A comparative study of trace element analyses by argon plasma emission and atomic absorption spectrophotometry.

K. Daniel. Mitchell

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RECEUE.
A COMPARATIVE STUDY OF TRACE ELEMENT ANALYSES BY ARGON PLASMA EMISSION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

BY

K. DANIEL MITCHELL

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES THROUGH THE DEPARTMENT OF GEOLOGY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE AT THE UNIVERSITY OF WINDSOR

WINDSOR, ONTARIO
SEPTEMBER, 1979
ABSTRACT

An atomic absorption instrument (Varian Techtron AA-5) has been modified for argon plasma emission by the addition of a D.C. argon plasma jet (Spectrajet II argon plasma jet). In this study, the feasibility of using such a system as an add-on device on an atomic absorption instrument has been evaluated for fourteen trace elements frequently measured in rock and soil analyses. They are arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, molybdenum, nickel, rubidium, selenium, silver, strontium and zinc.

Assessing the detection limits, slope of the line, drift, repeatability and noise levels, it appears that four elements (arsenic, boron, cobalt and chromium) would be better determined by argon plasma emission than by atomic absorption.

A comparative study of both methods has been done using ionic standards as well as the analyses of four rock and soil reference standards. While in many cases plasma emission has the advantage of lower detection limits, improved drift, repeatability and noise levels, severe interferences do exist which result in problems which are still unsolved. The effect of iron enhancement and silica suppression of peaks at several analytical wavelengths is reported.
Atomic absorption also has its limitations in that only five elements could be determined at the levels present in the prepared solutions, and also matrix effects similarly caused some high values. Attempts to overcome these interferences by the use of the method of standard additions, while indicating some improvement, has been unsuccessful. The cause of erroneous concentrations obtained by plasma emission is attributed to spectral interferences and non-atomic emission, as well as chemical interferences, in particular the total ion strength of the solution. It is inferred that for dilute, chemically simple solutions, argon plasma emission is a viable analytical method.
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INTRODUCTION

Atomic absorption spectrophotometry is a well established analytical method for the determination of numerous elements, and is based on the absorption of radiation by free atoms. In 1860, Kirchhoff and Bunsen were the first to demonstrate that by using emission or absorption techniques atomic spectra could form the basis of a new and useful method of analysis. It was not, however, until 1955 that Walsh demonstrated the real potential of atomic absorption.

Today's instruments vary in construction from simple filter flame photometers to sophisticated and expensive spectrophotometers which are capable of determining up to twenty elements consecutively.

The use of an atomic absorption instrument in the emission mode is limited by the relatively low temperatures (2000° - 3000° C) produced by conventional flames. The flames used are only hot enough to excite a small fraction, generally less than one percent, of the atoms aspirated into it (Ewing, 1969), therefore flame emission is limited to the determination of alkali and alkaline earth metals. However, by using an alternate excitation source, such as an argon plasma, a much larger number of atoms can be excited, due to higher temperatures (6000° - 10000° K).
Argon plasma emission is a known emission spectroscopy technique, although it is still somewhat in the experimental stage. It is, however, used in chemical analyses, but the available instruments are very expensive compared to atomic absorption instruments.

In North America there are three companies that manufacture argon plasma instruments. Applied Research Laboratories and Jarrell-Ash instruments are both inductively coupled plasma instruments and they cost approximately $69,000.00 and $66,000.00, respectively. Spectranetics Inc. manufactures a I.C. arc plasma instrument which costs approximately $32,000.00.

In this study, a Model 53000 Spectrajet II argon plasma jet, which is a component of an instrument manufactured by Spectranetics Inc., has been added to a Varian Techtron Spectrophotometer Model AA-5 at a cost of only $3,500.00. Although only one element can be determined at a time, it greatly expands the usefulness of the atomic absorption instrument, making it effectively an emission spectrograph. Such a modification allows the determination of many elements otherwise difficult or impossible to determine by atomic absorption, such as silica, which combines with the acetylene of the flame to form a silica carbide that causes burner blockage and
loss of signal, or phosphorus, which is present in solution as complex anion and therefore cannot be determined directly by atomic absorption.

Chemical interferences and matrix effects, which are significant limitations in atomic absorption analyses, should theoretically be nonexistent when using plasma emission techniques because of the much higher temperatures produced by the plasma, which breaks all chemical bonds. However, this is shown not to be the case in the determination of trace elements in highly concentrated solutions of rocks. These interferences are shown to be the greatest limitation in the application of argon plasma emission to trace element analyses.

In this study only liquid samples were investigated in order to make a true comparison with atomic absorption analyses. However, the use of a plasma jet also enables the analysis of gases and solid samples, which cannot be analysed by conventional atomic absorption.

This study is an assessment of the capabilities of an argon plasma jet, for use as an alternate excitation source to the conventional burner assembly of an atomic absorption instrument, in the determination of trace elements. However, for rubidium and strontium, comparisons were made between flame emission and plasma emission since hollow cathode lamps were not available for absorption analyses.

