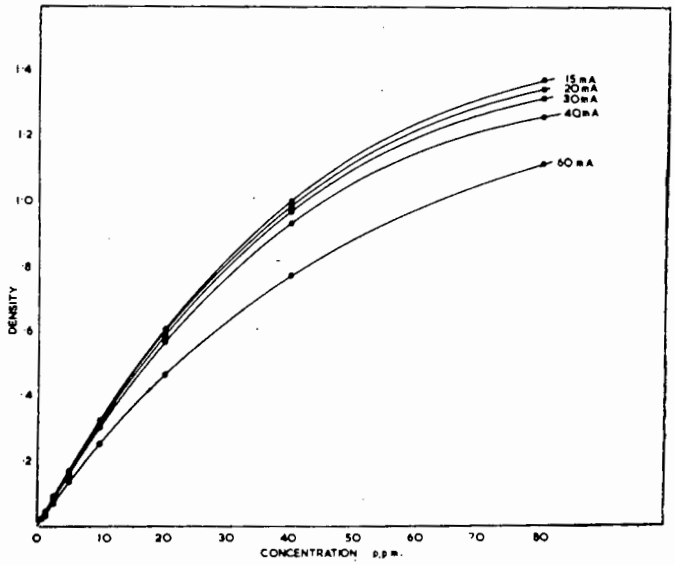

Fig. 3—Influence of anode current of hollow cathode lamp on analytical curve

TABLE II

Influence of other elements and acid radicals on results

Extraneous element or acid present in solution	Concentration present	Cu detected by atomic absorption, p.p.m.
Ca	0 p.p.m.	1·48
	1000 ,,	1·46
	10000 ,,	1·45
Na	0 ,,	2·5
	1000 ,,	2·5
	10000 ,,	2·4
Fe	0 ,,	1·57
	500 ,,	1·55
	5000 ,,	1·56
K	0 ,,	1·03
	1000 ,,	0·91
	10000 ,,	0·95
Al	0 ,,	1·25
	5000 ,,	1·26
	10000 ,,	1·26
Co	0 ,,	1·25
	5000 ,,	1·25
	10000 ,,	1·25
H_2SO_4	No H_2SO_4	4·10
	0·01 N	4·16
	0·1 N	4·14
	1·0 N	4·14
HCl	No HCl	1·10
	0·01 N	1·10
	0·1 N	1·08
	1·0 N	1·11

(ii) for routine use of the method an extraction time of 20 minutes may suffice, if relative standards are used for the preparation of the analysis curves.

In the latter case, normal routine samples of known copper content can be used as standards. The advantage of this method is that the standards and unknown samples are subjected to the same chemical treatment.

TABLE III

Influence of extraction time on analytical values.

Samples	Concentration of Cu based on mine chemical values for ores, % Cu	Extraction time for atomic absorption, (min)	Atomic absorption values, % Cu	% Difference between chemical and atomic absorption values
426	19·6	5	15·5	—21·1
3677	27·5		13	—52·9
3685	30·64		22·8	—25·5
				Average —32·2
426	19·6	10	17·5	—10·9
3677	27·5		25	— 9·1
3685	30·64		27·44	—10·5
				Average —10·2
426	19·6	20	18·5	— 5·7
3677	27·5		26·1	— 5·2
3685	30·64		28·54	— 6·7
				Average — 5·9
426	19·6	40	19·4	— 1·02
3677	27·5		25·7	— 6·71
3685	30·64		29·14	— 4·88
				Average — 4·20
426	19·6	Treatment A	19·6	— 0·135
3677	27·5	60	26·6	— 3·27
3685	30·64		29·5	— 3·83
				Average — 2·41
426	19·6	Treatment B	18·3	— 6·39
3677	27·5	60	27·9	+ 1·35
3685	30·64		30·38	— 0·84
				Average — 1·9

Treatment A: Ores dissolved directly and treated for 60 min.
Treatment B: Ores ignited first in porcelain crucible then treated as in A.

RESULTS

From the analytical curve illustrated in Fig. 1, it is evident that the linear portion of the curve extends to approximately 30 p.p.m. of copper. Above this value accurate results are still obtainable, but as concentrations become higher, they become less reproducible. The lower limits of analysis are limited by statistical fluctuations inherent in the apparatus.

From Table IV it can be seen that a concentration of 0·1 p.p.m. of copper can be detected. At this concentration the coefficient of variation is, however, above 10%. From 1 to 50 p.p.m. the average coefficient of variation is 1·76%, while at about 100 p.p.m. this value increases to about 3%.

