AN INVESTIGATION INTO THE DETERMINATION OF SOME VOLATILE ELEMENTS IN SILICATE ROCKS EMPLOYING D.C. ARC EMISSION SPECTROSCOPY IN ARTIFICIAL ATMOSPHERES

by

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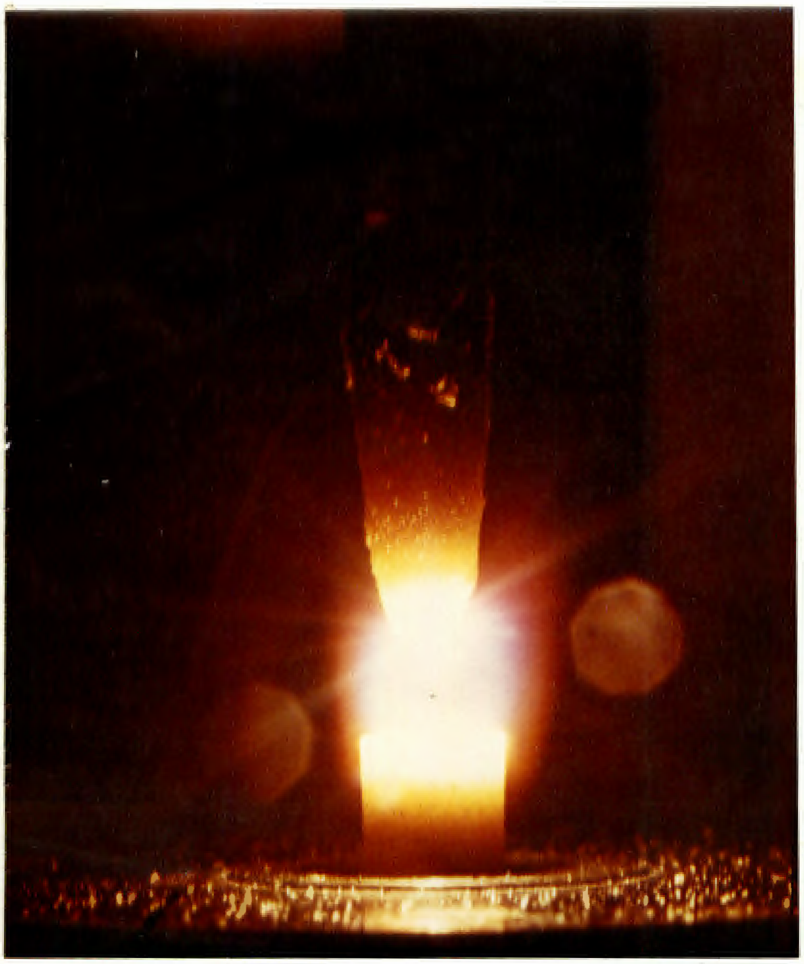

FRONTISPIECE

Photograph of a 25 amp d.c. arc burning in an atmosphere of argon and demonstrating the carrier distillation effect obtained when a carrier type electrode is employed.

VOLUME 1

ABSTRACT

The determination of 14 trace elements, namely As, Ag, Bi, Cd, Cu, Ga, Ge, Hg, In, Pb, Sb, Sn, Tl and Zn, in silicate rocks using d.c. arc optical emission spectrography (O.E.S.) and X-ray fluorescence spectroscopy (X.R.F.) was investigated.

X.R.F. was shown to be capable of determining Cu, Ga, Pb and Zn in normal silicate rocks and Sn, As and Ge in samples enriched in these latter three elements.

Improvement of the sensitivity of the trace elements selected employing d.c. arc excitation in artificial atmospheres was examined in detail.

A Margoshes and Scribner (M & S) design gas jet was constructed, and proved to have numerous advantages over those gas jets which incorporate a glass canopy.

Excitation in argon, argon-oxygen and nitrogen resulted in many advantages. The most prominent were, remarkable enhancement of the element Zn, and selective distillation of the volatile elements when the d.c. arc was surrounded by argon. The drastic reduction in electrode temperature associated with excitation in argon resulted in an unacceptable decrease in the volatilization rates of the more abundant volatile elements.

Several successful methods of overcoming these reduced volatilization rates were found. Increased amperage coupled with a special electrode design was one while the use of a small carrier electrode was another. It was also found that the carrier design electrode was most suitable for use with argon and nitrogen atmospheres as its use promoted selective distillation of the volatile elements.

The lack of improvement in volatilization characteristics through the use of additives was attributed to the dominating influence of argon on electrode temperature. The principal advantage of excitation in argon-oxygen was the suppression of CN emission essential for ultimate sensitivity of the element Tl. While excitation in nitrogen improved the volatilization characteristics of the more abundant elements, severe CN emission and increased spectral background limited the use of nitrogen to those elements with spectral lines not affected by CN emission.

Detailed moving plate experiments indicated that the group of elements should be subdivided into two main subgroups on the basis of their different volatilization rates. The less volatile subgroup consisted of the elements Ag, Cu, Ga, In, Ge, Sn and Zn while the more volatile subgroup contained the elements Bi, Cd, Pb, As and Sb.

The formation of silicon carbide in the electrode cavity during excitation in argon of samples buffered with additives containing graphite was demonstrated. The volatilization characteristics of several elements were shown to be adversely affected by this formation of silicon carbide. The in situ formation of silicon carbide was thought to be responsible for the poor precision obtained when the d.c. arc was surrounded by argon. Internal standardization did not improve this poor precision. By contrast the precision obtained with a d.c. arc surrounded by nitrogen was, for the majority of the elements, superior to that obtained with argon.

Visual estimates of lower limits of detection were made. The detection limits obtained employing argon were 1ppm for Zn, Cd, Bi, Sn and Pb and represent a considerable improvement when compared to their normal O.E.S. detection limits. Comparison of these detection limits with the average geological abundance levels of these elements revealed that Zn, Sn and Pb could be determined employing excitation in argon. The determination of Bi and Cd at the 1ppm concentration level could be useful in a geochemical prospecting application.

The investigation demonstrated that all the elements chosen could not be determined using a single spectrographic method. If the group was subdivided into subgroups, and the problems associated with carbide formation and slow volatilization rates are solved, viable analytical procedures employing d.c. arc excitation in artificial atmosphere may be possible. The application of d.c. arc excitation in an atmosphere of argon to the determination of the volatile trace elements in non-silicate or other matrices, which do not form carbides, would appear to be a promising possibility.

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INTRODUCTION

This investigation was undertaken in order to improve the detection limits of some volatile trace elements occurring at low levels of concentration in silicate rocks. The trace elements selected were As, Ag, Bi, Cd, Cu, Ga, Ge, Hg, In, Pb, Sb, Sn, Tl and Zn.

It is relevant to record that Ahrens and Taylor (1961) in their book on Spectrochemical Analysis observed that these elements complete their distillation into the d.c. arc before or simultaneously with the alkali metals and consequently referred to them as the volatile group.

For the sake of convenience the elements selected for this investigation are referred to as the volatile elements throughout this discussion.

Although this investigation is primarily analytical, a brief discussion on the contribution which data for the volatile elements make to geochemical interpretation, is given.

Geochemically the elements of the group are classified as chalcophilic because of their preference to enter sulphide matrices. For this reason their abundance in silicates is often low and consequently their determination difficult.

In the igneous environment inter-element ratios such as Rb/Tl, Ca/Cd, K/Ag, Si/Ge and Ga/Al are examined and used to (a) confirm observations of late stage magmatic differentiation (b) form the basis of explanations for obvious geochemical associations (c) interpret complex geological problems. (Refer to Taylor (1964)).

In the sedimentary sphere, attempts have been made to use several of the volatile elements as (1) indicators of depth of deposition (2) pointers to possible source rocks (3) indicators of possible sources of heavy metal pollution (Refer to Hirst (1962), de Groot (1966), de Groot et al (1971) and Heinrichs et al (1980)).

In cosmochemistry both absolute abundances and interelement ratios involving volatile elements are extremely useful with regard to fractionation processes which occurred in the solar nebula during cooling and condensation, prior to the formation of the solid planetary bodies. (Refer to Larimer et al (1967) and Grossman (1972)).

Geochemical prospecting used as a means of searching for hidden ore bodies has become increasingly important as the world's known mineral deposits and energy resources are being depleted. While some of the volatile elements are not themselves of economic importance, their presence often indicates potential ore bodies of geochemically related elements. (Refer to Rose et al (1979) and Levinson (1974)).

These are but a few examples of the geochemical application of volatile trace element data and are intended merely to indicate the range of problems in which acquisition of volatile element data can be helpful and desirable.

More detailed discussions relating to geochemical interpretation are to be found in the Handbook of Geochemistry Series. Vols. I. II-1 to II-5 edited by K.H. Wedepohl.

Optical emission and X-ray fluorescence spectroscopy were available to the writer as potential instrumental techniques for the determination of the volatile elements. Several other instrumental techniques exist which deserve consideration and which could equally have been employed had the facilities been available. For comparative purposes a brief discussion of these techniques is given below.

<u>Atomic absorption spectroscopy (A.A.S.)</u> has been in use for some 20 years, and there are probably few geochemical laboratories that do not employ the technique. One of its particular attractions is the relatively low cost of the apparatus when compared to other spectroscopic techniques.

A.A.S. is particularly suited to routine analytical procedures as various aspects of the technique such as sample preparation, dilution, aspiration and final analysis can be handled by relatively unskilled labour.

A somewhat serious disadvantage especially when analysing silicate rocks is the necessity for sample dissolution. Dissolution of silicate rocks requires rather complex handling, particularly when total sample dissolution is required. Another disadvantage is the fact that the technique is usually capable of determining only one element at a time although multi-element systems have been suggested.

Publications of Slavin (1968) and Angino and Billings (1967) deal with the application of atomic absorption spectroscopy in analytical chemistry; much of the book by Angino and Billings being devoted to geological and geochemical applications. The suitability of atomic absorption spectroscopy for the analysis of the volatile elements is demonstrated in Table 2. From this table it is evident that Ag, Cu, Ga, Pb, Sn and Zn can be analysed in typical silicate rocks. For the remaining elements in the group enrichment procedures are necessary to elevate their concentration levels to within the detection limits of the technique. A typical example of an enrichment procedure is given in the work of Heinrichs et al (1980) who volatilized the elements Cd, Bi, Tl, Pb, Zn and Rb from silicate materials by electrically heating the samples in a quartz tube and then analysing the condensed vapours using flameless atomic absorption. Elson et al (1978) on the other hand preferred a solvent extraction enrichment procedure followed by flameless atomic absorption when analysing silicate reference materials for Ag, Cd and Pb.

Nuclear Activation Analysis (N.A.A.) is one of the more sensitive analytical techniques available at the present time. With the advent of solid-state detectors and the use of computers, the technique has the potential of being applied to large scale geochemical analyses.

The application of nuclear activation analysis is however somewhat complex and requires a rather intimate knowledge of nuclear reactions and their products. As most of the elements present in a sample become radioactive when bombarded with thermal neutrons, radioisotopes are often produced that can interfere with the measurement of the desired radioactivities and it is usually necessary to employ radiochemical separation techniques to remove the unwanted radioisotopes in order to achieve ultimate sensitivity.

N.A.A. requires some form of irradiation source such as a nuclear reactor, neutron generator, isotopic neutron source or cyclotron. These are either expensive or may require transportation of samples to a centre where these facilities are available. Table 1 indicates the experimental detection limits possible with nuclear activation analysis using a nuclear reactor as irradiating source. It is evident that N.A.A. is capable of determining many of the less abundant volatile elements (for example As, Cd, Hg, In and Sb.)

Because the detection limits attainable by N.A.A. for many of the rarer volatile elements are low, its use as an analytical technique for the acquisition of geochemical data is expanding. Many texts on the application of nuclear activation analysis in geochemistry and geology are available. For example Fite et al (1971) have written a chapter on N.A.A. in a book discussing modern methods of geochemical analysis.

Brunfeldt and Steinnes (1971) have drawn on many years experience applying neutron activation analysis to geological problems to edit a book on activation analysis in geochemistry and cosmochemistry.

A recent paper by Hertogen et al (1980) describes the analyses of ocean floor basalt pillows using radiochemical neutron activation analysis. Among the 20 trace elements determined were the volatile elements Ag, Bi, Cd, Ge, In, Sb, Tl and Zn.

Another important application of N.A.A. is in the analysis of international rock reference samples. Smet and Roelandts (1978) for example analysed low concentrations of Sb, Cu, Zn and Ga in the two U.S.G.S. ultrabasic rock standards PCC-1 and DTS-1.

The development of the inductively coupled plasma (I.C.P.) as an excitation source in optical emission spectroscopy (O.E.S.) has provided this technique with a facility which places it back in the forefront of trace element analysis.

The advantages of the I.C.P. as a spectral source are:

(a) effective injection of the sample into the hot portion of the plasma

(b) relatively long residence time of the sample in the plasma

(c) higher gas temperature compared to combustion flames

(d) free atoms may be generated in hot zones of the plasma and observed in cold zones where background continuum is lower.

(e) chemical environment can be manipulated within certain limits

(f) electrode contamination is absent.

There are however some serious limitations:

(1) Samples have to be taken into solution

(2) the total concentration of elements present in the sample solution can affect the plasma performance and may in fact extinguish the plasma

(3) chemical interference effects are known to be present although there are methods available for overcoming these.

Compared to atomic absorption the technique is multi-elemental and conventional optical emission spectrographs can be fitted with an I.C.P. torch and suitable generator unit. Detection limits attainable with the I.C.P. are included in Table 1 for comparative purposes. They indicate that potentially many of the volatile elements can be determined in silicate rocks using the I.C.P. as spectral source.

The I.C.P. is a comparatively new development showing great promise. Currently work is in progress to permit the introduction of powders directly into the plasma, an improvement which would eliminate the dissolution procedure and would greatly facilitate I.C.P.-O.E.S. analysis of geological materials.

A comprehensive review of the application of the I.C.P. technique in analytical chemistry is beyond the scope of this investigation and consequently a few selected references will be given. For an excellent review of the history and development of the I.C.P. technique as a viable analytical procedure the address given by Fassel to the Analytical Chemistry Society Congress in April 1979 should be consulted. (Fassel 1979).

The application of the I.C.P. technique to geochemical analysis is expanding rapidly, adequate evidence being provided by the increasing number of papers dealing with I.C.P. which are appearing in analytical journals. For example, Walsh and Howie (1980) have made an evaluation of the performance of an I.C.P. spectrometer for the determination of major and trace constituents in silicate rocks and minerals. Although only two of the elements in the volatile group (Cu and Zn) are included in the elements tested by Walsh and Howie (op cit) they recommend the use of the I.C.P. source as a technique suitable for geochemical analysis because of the rapidity of analysis and the number of samples which can be handled in a normal working day. Church and Dahlquist (1980) have investigated in detail the analysis of 58 geological reference materials employing the I.C.P. technique. Comparison of the results obtained by Church and Dahlquist with the "recommended values" indicates that using an $HF/HNO_3/HClO_4$ digestion procedure the abundance of major elements can be routinely determined with an accuracy of ± 2 to 3% of the recommended value. Of the trace elements studied those of interest to this investigation namely, Cu, Zn, Sn and Pb can be routinely determined in igneous rock suites while Ag, Cd, Bi, As and Sb can be routinely determined at ore anomaly levels.

Thompson et al (1978) conducted a detailed investigation into the simultaneous determination of trace concentrations of As, Sb, Bi, Se and Te present in materials encountered in applied geological research employing the I.C.P. as spectral source. The detection limits obtained for these elements using conventional aqueous solution pneumatic nebulization into the plasma were not low enough for practical geochemical analysis. Reduction of the elements to their hydrides provided a useful method of separating the elements from the major interfering elements and a method for introducing the elements into the plasma source. The detection limits achieved under these conditions namely, 0.8μg/ml for As, 1.0μg/ml for Sb, 0.8μg/ml for Bi, 0.8μg/ml for Se and 1.0μg/ml for Te permitting determination of these elements in geochemical samples.

In describing some of the alternative analytical techniques which are applicable to the analysis of the volatile elements, only a few specific references are quoted for each technique. An indication of the advantages and disadvantages of each alternative technique is given together with some idea of the detection limits attainable by each technique. (Table 1).

These should be borne in mind when considering the work to be described in this dissertation, as access to these alternative techniques would clearly allow for the determination of some of the volatile elements.

Examination of Table 1 and, comparison of the limits of detection achieved with normal optical emission spectrographic (O.E.S.) methods, with the average igneous abundance levels of the volatile elements, reveals that for many elements O.E.S. is inadequate.

The main thrust of this investigation, therefore, was to attempt to improve the detection limits of the volatile group of elements in silicate rocks by means of improved d.c. arc optical spectrographic methods.

A method which displayed great potential was to employ a d.c. arc surrounded by atmospheres other than air. Previous work done in the Department of Geochemistry, U.C.T. and in other laboratories (fully documented in Chapter 2), revealed markedly improved detection limits for many of the volatile elements when excitation was carried out in pure argon, for example. Much of the work described in this dissertation is thus concerned with an evaluation of the excitation characteristics of the d.c. arc in various atmospheres (argon, nitrogen, helium, oxygen and carbon dioxide) and the attempts that were made to develop viable analytical methods for the optical emission spectrographic determination of the designated volatile elements.