The only previous studies in the use of an argon plasma
jeet on an atomic absorption instrument were done by Mitchell (1977), and subsequently, Quirt (1978) has investigated the above instrumentation with respect to major element analyses of rocks. A comparison between atomic absorption and argon plasma emission is made, using ionic standards, by experimentally determining the detection limit, slope of the line, repeatability, the drift, and noise level for the following trace elements: Ag, As, B, Be, Cd, Co, Cr, Cu, Mo, Ni, Rb, Se, Sr and In. This was then applied to rock and soil samples by determining the concentrations of the above elements in standard reference samples G-2, BCR-1, GAN-5 and SR-1050.

Both G-2 and BCR-1 are international geochemical standards issued by the United States Geological Survey. G-2 is a granite and BCR-1 is a basalt. GAN-5 is a soil standard taken from the B-zone of a moderately well developed podsol soil in Maine issued by the United States Geological Survey and the Association of Exploration Geochemists. SR-1050 is an altered volcanic in proximity to a lead-zinc deposit (Sherritt Gordon—Fox Mine) and is an 'in house' standard.

The elemental concentrations for the above reference samples have been reported by Flanagan (1973) for BCR-1 and G-2, Allcott and Lakin (1974) for GAN-5, and Lonercy (1975) for SR-1050.
THEORY OF ABSORPTION AND EMISSION SPECTROSCOPY

The flames used in atomic absorption spectrophotometry are only hot enough to excite a small fraction of the atoms introduced into it. By using the Boltzmann principle it can be shown that for any given temperature \( T \), the number of excited atoms \( N_j \) is related to the number of ground state atoms \( N_0 \) by the following formula:

\[
N_j = N_0 \cdot \frac{\frac{E_j}{P_0}}{\exp \frac{-E_j}{kT}}
\]

where \( E_j \) and \( E_0 \) are the statistical weights for the states of energy \( E_j \) and \( E_0 \) respectively (Browning, 1969). The ratio \( N_j/N_0 \), which is the fraction of excited atoms, is therefore a function of temperature.

In the case of unexcited atoms, the electrons occupy as many levels as needed, starting with the lowest (1s) and proceeding upwards according to the quantum rules. For example, sodium has eleven electrons, designated \( 1s^2 \ 2s^2 \ 2p^6 \ 3s^1 \). The 3s electron is held least strongly and therefore can easily be pushed up to the 3p level, the next highest level, when excited. The excited electron has a strong tendency to return to its normal or stable state, the 3s level, and in doing so emits a quantum of radiation called a photon (i.e. the yellow flame of sodium).
Quantum theory shows that, in general, the energy $E$ of a molecule can have certain "quantized" values only, and that when a molecule changes its energy from one to another of these permitted values it may emit or absorb the energy difference as a photon in accordance with the relation:

$$h\nu = E_1 - E_2$$

where: $h =$ Planck's Constant  
$\nu =$ frequency  
$E_1 =$ first energy level  
$E_2 =$ second energy level

Thus the spectrum of an element is a line spectrum.

The simple case of the outer electron being raised by one energy level and then returning is known as resonance radiation (Ewing, 1969). The intensity of the emitted radiation is directly proportional to the concentration of the particular element being excited.

The number of atoms excited to a given quantum level increases exponentially with temperature, and it is apparent, therefore, that small temperature fluctuations in the plasma will drastically decrease the reproducibility of measurements obtained by this method (Howery and Test, 1971).

The atoms that remain unexcited are capable of
absorbing radiation transmitted from an external source through the flame at the same characteristic wavelength as the emitted radiation. Therefore, while emission spectrophotometry is dependent on emission by excited atoms, atomic absorption is based on the absorptivity of atoms in the ground state, and is essentially the opposite of emission spectroscopy.

For atomic emission a higher temperature is required in order to excite a larger number of atoms and increase the amount of radiation. With a more effective source of energy capable of producing such higher temperatures, not only the outermost electron, but many electrons in any element can be excited to various degrees. The resulting radiation can be comprised of several thousand discrete and reproducible wavelengths, most of which are in the visible and ultraviolet regions of the spectrum. Quantitative analyses by emission spectrophotometry techniques are dependent on the relation between the power of the emitted radiation at a particular wavelength and the concentration of the corresponding element in the sample.

Argon plasma offers great potential as a source of high energy. It is capable of producing temperatures up to 10000°K, and therefore most chemical interferences are eliminated, the linear operating range is increased and it
The direct analyses of refractory elements (e.g., Si, Al) became possible (Spectrometrics Inc., 1974).

A plasma is a gaseous cloud composed of free electrons, positive ions, neutral atoms and molecules, and is referred to as the fourth state of matter. The generation of a plasma involves the imparting of sufficient energy to an inert gas to cause at least partial ionization. This can be achieved by accelerating electrons between two electrodes in a gaseous environment. These electrons collide with and excite the atoms and molecules in the gas and cause them to ionize. Electrons freed by the initial ionization are also accelerated toward the anode, resulting in more collisions and further ionization. The result is a highly conductive gas through which electrical sparks can pass.

With an increase in the number of collisions between electrons and larger particles, the gas becomes increasingly hot, providing a high temperature environment into which solutions to be analysed can be introduced and thus excited (Serdeman, 1972).

One of the characteristics of argon, as well as all rare gases, is that when excited the electrons go into a metastable state from which they can not return directly to the ground state. The excited atom must transfer its energy to another body by collision and thus return to the
ground state. Therefore, energy is transmitted to the sample, introduced into the plasma, by this process.