TABLE IV

The change of coefficient of variation with different concentrations of copper solution

Concentration of Cu in solution, p.p.m.	Coefficient of variation on 5 repeat analyses
0·106	11·8 %
0·128	14·3 %
0·182	10·1 %
0·32	8·4 %
0·44	9·7 %
0·68	5·7 %
1·19	3·80%
1·88	2·31%
2·4	1·16%
2·6	2·60%
3·3	1·20%
4·5	1·69%
9·5	0·80%
19·03	1·40%
38·0	1·07%
47·8	2·59%
96·94	2·91%

When analysing solutions with high copper concentrations, dilutions have to be made. Personal error in measurement is magnified under these circumstances. Very concentrated solutions should also be avoided as these gave consistently low readings. This is probably due to poor spraying in the atomiser.[7]

The day to day reproducibility of the analytical curve is good, provided that all components are adjusted to optimum conditions.

Information in connection with the accuracy of the method may be gained from the results tabulated in Tables V, VI and VII. The chemical values are based on results of a standard chemical method[8] using the iodide-thiosulphate titration with starch as indicator. From these results the following may be concluded:

(i) Using a 20-minute extraction procedure and relative standards, copper concentrations in ores can be determined with an accuracy of 5·3%. This accuracy seems satisfactory when compared with the results obtained by the two chemical methods.

(ii) Using absolute standards, low values are recorded for high copper concentrations. The X-ray fluorescent method, however, gives results which are in agreement with the atomic absorption results. The accuracy of the method under these conditions is $\pm 6{\cdot}2\%$ for copper concentrations varying from 0·18% to 24% copper.

(iii) The atomic absorption method seems especially suitable for the determination of copper in ores with concentrations varying from 0·1% to 5% when absolute standards are used. With proper extraction techniques, the results given in Table VII seem to indicate that with the use of relative standards, copper concentrations as high as 25% can very satisfactorily be determined.

(iv) The chemical method as used at the mines seems unreliable for low copper concentrations.

TABLE V

Comparison of chemical analysis of ores and atomic absorption analysis of solutions obtained with 20 minute extraction using relative standards. Results given in percentage copper

Sample No.	C.S.I.R. chemical values	Atomic absorption values (rel. stds)	Percentage difference between chemical and atomic absorption values
1	24·18	24·18	0
2	19·58	19·58	0
3	9·58	8·81	— 8·04
4	4·16	4·42	+ 6·25
5	4·12	4·00	+ 2·91
6	3·34	3·67	+ 9·88
7	2·70	2·80	+ 3·70
8	2·38	2·30	— 3·36
9	1·95	1·95	0
10	0·81	0·76	— 6·17
11	0·54	0·595	+10·19
12	0·37	0·35	— 5·41
13	0·26	0·285	+ 9·62
14	0·21	0·20	— 4·76
15	0·18	0·17	— 5·56

Percentage standard deviation = 5·28

TABLE VI

*Comparison of results obtained with different analytical methods. All atomic absorption results were obtained with the use of absolute standards. Results are given in percentage copper. Values marked * were not included in the calculation of standard deviation*

Extraction time	Atomic absorption values		X-Ray fluorescence values	C.S.I.R. chemical values	Mines chemical values	Percentage difference of 40 min. extraction atomic absorption values from C.S.I.R. chemical values	Percentage difference between C.S.I.R. and Mines chemical values
	20 min	40 min	40 min				
Sample No.							
1	22·6	23·78	22·81	24·18	24·69	— 1·65	— 2·11
2	18·1	18·43	18·0	19·58	19·77	— 5·87	— 0·97
3	7·63	9·06	9·48	9·58	9·57	— 5·43	+ 0·10
4	3·59	3·95	3·5	4·16	4·15	— 5·05	+ 0·24
5	3·97	4·01		4·12	3·99	— 2·67	+ 3·16
6	3·40	3·25		3·34	3·19	— 2·69	+ 4·49
7	2·59	2·57		2·70	2·6	— 4·81	+ 3·70
8	2·12	2·15		2·38	2·35	— 9·66	+ 1·26
9	1·87	1·82		1·95	1·86	— 6·67	+ 4·62
10	0·773	0·83		0·81	0·84	+ 2·47	— 3·70
11	0·564	0·60		0·54	0·69	+11·11	—27·78*
12	0·339	0·35		0·37	0·45	— 5·41	—24·32*
13	0·262	0·25		0·26	0·35	— 3·85	—34·62*
14	0·206	0·23		0·21	0·22	+ 9·52	— 4·76
15	0·177	0·186		0·18	0·19	+ 3·33	— 5·55
			Percentage standard deviation			6·23	3·56

TABLE VII

Comparison of results obtained by chemical analysis with those from atomic absorption using a standard chemical extraction method[8]