A further but minor aspect of this investigation was concerned with an evaluation of the detection limits that could be achieved for some of the volatile elements employing X-ray fluorescence (X.R.F.) methods of analysis and an assessment of potential methods for specific volatile elements.

Since both O.E.S. and X.R.F. instrumentation was available in the laboratories of Department of Geochemistry, the determination of a particular element by both methods would be useful for comparative or internal standardization purposes.

Additionally, in the event that one or other of the two techniques could not determine some of the volatile elements, it was hoped that the combination of the two techniques would allow the determination of all the designated volatile elements in common silicate rocks.

CHAPTER 1

X-RAY FLUORESCENCE SPECTROGRAPHY

1-1 INTRODUCTION

X-ray fluorescence (X.R.F.) spectrography was, for a long time, employed in estimating major element concentrations in samples of diverse origin. The development of more efficient spectrometer components and improved spectrometer geometry has, however, led to an ever increasing application of the technique to the analysis of trace elements in, amongst others, silicate materials. A detailed discussion on the theory of X.R.F. will not be presented here as many excellent texts are available (Refer to Jenkins and De Vries (1967), Bertin (1975), Norrish and Chappell (1967)).

Because of the relative simplicity of the technique, the potential of X.R.F. to analyse for the volatile trace elements was examined first. In order that a critical evaluation can be made, it is necessary to discuss some of the problems associated with trace element analysis.

1-2 TRACE ELEMENT ANALYSIS

The three most critical factors affecting the accuracy and sensitivity of X.R.F. trace element analysis are the correction for mass absorption coefficient (m.a.c.) differences between samples and standards, the accurate estimation of background, and the correction for spectral line overlap. Several methods are available for determining m.a.c. and background, the choice being governed by the degree of analytical accuracy required.

1-3 M.A.C. CORRECTIONS

Reynolds (1963, 1967) showed that the m.a.c. and the Compton scattered peak intensity of a Mo Kα primary beam are inversely related. By measurement of the Mo Kα Compton peak produced by various substances of known m.a.c. a calibration curve can be constructed.

This curve enables m.a.c.'s for the unknowns and standards to be determined and corrections for m.a.c. differences to be effected mathematically.

Establishment of m.a.c.'s of pure compounds, mixtures of compounds, rocks and pure elements relied initially on the accuracy of absorption coefficient tables. Willis (1968) pointed out the errors which can arise due to the uncertainty in the values in these tables.

Norrish and Chappell (1967) described a method for the direct measurement of m.a.c. The method required preparation of a separate thin wafer of the sample. The advantage is that the mass absorption coefficient can be measured directly at the specific wavelength of the element being determined. This transmission method however has a wavelength limitation, as the point is reached where the specific radiation is totally absorbed by the thin wafer and preparation of a wafer which will permit transmission of the longer wavelength radiation is impractical. In practice the longest wavelength m.a.c. that can be measured by the transmission method is for the element Ti (2.75A).

Willis (1973) has shown that the inverse relationship between the Mo Kα Compton peak and m.a.c. measured by the transmission method of Norrish and Chappell is very close. These measured m.a.c.'s are therefore preferred for setting up the calibration curve which is then used for the subsequent determination of the m.a.c.'s of unknown samples employing the original Reynold's method.

This is probably the most accurate method of m.a.c. determination available at present.

M.A.C.'s can also be calculated if the major element composition of the sample is known, but the accuracy is again dependent on the reliability of published m.a.c. values for the elements.

Feather and Willis (1976) described a method whereby a single measurement of background can be used to calculate both the background and the m.a.c. of the standards and samples at specific spectral positions. The accuracy claimed for this method is between 2% and 5% relative.

1-4 BACKGROUND DETERMINATION

The accurate determination of background interference of an X-ray spectral line is somewhat complex.

The most accurate method of background determination is by measuring the background at two or more off peak interference free spectral positions and then interpolating the background by graphical means or by calculating the background using factors derived from blank samples. This method is rather time-consuming as it is used on sequential X-ray spectrometers. Generally it is applicable when highly accurate analytical data is required.

The method of Feather and Willis (1976) has been referred to in Section 1-3. It was especially developed for simultaneous spectrometers and is particularly attractive when large batches of samples have to be analysed, as for example, in geochemical prospecting programs.

1-5 TRACE ELEMENT REFERENCES

As X.R.F. formed a minor aspect of the investigation a comprehensive review of references relating to trace element analysis employing X.R.F. was not warranted. A few references selected as examples of the different methods of background or m.a.c. determination will be cited.

The chapter on X-ray fluorescence spectrography written by Norrish and Chappel appearing in Physical methods in Determinative Mineralogy edited by Zussman gives details of various methods of background and m.a.c. determination. Sweatman et al (1967) determined Sn in ores and concentrates using the transmission method of Norrish and Chappel for measuring m.a.c. Background was determined by reading two off peak background positions and calculating the background at the Sn kα position. The overall method was shown to be applicable to samples of widely varying matrix and covered the concentration range 0.06 to 77% Sn, adequate for metallurgical process analyses but unsuitable because of lack of sensitivity for geochemical prospecting samples.

Kaye (1965) analysed several international reference materials for the elements Cu, Ni, Rb, Sr, Zn and Zr using an X.R.F. method similar to that proposed by Hower (1959). M.A.C.'s were calculated using the major element composition of the standards and absorption data from Liebhafsky et al (1960). The calibration standard used consisted of specpure SiO_2 spiked with each of the analytical elements. Matrix correction was effected by comparison of the calculated m.a.c. of the samples with the calculated m.a.c. of SiO_2 at a wavelength of $0.9A^o$. The results obtained on the international standards compared favourably with those reported by other analysts.

Hofmeyer (1971) employed the m.a.c. correction method of Reynolds (1963, 1967) (described in section 1-3) for determining the elements Cu, Ni, Zn, Zr, Nb, Y, Th, Pb and Ga in South African shale samples during an investigation to establish whether any of these trace elements could be used as indicators of depositional environment. Background corrections were effected for each sample by calculation of the background under the peak from adjacent background positions.

1-6 EVALUATION OF X-RAY FLUORESCENCE

At the time of the investigation, many of the trace elements had not previously been examined in the Department of Geochemistry. As X.R.F. techniques formed an integral part of the Department's analytical instrumentation, the feasibility of determining some of these trace elements would be of great value.

The establishment of detection limits for those elements which could be determined by X.R.F. was also important, as an alternative method of analysis would then be available for those elements showing adequate sensitivity.

An important prerequisite of the investigation was the ability to handle large batches of samples, and consequently it was desirable that sample preparation should be as simple as possible.

X.R.F., because of the relative speed with which results are obtained, was also ideally suited for checking the accuracy of the dilution procedure used in the preparation of the synthetic standards for this investigation.

Chart recordings of the 1% and 0.1% synthetic trace element standards were obtained. It was apparent that only a limited number of elements could be determined as excessive spectral line overlap was present.

Of the fourteen trace elements selected for this study, the following showed promise: Ag, Bi, Cd, Cu, Ga, Zn. Optimal instrument settings were established for each of these elements using different X-ray tubes and crystals.

Generally, it was found that a Au or W tube gave best sensitivity except for the elements Ga and Bi where the Mo tube provides optimal excitation efficiency.

A topaz crystal had to be used for the analysis of the artificial standards as maximum resolution was necessary due to the fact that the elements of the group are adjacent to one another in the periodic table and consequently excessive spectral line overlap takes place.

In natural materials such as silicate rocks, minerals, ores or soils such excessive overlap would probably not be present and a Li F (200) crystal having greater reflectivity could be used. The dilution procedure was checked by measuring the appropriate X-ray spectral lines of the elements that showed promise. Background was measured at two adjacent interference free spectral positions. As the offset background positions were equidistant from the spectral peak, the background correction applied was calculated as the mean of the two background readings taken. This calculated background was subtracted from the peak readings obtained and was also used as a measure of the m.a.c. of the samples. Background can usually only be used as a measure of m.a.c. for samples of similar composition, such as the artificial standards used in this investigation. The nett peak was divided by the mean calculated background to effect the m.a.c. correction. Graphical plots of nett peak to background ratio versus concentration (Figures 1 to 6) resulted in straight line plots for all the elements tested, indicating that the successive dilutions were accurate and any error present was not detectable by X-ray spectrographic means.

1-7 LIMITS OF DETECTION

The limit of detection in X.R.F. spectrometry is defined as the concentration equivalent to the nett peak which exceeds the background by three standard deviations of the background measurement.

A useful formula for determining detection limit using samples of known concentration is -

$$C_d = \frac{\text{Conc. std.}}{N_p - N_b} \times 3\sqrt{N_b}$$

where:

C_d = Detection limit.
N_p = Total counts at peak.
N_b = Total counts at background, Willis (1968).

When comparison of different methods and spectrometers is to be made, time normalization of this equation is essential and the formula becomes -

$$C_d = \frac{\text{Conc. std.}}{R_p - R_b} \times \frac{3\sqrt{2}\sqrt{R_b}}{\sqrt{T}}$$

where:

C_d = Detection limit.
R_p = Count rate on peak.
R_b = Count rate on background.
T = Total counting time, Willis (1968).

Table 3 sets out the detection limits obtained with different instrumental conditions for those elements which showed promise by X.R.F. From this table it is obvious that only Cu, Zn and Ga could be determined in normal silicate materials with the X-ray spectrometers available at the time of this investigation.

1-8 RELATIVE STANDARD DEVIATION

For comparative purposes the theoretical relative standard deviation of the 100ppm artificial standard was calculated. These results give a good indication of the precision obtainable with each of the instrumental conditions investigated.

The formula used is -

$$E\% = \frac{100}{\sqrt{T}} \times \frac{\sqrt{R_p + R_b}}{R_p - R_b}$$

where:

R_p = count rate on peak.
R_b = count rate on background.
T = Total time ($T = T_p + T_b$ and $T_p = T_b$)

The results obtained appear in Table 3.

1-9 CURRENT CAPABILITIES

Since the X-ray fluorescence part of this investigation was undertaken, vast improvements in X-ray spectrometer geometry and components have taken place and this has led to greatly improved detection limits. Currently the detection limits for members of the volatile group are:-

Element	L.L.D.	L.L.Dt.	Crustal Abundance
As	1.2	3.6	2.0
Bi	2.0	6.0	0.2
Cu	1.2	3.6	55
Ga	1.2	3.6	19
Ge	1.0	3.0	1.1
Pb	2.4	7.2	15
Sn	2.2	6.6	2.0
Zn	0.8	2.4	40

Viewed against the crustal abundance levels these detection limits, when converted to the lower limit of determination (L.L.Dt.) i.e. 3 times the lower limit of detection (Refer Jenkins (1974), now make it feasible to determine Cu, Ga, Pb and Zn. Sn, As and Ge have also been determined in samples showing enrichment in these elements. (Willis et al (1980)).

CHAPTER 2

A DETAILED DISCUSSION OF THE OPTICAL SPECTROGRAPHIC TECHNIQUE WITH EMPHASIS ON PROCEDURES FOR INCREASING THE SENSITIVITY OF THE VOLATILE ELEMENTS

2-1 INTRODUCTION

The general principles of this technique are adequately described in Ahrens and Taylor (1961) and will not be repeated. Examination of Table I and comparison of abundance levels and detection limits for the "volatile" elements using normal optical emission procedures emphasises the need for specialized techniques in many instances. Several of the volatile elements namely Ga, Cu and Pb are normally present in igneous rocks at levels exceeding their optical spectrographic detection limits and can be determined with little difficulty.

2-2 NORMAL TECHNIQUES

Ahrens (1954) studied the behaviour of what he defined as volatile elements in the d.c. arc and as a consequence of his investigations proposed low amperage excitation and alkali type distillation with In as the added internal standard for the determination of these elements.

Siedner (1965) used a method applicable essentially to involatile elements to determine Ga, Cu and Pb in a fractionated alkali igneous suite. This method employed d.c. arc excitation with a current of 7 amps on sample mixed with a graphite - palladium buffer in the ratio of 1 part sample to 2 parts buffer. Sodium was used as variable internal standard for this method.

These methods were however for a very small proportion of the elements in the volatile group. Determination of the remainder of the elements requires specialized techniques which are discussed in turn.

2-3 SIMPLE PROCEDURES

One such method was the improvement in the detection of Tl in granites achieved by Willis et al (1964). Potassium sulphate (in conjunction with low amperage excitation) was used as the buffer to reduce cyanogen band emission which masks the Tl spectral line occurring at 377,5nm. Ag was added as internal standard thereby improving the relative deviation from 16% to 8,4%. By using a large carbon anode the detection limit was reduced to 0,5 ppm, adequate for the determination of Tl in granitic rocks. Rusanov, Khitrov and Batova (1959) also used potassium sulphate as a buffer but only achieved a detection limit of 3 ppm, somewhat inadequate for determining Tl in silicate rocks.

2-4 ENRICHMENT PROCEDURES

The purpose of these procedures is to upgrade the concentrations of the elements so as to bring them within the range of normal spectrographic detection limits.

Chemical precipitation enrichment was developed by Mitchell and co-workers (1948, 1954) whereby elements are precipitated from acid solution. Numerous other similar methods are available, in some instances specific procedures being employed to precipitate a specific group of elements.

Ion-exchange enrichment is a further useful method of pre-concentration. A combined anion-exchange spectrochemical technique was applied by Brooks, Ahrens and Taylor (1960) for the determination of 10 elements occurring in silicates at levels well below their normal detection limit. The elements were Tl, Bi, Sn, Cd, Zn, Ag, Pb, In, Mo and Nb of which all but the last two fall into the so-called volatile element group.

It was most convenient that the elements which form a distinct group from a spectrochemical point of view also behaved as a group during elution from the ion-exchange column.

By using 20 g of material Sn, Zn, Cd, Tl and Bi were determined in 19 rock specimens including the U.S. Geol. Survey standards G-1 and W-1.

2-5 DOUBLE-ARC-TECHNIQUE

Probably one of the earliest techniques used to improve the detection of the volatile elements was fractional distillation of the elements from a large quantity of sample.

Rose and Bose (1935) were the first to investigate this technique when they studied the condensed sublimates of a fractional distillation process.

Pruess (1940) using the same idea eliminated the condensation step and led the vapours of the volatile elements into a hollow electrode where they were excited. The principle of the double arc technique is to combine the two processes, namely, vaporization and excitation into a single procedure.

By using a relatively large graphite crucible and striking two independent arcs - one between the lower electrode and base of the crucible and the other between the upper electrode and cap of the crucible - the vaporization step is closely followed or accompanied by the excitation step.

Shaw, Joensuu and Ahrens (1950) and Wedepohl (1953) independently developed two practical methods utilizing the double arc technique. The former workers were able to improve the estimations of Tl and In in geological materials while Wedepohl used this technique during his study of the geochemistry of Zn. The precision obtainable in both cases was in the region of 30% despite the use of internal standardization.

Schroll and his co-workers (Schroll 1963, 1964, Schroll and Weninger 1965, Janda and Schroll 1959, Brandenstein, Janda and Schroll 1960, Janda, Schausberger and Schroll 1963, Weninger 1965) have investigated the technique of the double arc furnace very intensively and have published numerous papers reporting great improvements in detection of the volatile elements. Schroll (op cit) emphasises the importance of distinguishing between the various processes taking place during the arcing of a sample. The processes are vaporization and excitation and it is the vaporization step that has been studied at length by Schroll and his co-workers (op cit).

Numerous parameters such as electrode design, amperage and additives influence the vaporization procedure taking place during arcing. Of these, additives and the reactions taking place in an electrode, have been shown to be important and occupied most of Schroll's (op cit) investigations.

Before passing on to a detailed discussion of additives, mention should be made of the boiler electrode used by Hall and Lovell (1958) to determine As in anthracite coal ash. In principle very similar to the double arc furnace, the distinguishing feature of this technique was that a single arc was struck which was responsible for both heating the "boiler" to vaporize the sample and exciting the vapours emanating from the orifice in the cap.

2-6 ADDITIVES

The term additives embraces all chemical compounds that are added to a sample prior to its excitation. They can be sub-divided into groups on the basis of the part each plays during the arcing process. An attempt will be made to discuss these various roles bearing in mind the fact that there are differing opinions on the roles and on the terminology that is used when describing the mechanisms by which additives work.

2-6(a) Carriers

The generally accepted meaning of the word carrier is according to Scribner and Mullin (1946) an added material that will " sweep out slowly the minute quantities of impurities volatilized by the heat of the electrode" while the more refractory matrix is left unvolatilized. Hence gallium oxide was added to uranium oxide for the determination of trace impurities in this nuclear fuel. Zakhariya et al (1958) showed that the carrier influenced the kinetics of distillation. There was however some doubt about this being the mechanism and so Vainshtein and Belyaev (1958) investigated the carrier action using radio-active isotopes. They came to the conclusion that the carrier exercised no influence on the vaporization of the impurities from the matrix but rather influenced their excitation. The carrier added in an empirically determined proportion dictated the distribution of the impurity elements in the arc plasma. The carrier atoms were found to assume a symmetrical distribution with a sharp maximum at the centre of the arc, the impurity elements showing a similar distribution. The increased intensity of the radiation from the impurity elements was therefore a consequence of the fact that they are also concentrated in the centre of the arc plasma and not randomly distributed.