The excitation region which forms at the juncture of the plasma (Figure 1) is approximately 6000°K. Liquid samples are fed into a nebulizer and spray chamber by a peristaltic pump, and from there they are introduced into the excitation region as an aerosol spray consisting of drops of 1 to 5 microns in diameter. The entire cycle of de-solvation, molecular dissociation and excitation takes place during the residence time of the sample within the excitation region.
INSTRUMENTATION

A conventional atomic absorption spectrophotometer is comprised of four fundamental components: a light source (hollow cathode lamp) which emits a narrow line spectrum of the element to be determined; a means of producing an atomized vapour (nebulizer) of the sample to be analysed; a wavelength selector (monochromator) to separate the resonance line required; and a detector, amplifier and readout system.

In this study, a Varian Techtron Model AA-5 Spectrophotometer was used. The line source consists of a modulated lamp supply (Varian Type MLS-5) that supplies current, variable from 0 to 50 mA, to the lamp turret assembly. This assembly consists of four lamp quadrants and a lens through which the line spectrum is focused on the entrance slit of the monochromator.

The monochromator isolates the required narrow spectral band from the spectrum of the light source. The monochromator used in this study was an Ebert type, which uses a 50 mm by 50 mm plane grating ruled with 635 lines per millimeter. This produces a 3.3 mm/μm linear dispersion, in the first order, at the exit slit. The width of the wavelength band isolated by the monochromator is determined by the width of the entrance and exit slits. Both
slits are continuously variable and are adjusted simultaneously by one drum control. The maximum width available is 300 microns which gives a spectral band width of 0.99 mm. The monochromator is capable of selecting wavelengths between 0.0 nm and 1015.0 nm, however there is a mechanical limit that prevents operation below 166.0 nm.

The photomultiplier is an HTV Type R213 that has a recommended range of optimum sensitivity between 200 nm and 780 nm. The indicating module (Type II-5) provides a one channel analogue readout directly in transmittance and absorbance units, and is also connected to a chart recorder. The readout module has an auto set system that compensates for baseline drift due to lamp fluctuations and drift in the electronics (Varian Techtron, 1971).

For atomic absorption the conventional burner system was used as an excitation source, but for plasma emission a Spectrajet II Model 55000 Argon Plasma Jet was used.

The Spectrajet II has an inverted 'V' configuration (Figure 1) which gives good performance capabilities in regard to detection limits, stability, reproducibility and ease of operation.

The liquid samples are fed into a nebulizer and spray chamber, at a recommended rate of 0.8 ml/min., by a peristaltic pump. The ceramic nebulizer is approximately
efficient in converting the liquid sample to an aerosol made up of particles 1 to 5 microns in diameter. Once in aerosol form the sample is carried through the spray chamber by the flow of argon from the nebulizer, and is directed into the plasma from below by a teflon tube. In this way the argon not only delivers the sample to the plasma but it helps to stabilize the arc as it flows around it.

A region of sample concentration is created just below the bend in the arc by the three streams of argon gas flowing from the two electrodes and from the sample delivery tube. It is in this region that the atoms are excited. It should be noted that this region of concentration and excitation develops near the bend in the arc but outside the plasma continuum, for it is under these conditions that the best signal-to-background ratio is obtained.

The plasma produces effective temperatures which are high enough to enable the direct analysis of such non-metals as boron and phosphorus as well as refractory type metals. The measurement of elemental concentrations using the ionized spectral lines available with this excitation source often gives a greater linear range to the calibration curves. Calcium, for example, is linear from 0 to 20,000 μg/ml.
SET UP AND CALIBRATION

The only gas required in the operation of the Spectra-jet II is welder's grade argon. It is supplied from a cylinder at approximately 200 kPa (30 psi) by a luxon 2-stage L-2055 regulator. In order to permit easy and rapid conversion between flame and plasma, the argon gas supply was set up in such a way that it is connected directly to the jet and can be removed by the removal of the jet itself. In this way the gas supply for the conventional burner can remain connected to the gas control unit (GCU-5) of the spectrophotometer.

A problem frequently encountered in flame analyses is the oxidation of the sample in the flame. However, the inert nature of argon gas decreases the extent of oxidation.

Argon is also non-toxic and non-explosive as opposed to the gases used in the operation of conventional burners.

The jet requires a cooling system to prevent the bonding of the electrodes to the holders. Cooling is accomplished by passing water at a recommended rate of 0.25 liters per minute through the cooling blocks of the jet. As is the case with the supply of argon, the water supply is also connected to the jet and is removed by the removal of the jet (Figure 2).
PLASMA JET AND ADJUSTMENT ASSEMBLY

CERAMIC SLEEVE
DELIVERY TUBE
COOLING BLOCK
ELECTRODE AND HOLDER
EXTENSION BLOCK

Figure 2.
In adapting the jet assembly to the atomic absorption instrument a few minor modifications had to be made. Due to the construction of the jet, the plasma is not produced directly over the base that fits into the burner adjustment assembly of the spectrophotometer. For this reason an extension (Figure 2) had to be added to the adjustment assembly to move it forward and bring the plasma into alignment with the instrument. With this new extension the whole assembly can be fixed to the optical rail of the unit for either plasma or flame analysis simply by loosening one screw and moving the assembly forward or backward. This enables the three controls that are used to make X, Y and Z coordinate adjustments of the burner to be used for the plasma jet as well.