Sample	Chemical values	Atomic absorption values	% Difference
1	24·18	23·4	—3·23
2	19·58	18·6	—5·01
3	9·58	9·22	—3·76
4	4·16	3·99	—4·09
5	4·12	3·94	—4·37

Percentage standard deviation =4·62%

CONCLUSION

It is evident from the results given in this paper that atomic absorption spectroscopy provides a relatively quick method for the analysis of copper in solutions and in materials containing copper that can be brought into solution. Analysis of copper ores, concentrates and tailings can be done satisfactorily for production control using a 20-minute extraction.* For accurate analytical results, atomic absorption measurements at two different concentration values are recommended. Satisfactory results were also obtained using the Zeiss spectrometer with the Hilger Atomic Absorption Attachment.

Thanks are due to Messrs. Hilger and Watts for the loan of the Uvispek spectrometer, to Misses M. C. Maskew and R. E. Rethemeyer, Mrs. C. J. C. Bothma and Messrs. E. J. de Villiers and R. P. M. Procter, of this Laboratory, for technical assistance; to Dr. A. J. Rossouw, of Rand Mines, Ltd. for his help with the X-ray fluorescence results and to Dr. J. N. van Niekerk, of this Laboratory, for the ore samples.

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South African Council for Scientific and Industrial Research,
Pretoria. *Received February* 11, 1960.

REFERENCES

[1] Walsh, *Spectrochim. Acta*, 1955, **7**, 108.
[2] Russel, Shelton and Walsh, *ibid.*, 1957, **8**, 317.
[3] Allan, *Analyst*, 1958, **83**, 466.
[4] David, *ibid.*, 1958, **83**, 655.
[5] Dean, *Anal, Chem.*, 1955, **27**, 1224.
[6] Foster and Hume, *ibid.*, 1959, **31**, 2028.
[7] Baker and Vallee, *ibid.*, 1959, **31**, 2036.
[8] Hillebrand and Lundell, *Applied Inorganic Analyses*, John Wiley and Sons, Inc., New York, Shepman and Hall, Ltd., London, 1953, p. 248.

*This extraction time may possibly be reduced by 5 minutes if the platinum crucibles are slightly embedded in a sand bath.

C.S.I.R. RE 81

A Versatile Hollow Cathode Lamp for Atomic Absorption Spectroscopy

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A Versatile Hollow Cathode Lamp for Atomic Absorption Spectroscopy

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One of the most important items of equipment necessary for atomic absorption spectroscopy (*1-3*) is the hollow cathode lamp. Of all light-sources available, it has been found to give the narrowest spectral lines with reasonable intensity, and it has the added advantage that it also provides very constant light output. Several types of hollow-cathode lamps have been developed in the past. The gas circulating system described by Tolansky (*4*) is not necessary, since sealed off hollow cathode tubes have successfully been made (*2, 5*). In these cases efficient outgassing of tubes has been achieved by the use of getters, but Walsh (*6*) has shown that, provided pure gas is used and careful outgassing of the tube is achieved, the use of a getter is not essential. Zeeman and Butler (*7*) described a lead lamp with a water cooled cathode, which could be dismantled. This lamp proved to be so successful that a similar type of lamp, using other cathodes which were not watercooled, was designed and built. In Fig. 1 a diagram of this new type of lamp is shown.