Raikhbaum and Malykh (1961) came to a similar conclusion about the mechanism by which a carrier substance enhances spectral line intensity. They found a dependence of the carrier effect on the ionization potential of the carrier atoms. Atoms having lower ionization potentials caused greater increases in spectral line intensities. The explanation given was that the carrier atoms influence the residence time of the impurity atoms in the arc plasma. These views are closely allied to those of Ahrens L.H. (Personal communication) that the carrier atoms influence anode and arc temperature. Carrier atoms having a low ionization potential will reduce the extreme temperature of a normal carbon arc thereby inhibiting volatilization of undesirable matrices and aiding selective distillation of the volatile impurities.

On the evidence presented then, it seems reasonable to conclude that "carriers" can influence both vaporization and excitation and that they should be assessed in terms of their ability to increase the intensity of trace elements.

Pszonicki and Minczewski (1962) set about trying to determine which of the two processes was more important.

Besides the carrier's influence on vaporization and excitation they shared the ideas of Schroll (op cit) that the carrier could also influence chemical reactions in the electrode crater.

In order to test whether vaporization or excitation was more dominant they compared spectral line intensities of impurity elements resulting from arcing a sample mixed with "carrier", to those obtained by, first distilling the impurity elements from the sample, and then arcing the condensed material mixed with the same carrier. They found the spectral line intensities to be similar and concluded that the carrier was influencing the excitation of the impurity elements.

In contrast however, they showed that less volatile elements such as Be, Ni, Mo and V can be made more volatile by the addition of a suitable carrier such as $AgCl_2$.

This seemed to be an example of electrode reactions, where the oxides of the impurity elements are chlorinated, the resultant chlorides having lower boiling points and therefore greater volatility.

As already mentioned much of Schroll's (op cit) work was devoted to obtaining an understanding of the chemical reactions taking place in an electrode as it was felt that this knowledge could be used to single out selected additives to be used for specific problems. Additives such as ammonium sulphate, lithium carbonate, barium sulphate, sulphur and gallium oxide were used. The last three formed a mixture that operated as a sulphidizing agent for converting the volatile elements into their more volatile sulphides.

Schroll and Sauer (1966) advanced the idea of using a graphite beaker that could hold 10 grams of material. A mixed arcing source was used, the heating arc being 24 amps d.c. while excitation was by means of a high voltage spark.

Detection of elements such as Hg and Mo was well below the 1,0 ppm level using this specialized double arc method. Double arc procedures had always been subject to poor reproducibility, a problem which Schroll et al (1965) seemed to overcome. Sn and Ge were for example determined at the 1,0 ppm level in a suite of graphite and talc bearing rocks with a reproducibility of 10%. Janda and Schroll (1959) determined the volatile elements in graphitic rocks employing the double arc procedure and a lithium carbonate-ammonium sulphate additive.

The reproducibility obtained, ranged from 2% for Ga to 16% for Zn. The poor reproducibility obtained for the elements Zn, Hg and As was the result of In, used as internal standard, exhibiting rather different volatilization characteristics compared to those of the analytical elements.

2-6(b) Buffers

Buffers are those additives whose function is primarily to remove variations in matrix between samples and standards and not necessarily to improve sensitivity. In most cases the buffer is added in such proportions as to make it the matrix. The most commonly used buffers are alkali and alkali earth salts because of their smoothing effect on the arc. Strock (1945) made use of a mixture of sodium chloride and graphite when determining In, Ga, Ge, Sn, Bi and Sb in zinc sulphide ores.

Marks and Hall (1946) found that by buffering samples with calcium carbonate and graphite they were able to remove extreme variations in line intensity due to matrix differences.

Mohan and Fry (1958) while developing a semi-quantitative universal method of spectrochemical analysis showed that lithium carbonate and gallium oxide are by far the most effective buffers for eliminating matrix variation.

Several workers, among them Holdt (1962) and Maritz and Strasheim (1964) have reported extensive investigations into methods of assessing buffer efficiency and determining optimal buffer concentrations.

Of much greater importance are those investigations which have determined optimal buffer concentrations for the determination of the volatile elements in geological materials.

For example Joensuu O.I. (Personal communication A.J. Erlank) recommended a mixed buffer of calcium carbonate and potassium sulphate for the determination of the volatile elements, while Ingamells and Suhr (1963) preferred a potassium sulphate-graphite buffer and Wang and Cave (1964) used a lithium carbonate-graphite mixture.

Tennant (1967) on the other hand used a buffer mixture of aluminium oxide, calcium carbonate and potassium carbonate and developed a method for the general spectrographic determination of volatile trace elements in silicates achieving remarkable detection limits. Thus he quotes for Ag, Ga, In and Tl 0,1 ppm, Pb, Sb, Sn and Zn 1 ppm and As 10 ppm in normal silicate matrices. Compared to their geochemical abundances this is a significant achievement.

2-6(c) Graphite

A substance which can neither be termed buffer nor carrier but which is probably the most widely used additive is graphite powder. Its chief usage is to steady the arc and reduce selective volatilization. A considerable disadvantage however is its promotion of cyanogen band emission.
Nickel (1968) studied the effect graphite has on oxide compounds when excitation in a d.c. arc takes place. He used an enclosed gas chamber into which argon or argon-oxygen mixture flowed. His primary concern was to establish what thermochemical reactions or physical processes take place inside the electrode which could have a bearing on the subsequent volatilization characteristics of the elements present in the sample.
After excitation at 10 amps for 20 secs. in the surrounding atmosphere, the oxide bearing graphite electrodes were microtomed and the resultant sections subjected to X-ray diffractometry to identify the compounds present, and the depth at which they had been formed. It is interesting to note that his experiments did not reveal the formation of carbides of any of the volatile elements. Instead CuO was reduced to metallic copper and mixtures of copper oxides while AgO was reduced to metallic Ag.

Nickel found many elements that did form carbides and among the major rock forming elements Fe_3C, SiC, CaC_2 and to a lesser extent Al_4C_3 were present. Of these Fe_3C decomposes at 1075°C, CaC_2 at 2300°C, SiC at temperatures beyond 2200°C and Al_4C_3 at temperatures near 2000°C. Of these carbides SiC and CaC_2 are the most stable and probably will not decompose in the lower temperatures of a d.c. arc surrounded by argon.

2-7 ATMOSPHERES

Vallee and co-workers (1950, 1952a, 1952b, 1956a, 1956b, Thiers and Vallee 1956, Baker, Adelstein and Vallee 1956) studied the effect of artificial atmospheres on the d.c. arc. Among the atmospheres were helium, argon, oxygen, carbon dioxide, krypton and neon. By surrounding a direct current arc with noble atmospheres it becomes a spectrochemical source having several advantages. These will be discussed in turn.

There is a reduction of general background besides the elimination in many instances of cyanogen bands. This reduction is a consequence of the lower electrode temperatures that result when noble gases surround the arc.

Thiers and Vallee (1956) measured anode temperatures by means of a projection thermister pyrometer and reported the temperatures shown in the following table.

GAS	ANODE TEMPERATURE	
He	1360°C	
Ne	1080°C	
A	965°C	
Kr	925°C	
Air	3927°C	Von Engel (1955)

The greatly reduced temperatures relative to those in air slow down electrode reactions and electrode consumption, thereby reducing the number of incandescent solid particles entering the arc column. It is these incandescent particles that are chiefly responsible for the background continuum. The reduced temperatures make longer arcing times necessary with a possible increase in background. This increase leads to reduced line to background ratios and a raising of detection limits. It was found, however, that several spectral lines were enhanced and that line to background ratios were improved.

Two types of spectral line enhancement were found during excitation in argon atmospheres. They were respectively enhancement of ion lines and of atom lines. The enhancement of ion lines appears to be a function of the excitation potentials of the lines and their relationship to the excitation potential of the noble gas. This is borne out by the observed maximal enhancement of lines whose total excitation potential corresponds to the lowest excited state of argon.

The enhancement is probably due to "inelastic collisions of the second kind" between gas and metal atoms, these collisions being most likely to transfer energy when there is a proximity of total excitation and resonance potentials.

Erlank (1964) reported this selective line enhancement for the element Beryllium which has two ion lines at 313,1nm. The total excitation potential of these lines is 13,2 eV coinciding with the resonance potentials of argon which lie between 11,548eV and 13,479eV. The enhancement of atom lines in argon is apparently due to the effect of reduced temperatures on the volatilization rates of the elements. As already mentioned electrode temperatures are greatly reduced in argon. Volatilization times are consequently greatly prolonged and the slower distillation of the volatile elements allows longer residence times in the arc plasma, improved excitation and hence enhanced atom line intensities.

Vallee and Thiers (1956b) demonstrated that, in contrast to their influence on anode temperatures during excitation in air, alkali and alkali earth chlorides exercise no temperature control when an arc is surrounded by argon and consequently fractional distillation of the volatile elements is likely to take place.

The effects of helium, krypton and neon were also recorded but the most important observations made throughout the reports of Vallee et al (op cit) were the obvious advantages of excitation in argon for the determination of the volatile elements. For example, Vallee and Adelstein (1952a) comment that "volatile elements such as zinc, cadmium, lead, tin and and silver could be detected in argon with considerable ease when they could only be demonstrated in 100% helium or air with difficulty or not at all".

Mention should be made that most of the materials studied by Vallee and his co-workers (op cit) were biological in nature. There are some references on the use of atmospheres other than air for the analysis of geological and related materials and a few selected examples will be given. Ingamells and Suhr (1963) were among the first to determine several volatile elements in standard silicate samples using an argon atmosphere. Cruft (1964) used pure argon when analysing soils and stream sediments for Lead and Zinc. He also observed the exceptional increase in sensitivity for Zinc in pure argon as did Nash (1965).

Kolbe (1965) on the other hand preferred pure oxygen as the enveloping arc gas when determining Lead, Thallium, Gallium, Copper and Tin in some silicate rocks and minerals.

Morrison et al(1960) and Rupp et al (1960) employed an argon atmosphere to obtain selective distillation of trace impurities from refractory matrices such as silicon carbide and nickel. Further applications of atmospheres are those of O'Neil and Suhr (1960) for the determination of trace elements in lignite ash where carbon dioxide was used to suppress cyanogen bands and Joensuu and Suhr (1962) who also used carbon dioxide in a method for determining major elements in geological materials.

Among the atmospheres that have been used only argon-oxygen mixtures remain to be discussed. The primary use of this atmosphere mixture is to provide a nitrogen free environment for the arc discharge, thereby eliminating the formation of cyanogen. The three ultraviolet cyanogen bands occurring with band heads at 421,6nm, 388,3nm and 359,0nm mask many sensitive spectral lines that become usable when cyanogen emission is eliminated.

Danchin and Baumgartner (1964) for example used an argon-oxygen atmosphere to eliminate cyanogen interference of the Tl spectral line at 377,5nm and indicated that the detection limit for Tl could be lowered to 0,1ppm in common silicate materials by this means.

In an excellent review article in the Spex Speaker (1962) on the application of the Stallwood jet in optical emission spectrography the emphasis throughout is on the use of argon-oxygen atmosphere mixtures. Shaw (1962) reviewing the use of the Stallwood jet in the Geology Laboratory of McMaster University stresses the vast improvements in usable spectral lines, background elimination and sensitivity when an argon-oxygen mixture is used with the Stallwood jet.

2-8 GAS SHEATHING DEVICES

The development of the air jet by Stallwood in (1954) was primarily intended to improve quantitative spectrographic analysis. Factors which caused inaccuracies in analyses were attributed to:

(1) Selective volatilization effects

(2) Matrix effects.

(3) Self absorption.

(4) Instability of the arc.

During quantitative spectrographic analysis internal standardization is necessary if precise results are to be obtained. Careful choice of an internal standard which exhibits volatilization characteristics closely similar to those of the elements being determined is therefore necessary. As selective distillation is a prominent feature of emission spectrography, internal standards can usually be used for only a limited number of elements at any one time.

Matrix differences between samples also seriously affect the analytical results obtained as spectral line intensities from elements present in dissimilar matrices differ.

Among the methods that have been employed in attempts to minimize matrix effects are 1) dilution with spectroscopic buffers and 2) internal standardization. Dilution of the samples results in loss of sensitivity and so has limited application.

Stallwood (1954) undertook an investigation which involved attempts to reduce matrix effects.

A marked enhancement of spectral line intensity of the more volatile elements was noted when samples were placed in deep narrow cratered electrodes. As it appeared that sample cooling influenced volatilization, further cooling was proposed by directing a stream of air against the outer walls of the electrode.

A Stallwood jet was designed for this purpose. Not only was the unburned portion of the sample cooled throughout the exposure but the arc discharge itself was stabilized by the vertical air currents.

Some of the results of Stallwood's (op cit) investigation can be summarised as follows:

(i) Of the more volatile elements, such as Mercury, Lead, Antimony and Tin, volatilization times were extended in addition to being uniform.

(ii) The linearity of intensity-concentration plots was significantly improved. This was attributed to the more uniform volatilization of the sample and the removal of the outer flamy fringe of the arc that is thought to be responsible for self-absorption.

(iii) Establishment of calibration curves for Mercury and Lead using widely different matrices produced a single curve indicating that matrix effects were overcome.

Substitution of the air normally used with the air jet by other atmospheres could be reasonably expected to result in a combination of the advantages of the air jet with those of excitation in an atmosphere. Prior to the modifications and adaptations of the Stallwood air jet for surrounding electrodes in atmospheres other than air, Vallee, Riemer and Loofbourow (1950) used an air tight arc stand into which the gases flowed.

This type of apparatus was not suitable for routine operation and so it was Shaw et al. (1958) who "positioned a simple glass chamber on top of the jet so as to nearly exclude air and using a nitrogen free atmosphere practically eliminate CN bands". By careful experimentation varying electrode and jet dimensions Shaw (op cit) was also able to achieve an adequate reduction in cyanogen band emission without the aid of a glass canopy.

Arc control devices essentially individualistic designs or modifications of the Stallwood jet with or without a glass canopy have been described by, inter-alia Annell and Helz (1960), Philcox (1959), Curtis (1962) Wang and Cave (1964) and Margoshes and Scribner (1964).

Broadly speaking two types of gas sheathing device exist, those with and those without a glass canopy.

The advantages and disadvantages of the two designs will not be discussed here as they are adequately covered in the original papers and will be dealt with briefly in Chapter 3 in the section discussing the selection and design of a gas sheathing device for this investigation.

CHAPTER 3

AN INVESTIGATION INTO PROCEDURES FOR IMPROVING THE OPTICAL SPECTROGRAPHIC DETERMINATION OF THE VOLATILE ELEMENTS USING ARTIFICIAL ATMOSPHERES

3-1 THE USE OF ARTIFICIAL ATMOSPHERES

In the discussion on procedures for improving the sensitivity of the optical spectrographic technique (Chapter 2), the improvement obtained in lowering the detection limit of Tl employing excitation in a mixed atmosphere of argon and oxygen was mentioned. This success, coupled with the observations of Danchin and Baumgartner (1964) and Vallee et al (1950, 1956), that the intensities of several elements such as Be, Zn, Ag and Pb were enhanced when the d.c. arc was surrounded by argon atmospheres, prompted a more detailed study of the application of artificial atmospheres to the analysis of silicate rocks.

3-2 SELECTION AND DESIGN OF A GAS SHEATHING DEVICE

The gas sheathing device initially used in this study was similar to that designed by Annell and Helz (1960). It consisted of a ceramic collar which directs a flow of gas past the electrode containing the sample. For optimum sensitivity of the element Tl, using the Tl 377.5nm spectral line complete elimination of cyanogen emission is necessary. This was found to be possible by the introduction of a glass canopy fitted with a quartz window to allow the passage of radiation to the spectrograph.

This gas device had several disadvantages:

a. The glass canopy and quartz window required removal and cleaning between successive arcings, a time consuming and cumbersome operation.

b. As the gas device was clamped in the lower electrode holder of the arc stand, the lower electrode containing the sample could not be raised or lowered independently during the arcing procedure.

As electrode temperature is dependent on arc gap it is desirable that the arc gap is kept constant during arcing of samples.

Replacement of the existing gas device with one similar in design to that proposed by Margoshes and Scribner (1964) promised to be a more satisfactory means of surrounding the electrodes and the arc with artificial atmospheres.

The National Physical Research Laboratory (N.P.R.L.) at the Council for Scientific and Industrial Research, (C.S.I.R.) Pretoria had already constructed a gas device employing the basic design of Margoshes and Scribner (M & S) and a detailed drawing of the C.S.I.R. device was obtained. The essential differences between the M & S and N.P.R.L. devices were, the use of perspex instead of copper for the main body, and the fitting of a stainless steel water cooled top section to this perspex body.

A gas sheathing device was constructed using the drawings obtained from the N.P.R.L. and the device was installed in a Hilger and Watts arc spark stand. For convenience this gas device will be referred to as the M & S gas jet. The advantages of this device were:

(1) independent control of the lower electrode holder enabling the analytical gap to be adjusted during arcing.