Because of the greater intensity of the ultraviolet radiation emitted by the plasma, the original protective shield had to be replaced by a new one made of shade 12 welder's glass.

The final modification made was the relocation of the spray chamber. In order to fit the jet assembly into the exhaust hood of the atomic absorption unit, the spray chamber, which was originally attached by a spring clip to the jet itself, had to be fixed to the back of the exhaust hood.
Figure 3a illustrates how the spray chamber and the drainage system was originally positioned and how water accumulated in the drain tubes.

Figure 3b shows the drainage system after the modifications. During the course of this study it was found that water accumulation still occurred at the restriction in the tube beneath the spray chamber as well as at the connection between the 'T' and sample delivery tube. However, this can be limited by careful control of the water level in the drainage reservoir.

(a)  (b)

Figure 3.

With these modifications and the assembly complete, the atomic absorption instrument was ready for operation by plasma emission. Operating instructions are given
briefly in Appendix I and II for both plasma and flame analyses. For a more detailed description of the set-up see Mitchell (1977) and Quirt (1978).
THEORETICAL PARAMETERS

The criteria used in this study for the comparison of argon plasma emission and atomic absorption spectrophotometry are detection limit, slope of the line, drift, repeatability and noise levels.

Detection Limit

The detection limit, as defined by the Second International Atomic Absorption Conference (1969), is the concentration, in solution, of an element which can be detected with a 95% certainty. This is that quantity of the element that gives a reading equal to twice the standard deviation of a series of at least ten determinations at or near blank level (Varian Techtron, 1971).

Slope of the Line

Since there is no mathematical relationship between the sensitivities obtained by absorption techniques and those by flame and plasma emission, which is one of the conventional parameters for atomic absorption and emission spectrophotometry, the slope of the lines obtained for both methods are reported as an alternative to the sensitivities (Winefordner, 1976).

Drift

For purposes of this study, drift is defined as a measure of the degree of fluctuation in the signal produced while aspirating a standard over an extended period of time.
(approximately seven minutes) (Winfordner, 1976).

Repeatability

The accepted definition for repeatability is that it is equal to the "standard deviation of a series of results obtained for a particular determination, by a single analyst making all determinations at or about the same time." (Jeffery, 1975).

Noise Level

Two distinct types of noise are observed in the readout output for both methods of analysis. The first is the noise produced by the instrument as a whole, including lamp noise, recorder noise and electronic noise. This noise is seen as fluctuations in the recorder plot produced while aspirating triple distilled water, and will therefore be referred to as base line noise. This noise varies from element to element and method to method due to the use of different instrument parameters, and lamps in the case of absorption, as well as being dependent on the element in question.

The second noise, signal noise, is produced solely by the analyte element when aspirating a solution other than a blank.

Definitions for both base line noise and signal noise are given as follows:
Base line noise (noise level) is "that concentration of the analyte element that would give a signal equal to one fiftieth of the sum of twenty measurements taken as follows:

The output of an atomic absorption spectrometer operating on a blank solution is recorded for ten time periods, each of ten times the time constant of the instrument. The maximum displacements that occur to both sides of the median line in each of the ten time periods are measured. These are the twenty measurements referred to above.

The figure obtained approximates to the standard deviation of the noise expressed in terms of element concentration" (Price, 1972), and is approximately equal to the 95% confidence limit.

For purposes of this study, signal noise is defined as being equal to the ratio $\frac{S}{N}$; where: $S$ is equal to the average of six measurements of the signal height; and $N$ is the average of six measurements of the peak to peak fluctuation in the signal minus the average of six measurements of the peak to peak fluctuation of the base line (Figure 4).

![Figure 4: Signal Noise](image_url)
In order to get a true picture of how noisy a method is, it is necessary to consider both types of noise together.
STATISTICAL METHODS

In the evaluation of the collected data, several statistical procedures were used. The basic parameters, which are characteristic of the calibration curves, such as the slope, intercept and correlation coefficient, were calculated using a Wang 2200 computer (Appendix III). In both absorption and emission techniques, these parameters are based on the direct relationship which exists between the instrument reading, in arbitrary units, and the concentration, in µg/ml. Therefore comparisons are valid since both units concerned are the same for each of the two methods. The results were printed out in table form and are presented in this study. Table 51 is an example of the detection limit tables developed by this program.

**Slope and Intercept**

The slope (m) of the calibration curve was obtained by least square simple regression with Y regressed on X for no error in X. The regression lines were forced through zero, as theoretically the lines have to pass through zero on a blank reading, by including the coordinates (0,0) in with the other coordinates that were determined by running the standard solutions.

The following equations were used in calculating the slope (m) and intercept (b):
\[
m = \frac{\varepsilon(X_i - \bar{x})(Y_i - \bar{y})}{\varepsilon(X_i - \bar{x})^2}
\]  
(1)

\[
b = \bar{y} - (m \times \bar{x})
\]  
(2)

where: \( \bar{x} = \frac{\varepsilon X_i}{n} \), \( \bar{y} = \frac{\varepsilon Y_i}{n} \)

(Moroney, 1965)

**Correlation Coefficient**

The correlation coefficient \( (r) \) is a measure of the degree of correlation between the line of best fit, as defined by 'm' and 'b' in the equation \( \bar{y} = (m \times \bar{x}) + b \), and the individual data points. A correlation coefficient of +1.0000 indicates a perfectly functional relationship with all data points perfectly described by the line of best fit (Moroney, 1965).