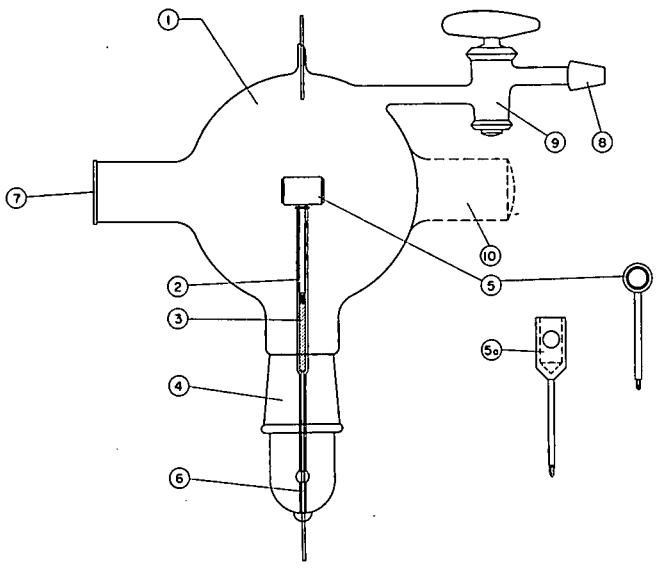

FIG. 1. DIAGRAM OF THE HOLLOW CATHODE LAMP

The body of the lamp, *1*, is a 750 ml pyrex flask. Walsh (*6*) found that the life of a lamp could be appreciably increased by using lamps with large volumes. The flask is provided with a high-vacuum tap, *9*, and joint, *8*, for connection to the vacuum system. A 34/45 joint, *4*, is connected to the neck of the flask. Another 3 cm-diam. neck is attached, onto which a quartz window, *7*, is cemented. A 1.5 mm-tungsten rod, *6*, is sealed into a 34/45 stopper to provide electrical connection to the cathode. The cathode is a cylindrically shaped metal electrode, 20.0 mm long, with an inside diam. of 9.0 mm and a wall thickness of 1.3 mm. The cathode is attached to a short rod which can be screwed onto a brass rod, *3*, which in turn is encased in a glass tube, *2*. Should the element to be investigated be suitable, the cathode can be machined directly from stock consisting of this element. In most cases however the cathode is machined from copper, and a cylindrical liner inserted into the copper cylinder, being held in position by swaging over the ends of

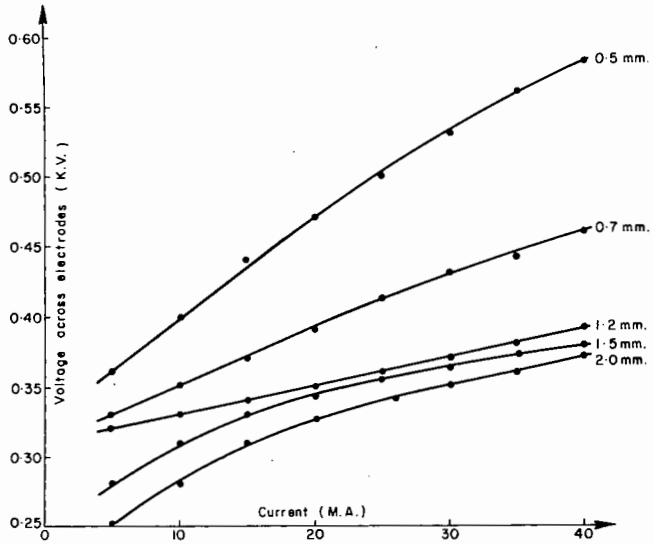

FIG. 2. INFLUENCE OF GAS PRESSURE ON VOLTAGE-CURRENT CHARACTERISTICS

the liner. In the case of metals having low melting points (e.g., Pb) a cuplike cathode, *5a*, can be used.

The lamps are evacuated by means of a simple vacuum system with a rotary pump and a two-stage mercury diffusion pump. Liquid air traps prevent mercury vapor from entering the lamps. Silicone grease is used on all ground glass joints. The lamps are degassed in much the same way as described by Walsh (6). It was also found that a getter is not necessary. The best argon gas pressure proved to be 1.2 mm Hg. The rate of sputter at this pressure is fairly high, but due to the fact that the lamps can be easily and cheaply reconditioned, and because the discharge is very stable, this pressure is used. It was found that when the gas pressure is correct, there is a linear relationship between voltage drop across the lamp, and the anode current. Figure 2 shows the voltage-current characteristics of a lamp at different gas pressures. With all the cathodes tested this linear relationship was evident, and it proved to be very useful as a means for determining the correct pressure in the lamp.

The main advantages of this type of lamp are: (a) it can be dismantled, cleaned, and the cathode reconditioned or changed very easily, and (b) a watercooled cathode can be introduced by replacing the 34/45 stopper with a watercooled metal stopper onto which the connecting rod, *3*, has been attached. In this case, mica guards are necessary to prevent sporadic discharges to the metal.

It is suggested that if more than one element has to be determined simultaneously (e.g., with direct reading spectrograph), a second projection, *10*, be made at the rear of the lamp and provided with a quartz lens instead of the quartz window. The image of the cathode of a second lamp, mounted in tandem behind the first lamp, can then be projected into the cathode of the first lamp, and both characteristic spectra then passed through the absorbing flame.

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Literature Cited

(1) A. Walsh, SPECTROCHIM. ACTA **7**, 108 (1955)
(2) B. Russell, J. P. Shelton, and A. Walsh, IBID. **8**, 317 (1957)
(3) A. C. Menzies, ANAL. CHEM. **32**, 898 (1960)
(4) S. Tolansky, *High Resolution Spectroscopy*, Methuen and Co., London, 1947
(5) G. Dieke and H. M. Crosswhite, J. OPT. SOC. AM. **42**, 933 (1952)
(6) W. G. Jones and A. Walsh, SPECTROCHIM. ACTA **16**, 249 (1960)
(7) P. B. Zeeman and L. R. P. Butler, TEGNIKON (SOUTH AFRICA) 96 (Oct. 1960)

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