(2) a water cooled top eliminating vaporization of the metal from which the device was constructed and also permitting excitation at much greater amperages than had previously been possible.

(3) different electrode sizes were readily accommodated in the lower electrode holder.

(4) the gas flow surrounding the lower electrodes could be adjusted by means of variable ring inserts which fitted the aperture in the top of the device.

(5) the ease of manipulation of this device was in fact comparable with normal excitation in air.

During the initial testing and familiarization period it was found that after arcing at high amperages (30 amps) for extended periods, the lower electrode holder became heated and jammed in the perspex base. A new base was therefore machined from aluminium and subsequently modified to become the gas inlet system to the device. The tangential flow of gas into the main body of the device was thought to inhibit laminar flow of gas past the lower electrode. The concentric holes in the aluminium base plate ensured that the incoming gas streamed upwards, surrounding the lower electrode holder, lower electrode, and the burning arc in a gaseous envelope. An aluminium section was also inserted between the water cooled top and the main perspex body of the device as after prolonged arcing water leaks developed because of softening of the perspex body. It was found that, because of the conical internal shape of the main body of the device, raising the lower electrode holder above a certain level caused undesirable variations in the gas flow past the lower electrode and it was thus advantageous to have as much as possible of the main body of the jet made from transparent perspex as this permitted visual adjustment of the lower electrode holder. A diagram and detailed description of the M & S gas jet in its final configuration is given in Appendix-D.

3-3 VISUAL OBSERVATIONS ON THE M & S GAS JET OPERATION

With the M & S gas jet in good working order, visual observations on the physical behaviour of the d.c. arc when surrounded by atmospheres other than air were made.

The greatly reduced temperature of an arc surrounded by argon was obvious from the intensity of the arc itself and from the intensity of the glowing electrodes.

The practical use of amperages as high as 30 amps was possible, this amperage being impractical under any other circumstances because of the vigorous and unstable nature of the arc itself, the rapid consumption of electrodes and the excessive temperatures capable of damaging the electrode holders.

When the arc was surrounded by a mixture of argon and oxygen in the ratio 4 parts argon to 1 part oxygen, excitation at low amperages (4-5 amps) was very poor, while at 15 amps it became rather vigorous.

Arcs surrounded by nitrogen were very stable up to 15 amps while the use of pure oxygen was soon discarded even at low amperages because of the extremely vigorous and unstable nature of excitation, it being similar to that experienced when high amperages (30 amps) were used for arcing in air.

A very noticeable benefit of the gases flowing past the electrode containing the sample was the stabilization of the arc and advantages similar to those found by Stallwood (1954), using an air jet were anticipated.

Plate 1 which is a collection of photographs of d.c. arcs enveloped by various atmospheres illustrates the advantages obtained from gases flowing past the lower electrode containing the sample. (Compare (a) no gas flow with the remaining figures). The greatly reduced temperatures of the electrodes and of the arc surrounded by argon are also evident in figure (c) of Plate 1 while figure (d) shows how the arc temperature in argon is increased by employing a higher amperage. Figures (e) and (f), showing arcs burning in argon-oxygen, clearly illustrates and contrasts, the carrier effect obtained with a carrier electrode (figure (e)), with total sample excitation achieved with an electrode filled with sample, (figure (f)). The merits of the various electrode designs investigated, are discussed in detail in section 4-3.

Plate 2 is a reproduction of spectra obtained employing 15 amp d.c. arc excitation of a granite sample mixed with graphite in the ratio 1 part sample to 1 part graphite. A large variety of atmospheres and atmosphere mixtures are represented on Plate 2. The most prominent features of the plate are:

(1) reduction of cyanogen band emission when argon-oxygen or helium-oxygen mixed atmospheres are used.

(2) selective distillation of certain elements when the arc is surrounded by argon. The spectral lines of the volatile elements Zn, Cu and Sn are clearly visible in a spectrum free of matrix elements e.g. Fe 310,0nm, Al 308,2nm, Na 330,2nm spectral lines absent in (a).

(3) the greatly reduced background associated with excitation in argon.

(4) the enhancement of the spectral line of Zn when the arc is surrounded by argon.

(5) enhancement of the spectral line of Sn when the arc is surrounded by nitrogen or argon-oxygen.

3-4 INSTRUMENTAL CONDITIONS

Table 4 lists the details of the optical spectrograph, plate calibration method, plate development procedure and lens system which were employed throughout the investigation. Variable parameters such as amperage, electrode design, sample additives and atmosphere composition are dealt with individually in Chapter 4 which describes the systematic study of the use of artificial atmospheres.

3-5 CHOICE OF ANALYTICAL LINES

Table 5 contains the most sensitive spectral lines and their relative intensities for the 14 elements in the volatile group.

Visual examination of many of these spectral lines was made during the reconnaissance study using the artificial standards (whose preparation is discussed in Appendix-C). The extremes of wavelength represented in Table 5 are the Zn lines at 213,8nm and 481,05nm. The Zn line at 213,8nm and the Cd line at 228,8nm both require ultraviolet sensitive photographic emulsions. These are specialized emulsions and require rather specialized handling procedures. Because these ultraviolet emulsions are only applicable in the far ultraviolet region of the spectrum (below 220,0nm) it was decided to exclude the spectral lines at 213,8nm and 228,8nm from further consideration.

The most sensitive spectral lines of In and Hg are at 451,1nm and 435,8nm respectively while the most sensitive line for As is at 234,98nm. This is a spectral range of 216,1nm. While this wavelength range is practicable with the Jarrell-Ash 3.4m Ebert mount spectrograph, 2 photographic plates are required to cover this spectral range. In a routine method it is preferable to use a single photographic plate for the following reasons:-

(a) photographic emulsion responses are rarely the same and therefore if two plates are used, each plate requires a separate plate calibration curve

(b) if internal standardization is employed a suitable spectral line on each plate is necessary, not always practicable with the addition of a single internal standard element.

In addition to these problems, spectral lines on the outer limits of the wavelength range were not perfectly focussed on the spectrograph used and so it was far more desirable to employ a centrally mounted single photographic plate. The wavelength range was thus reduced to

125nm, the range of a normal 10 inch photographic plate, and the choice of spectral lines restricted to covering this range.

The preliminary experimentation indicated that the elements Tl, Hg, As and Sb were problematic for a variety of reasons. Elimination of CN emission interference from the Tl 377,5nm spectral line required special excitation conditions which are discussed in detail in section 3-6.

According to Ahrens and Taylor (1961) the detection limit of the Hg 253,6nm spectral line is 100ppm. During the preliminary testwork neither the Hg 435,8nm nor Hg 253,6nm spectral lines were visible and so Hg was excluded from the group of elements. Testwork using spiked samples indicated that the As 278,0nm spectral line suffered interference from a Sn line at 277,98nm and the detection limits achieved in argon with the spectral lines of As at 286,0nm and Sb at 287,7nm were approximately 100ppm. These two elements, As and Sb, were therefore not included in the remainder of the investigation. Suitable spectral lines were thus chosen for the remaining 10 volatile elements in the group. Although the Pb line at 405,7nm and Ga line at 417,2nm were the most sensitive spectral lines of these two elements, they were not favoured because of possible interference from CN 421,6nm band emission. The remaining spectral lines fell within the range Zn 334,5nm and Pb 283,3nm, a spectral range of 51,2nm which was well within the capability of a single photographic plate placed in the centre of the camera of the spectrograph.

The final choice of spectral lines used in this investigation appear in Table 6.

3-6 COMPARISON OF GAS SHEATHING DEVICES

Although the new design Margoshes and Scribner gas sheathing device promised numerous advantages over the Annell and Helz device a comparison of several devices was made prior to the detailed study of the use of artificial atmospheres.

The devices compared were:

(1) The Annell and Helz jet with glass canopy.

(2) The Spex Industries Stallwood jet with and without a glass canopy.

(3) The Margoshes and Scribner (M & S) gas device with and without a glass canopy.

(4) The base plate of the Margoshes and Scribner (M & S) device used with a specially constructed glass canopy.

The criteria employed for the comparison were :-

(a) Efficiency of cyanogen elimination.

(b) Stability of the arc.

(c) Spectral line intensity.

All the gas sheathing devices achieved optimum cyanogen elimination when low amperage excitation (3-5 amps) of the sample was used in conjunction with an atmosphere of argon-oxygen mixture and a glass canopy. It also appeared essential that the flow of gaseous mixture to the device maintain a positive pressure inside the canopy, otherwise air was sucked into the canopy via the optical path aperture and cyanogen bands appeared in the spectra. Using pure argon all the devices with or without a glass canopy resulted in poor cyanogen emission elimination. Apparently the only way to achieve effective cyanogen elimination with pure argon is by means of a gas tight chamber similar to that used by Vallee, Riemer and Loofbourow (1950).

Very unstable arcs were produced during excitation in pure argon employing either the Stallwood jet or the M & S base plate, in conjunction with a glass canopy. The arc between the upper and lower electrodes exhibited either a bowing out effect or else the burning arc rotated on the outer rim of the lower electrode. Attempts to stabilize these arcs by varying the amperage or by increasing the gas flow rate were unsuccessful. This instability contrasted sharply with the very stable discharge achieved when argon gas streamed past the lower electrode using the Stallwood jet without a glass canopy or the M & S gas device. This streaming envelope of gas which encircled the lower electrode not only stabilized the arc, but also cooled the lower electrode and swept away the outer flamy fringe of the arc discharge which is thought to be responsible for self absorption phenomena. As it was the presence of the glass canopy on the jet which was held responsible for the instability of the arc discharge, use of the glass canopy was discontinued.

Visual comparison of the spectral line intensities of a few volatile elements obtained during excitation of a natural sample in argon and in argon-oxygen using the Stallwood jet and the M & S gas jet shows that the intensities are similar. Spectra recorded during excitation of samples surrounded by artificial atmospheres using the Stallwood jet (with and without its glass canopy) and the M & S gas jet are reproduced in Plate 3.

Comparison of these spectra reveals that efficient elimination of cyanogen emission with the Stallwood jet is only achieved with the glass canopy in position.

Reduction of cyanogen emission to a level comparable to that obtained with the Stallwood jet is also achieved using the M & S gas jet constructed for this investigation. Interference by CN 359,0nm band emission with the Zn 334,5nm spectral line is clearly demonstrated (spectrum (a) and (c) Plate 3) when the Stallwood jet is used without the glass canopy.

Comparison of the spectral line intensities recorded for Zn 334,5nm and Sn 317,5nm using the new gas jet and the Stallwood jet reveals that the intensities obtained with the two devices are comparable.

Enhancement of Zn in pure argon is clearly illustrated in Plate 3 by comparing the intensity of the spectral line of Zn 334,5nm obtained during excitation in argon (spectra (b), (d), (g), (h)) with the intensity obtained using argon-oxygen. (spectra (e), (f), (i), (j), (k)). The level of enhancement of Zn is similar whether the Stallwood jet or the M & S gas jet is used.

The M & S gas jet was however superior to the Stallwood jet as different electrode sizes were readily accommodated in the lower electrode holder. Variation of the ring inserts in the upper aperture of the M & S device also ensured that the flow of gas past the different electrodes containing the sample was kept constant. Furthermore, excitation of samples was more convenient when using the M & S gas jet than when using the Stallwood jet and consequently the M & S device was used exclusively throughout the remainder of this investigation.

3-7 RECONNAISSANCE EXPERIMENTATION (PART 1)

The new M & S gas jet replaced the ceramic jet of Annell and Helz (1960) that was used by Danchin and Baumgartner (1964) during the investigation into methods for improving the detection limit of Tl. To attain ultimate Tl sensitivity, one of the first requirements is that maximum suppression of cyanogen emission (as detectable on a photographic plate) is achieved, because the sensitive Tl spectral line at 377,5nm is masked by the cyanogen 388,3nm band system.

Considerable experimentation varying electrode design, gas composition, gas flow rate, amperage and sample additives was carried out using the new M & S gas device to determine the set of conditions which would eliminate cyanogen emission most effectively.

The conditions finally arrived at which achieved maximum suppression of CN band emission were:-

(a) a gaseous mixture of argon-oxygen in the ratio 4 parts argon to 1 part oxygen coupled with a glass canopy on the M & S gas device. The glass canopy was essential for efficient exclusion of air from the arc (N_2 in the air being responsible for CN emission).

(b) low amperage excitation (3,5 amps).

(c) addition of 25% Li_2CO_3 additive to the sample.

(d) a shallow cratered electrode which ensured immediate flooding of the arc with alkali metal atoms. These conditions were totally unsuitable for the other elements in the volatile group because of the extremely slow volatilization characteristics exhibited by some of these elements.

They also resulted in Tl spectral line intensity which was poorer than that achieved by Danchin and Baumgartner (op cit) using the Annell and Helz jet with its special canopy. It was therefore obvious that Tl required a very special set of excitation conditions and that the determination of Tl should be considered a separate analytical method. As the current investigation was unable to improve the detection limit of 0,1ppm for Tl achieved by Danchin and Baumgartner (op cit) details of the optimum conditions developed by them for the determination of Tl in silicate rocks is recorded here.

The conditions were:-

(a) Annell and Helz ceramic gas jet with glass canopy fitted with a quartz optical path window.

(b) 25% Li_2CO_3 additive.

(c) Carrier design electrode (3.96 x 8mm cavity).

(d) Argon-oxygen atmosphere in the ratio of 4 parts argon to 1 part oxygen.

(e) 3,5 amp excitation.

The superior Tl spectral line intensity achieved using the Annell and Helz (1960) gas device (A & H device) with special glass canopy, compared to that achieved with the new M & S gas device, was attributed to several factors. These were:-

(a) Cooling of the electrode containing the sample, was more efficient using the A & H device and resulted in slower distillation of Tl into the arc.

(b) This slower distillation rate of Tl into the arc combined with the lower arc temperature, a consequence of low amperage excitation and the presence of Li atoms in the arc derived from the Li_2CO_3 additive, resulted in more efficient excitation of Tl atoms in the arc discharge.

(c) The presence of the special glass canopy with quartz optical window achieved more efficient exclusion of air from the arc discharge and resulted in more effective control of cyanogen emission.

(d) Use of the carrier electrode compared to use of the shallow cratered electrode (details of electrode design are given in section 4-3) resulted in greater Tl spectral line intensity. These four factors combined to produce extremely efficient vaporization of Tl from the sample, excitation of Tl in the arc discharge and resulted in a detection limit of 0,1ppm using the Tl 377,5nm spectral line.

3-8 RECONNAISSANCE EXPERIMENTATION (PART 2)

A new set of optimum arcing conditions were sought for the determination of the remaining elements in the volatile group.

It was desirable that natural materials be used for the determination of these conditions. The natural samples chosen were a Cape granite, a Malmesbury shale and a Bushveld granite as large stocks of material were available.

Examination of Table 1 shows that except for the elements Cu, Ga and Pb, employing normal O.E.S. methods the elements in the volatile group are difficult to detect in natural materials because of their low abundance levels.

The three natural materials chosen were mixed with graphite in the ratio 1 part sample to 1 part graphite, loaded into shallow cratered electrodes and arced in argon at 10, 15 and 20 amps and in argon-oxygen (ratio 4:1) at 4 amps. The spectra were recorded using Kodak 103-0 ultra sensitive photographic plates. Examination of the spectra revealed the presence of 10 of the group of 14 volatile elements. The elements identified were Ag, Bi, Cd, Cu, Ga, Ge, Sb, Sn, Pb and Zn.

The fact that these elements were visible in the spectrograms of these materials was encouraging and meant that a large stock of natural material containing the volatile elements was available for use during the greater part of the reconnaissance study.

A noticeable property of several elements of the group was their slow rate of volatilization from the samples when the electrodes and arc were surrounded by an atmosphere of argon. Numerous methods were employed in an attempt to increase these volatilization rates. The methods were:-

(a) a great variety of additives were employed in an attempt to either influence the anode temperature or promote thermochemical reactions in the electrode. Increase in anode temperature or promotion of reactions in the electrode would both contribute to an improvement in the volatilization characteristics of the volatile elements. No general improvement in the volatilization rates was found with any of the additives employed.

(b) increased amperage to offset the drastic temperature reduction of the arc enveloped in argon. Amperage was however limited to a maximum of 17 amps as sample extrusion took place at higher amperages. Predrying the loaded electrodes in an oven as suggested by Suhr N.H. (private communication) or heating them to red heat in a bunsen flame (O'Neil and Suhr 1960) failed to prevent sample extrusion. This limit of 17 amps was unfortunately not high enough to improve volatilization times significantly.

(c) addition of an anode cap to a wide cratered deep electrode containing the sample (packed and vented at the bottom of the crater) allowed operation at 30 amps in an argon atmosphere and prevented sample extrusion taking place. Use of the graphite anode cap resulted in an increase in both the spectral line background and cyanogen emission recorded photographically. These increases were probably the result of a greater number of incandescent carbon particles entering the arc discharge,

The increased spectral background could be reduced by employing less sensitive photographic emulsions. The use of these less sensitive photographic plates did not adversely affect element sensitivity because the more abundant volatile elements Cu, Zn, Pb, Ga and Sn were involved. The cyanogen emission on the other hand was controlled by soaking the anode cap in an alkali metal salt solution so that when the arc was ignited it was immediately flooded with alkali metal atoms rather than incandescent carbon particles.