The following equation was used in determining the correlation coefficient \( (r) \):

\[
r = \frac{\varepsilon(X_i - \bar{x})(Y_i - \bar{y})}{\varepsilon(X_i - \bar{x})^2 \varepsilon(Y_i - \bar{y})^2}^{\frac{1}{2}}
\]  
(3)

where: \( \bar{x} = \frac{\varepsilon X_i}{n} \), \( \bar{y} = \frac{\varepsilon Y_i}{n} \)

(Moroney, 1965)
Mean, Variance and Standard Deviation

The mean ($\bar{x}$), variance ($\text{var}$) and standard deviation ($\sigma$) for the ten readings taken in determining the detection limit were calculated and tabulated by the Wang 2200 computer using the following equations:

$$
\bar{x} = \frac{\sum x_i}{n}
$$

(4)

$$
\text{var} = \frac{\sum (x_i - \bar{x})^2}{n}
$$

(5)

$$
\sigma = \left( \frac{\sum x_i^2}{n} - \bar{x}^2 \right)^{1/2}
$$

(6)

(Moroney, 1965)

Detection Limit

The detection limit was determined using the following equation:

$$
\text{Det. Limit} = 2 \times 3\sigma
$$

(7)

All of the statistical parameters mentioned so far in this section were computed using the computer program listed in Appendix III.

A second computer program (Appendix I) was used to test the values obtained for a given element in a particular standard, by both plasma and flame analyzers, and an example of the output is given in Table 52.
t-test for Rejection of Values

A t-test (Turek, 1966) was applied to the concentrations obtained for replicate samples as a means of rejecting those which do not belong to the sample as defined by the 95% confidence limit.

By calculating $t_{calc}$ (Equation 8) and comparing it to the $t_{table}$ value (Equation 9) for the appropriate degrees of freedom, those values for which $t_{calc}$ is greater than $t_{table}$ were rejected.

$$t_{calc} = \frac{|\bar{X} - X_i| (n - 1)^{-1}}{SD} \quad (8)$$

For computer processing purposes, Equation 9 was used in the calculation of the Student's $t$-value for the 95% confidence level.

$$t_{table} = 1.96 - 0.00554565/(n - 0.55) + 2.4059333/\left((n - 0.55) + 0.671777/(n - 0.55)^2 - 0.3531214/\left(n - 0.65\right)^3\right) \quad (9)$$

where: \(n = \text{number of values}\)

The number of degrees of freedom \((k)\) was determined using the following formula:

$$\frac{(Var_1 + Var_2)^2}{X} = \frac{Var_1^2}{n_1 - 1} + \frac{Var_2^2}{n_2 - 1} \quad (10)$$

(Turek, 1966)
Upon completing the rejection test, the new means and standard deviations were computed using Equations 4 and 5. The relative standard deviations (R.S.D.), also known as the coefficient of variance (C of V), were calculated using Equation 11 in order to show a relative measure of dispersion for both the flame and plasma techniques.

\[ \text{R.S.D.} = \frac{SD}{X} \times 100 = \text{C of } V \]  

(11)

This second computer program then applied Snedecor's F-test of variances and Student's t-test of means to the results of both methods of analysis in order to determine whether or not the means and variances were significantly different at the 5% level of significance.

Snedecor's F-test of Variance

In comparing the two variances, Equation 12 was used to determine F-calc. If the value thus obtained was greater than that given in the F-tables (Kennedy and Keeping, 1954) the difference between the variances was considered significant at the 5% level.

\[ F_{\text{calc}} = \frac{\text{Var}_1}{\text{Var}_2} \]  

(12)

Student's t-test of Means

The Student's t-test of means was used in comparing the means obtained for elemental concentrations in the
standard rock samples.

If \( t_{-\text{calc}} \) (Equation 13) was greater than \( t_{-\text{table}} \) (Equation 9) then the means were considered significantly different at the 5\% level of significance.

\[
  t_{-\text{calc}} = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{\text{Var}_1 + \text{Var}_2}{n_1 + n_2}}}
\]  

(13)

**Drift**

Drift is the standard deviation of ten peak values measured from a recorder plot obtained while running a standard for an extended period of time. It was calculated using Equation 6.

**Repeatability**

Repeatability is the standard deviation of the six peak values measured from a recorder plot obtained while making six consecutive runs of a standard. It was calculated using Equation 6.
INTERFERENCES

Elemental analyses by atomic absorption or emission spectrophotometry can be subject to four types of interferences. They are: (1) matrix effects; (2) chemical interferences; (3) non-atomic absorption; and (4) spectral interferences (Varian Techtron, 1974).

Matrix Effects

Matrix effects, which influence the amount of sample reaching the flame, can cause inaccurate results. They are commonly the result of precipitation of the element of interest, such as the hydrolysis of silicon and tin compounds, and the formation of insoluble chlorides and sulphates.

The amount of sample aspirated by the nebulizer and the proportion which reaches the flame are dependent on the viscosity, surface tension, density, and solvent vapour pressure of the solution. Therefore, it is necessary for the physical properties of the samples and standards to be matched as closely as possible to avoid differences in the amount of sample and standard which reach the flame.