Although the anode cap allowed excitation at 30 amps, which in turn increased the volatilization rates of some of the elements, it was not entirely satisfactory as preparation of the anode cap was rather time-consuming and the caps available contained Ag and Cu as contaminants.

(d) smaller amounts of sample placed in smaller electrodes also overcame the excessive volatilization times shown by the more abundant elements. Use of a smaller sample was only applicable to the more abundant elements as the spectral lines of the less abundant elements were not visible in the test spectra recorded.

3-9 CONCLUSIONS

The results of the investigation carried out during the design and testing of the new M & S gas jet were based entirely on visual observations of arc behaviour and visual estimates of arc and electrode temperatures.

Parameters such as efficient removal of cyanogen emission, spectral line enhancement, choice of suitable spectral lines, comparison of gas sheathing devices and finally comparison of the volatilization characteristics of the volatile elements during excitation of samples surrounded by artificial atmospheres, were evaluated by visual inspection of the photographically recorded spectra.

The most significant fact to emerge from this reconnaissance study was that the group of elements chosen should be subdivided, the geological abundance levels forming a guideline for this division.

The elements Cu, Zn, Ga, Sn, Pb and Ag which were abundant in the natural materials examined, exhibited slow distillation rates when excitation in argon took place and were defined as the "less volatile" group/elements, while the elements Bi, Cd, In, Ge (As and Sb), having lower abundance levels, were defined as the "more volatile" group/elements.

This classification is used throughout the succeeding discussions.

CHAPTER 4

A SYSTEMATIC STUDY OF THE USE OF ARTIFICIAL ATMOSPHERES

4-1 INTRODUCTION

As the conclusions discussed in section 3-9 indicated that a general method of analysis for the volatile elements as a group was unlikely to be achieved, a systematic study of the behaviour of these elements during excitation in artificial atmospheres was undertaken.

For such a study, samples containing all the volatile elements at known concentration levels were required. Consequently, a set of artificial standards was prepared and used for this purpose. A detailed description of the preparation procedure is given in Appendix-C.

4-2 DETERMINATION OF OPTIMUM ATMOSPHERE

It was considered advisable to employ the same exposure time, amperage and additive for the determination of optimum atmosphere for each element in the volatile group, so that an unbiased assessment of atmosphere performance could be made. In the succeeding discussion on electrode design in section 4-3, the choice of suitable electrode for use with the various atmospheres to be tested is given. For pure atmospheres the choice was a carrier electrode while the shallow cratered electrode was preferred for excitation with carbon dioxide, air and the mixed atmospheres of argon-oxygen and helium-oxygen.

Vallee and Adelstein (1952) had recommended arcing times of eleven minutes to make allowance for the slow distillation rates of the volatile elements when surrounding an arc in argon. This time was considered impractical for the current investigation, which sought to determine a routine method of analysis, and an arcing time of one minute was arbitrarily chosen for all the atmospheres being tested. The 31.6ppm artificial standard was mixed with spectrographic grade graphite in the ratio of 1 part sample to 1 part graphite, packed into the appropriate electrode and arced in duplicate at 15 amps. in nine different atmospheres. They were 100% argon, 100% helium, 100% nitrogen, 100% CO_2, 100% air, 80% Argon -20% oxygen, 90% argon - 10% oxygen, 95% argon - 5% oxygen and 80% helium - 20% oxygen respectively. Ilford ordinary N-30 photographic plates were used to record the spectra.

Relative intensities of background, (B) spectral line minus background (P-B) and nett line to background $(\frac{P-B}{B})$ ratio were determined and plotted against atmosphere composition. The results are depicted graphically in Figures 7 to 16 .

The reduction in background of an arc surrounded by argon, helium and helium-oxygen mixture is obvious, but, except for Zn and Cd, there is a corresponding reduction in spectral line intensity. Bi, Ga, Ge, In, Pb and Sn show maximum nett spectral line intensity (P-B) in nitrogen while Ag displays its highest intensity in 90% argon - 10% oxygen mixture and Cu its highest in 100% carbon dioxide.

Comparison of nett peak to background $(\frac{P-B}{B})$ ratio obtained in the various atmospheres yields similar results except that the optimum atmosphere for Bi is argon instead of nitrogen.

The behaviour of As, Sb and Hg could not be evaluated as their spectral lines were not visible and the problems associated with Tl have been discussed in section 3-7. The relative intensities obtained in argon for the elements Pb, Ag, Sn and Cu were somewhat disappointing in the light of the observations of Vallee and Adelstein (1952) and Thiers and Vallee (1956) who reported remarkable enhancement for the volatile elements Cd, Sn, Pb, Ag and Zn when a d.c. arc was surrounded by argon. They also stressed the importance of "adjusting the exposure times in argon to allow for the prolonged volatilization". The short exposure time used in this test was therefore probably responsible for the poor spectral line intensities obtained for Bi, Ga, Ge, In, Pb, Sn, Ag and Cu when compared to those obtained in nitrogen. Vallee et al (1950) examined the effect of prolonged exposure times on signal (P-B), noise (background) and signal to noise $(\frac{P-B}{B})$ ratios of spectra produced by a d.c. arc surrounded by argon. They concluded that "the use of 100% argon enhanced lines without significantly affecting background". To test whether prolonged arcing in argon would improve spectral line intensities and signal to noise ratio the 100ppm artificial standard was mixed in the ratio of 1 part sample to 1 part graphite, loaded into carrier electrodes and replicate arcings at 15 amps. in argon were made. Exposure times of one, two and five minutes were used. As a basis for comparison the same sample-additive mixture was loaded into shallow cratered electrodes and arced in air for one minute.

Background and spectral line intensities were measured and nett peak to background ratios calculated. The results obtained are depicted in Figures 17 to 22.

Examination of these results reveals that background increases at a greater rate than spectral line intensity and consequently signal to noise ratio $(\frac{P-B}{B})$ decreases with longer arcing times in argon. There was therefore little advantage to be gained by using longer arcing times in argon.

Comparison of the signal to noise ratios obtained in argon and in air confirmed the "remarkable enhancement" of the volatile elements reported by Vallee and Adelstein (1952) and Thiers and Vallee (1956). This enhancement in many instances (Sn, Bi Ge and Pb) was the result of greatly reduced background in argon rather than increased spectral line intensity. For Cd it was the spectral line intensity that was enhanced relative to the intensity obtained in air. The enhancement of Zn was even more remarkable as its spectral line was not detectable in air, but was readily visible in argon.

Of the nine atmospheres tested, optimum $(\frac{P-B}{B})$ ratios of volatile elements were obtained using either argon, 90% argon - 10% oxygen, nitrogen or carbon dioxide. As carbon dioxide was specific for one element only, Cu, and the signal to noise ratio obtained for Cu using nitrogen was only slightly lower than that obtained in carbon dioxide, the continued use of carbon dioxide was considered non-essential.

The final choice of atmospheres for the systematic investigations was thus 100% argon, 90% argon - 10% oxygen mixture and 100% nitrogen. The 90% argon - 10% oxygen mixture will, for the sake of convenience, be referred to as argon-oxygen.

Mention should be made of the fact that the use of nitrogen was accompanied by excessive cyanogen emission which masks the spectral lines of many elements. Of the volatile elements under investigation the Zn spectral line at 334.5 nm was rendered totally unusable when nitrogen was employed as an atmosphere.

4-3 ELECTRODE DESIGN

During the reconnaissance experimentation described in section 3-8, four electrode designs applicable to the systematic study emerged.

Figure 23 shows their shape and dimensions.

The four designs were designated as:

a. carrier electrode

b. shallow cratered electrode

c. carrier electrode with anode cap

d. small carrier electrode.

a. Carrier electrode

The carrier electrode is characterised by a deep crater, the sample being placed at the bottom of this crater. When the arc is ignited direct excitation of the sample cannot take place because of its location in the electrode crater.

Initially the arc burns between the upper electrode and rim of the carrier crater. As the temperature of the carrier electrode increases and exceeds the boiling points of the sample's components they distil from the sample and enter the arc plasma in the so called "carrier effect".

For this carrier effect to function efficiently, it is necessary for sample, plus additive if required, to be compacted into the bottom of the crater. A small central vent hole is made in this plug of material to allow the gaseous components of the sample to escape freely when the arc is initiated, thus minimizing extrusion of material from the electrode crater. It is a feature of efficient operation of the carrier effect that a sintered plug of material remains at the bottom of the electrode after arcing.

The carrier electrode was originally designed for use with the carrier distillation method of analysis for determining impurity elements in nuclear fuels (Scribner and Mullin (1946)). It had already been used with success by other workers in the Department of Geochemistry and the current investigation sought to improve the design and test its applicability. Tests using different electrode designs indicated that the carrier electrode was the most suitable design for use with argon, nitrogen and helium atmospheres. The standard carrier electrode used in this investigation had a crater 5mm deep and 3,96mm wide and will be referred to as a D-5 carrier electrode.

b. Shallow cratered electrode

The addition of oxygen to the artificial atmospheres argon and helium, seemed to adversely affect the "carrier effect" when it developed using a carrier electrode with argon-oxygen and helium-oxygen mixtures. In addition, the spectrograms photographed recorded high background continuum.

It was apparent that the addition of oxygen to the inert atmospheres argon and helium elevated electrode temperatures and consequently electrode consumption. This resulted in the entry of incandescent carbon particles into the arc, these particles probably being responsible for the high spectral background recorded. It was therefore necessary to employ a different electrode design.

The shallow cratered electrode, filled with sample, turned out to be most suitable for use with atmospheres which contained oxygen. On ignition of the arc, because of the higher electrode temperatures attainable, immediate sample vaporization took place flooding the arc with sample atoms. Because of the absence of incandescent electrode particles in the arc, spectral background was reduced to acceptable levels.

The standard shallow cratered electrode had a crater 2.5mm deep and 3.96mm wide and will be referred to as a D-2 electrode.

c. Carrier electrode plus anode cap

Although the carrier electrode was most suitable for use with helium, nitrogen and argon atmospheres, it was noted that when the arc was surrounded by argon, distillation times of several of the elements being studied were extremely long. Typical volatilization times are recorded in Table 7.

Undercutting the carrier electrode, which has the effect of raising the temperature of the electrode cup, resulted in too great a heat localization, the plug of material rising to the rim of the electrode crater and the carrier effect being eliminated.

The elevation of electrode temperature by the use of increased amperages is discussed in section 4-5. Although the ordinary carrier electrode could be used with elevated amperage in the manner described in section 4-5, an improved carrier electrode design was sought which would allow direct excitation at 30 amps. in argon. It was thought that widening the carrier electrode crater coupled with the introduction of an anode cap would satisfy this requirement. Direct excitation at 30 amps still resulted in sample extrusion and the procedure for increasing amperage from 15 amps to 30 amps, discussed in section 4-5 had to be employed. The combination of wide cratered electrode, anode cap and 30 amp excitation in argon did improve the volatilization characteristics of the less volatile elements and is demonstrated in Table 8.

The disadvantages of the anode cap are discussed in section 3-8c.

The carrier electrode used with the anode cap had a crater 4mm deep and 4.76mm wide and was designated I.S.-4.

d. <u>Small carrier electrode</u>

A simple method of overcoming the long volatilization times exhibited by the less volatile elements was the use of a carrier electrode with smaller dimensions and holding much less sample. The dimensions of the crater were 3.18mm wide and 6mm deep and this design was designated C-6. A moving plate exposure of the natural material (Z2 Bushveld granite) mixed in the ratio of 1 part sample to 1 part graphite was loaded into a small carrier electrode and arced in argon at 17 amps. The visual scanning method described in section 4-4 was used to determine when volatilization of the less volatile elements was complete.

The volatilization times are set out in Table 9 and indicate that Ag, Ga and Pb complete their distillation from the sample in one minute while Zn has not completed its distillation after three minutes. The constant intensity of the spectral lines of Cu and Sn in the last two minutes of the burn, are indicative of carbide formation which is dealt with in section 4-7.

Electrode material

Comparison of the use of graphite rod and carbon rod as electrode material soon revealed that carbon was far superior. Graphite was consumed too quickly after arc ignition, this rapid consumption of the carrier design electrode resulting in elimination of the carrier effect. Electrodes machined from carbon rod on the other hand were generally more robust, especially during high amperage excitation in argon and consequently carbon rod was used exclusively in this investigation as the electrode material.

4-4 THE USE OF ADDITIVES

Boumans (1966) and Slavin (1971) agree that there appears to be little rationale in selecting a suitable additive for a particular investigation, and that the ultimate choice of a suitable additive is made empirically. This empirical approach has resulted in a great variety of additives being reported in the literature.

In section 2-6 the role of additives in improving the detection limits of the volatile elements was discussed in detail and selection of suitable additives for this investigation was made from among the additives quoted in section 2-6. In the current investigation the influence of additives on (a) spectral line intensity (b) volatile element distillation rates (c) thermochemical reactions and (d) burning characteristics of the arc was studied.

(a) Spectral line intensity

The influence of additives on background (B) nett peak (P-B) and nett peak to background ratio ($\frac{P-B}{B}$) was assessed using a Bushveld granite sample blended individually with six (LiF, $Li_2 CO_3$, CaF_2, K_2SO_4, $CaCO_3$ and NaF) of the additives selected. The blended samples were loaded into carrier electrodes (3.96mm diam. x 8mm deep crater) and arced in argon at 15 amps for 60 seconds. Figures 24 to 26 illustrate the measured background, nett peak and nett spectral line intensity to background ratios for the elements Cd, Sn and Zn obtained with the additives used. Comparison of the results obtained reveals that superior signal to noise ($\frac{P-B}{B}$) ratios for all three elements was not achieved using the same additive. These results combined with further visual comparisons of spectral line intensities led to the conclusion that spectral line enhancement of all the elements in the volatile group using the same additive was not possible. The enhancement of specific volatile element spectral lines by specific additives was not investigated as this study sought to determine the volatile elements using a single spectrographic method.

(b) Distillation rates

The role of additives in improving the volatilization rates of the less volatile elements was examined by means of moving plate experiments. The Bushveld granite sample was mixed with five (Li_2CO_3, LiF, K_2SO_4, CaF_2 and NaF) of the selected additives, loaded into D-5 carrier electrodes and arced in argon at 20 amps. The photographic plate was racked every 30 seconds while the carrier effect was visible. Visual estimation of the time taken by an element to complete volatilization from the sample was made by examining the recorded spectra and noting when the spectral line of the element disappeared from the recorded spectra. As this method of determining volatilization times was used extensively throughout this investigation it will be referred to as the visual scanning method. Table 7 sets out the volatilization times taken by the less volatile elements and examination of the table reveals that improvement in the distillation rates of all the elements using the same additive was not possible. Specific additives are capable of improving the volatility of individual elements but this aspect was not pursued as determination of a suitable additive for each individual element in the volatile group was not within the scope of this investigation.

(c) Thermochemical reactions

Contrary to the assertions by Boumans (op cit) and Slavin (op cit) that there appears to be little reasoning attached to the selection of additives, Schroll (1964), placed great emphasis on understanding the thermochemical reactions which take place in the electrode cavity during arcing of a sample. A knowledge of the thermochemical reactions which take place would facilitate the addition of a specific additive capable of improving the volatilization rates of the volatile elements.

The chalcophilic nature of the volatile elements almost certainly contributed to the successful improvement in the normal d.c. arc detection limits of the elements Sn, Pb, Bi, Zn, As and Sb achieved by Schroll and Weninger (1965) who employed sulphidizing agents to convert the elements into their more volatile sulphides.

Mixtures similar to those employed by Schroll and Weninger (1965) ($BaSO_4$ and S), Janda and Schroll (1959) (NH_4Cl and Li_2CO_3) and Joensuu O.I. (private communication A.J. Erlank) were tested in the present investigation, as possible promoters of thermochemical reactions. The admixed samples were loaded into the modified carrier electrode with anode cap (section 4-3c) and arced in argon at 25 amps. The photographic plate was moved every 60 seconds for

4 minutes and the volatilization times of the less volatile elements determined using the disappearance of the spectral line of the element as evidence of its complete volatilization from the sample. The volatilization times established are shown in Table 10. Comparison of the volatilization times presented in Tables 7 and 10 shows that the distillation times are similar and indicates that the volatilization characteristics of the less volatile elements are probably not influenced by thermochemical reactions if indeed any were able to take place in the arc surrounded by argon. Experiments described in section 4-13 indicate that the anode temperatures of an arc burning in argon are depressed and are independent of the ionization potential and boiling point of the alkali or alkali earth compounds present in the sample. Consequently it is possible that no useful thermochemical reactions can take place in the electrode cavity at these reduced temperatures. Although the evidence presented indicates that specific additives have discrete advantages for individual elements it does not single out any specific additive as being able to improve the volatilization characteristics, enhance spectral line intensities or promote thermochemical reactions for the less volatile elements as a group.

(d) Burning characteristics of the arc

Some important observations on the carrier effect described in section 4-3a were made and must be discussed.

It was noticed that those samples which contained appreciable amounts of alkali metal compounds required only the addition of graphite powder for the carrier effect to operate efficiently when the d.c. arc was surrounded by argon or nitrogen. When the sample contained low alkali metal concentrations, it was necessary to include alkali metal compounds with the graphite additive to obtain a good carrier effect.