Chemical Interferences

Chemical interferences are those interferences which inhibit the formation of ground state atoms in the flame.
The two general forms of chemical interferences are: (1) incomplete dissociation of compounds and (2) ionization.

Incomplete dissociation of compounds is most commonly the result of the formation of refractory compounds in the flame, such as calcium phosphate and potassium fluoro-tantalate. Compounds formed by such interferents are not completely dissociated at the temperature of the flame and hence prevent the formation of neutral ground state atoms. This problem is negligible in plasma emission analyses because of the higher level of energy available from the plasma.

High temperature flames such as air-acetylene or nitrous oxide-acetylene can cause a significant degree of ionization of the analyte element. The alkali and alkaline-earth metals are more susceptible to ionization than the transition elements.

Ionization of the analyte can be controlled by the addition of a suitable cation having a lower ionization potential than the analyte. These elements are referred to as ionization suppressors. For example, the addition of readily ionized elements such as sodium, potassium and caesium at concentrations of 2000 to 5000 μg/ml effectively suppresses ionization of the analyte by creating an excess of electrons in the flame.
Although thermal ionization does occur in an arc, the energy provided by arc sources is generally low enough that the lines of neutral atoms tend to predominate in an arc spectrum. However, since the energy can vary considerably, most spectra contain a mixture of lines from both atoms and ions. The relative intensities of the two types are dependent upon the energy provided by the source (Shoog and West, 1971).

**Non-atomic Absorption**

At high concentrations, the presence of molecules in the optical path can cause non-atomic absorption. Each molecule is capable of absorbing radiation at a characteristic wavelength and non-atomic absorption will occur when this characteristic band coincides with the atomic absorption line. Generally, the degree of non-atomic absorption will increase as the wavelength decreases and will decrease as the molecular concentration is reduced. The use of a higher wavelength or higher temperature flame will sometimes reduce this form of interference. Non-atomic absorption is normally corrected for by using a hydrogen continuum lamp (background corrector).

**Spectral Interferences**

Spectral interferences are a result of the overlap between the desired analytical line and other elemental
lines. This condition exists because of the necessary compromise between resolution and light throughput.

A monochromator views a specific band of wavelengths or, either side of the analytical wavelength and any other elemental line that falls within that wavelength region will be interpreted by the monochromator as light emanating from the analyte (Merciello and Ward, 1979). This is not important in atomic absorption spectrophotometry however, because the radiation detector is a sharp-line spectrally-attenuated by a hollow cathode tube. However, in emission spectrophotometry this is a very important interference which is usually controlled by use of very narrow slit widths, as well as by use of alternate wavelengths.
EXPERIMENTAL METHODS

PREPARATION OF SAMPLES

In order to have sample solutions containing high enough concentrations of the trace elements to enable quantitative analyses to be made, and yet keep the concentration of the sample within the practical limits of the method of analysis used, it was necessary to use the methods of dissolution.

Since very highly concentrated solutions can result in chemical interferences and reabsorption of the transmitted radiation, as well as an increased possibility of burner blockage, samples were prepared by the 'Solution B' method (Shapiro and Brennok, 1962) for analysis by flame techniques.

Because of the high temperatures produced by the flame, the interferences encountered with the samples reduced, and it was believed that solutions of much higher concentration could be used. Also, the high acid content of concentrated solutions, which would have a deleterious effect on the tantalum-tantalum nebulizer and teflon burner lamp of the atomic absorption unit, has no effect on the ceramic and teflon components of the plasma jet assembly.

The very highly concentrated solutions for analysis by plasma emission were prepared by the 'Solution A' method.
other (Hare, 1977).

1. Solution 1

In the preparation of Solution 1 about 0.5 g of finely dried rock powder was accurately weighed and placed in a small platinum dish. It was then wetted with about 0.1 ml of triple distilled water to reduce any effervescence on subsequent addition of acids. Ten millilitres of reagent grade hydrofluoric acid (40% w/w) were added and evaporated to dryness on a hot plate set at 250 (approximately 60°C). This step was then repeated. When dry for the second time, the dish was removed from the hot plate and allowed to cool for 5 minutes. Approximately 5 ml of hydrofluoric acid (40%) and an equal volume of reagent grade perchloric acid (70-72% HClO₄) were then added and the dish was replaced on the hot plate at a setting of 350 to 400 (approximately 80°-100°C). When the sample was down to dryness, the hot plate setting was turned to maximum until all the fumes were given off and then it was left for half an hour at the top setting to bake. After cooling, the sample was dissolved in about 20 ml of 2.5 M hydrochloric acid (HCl), and transferred to a 200 ml volumetric flask. The solution was then made up to volume and transferred to a nalene bottle.

For plasma emission analyses 1.5 grams of rock powder
as used and the volumes recommended by Shapiro and
Johnson were tripled. After baking and cooling the
samples, they were transferred to 50 ml volumetric flasks
and made up to volume with 2.5 N reagent grade hydrochloric
acid (HCl).

2/ Solution 2A

The method of preparing Solution 2A as given by Lord
(1977) has been modified for use with a Parr acid digestion
bomb. This method of dissolution is outlined below.

An accurately weighed sample of about 2 grams of
dried rock powder was placed into the stainless liner of a
Parr bomb. To it was added 10 ml of reagent grade hydro-
fluoric acid (40% HF), 4 ml of reagent grade hydrochloric
acid (37.5% HCl) and 2 ml of reagent grade nitric acid
(70–71% HNO₃). The sealed bomb was then heated in an
oven at 95°C for one week, cooled for 30 minutes and then
the contents were quantitatively transferred to a 50 ml
volumetric flask, rinsing with a saturated solution of
boric acid (B₂O₅). The solution was then brought up to
volume and quickly transferred to a nalgene bottle. It is
important that the solution be in contact with the glass
volumetric flask for as short a time as possible in order
to minimize the effects of the hydrofluoric acid on the
glass.
Replicate solutions for BCI-1, G-2, GIX-5 and
3 - D1050 were prepared by the 'Solution B' method and
two solutions of BCI - D1050 were prepared as 'Solution A',
or well as a blank for each method.

Preparation of Standards

All of the standards, except rubidium, were prepared
for Fisher Scientific Company certified atomic absorption
standard reference solutions. The 1000 µg/ml stock solution
was diluted with triple distilled water to obtain standards
that were within the lower limit of the recommended working
range of the instrument, and also to bracket the samples
being analysed, where possible.

The stock 1000 µg/ml Rb solution was prepared by dis-
solving 0.7001 grams Reanal (99.9% pure) in 500 ml of triple
distilled water.

Analytical Procedure

In doing the flame analyses, relatively rapid instru-
ment set up was possible since the optimum working con-
ditions are well established (Varian Techtron, 1971).
However, for the plasma emission analyses, it was neces-
sary to test many of the more intense spectral lines in
order to determine which wavelength settings gave the
best results. References used in the selection of
analytical wavelengths to be tested by plasma emission.
include: Sperber, et al (1961), Varian Techtron (1974), Weast (1973) and Leidel, et al (1970). After optimizing the wavelength setting and gain for the desired signal intensity, the standards, samples and blank were aspirated into the instrument and then the standards were repeated to check for any drift in the instrument.

After running the standards and samples, the lowest readable standard was run ten times, consecutively, in order to determine the detection limit from the standard deviation of the ten peaks.

Next, standard solutions of eight of the major elements present in the rock standards were run to determine if they produced any spectral interferences. The elements tested for interference and their concentrations in the solutions run are listed below:

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. (μg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>100</td>
</tr>
<tr>
<td>Ca</td>
<td>60</td>
</tr>
<tr>
<td>Fe</td>
<td>40</td>
</tr>
<tr>
<td>Mg</td>
<td>32</td>
</tr>
<tr>
<td>Mn</td>
<td>35</td>
</tr>
<tr>
<td>Na</td>
<td>40</td>
</tr>
<tr>
<td>K</td>
<td>560</td>
</tr>
</tbody>
</table>

After testing for interferences, one standard which
produced a peak of approximately 20 units was run to obtain drift and repeatability plots. This was accomplished by running the standard for an extended length of time (approximately seven minutes), and then running the same standard for six consecutive runs at a normal sampling speed. When doing absorption analyses, the instrument is initially set up for 0% T and 100% T when aspirating water and therefore the operating conditions for a given element are fixed. For this reason, the absorption work was done first, and then when repeating the element by plasma emission, the same standard could be run using instrument settings to give the same peak height. In this way, the instrument settings required to obtain that peak could be compared for the two methods.
RESULTS AND DISCUSSION OF EXPERIMENTAL PROCEDURES

INTRODUCTORY STATEMENT

The following is a report of the analytical procedure and results for the fourteen elements investigated in this study. They are arranged alphabetically. The choice of the fourteen elements is simply based on the interest in these elements in various geochemical studies done in this laboratory in the past. Also for some of the elements studied, there is a need for the development of superior analytical techniques.

The first few paragraphs of each section give a very brief statement on the crustal abundance and source of the respective element. Detailed abundances and lists of minerals containing the particular element are reported in numerous texts. The Handbook of Geochemistry by Wedepohl (1969) is the most comprehensive and up-to-date source.

The last paragraph is a statement regarding the superiority of one method over the other. This is based, in most cases, on the detection limits, drift, repeatability and noise levels, as well as the slope of the calibration curve.

In each section, the diagrams and figures are given at the end. These are systematically ordered as follows: experimental data for calibration curves by flame, and by
argon plasma emission, corresponding calibration curves and actual recorder plots showing drift, repeatability and noise levels. This is followed by a table listing optimum instrument parameters. In the text, reference to the figures and tables does not appear consecutively and this is recognized as a departure from conventional practice. Also, summary tables (Tables 45 - 50) which are frequently referred to throughout the text are in the Summary and Conclusions section of this thesis.
ARSENIC

Arsenic is a very important pathfinder element in geochronical exploration. It has an average crustal abundance of 1.5 ppm.

Arsenopyrite, AsFe3, is a widespread arsenic mineral, and arsenic is found in small amounts in almost all soils. Because of this, arsenic is widely distributed in plants and can be accumulated in the roots of some plants.

The determination of arsenic in soils is most commonly done by either a colorimetric method involving its reduction and reaction with ammonium molybdate, \((\text{NH}_4)_2\text{MoO}_4\), or by the Gutzeit method in which arsenic is reduced to arsine and reacted with mercury (II) bromide, \(\text{HgBr}_2\). Although not sensitive enough for very small quantities, arsenic can also be measured spectrographically. Further methods of determining arsenic are outlined by Vogel (1961).