Excitation in argon-oxygen produced a poor carrier effect and resulted in the shallow cratered electrode design discussed in section 4-3b.

To minimize spectral background when using these shallow cratered electrodes it was desirable that on striking the arc it was flooded immediately with alkali metal atoms. Samples which inherently lacked alkali metal content required suitable additive supplements. This investigation however, did not examine in detail the role played by additives when the arc was surrounded by argon-oxygen.

(e) Final additive choice

In view of the fact that additives do not influence anode temperature when the arc is surrounded by argon, choice of suitable additives for the systematic study was somewhat empirical.

The advantages of having the arc flooded with alkali metal atoms when using argon-oxygen have been discussed. Alkali metal atoms and graphite appeared to be essential additives for an efficient carrier effect to take place.

As the mixture used by Wang and Cave (1964) contained Li_2CO_3 and graphite and that of Ingamells and Suhr (1963) K_2SO_4 and graphite the choice was narrowed to one of these mixtures. The Ingamells and Suhr (op cit) mixture prepared by adding 80% sample to 8% K_2SO_4 and 12% graphite and designated 20/2/3 had been used in the determination of the volatile elements in silicate rock reference materials and was thus selected for the systematic study.

Although the addition of pure graphite was only advantageous when the sample contained appreciable amounts of alkali metal atoms, graphite was also selected for the systematic study and its performance used solely for comparative purposes.

A procedure which allowed excitation at amperages as high as 25 and 30 amps was initiation of excitation at a low amperage (15 amps) and then, once the carrier effect was in operation, increasing the amperage to the desired level. This procedure was facilitated by the fact that the varisource unit was equipped with a low-high range switch on the amperage selector. For example, it was possible to immediately change the amperage from 10 amps to 20 amps by use of this switch. Application of this procedure in a routine analytical method would require internal standardization with the added internal standard element displaying volatilization characteristics closely matching those of the analytical elements.

In section 4-3b the modified carrier electrode with anode cap has been described. It was designed specifically for use with special additive mixtures and 30 amp. excitation in argon.

The same "switching up" procedure used with the normal carrier electrodes had to be employed with the modified carrier. A moving plate study of the distillation trends of the less volatile subgroup present in a natural sample (Bushveld granite Z2) arced in argon at 30 amps, revealed that their volatilization characteristics could be improved. The results derived by the visual scanning method of interpretation described in section 4-4 are listed in Table 8 and demonstrate that the average distillation time is one and a half minutes and independent of the additive used. When the volatilization times listed in Tables 7 and 8 are compared it can be seen that 30 amps. excitation has improved the volatilization trends of the less volatile subgroup.

Copper displays no improvement in volatilization time, although close examination of the recorded spectra reveals that the intensity of the Cu spectral line in the last one and a half minutes of the arcing period (recorded in Table 8) is constant and indicative of carbide formation, a phenomenon encountered in section 4-4 and discussed in section 4-7.

The use of increased amperages in argon-oxygen was restricted to an upper limit of 15 amps. The presence of oxygen in the mixture caused the excitation process to become so vigorous and temperatures (gauged by electrode incandescence) to be elevated to such an extent that damage to the gas device and arc spark stand was possible when amperages in excess of 15 amps were employed.

The increased amperages used with argon were also possible with nitrogen. Cyanogen emission, already a problem associated with excitation in nitrogen atmospheres, increased as amperage increased. In section 4-6 the influence of varying amperage on the volatilization characteristics of the volatile elements is examined in greater detail.

4-6 MOVING PLATE EXPERIMENTS

The slow volatilization rates of the elements Cu, Ga, Pb, Sn and Zn, during excitation of natural materials in argon are described in section 3-8, and the relatively long volatilization times taken by these elements are demonstrated in Table 7.

To obtain a more precise assessment of the volatilization rates under varying experimental conditions a comprehensive moving plate study was undertaken.

The sample selected for this moving plate study was the 31.6 ppm artificial standard as it was most likely to yield reasonable spectral line intensities for the greatest number of elements in the volatile group. The standard was mixed with the two additives finally selected in section 4-4 (sample/graphite = 1/1 and Ingamells and Suhr 20/2/3) and loaded into D-5 carrier electrodes. The three atmospheres chosen in section 4-2 (argon, argon-oxygen and nitrogen) were employed. Excitation at different amperages was used to determine the influence of amperage on rates of volatilization.

Ilford ordinary N-30 plates which have a slow emulsion response were selected for recording the spectra. Their slow response results in low spectral background being recorded and also makes them suitable for recording the wide range of spectral line intensities which the different elements in the volatile group produce at their concentration levels in the sample used.

Volatilization curves were constructed by plotting, the relative intensities of the spectral lines of the elements measured in the consecutive spectra of the moving plate against time. The volatilization curves which are shown in Figure 27 are those obtained for Ge and are typical of the curves for Ag, Cu, Ga, In, Sn and Zn.

The practical implementation of amperages in excess of 17 amps is discussed in section 4-5 and was used to obtain the volatilization curves at 20, 25 and 30 amps in nitrogen and argon atmospheres. Excitation in argon-oxygen was restricted to 5, 10 and 15 amps.

The curves in Figure 27 illustrate the slow distillation rates of the elements, designated less volatile, from samples arced in argon, argon-oxygen and nitrogen when low amperage excitation is employed. The improvement in volatilization rates achieved by increasing the excitation amperage is clearly seen.

Comparison of the curves for Ge during excitation in argon and in nitrogen using 20 and 25 amps (Figure 27 (a)(b)(e)(f)) reveals that the distillation rates in nitrogen are greater, probably a result of the higher temperatures attained with nitrogen. This increased volatility of the less volatile elements during excitation in nitrogen is probably the reason greater spectral line intensities were obtained for these elements during the determination of optimum atmosphere (described in section 4-2) when parameters such as excitation amperages and exposure times were kept constant.

Comparison of the volatilization curves obtained for Ge employing the two additives chosen, (Figure 27(c)(d)(e)(f)) shows that the presence of alkali metal atoms in the arc decreases volatilization rates when excitation at low amperage (10 amps) takes place in argon-oxygen and nitrogen. This decrease in volatilization rate is the result of the reduction in electrode temperature by the alkali metal atoms. The mechanism whereby electrode temperature is reduced is indirect. The alkali metal atoms (because of their low ionization potentials) actually lower the arc gap voltage and it is this lower voltage across the arc gap that results in the lower electrode temperature. These reduced volatilization rates are increased by using higher amperages (in argon-oxygen 15 amps and in nitrogen 25 amps) which effectively overcome the temperature quenching effect of the alkali metal atoms.

Comparison of the distillation rates of Ge from a sample buffered with graphite and a sample buffered with Ingamells and Suhr mixture (20/2/3) Figure 27(a) and (b) reveals that during excitation at 20 amps in an arc surrounded by argon, distillation of Ge from the graphite buffered sample is slower and is probably related to the formation of silicon carbide in the electrode crater (Discussion section 4-7).

In section 3-9 Ge and In were designated more volatile but in this moving plate study they display less volatile characteristics. The reason for this duplicity is because the concentration levels of Ge and In in the sample employed in this moving plate study are greater than their concentration levels in the natural materials used in section 3-9, and at these greater concentration levels they distil from the sample for a longer period of time.

The volatilization curves constructed for Cd are shown in Figure 28 and are typical of the curves obtained for Bi and Pb. Rapid volatilization rates are displayed in all three atmospheres using both additives and are independent of the amperage employed. These findings for Bi and Cd confirm their designation as more volatile made in section 3-9.

In section 3-9 Pb was defined as less volatile and in Tables 7 and 8 this classification was confirmed. Closer examination of Tables 7 and 8 reveals that Pb displays less volatile characteristics when the additives LiF, CaF_2 and NaF are used and more volatile characteristics with the additives Li_2CO_3, K_2SO_4, SCHROLL 1 and SCHROLL 2. The latter additives are obviously a selection of additives suitable for improving the volatilization of Pb and emphasises the need for a more detailed examination of the influence additives have on individual volatile element volatilization behaviour.

Volatilization curves for As, Sb, Hg and Tl were not obtained with the artificial standard employed because of lack of sensitivity but they would probably display distillation characteristics similar to those of Cd.

The different volatilization characteristics depicted in Figures 29, 30, 31 a composite of several volatile element volatilization curves, confirms the recommendation in section 3-9 that the volatile group be sub-divided. While the designation as less volatile and more volatile is substantiated by the moving plate study, the elements assigned to the two subgroups differ. Based on the volatilization curves obtained in this moving plate study the less volatile group consists of Ag, Cu, Ga, In, Ge, Sn and Zn while the more volatile group contains Bi, Cd, Pb (As and Sb).

The apparently dual volatilization characteristics exhibited by the elements Ge, In and Pb emphasizes the need for caution when employing volatilization curves established using volatile element oxides added to an artificial matrix for predicting the distillation behaviour of the same elements from silicate materials where the elements are usually incorporated in complex structures.

The formation of silicon carbide in the electrode cavity during arcing in argon (demonstrated in section 4-7) also plays an important role in influencing the volatilization characteristics of some of the volatile elements and this factor should not be overlooked when interpreting the results of a moving plate study.

4-7 CARBIDE FORMATION

Nickel (1968), Ahrens and Taylor (1961) and Schroll (1963) all point out that the volatility of an element can be influenced by a variety of electrode reactions and by thermal conditions in the electrode cavity. Of the numerous reactions that are possible, the reduction of oxide to metal and the formation of involatile carbide (especially when carbon or graphite powder is present as an additive) is significant to this investigation.

Erlank (1964)while examining the behaviour of Be in a d.c. arc surrounded by argon, observed that the Be 313,1nm spectral line decreased in intensity in successive exposures of a moving plate. Under normal circumstances the disappearance of the spectral line of an element from the recorded spectra is indicative that that element has completed its distillation from the sample. On arcing the residue of the Be sample, mentioned above, in air, the Be 313.1nm spectral line reappeared in the recorded spectra indicating that, although the burn in argon had been in progress for 20 minutes, Be had in fact not completed its distillation from the sample.

An X-ray diffractogram of the residue from a similar sample arced in argon revealed the presence of silicon carbide. The formation of silicon carbide (or beryllium carbide) in the electrode crater was thought to have inhibited the volatilization of Be into the arc. The arc in air however, capable of attaining a higher electrode temperature, permitted Be to recommence volatilization from the residue.

The investigation by Nickel (1968) into carbide formation during d.c. arc excitation is discussed in section 2-6c. He reported that "most alkaline earth oxides, when reacting at high temperatures with carbon are converted into thermally stable heteropolar carbides". Nickel's (op cit) experimentation confirmed not only the formation of silicon carbide (SiC) in the electrode but also the formation of beryllium carbide (Be_2C), the temperature of formation of Be_2C being estimated at 2030°C. The decomposition temperature of Be_2C is quoted as 2200°C while that of SiC is quoted as $\sim$ 2700°C (Nickel 1968 pg. 343) both temperatures being easily attainable by a d.c. arc in air. Arcing a Be sample residue in air would therefore result in decomposition of the Be_2C and SiC formed during excitation in argon permitting Be to re-enter the arc.

The observation of Erlank (1968) of significance to this investigation was that the disappearance of a spectral line of an element from moving plate spectra should not be regarded as conclusive evidence that the element has completed its distillation from the sample.

Schroll (1963), Nickel (1968) and Slavin (1971) list the refractory elements as being the main carbide formers and it is therefore reasonable to assume that the volatile elements will not themselves form carbides which could influence their volatilization characteristics.

Morrison et al (1960) developing a method of analysis for the determination of volatile element impurities in silicon carbide found that 20 amp. excitation in argon enhanced selective distillation of the volatile elements from the silicon carbide matrix. These findings suggest that distillation of the volatile elements are not likely to be influenced by the presence of silicon carbide. It was nevertheless decided to check whether or not any of the volatile elements exhibited behaviour similar to that displayed by Be during prolonged arcing of samples in an argon atmosphere.

An artificial standard containing the volatile elements at the 31,6 p.p.m. concentration level was mixed with K_2SO_4 and graphite in the ratio 20 parts sample: 2 parts K_2SO_4: 3 parts graphite and arced in argon at 15 amps. The photographic plate recording the spectra was moved every minute for 11 minutes. The residue was then arced in air at 10 amps. and the resultant spectrograms examined for evidence of incomplete volatilization during excitation in argon. The results obtained are illustrated by means of volatilization curves and are found in Figures 32 to 36. In these figures Sn appears to complete its distillation into the arc in three minutes and Ge in five minutes while Ga and Cu exhibit a slow decrease in intensity and after 11 minutes have apparently not completed their distillation into the arc. On arcing the residue in air, the spectral lines of Ga, Sn and Cu reappear strongly, while the spectral line of Ge is only just visible.

Because many of the volatile elements have poor sensitivity in air, this experiment was repeated with the 316 p.p.m. artificial standard. Bi appears to complete its distillation from the sample in 6 minutes when the arc was surrounded by argon but the spectral line re-appeared when the residue was arced in air. The previous findings for Cu, Ga, Sn and Ge were confirmed.

Excitation in atmospheres of argon-oxygen and nitrogen resulted in complete consumption of the samples and no residue remained. It was therefore not possible to determine whether carbide formation takes place when the arc is surrounded by argon-oxygen and nitrogen.

A further test using the 316 p.p.m. artificial standard buffered in the same way as the 31,6 p.p.m. standard but arced at 30 amps in argon also resulted in complete sample consumption. The possibility of carbide formation during high amperage excitation in argon could therefore not be investigated.

X-ray diffractometry confirmed the formation of silicon carbide in the electrode cavity during arcing of graphite buffered samples at 20 amps in an argon atmosphere.

Typical diffractograms of arced and unarced samples are shown in Figures 37 to 39. Several other additive mixtures which contained graphite and were used during the additive testwork described in section 4-4 were mixed with silica-rich samples and arced in argon. The residues were examined for silicon carbide formation. X-ray diffractometry confirmed the formation of silicon carbide whenever graphite was present in the additives mixed with the samples.

Pikhtin (1965) states that silicon carbide formation only begins at temperatures of 1727°C while Nickel (1968) found that silicon carbide formation is possible at a temperature of about 1480°C. The decomposition temperature of silicon carbide is given as approximately 2700°C (Handbook of Physics and Chemistry).

Morrison et al (1960) measured the electrode temperature of an arc burning at 20 amps in argon to be 2600°K (2327°C) this temperature being high enough for silicon carbide formation to take place in the electrode cavity.

This electrode temperature is however too low for the SiC formed in the electrode to decompose. In seeking an explanation for the retention of the elements Cu, Ga, Sn, Ge and Bi during excitation in argon, the observations of Nickel (1968) and Morrison et al (1960) are pertinent. Nickel (op cit) demonstrated that the volatile elements do not themselves form carbides and so retention of the elements Cu, Ga, Sn, Ge and Bi cannot be ascribed to formation of their carbides.

The ability of Morrison et al (op cit) to selectively distil the volatile elements from a silicon carbide matrix by excitation in argon suggests that silicon carbide is not responsible for inhibiting volatilization of the volatile elements. As the temperature in the electrode cavity permitted the formation of silicon carbide (according to the reaction $SiO_2 + 3C \rightleftharpoons SiC + 2CO$ Nickel op cit) in situ, reaction of graphite with some of the volatile element oxides present in the artificial standard may also be possible. Reduction of the oxides to metal (Nickel op cit) and the possible formation of intermetallic compounds (Török et al 1978) should also be considered as possible explanations for the retention of the elements. Examination of the volatilization curves for Cu and Ga (Figures 33 and 34), illustrating the distillation of these elements during excitation of the sample in argon, reveals that Cu and Ga initially exhibit a normal distillation pattern but after approximately 4 minutes the rate of distillation becomes constant. It is thought that this constant rate of distillation is related to the formation of silicon carbide in the electrode crater. Only when the electrode temperature is elevated by excitation in air is the silicon carbide structure broken down thereby releasing the elements Cu and Ga and enabling them to complete their distillation into the arc.

The retention of the elements Cu, Ga, Sn and Bi during excitation in argon is thought to be responsible for the poor reproducibility achieved during excitation in argon (Section 4-9), and the inability to improve reproducibility by means of internal standardization (Section 4-10).

The slow volatilization characteristics demonstrated by the elements Cu, Ga, Ge and Sn (Section 4-6) is probably also a consequence of the formation of reaction products like silicon carbide.

In establishing optimum conditions for a quantitative spectrochemical procedure the possibility of thermochemical reactions resulting in carbide formation should therefore not be overlooked, as carbides obviously influence the volatilization characteristics of the elements present in a sample.

4-8 CALIBRATION CURVES

The original aim of this investigation was to develop, if possible, a general spectrographic method of analysis for the volatile group of elements at trace levels in silicate rocks.

For reasons that have been discussed in detail this was not practicable. The lack of reproducibility of the d.c. arc when surrounded by argon and argon-oxygen led to the conclusion that construction of reliable calibration graphs may not even be possible. Nevertheless, the 3, 10 and 31,6ppm artificial standards were selected and arced in the three atmospheres chosen for the detailed investigation.

The standards were buffered with the Ingamells and Suhr (20:2:3) additive, loaded into D-5 carrier type electrodes and arced using various amperages. The exposure times for each amperage were adjusted so that only the "carrier type distillation" portion of the burn was recorded. Each standard was arced in duplicate with a 7 step sector mounted on the optical path to provide graded intensity lines. Ilford ordinary N-30 photographic plates were used to record the spectra.
The self-calibration method was used to convert optical density readings to intensity. Background corrections were made where applicable. In view of the results obtained in section 4-10 no internal standardisation was employed.

Figures 40 to 42 depict the calibration curves for Ag obtained during excitation in the various atmospheres tested and are typical of the curves drawn for the elements in the less volatile group.

Figure 40 illustrates that when excitation takes place in argon, improvement in the linearity of the working curves is achieved by the use of increased amperage. This improvement in linearity is probably related to more efficient volatilization achieved with the higher temperature.

Figure 41 depicts the poor linearity of the working curves obtained employing argon-oxygen as the surrounding atmosphere. The non-linearity of the curves in argon-oxygen is attributed to three different phenomena. At the lower amperage (15 amps), the background contribution to the intensity of the 3ppm standard causes the curve to deviate from linearity. Using the higher amperage (20 amps), deviation from linearity occurs at the higher concentration level because of either incomplete volatilization of the less volatile element or the presence of self-absorption.

Figure 42 which contains the curves obtained in nitrogen shows that using 15 amp excitation and 60 second exposure the curve is linear while at 20 amps excitation and 40 seconds exposure the curve is non-linear.

Comparison of the working curves obtained in nitrogen and argon exploying 15 amp excitation reveals that in nitrogen the curve is linear and in argon non-linear. The linearity in nitrogen is almost certainly related to the higher electrode temperature achieved by excitation in nitrogen.

The non-linearity of the working curve at 20 amps in nitrogen appears to be related to incomplete volatilization of the upper standard as the intensities of the lower standards are similar to the intensities obtained employing only 15 amp excitation.

Before discussing the calibration curves obtained for the more volatile elements it should be noted that calibration curves for certain excitation conditions could not be drawn as the background contribution to the spectral line intensities of these elements was so great that the lines could not be measured.

The excitation conditions were 25 amps in argon, 15 and 20 in argon-oxygen employing 120 and 90 second exposures respectively and 20 amps in nitrogen.

Special short exposure excitations in argon-oxygen and nitrogen were recorded so that a comparison of calibration curves in various atmospheres could be made.

Figures 43 to 45 show the calibration curves for Bi in the three atmospheres and are typical of the curves obtained for the more volatile elements in the group. Figure 43 illustrates that the working curves obtained during excitation in argon are linear and that linearity is not dependent on amperage. The calibration curves in nitrogen (Figure 45) are also linear. In argon-oxygen the curve (Figure 44) deviates from linearity and shows curvature at high Bi concentration, the curvature being caused either by self absorption or by incomplete volatilization.

Figure 46 showing the calibration curves obtained for Ga during excitation in argon are included as they depict the curves obtained with an element that displays incomplete volatilization because of the formation of silicon carbide (Section 4-7).

Comparison of Figures 40 and 46 reveals that the deviation from linearity shown by the Ga curves at 15 and 20 amps is greater than the deviation from linearity shown by Ag at equivalent amperages. In addition, excitation at 25 amps in argon is unable to improve the linearity of the working curve of Ga to the same degree as that achieved for Ag.

The spread of plotted points is much greater for Ga compared to the spread for Ag. The formation of silicon carbide in the electrode crater during excitation in argon probably causes irregular vaporization of the element Ga to take place. This irregular vaporization is in turn thought to be responsible for the greater spread of plotted points.

Figures 47 and 48 show the calibration curves obtained for Ga during excitation in argon-oxygen and nitrogen.

Comparison of these curves with those obtained for Ag (Figures 41 and 42) reveal that the curves are similar. This similarity is taken as an indication of the absence of the formation of silicon carbide during excitation in argon-oxygen and nitrogen atmosphere and consequently the volatilization of Ga is unaffected.

In spite of the poor reproducibility of the d.c. arc when surrounded by argon, linear calibration graphs are possible under certain conditions. For the less volatile elements, increased amperage in argon results in linear calibration curves while for the more volatile elements linearity is independent of the amperage used. Non-linearity of calibration graphs in argon-oxygen are apparently caused by background interference at low concentration levels. Incomplete volatilization or self-absorption causes deviation from linearity at the high concentration portion of the graph.

4-9 PRECISION

The precision obtainable with a d.c. arc surrounded by argon, argon-oxygen and nitrogen was estimated by replicate arcings (10 or more) of the 10 ppm artificial standard buffered with the Ingamells and Suhr (20/2/3) additive. The buffered samples loaded into D-5 carrier electrodes, were arced at 15 amps, the exposure times selected being 90 secs for argon, 40 secs for argon-oxygen and 30 secs for nitrogen. These exposure times were chosen as they represented the major portion of the carrier distillation effect (See section 4-3).

Intensities for the principal spectral lines of the volatile elements were obtained using the self calibration method of Ahrens and Taylor (1961). The coefficient of variation (c.o.v.) of the intensities was calculated using the formula suitable for computation with a desk-top calculator where $S = \sqrt{\frac{\Sigma x^2}{n} - (\bar{x})^2}$ and $\text{c.o.v.} = \frac{S\times 100}{\bar{x}}$ ($\bar{x}$ = Arithmetic mean). The results obtained are presented in Table 11 and are discussed for each atmosphere in turn.

a. Argon atmosphere

Considering the elements in the less volatile group, the c.o.v. for Ge is close to 10%, an acceptable value for d.c. arc excitation. The c.o.v.'s for the other less volatile elements namely Ag, Ga, In, Sn and Zn range from 16.8% for Sn to 26.3% for Ga, these being the values expected in an approximate method of analysis (Ahrens and Taylor 1961, pg. 117), while the value of 50% for Cu is extremely poor. The volatilization rates of the less volatile elements are slow (Figure 29) and for some elements irregular (Figure 29). In section 4-7 it is demonstrated that the formation of silicon carbide in the electrode cavity inhibits the volatilization of the elements Cu, Ga, Ge and Sn. The precision obtained for these elements ranges from good (Ge 10%) to moderate (Ga 26.3%).

The reasons for the extremely poor c.o.v. obtained for Cu and the moderate values of c.o.v. obtained for the other less volatile elements (Ge excluded) are probably related either to their slow and irregular volatilization from the sample or to the formation of silicon carbide in the electrode cavity during excitation in argon.

The remarkable enhancement of Zn, which resulted in an improvement in the detection limit for Zn employing excitation in an argon atmosphere, (Section 4-11) suggested that the determination of Zn in silicate rocks using argon was feasible. The c.o.v. of 20% for Zn however, emphasises the importance of first overcoming the problem of the slow distillation of the less volatile elements before a viable method of analysis is possible. With the exception of Cd (c.o.v. 9.4%) the c.o.v.'s of the other elements in the more volatile group (Bi 20.8% and Pb 14.1%) are disappointing. The reason for this moderate precision cannot be ascribed to incomplete volatilization but may in the case of Bi be caused by the formation of silicon carbide (section 4-7) which inhibits volatilization of certain volatile elements.

b. Argon-oxygen atmosphere

In general the c.o.v.'s attainable with excitation in an atmosphere of argon-oxygen are poor in spite of the higher temperatures attained with this mixed atmosphere. The range of values for the less volatile elements are from 15.5% for Ge to 31.5% for Cu.

The c.o.v.'s obtained for Cd and Bi, elements in the more volatile subgroup, are 12.8% and 11.5% respectively, values which are just greater than the acceptable level of 10%.

The reason for the poor precision obtained for the less volatile elements is probably again related to their incomplete volatilization during excitation in argon-oxygen. This supposition is actually strengthened by the fact that the precision obtained for the more volatile elements Cd and Bi are only marginally greater than the acceptable levels of 10%.

c. Nitrogen atmosphere

The reproducibility obtained, particularly for the less volatile elements, employing excitation in nitrogen, is most certainly far superior to that obtained using argon or argon-oxygen atmospheres. For example, the c.o.v.'s were 6% for Ag, 12% for Ga, 8% for Sn and 25% for Cu. The greatly improved reproducibility of the less volatile elements is largely attributable to the higher temperatures attainable with nitrogen (Section 4-12) resulting in more complete volatilization of these elements from the sample.

The improvement in the c.o.v. for Cu from 50% in argon, 32% in argon-oxygen to 25% in nitrogen seems to support the idea that the poor reproducibility in argon and argon-oxygen is attributable to suppressed volatilization rates which in turn are the result of greatly reduced electrode temperatures.

The possible role of in-situ carbide formation inhibiting volatilization has been discussed. The temperatures achieved with nitrogen appear to be high enough to dissociate the silicon carbide formed in the electrode cavity thus releasing the carbide bound elements.

d. Internal standardization

Ahrens (1954), suggested In as an internal standard for the determination of the volatile elements using normal d.c. arc excitation conditions. As an initial trial, intensity ratios for all the volatile elements employing In as an internal standard element, were calculated and the c.o.v.'s of these ratios computed using the formula given in section 4-9.

These c.o.v.'s are included in Table 11. Comparison of the c.o.v.'s obtained with and without internal standardization reveals that no exceptional improvements in reproducibility result from the use of In as internal standard. The choice of a more suitable internal standard for the volatile elements is examined and discussed in section 4-10.

4-10 INTERNAL STANDARDIZATION

The choice of a suitable internal standard for improving the analytical precision of an optical spectrographic method is governed by several factors which are clearly set out in Ahrens and Taylor (1961, p.91).

Amongst these, one of the major factors is similarity in volatilization characteristics. The volatilization characteristics of the volatile elements determined in section 4-6 confirmed the subdivision of the volatile elements (suggested in section 3-9) into two subgroups. On the basis of the extremely different volatilization characteristics of the two subgroups, a different internal standard for each group was essential. The approach adopted in the choice of a suitable internal standard for each subgroup was to select a typical element, already present in the artificial standards, from each of the two subgroups and use them as potential internal standards for the remaining elements in the volatile group. Silver as a typical element from the less volatile group and Cadmium typical of the more volatile group were chosen as potential internal standard elements.

Intensity ratios were calculated for all the volatile elements using both the internal standard elements chosen. The coefficient of variation (hereafter referred to as c.o.v.) of these ratios was determined using the formula described in section 4-9.

The c.o.v.'s obtained are presented in Table 12 and the effectiveness of the potential internal standard elements chosen is discussed.

(a) Argon atmosphere

The use of Ag as an internal standard, results in a significant improvement (for example Ga 26,3% to 17%) in the c.o.v. obtained for Ga and In. As the elements Ga and In are present in the same subgroup as Ag the improvement is not unexpected. On the other hand, use of Ag as internal standard for Ge, Pb, Sn and Zn (present in the same subgroup as Ag) resulted in a deterioration in c.o.v. (for example the c.o.v. of Ge increased from 11% to 20%). The deterioration in c.o.v. for Cd (9,4% to 28,0%) is large and for Bi (20,8% to 27%) relatively small. Both Cd and Bi are elements in the more volatile subgroup, while Ag, the internal standard, is classified as less volatile. The deterioration in c.o.v. is therefore probably a consequence of difference in volatility. The use of Cd as internal standard for elements present in both of the volatile subgroups produces neither appreciable improvement nor deterioration in the precision obtained without internal standardization. The very poor precision obtained for Cu is not improved by using either silver or cadmium as internal standard. The improvement in c.o.v. for Copper (50% to 39%) achieved using Indium as an internal standard (see Table 11) is insignificant.

(b) Argon-oxygen atmosphere

Ag as potential internal standard for the volatile elements during excitation in an atmosphere of argon-oxygen improves the c.o.v. for the elements Pb, In, Ga, Cu and Sn (for example In from 26,7% to 17%). In this instance internal standard and analytical elements belong to the less volatile subgroup. Examining the potential of Ag as internal standard for the more volatile elements Cd and Bi, the c.o.v.'s attained become poorer, (for example Cd 12,8% becomes 19%) presumably because of the difference in volatility between internal standard and analytical element. The use of Cd as internal standard improves the c.o.v. for Bi to an acceptable level (11,5% to 9,0%) while the improvement for the elements Ge, Pb, Sn, Zn and Ag (for example Ge 18% becomes 13%) is only marginal. Cd and Bi belong to the more volatile group, an improvement in c.o.v. is therefore expected. The slight improvement in c.o.v. for Ge, Zn, Pb, Sn and Ag, elements in the less volatile group, is better than anticipated as the internal standard Cd is in a different subgroup to the analytical elements.

(c) Nitrogen

In nitrogen where the precision for several elements without internal standardization is good and superior to that achieved in either argon or argon-oxygen, neither Ag nor Cd used as internal standard significantly improves the c.o.v.'s of any of the volatile elements. The use of Cd as internal standard in fact results in poorer c.o.v.'s for many of the elements (for example, In 15% becomes 29% and Pb 12% becomes 19%).

Examination of the results achieved with the potential internal standards chosen reveals that the precision of some elements in a subgroup is improved, while for others in the same subgroup, and using the same internal standard, the precision is poorer. (For example in argon, silver improves the precision of Ga and In and makes it poorer for Ge, Pb, Sn and Zn). The formation of silicon carbide in the electrode during excitation in argon is probably responsible for these contradictory results. In argon-oxygen there is only one example of a significant improvement in precision (Cadmium improves the precision for Bismuth) while in nitrogen the internal standardization attempted, produces poorer precision. To achieve significant improvement in precision, the problem of carbide formation would first have to be overcome after which a systematic investigation into the choice of suitable internal standard elements could be undertaken. In view of the fact that a viable, general method of analysis for the volatile elements was not achieved in this study, such a systematic investigation was not warranted.

4-11 DETECTION LIMITS

Examination of Table 1 reveals that the geochemical abundance levels of many of the volatile elements are below 1 ppm and calibration standards below 1 ppm were therefore required.

Before preparing these calibration standards a stringent examination of the individual base material components was undertaken using the most sensitive optical spectrographic methods available at the start of this investigation.

Preparation of the artificial standards required for calibration purposes is discussed in detail in Appendix-C. Because the lowest standard was at the sub ppm level, elaborate precautions were taken during the preparation of these standards to prevent contamination.

In spite of the precautions taken it was found that the base mix contained several of the volatile elements, notably Ag, Bi, Cu, Cd, Pb, Sn and Zn.

Determination of the detection limits was nevertheless carried out employing the artificial standards buffered with Ingamells and Suhr (20/2/3), additive, loaded into D-5 carrier electrodes and arced in argon at 17 amps, argon-oxygen at 10 amps and nitrogen at 15 amps.

Kodak 103-0 photographic plates were used initially as they are generally accepted as the most sensitive plate for the spectral region 380.0nm to 255.0nm, which contains the spectral lines chosen for the volatile elements. Because of the difficulties mentioned above with regard to base mix impurities no attempt was made to estimate the detection limits using the generally accepted criteria for obtaining detection limits.

The most practicable detection limits that could be estimated, using visual observations, and assuming that the designated concentrations of the standards were correct and not increased due to contamination, are shown below. The contamination levels of Cu and Ge in the base mix rendered estimation of their detection limits impractical.

	Zn	Ag	Cd	In	Sn	Bi	Ga	As	Pb	Sb
Argon	1	,3	1	1	1	1	3	31.6	1	31.6
A/O_2	-	1	3	1	1	1	3	31.6	1	31.6

No estimates were possible for samples arced in nitrogen because of excessive cyanogen band masking of the spectral lines of the volatile elements. Ilford ordinary N-30 plates, usually used as a general purpose plate when extreme sensitivity is not required, were also tested and showed remarkably good sensitivity for the volatile elements, probably because of the lower inherent background recorded.

The detection limits attained were as follows:-

	Zn	Ag	Cd	Sn	Bi	In	Ga	Pb	As	Sb
Argon	1	1	3	3	3	3	3	3	31.6	31.6
A/O_2	-	1	10	1	10	10	3	3	-	-
N_2	-	1	10	3	3	3	3	3	-	-

The Zn spectral line was masked by CN band interference during excitation in argon-oxygen and nitrogen and no detection limit estimate was possible.

An alternative method of assessment not influenced by base mix contamination and which gives some idea of the detectability of the volatile elements in natural materials was used.

Several International Geological reference materials were arced employing the most sensitive conditions for each atmosphere. The volatile element spectral lines were identified and their relative strengths estimated visually.

The results appear in Table 13.

Examining Table 13 it is clear that the elements Ga, Cu and Pb are present, in the samples studied, at concentration levels above their normal detection limits and therefore they presented no problem with regard to sensitivity.

The spectral lines of the elements that are present at or near their normal detection limits, Ag, Bi, Cd, Ge, Sn and Zn are shown to be visible during excitation in artificial atmospheres. Comparison of the relative ratings for the spectral lines of Ag, Bi, Cd, Ge and Zn shows that there is little difference in sensitivity obtained during excitation in argon and argon-oxygen while Sn demonstrates superior sensitivity in nitrogen. Background recorded in the different atmospheres is however very different and as no correction for these differences was made during visual estimates of the strength of the spectral lines, the conclusion that Ag, Bi, Cd and Ge display equivalent sensitivity in argon-oxygen and argon is not strictly correct.

As already mentioned in section 3-3, background associated with excitation in argon is much lower than that produced during excitation in argon-oxygen or nitrogen. For ultimate sensitivity of the elements Ag, Bi, Cd, Ge and Zn argon would therefore be preferred and parameters such as photographic plate, amperage, electrode design and exposure optimized for each element.

The superior sensitivity of Sn in nitrogen is a result of the greater volatility of Sn during excitation in this atmosphere.

Estimates of the detectability of Ga, Cu, Pb and Zn were not possible because of their elevated abundance levels in the natural materials used. Of these, only Zn has an igneous rock abundance level that is below its normal optical spectrographic detection limit.

Zn is present at concentration levels below this optical spectrographic detection limit in two of the International reference materials examined and the rating of strong for the spectral line of Zn in these two samples is indicative of the enhancement of Zn in artificial atmospheres.

In spite of the contamination problems which precluded an accurate estimation of the ultimate detection limit for Zn, the detection limit for Zn using excitation in argon is probably near 10 ppm. This represents a considerable improvement in the normal optical spectrographic detection limit.

4-12 THE EFFECTS OF ATMOSPHERES ON CHARACTERISTICS OF THE D.C. ARC

Vallee and Baker (1956) and Thiers and Vallee (1956) examined the effect noble gas atmospheres have on specific characteristics of the d.c. arc. These included the influence of the atmospheres He, A, Kr and Ne on anode temperatures and arc gap voltage and the influence of alkali and alkaline earth chlorides on the anode temperature of a d.c. arc surrounded by helium and argon.

The matrix, containing the volatile elements, used by Vallee et al (1956) in their investigations was biological, very different to the silicate matrix used in this investigation and consequently an independent examination of the effect artificial atmospheres have on the d.c. arc was considered essential. Measurements of the temperature of electrodes surrounded by artificial atmospheres were not possible because of the non-availability of an optical pyrometer.

Thiers and Vallee (1956) however, demonstrated that when an arc is surrounded by noble gas atmospheres, gap voltage and anode temperature have a sympathetic relationship. In the absence of an optical pyrometer, measurement of gap voltage can therefore be used as an indication of anode temperature.

Figure 49 is a plot of gap voltage readings taken at 15 second intervals during an arc discharge between two carbon electrodes. The arc current used was 12.8 amps and the gap between the burning electrodes was maintained at 4.0mm. The fluctuations of gap voltage in nitrogen contrasts with the constancy of the gap voltage readings obtained in air, argon-oxygen and argon. The approximation of gap voltage in air to gap voltage in nitrogen indicates that electrode temperatures in these two atmospheres are probably similar. The low gap voltage recorded when argon surrounds the arc is in accordance with the measurements of Thiers and Vallee (1956) that electrode temperatures are depressed in argon. The presence of oxygen in the argon-oxygen atmosphere results in a slightly higher gap voltage than the voltage obtained in argon and the estimate of electrode temperature in argon-oxygen is accordingly marginally higher than that in argon.

Vallee and Baker (1956) noted that the gap voltages in argon are insensitive to variations in amperage, the amperage range tested by them being from 3 to 15 amps.

Figure 50 presents a comparison of gap voltage readings taken at different amperage settings, for a carbon arc surrounded by argon, argon-oxygen, nitrogen and air. Several important influences on d.c. arc characteristics are depicted in this figure.

Voltage across the gap of a d.c. arc surrounded by argon or argon-oxygen is independent of the amperage used and the gap voltage readings obtained at each amperage are relatively constant.

By comparison the gap voltage of a d.c. carbon arc decreases as amperage is increased, and the gap voltage readings obtained at each amperage are not constant when the arc is surrounded by air or nitrogen.

When a d.c. arc burns in air the alkali elements are known to have a depressant effect on arc temperature. Gap voltage measured across the electrode gap is also influenced by the alkali metal content of the sample and in fact completion of the distillation of the alkali elements into the arc can be gauged by the sudden increase in gap voltage, provided of course electrode separation is held constant. The magnitude of the depression on the d.c. arc temperature in air is related to the first ionization potential of the alkali elements present in the arc. Thus, it is found that arc temperature increases as ionization potential of the alkali element present in the arc increases.

Vallee and Thiers (1956) were able to demonstrate that when the arc is surrounded by argon, anode temperature is independent of the ionization potential of the alkali elements added to or present in the sample. They also showed that anode temperature is independent of the boiling point of the sample and speculated that "the volatile elements are probably vaporized into the arc unaccompanied by large quantities of alkali metals". It should therefore be possible to separate the volatile elements from their alkaline matrix by selective distillation, using argon to keep the electrode temperature at the optimum for this selective distillation.

Figures 51 and 52 record a series of gap voltage readings taken during excitation of some alkali element chlorides (with different ionization potentials) in air and in argon. The constancy of voltage in argon is contrasted quite markedly with the increase in gap voltage in air as the sample completes its vaporization from the electrode.

The dependence of gap voltage in air on the ionization potential of the alkali metal atom present in the arc is demonstrated in Figure 53. Gap voltage is also clearly shown in Figure 53 to be independent of the ionization potential of the sample when the arc is surrounded by argon.

Figures 54 and 55 are gap voltage readings taken during arcing in air and argon of a variety of silicate materials with varying alkali element content.

The independence of gap voltage on sample alkali element content when the arc is surrounded by argon is clearly illustrated in Figure 55. This independence contrasts markedly with the dependence of gap voltage on alkali metal content of the samples arced in air. The sharp increase in gap voltage which takes place when the sample completes its volatilization into the arc during excitation in air is demonstrated in Figure 54. Examination of Figure 55 reveals that gap voltage remains constant during excitation in argon irrespective of sample composition and is only slightly higher when the arc burns between two carbon electrodes. By contrast, gap voltage in air (Figure 54) fluctuates as the alkali elements distil into the arc and the gap voltage between pure carbon electrodes is considerably higher than that obtained with electrodes which contains samples.

A consequence of electrode temperature being independent of sample composition, when a d.c. arc burns in argon, is fractional distillation of those elements whose boiling points are below the prevailing temperature of the electrode.

Vallee and Thiers (op cit) speculated that "volatile elements are probably vaporized into the arc unaccompanied by large quantities of alkali metals" because the boilings points of the alkali and alkaline earth chlorides are greater than the temperature of the anode surrounded by argon.

Plate 2 clearly demonstrates this fractional distillation of the volatile elements during excitation of a sample in argon.

Although there is a tremendous advantage in selectively distilling the volatile elements from their matrix, this investigation has shown that the volatilization rates of some of the volatile elements are depressed to such an extent that complete volatilization of these elements cannot be achieved in reasonable arcing times (1-2 minutes).

The advantages of argon induced selective distillation are therefore only applicable to those elements which display sufficiently rapid volatilization characteristics for them to complete their distillation into the arc in practicable exposure times.

4-13 THE EFFECT OF ATMOSPHERES ON THE INTENSITY OF CERTAIN SPECTRAL LINES

Adelstein and Vallee (1954) reported that the intensity ratio of certain spectral lines of the same element are elevated in argon when compared to the ratio obtained in helium.

As an initial basis for comparison Ahrens and Taylor (1961) report an intensity ratio of 2 for the copper doublet Cu 324.7/327.4nm, this ratio being in accordance with the theory of multiplet ratios.

The Cu 324.7nm spectral line is known to be more susceptible to self-absorption and so in practice the ratio Cu 324.7/Cu 327.4 is often less than 2 and this fact, the deviation of the line pair ratio from 2, is used to ascertain whether self-absorption has taken place during excitation.

Adelstein and Vallee (op cit) on the other hand reported intensity ratios for the pair Cu 324.7/Cu 327.4nm ranging from 5 at the 67ppm level to 3 at the 1.3ppm level during excitation in argon. For the pair Ag 328.0/Ag 338.2nm they found ratios of 7 at the 67 ppm level and 1.4 at the 1.3ppm level.

In this investigation, several sets of data were examined in an attempt to substantiate the findings of Adelstein and Vallee (op cit). Data obtained during this investigation are shown in Table 14 and illustrate that the average ratios for the spectral lines of Cu 324.7/Cu 327.4nm and for Ag 328.0/Ag 338.2nm generally do not exceed the value of 2.0. An interesting aspect of the findings of Adelstein and Vallee (op cit) was that the spectral line ratio differed quite markedly at different concentration levels, the enhancement being greater at higher concentration levels. There was also a significant difference in the ratios obtained in the different atmospheres. The results of Adelstein and Vallee are reproduced in Table 15.

In this investigation the spectral line ratios of Cu 324.7/Cu 327.4nm and Ag 328.0/Ag 338.2nm for the 3, 10 and 31.6ppm artificial standards arced in argon, argon-oxygen and nitrogen were calculated and are shown in Table 16. Not only are the ratios for the different concentration levels similar but there is also little difference between the ratios of the spectral lines obtained in the different atmospheres. The findings of Adelstein and Vallee are thus not substantiated at all. A possible explanation for the remarkable enhancement of one of the spectral lines in the line pairs of Cu and Ag is advanced.

The report of Adelstein and Vallee (op cit) lists the elements added to the matrix material during preparation of the artificial standards for their investigation. Careful scrutiny of the elements added reveals that, in addition to several of the volatile elements, Mn was amongst the group. Ahrens and Taylor (1961, p. 406 and p.368) point out that spectral line interference from Mn 328.076nm with Ag 328.068nm and from Mn 324.754nm with Cu 324.754nm is possible unless a spectrograph with large wavelength dispersion is used.

Examination of Table 15 shows that the Ag 328.0/Ag 338.2 and Cu 324.7/Cu 327.4 line ratios increase as the concentration of added elements increases.

The spectral line intensity measured by Adelstein and Vallee (op cit) at 328.06nm is almost certainly a combination of the intensities of the spectral lines of Ag and Mn and that measured at 324.75 a combination of the lines of Cu and Mn.

The true intensity ratios calculated are thus (Cu 324.75+Mn 324.75)/ Cu 327.4 and (Ag 328.068+Mn 328.076)/Ag 338.2. The increase in ratio with increase in concentration is also explicable in terms of this spectral line interference.

The variation in ratio found by Adelstein and Vallee (op cit) for the different atmosphere compositions is a result of the differences in volatility of the elements Cu, Ag and Mn. To offset the greatly reduced element volatilization rates experienced when the arc was surrounded by 100% argon, Adelstein and Vallee (op cit) used longer exposure times than when the arc was surrounded by helium. During these longer exposure times, more Mn was able to volatilize into the arc thereby elevating the ratios obtained in argon when compared to those obtained in argon-helium or pure helium.

CONCLUSIONS

The results of this investigation indicate that although excitation in a d.c. arc surrounded by artificial atmospheres has many advantages, many problems have to be overcome before viable analytical procedures can be implemented.

The advantages of excitation in argon are a reduction in background intensity, improved sensitivity and selective distillation of the volatile elements. The volatilization rates of the geologically more abundant volatile elements (Cu, Ga, Pb and Zn) are however suppressed to such an extent that they are unable to complete their distillation into the arc in practicable times.

Although excitation in nitrogen overcomes this problem, cyanogen emission masks many useful spectral lines and its use is somewhat limited.

The chief advantage in the use of argon-oxygen is the suppression of cyanogen emission.

A serious problem encountered during excitation of samples in argon atmospheres was the formation of silicon carbide in the electrode cavity. The volatilization characteristics of several volatile elements were shown to be adversely affected by the formation of silicon carbide to such an extent that volatilization of the elements Cu, Sn, Ga, Bi and Ge was inhibited. The formation of silicon carbide was thought to be responsible for the poor precision obtained during excitation in argon.

From the combined observations made in this study certain guidelines for the determination of the volatile elements can be given. These guidelines are presented with certain reservations.

Firstly, it is assumed that the concentration levels of the volatile elements in the materials to be analysed are equivalent to their average igneous rock abundance levels. Secondly the problems associated with silicon carbide formation and the prolonged volatilization during arcing in argon should be borne in mind.

Furthermore, the unsuccessful determination of suitable internal standards for the volatile elements and the inability of the additives tested to improve the volatilization characteristics of the elements studied precludes any useful guidelines on choice of internal standard or additive being given.

Because of the different volatilization rates of the volatile elements it was necessary to subdivide the group into four separate subgroups.

(i) The method of analysis for the first subgroup, which consists of the elements designated less volatile i.e. Cu, Ga, Ge, Sn and Zn, employs small carrier electrode, 20 amps excitation, argon atmosphere and Ilford ordinary N-30 photographic plates. Exposure times would have to be determined empirically as they depend on the abundance levels of the elements in the materials being studied, but would be of the order of 1½ to 2 minutes. In instances where the analysis of only one or two specific less volatile elements may be required, the use of nitrogen which improves the slow volatilization rates of these elements is suggested. For example, nitrogen could be used in the determination of Sn and Ga as the spectral lines of these two elements are free from CN emission interference.

(ii) The elements in the second group viz. Ag, Bi, Cd, Pb and In have lower abundance levels in normal silicates and thus vaporize more rapidly. The spectrographic conditions applicable to their determination are a large carrier electrode, 20 amp excitation, argon atmosphere, Kodak 103-0 photographic plate and an exposure time of 60 seconds.

Although Ag has been included in this group because of its low geochemical abundance, it is very sensitive and exhibited less volatile characteristics during the moving plate experiments which employed artificial standards. Ag can also be determined using nitrogen with a carrier electrode or argon-oxygen with a shallow cratered electrode provided the materials being investigated are enriched in Ag.

(iii) The third subgroup As, Sb and Hg are generally present at such low concentration levels in normal geological materials and have such poor sensitivity, even in argon, that they should rather be considered as potential internal standard elements for the other volatile elements.

(iv) Finally, Tl has been shown to display greatest sensitivity when excitation in argon-oxygen at extremely low amperages is employed. The nature of the gas jet appears to be important as not only has cyanogen emission to be kept to an absolute minimum in order to allow the use of the 377.5nm spectral line, but the flow of gas past the electrode containing the sample seems to play a significant role in determining the lower limit of detection.

The practical application of d.c. arc excitation in artificial atmospheres to the analysis of silicate rocks is limited to those volatile elements whose abundance levels exceed their normal O.E.S. detection limits viz. Cu, Ga, Pb and Sn. Because the element Zn displays a considerable improvement in detection limit employing d.c. arc excitation in an atmosphere of argon it can be determined along with the elements Cu, Ga, Pb and Sn. (The detection limit for Zn by normal O.E.S. methods is 100ppm and employing excitation in argon 1ppm).

The elements Ag, As, Bi, Cd, In, Ge and Sb are present in silicate rocks at concentration levels below the detection limits attainable with excitation in artificial atmospheres. These elements are often enriched in sulphide ore bodies where their concentration levels may exceed the detection limits achieved during excitation in argon atmosphere. Excitation in argon could therefore be used to acquire quantitative data on the concentration levels of these elements in sulphide bearing rocks and ores.

Considering the two analytical techniques investigated, as potential methods of analysis for the volatile elements in geochemical prospecting samples, the success achieved with X.R.F. in determining Cu, Pb, Zn, Ga in normal silicates materials, and Sn, As and Ge when enriched, are features which favour the use of X.R.F. Furthermore the advent of large multi-channel X-ray spectrometers with automatic sample changers capable of holding 250 samples, the superior precision obtained with X.R.F., the simple sample preparation procedures employed and the non destructive nature of the technique combine to strengthen the choice of X.R.F. as the preferred technique for the determination of the elements Cu, Pb, Zn and Ga in prospecting samples. The high cost of multi-element channel X.R.F. equipment is an important consideration and this type of equipment can only be cost justified in applications where the number of samples to be analysed is large e.g. 6 000 samples per month.

The detection limits for Ag, Bi, Cd, In and Sb obtained employing X.R.F. and O.E.S. d.c. arc excitation in argon are inadequate when compared with the normal abundance levels of these elements. Other analytical techniques such as N.A.A., A.A.S. (with carbon rod) or I.C.P. - O.E.S. have superior sensitivity for these elements. These techniques are therefore more suitable for the analysis of these elements in normal silicates and prospecting samples.

The detection limits obtained employing O.E.S. d.c. arc excitation in argon suggests that Ag, Bi, Cd, In and Sb could be determined in geological materials which contain above normal concentration levels of these elements e.g. sulphides.

Although the original objective of developing a single O.E.S. method for the determination of the volatile elements, as a group, in silicate rocks was not achieved, the problems associated with d.c. arc excitation in artificial atmospheres have been highlighted. Development of a method for the determination of the more volatile elements employing d.c. arc excitation in argon shows promise.

Further experimentation should be carried out to:-

(1) Optimize carrier electrode design

(2) determine a suitable internal standard to improve the precision of excitation in argon.

(3) determine optimum exposure time

(4) determine the most suitable photographic plate

(5) optimize the selective distillation of the more volatile elements from the samples matrix.

Finally, the use of an argon atmosphere for determining volatile elements in matrices which do not form carbides or other refractory compounds, such as biological and plant materials, is a promising avenue for further investigation, as it seems likely that quantitative methods would easily be developed for this purpose.

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