The wavelength selected for atomic absorption determinations of arsenic was 193.696 nm. However, in testing several other wavelengths it was found that the line at 228.612 nm was the most sensitive and quiet line for plasma emission analyses. Table 4 gives the working conditions used for both methods.

Ionic standards ranging from 1 µg/ml to 200 µg/ml were prepared and used with each method and Tables 2 and 3
give the results obtained.

The calibration curves for arsenic by atomic absorption and plasma emission are presented in Figures 5a and 5b. The graph obtained by plasma emission is linear to 200 µg/ml As with a correlation coefficient of 0.99991. A lower correlation coefficient of 0.98875 was obtained by atomic absorption due to a negative deviation from Beer's law in the curve.

The slopes and the detection limits were obtained under normal operating conditions and it was found that the values for both are better by plasma emission than those by atomic absorption. The slopes for arsenic by these two methods are 0.2373 and 0.2085 respectively, and the detection limits are 0.8595 µg/ml and 1.5935 µg/ml. Tables 2 and 3 list the standards run and the readings obtained, as well as the statistical parameters derived from them. This information is given for the detection limits in Table 45.

Figures 6a and 6b are recorder plots obtained during the drift and repeatability tests of arsenic. Figure 6a is by atomic absorption and Figure 6b is by plasma emission. In both cases the standard used was 100 µg/ml As. Table 49 gives a complete list of the instrument parameters used in obtaining these plots. For the absor-
from these two tables was used to obtain the calibration curves which are presented in Figures 7a and 7b. Both curves are linear over the range tested with correlation coefficients of 0.99987 for atomic absorption and 0.99992 for plasma emission.

The experimentally determined slopes are 79.4680 by emission and 31.5418 by atomic absorption.

The standards and statistical parameters used in determining the detection limits for the two methods of analysis are given in Table 45. The detection limits by atomic absorption and plasma emission are 0.0077 µg/ml and 0.0019 µg/ml respectively.

The results of the drift and repeatability tests by atomic absorption and plasma emission are presented in Figures 8a and 8b. The ionic standard run by both methods was 0.7 µg/ml Be. The instrument parameters used in obtaining these plots are listed in Table 49. A gain of 4 was used for both methods while the slit width for atomic absorption was 100 microns and for plasma emission it was 25 microns.

The most pronounced difference between the two plots is the noise levels. Both methods have very low base line noise levels, although the value by absorption (0.0040 µg/ml) is slightly lower than that by plasma emission (0.0280 µg/ml).
bance test a gain of 17 and a slit width of 300 microns were required in order to produce a peak of approximately the same intensity as that obtained by plasma emission using a gain of 9 and a slit width of 10 microns. The standard deviation for drift over an extended period of time is 0.3400 by atomic absorption, and by plasma emission it is 0.3954. This suggests that the signal by absorption is slightly more stable than by emission. However, the difference between the variances for the two methods is not significant at the 5% level of significance (See Table 47).

The standard deviation for repeatability over six repetitions by plasma emission is 0.5273, more than twice the value for atomic absorption (0.2211). This indicates a better repeatability when using the conventional burner system than when using the argon plasma jet, and it is substantiated by the application of Snedecor's F-test of variances which shows a significant difference in the variances of the two sets of data at the 5% level of significance (Table 48).

In comparing noise levels for arsenic by the two methods of analysis it must be noted that the 'auto set' mode was not used in the atomic absorption tests as was the case for most of the other elements studied. The baseline noise levels for atomic absorption and plasma emission
are 0.4062 μg/ml and 0.1520 μg/ml, respectively, and the signal noise levels are 13.5000 and 16.4736. The much lower noise level by the emission technique is evident in Figures 6a and 6b. In comparing the signal noise levels it must be remembered that they are calculated by dividing the signal height by the peak to peak fluctuation in the signal minus the peak to peak fluctuation in the base line. Therefore, initially the signal noise by atomic absorption (13.5000) appears higher than by emission (16.4736). They are, however, very similar and the difference in the numeric values is due to the lower base line noise by plasma emission.

It was found that silica produced a strong depression when aspirated at the arsenic wavelength for plasma emission, and therefore it acts as a signal suppressor.

Taking these experimental factors into account, argon plasma emission is favoured over atomic absorption due to its superior performance.
Table 2

ARSENIC BY ATOMIC ABSORPTION

JOURNEY CONDITIONS: WAVELENGTH 193.7 nm, BAIN 17,
SLIT WIDTH 300 microns, LAMP CURRENT 7 mA
OXIDIZING AIR-ACETYLENE FLAME
ABSORPTION MODE

<table>
<thead>
<tr>
<th>CONC. OF STANDARD</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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</thead>
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THE SLOPE IS 0.2085

THE INTERCEPT IS 1.8555

THE CORRELATION COEFFICIENT IS 0.99875
Table 3

ARSENIC BY ARGON PLASMA EMISSION

* WORKING CONDITIONS; WAVELENGTH 228.8 nm, GAIN 5, SLIT WIDTH 50 microns, PLASMA CURRENT 7.0 A *

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THE SLOPE IS 0.2373

THE INTERCEPT IS - 0.0511

THE CORRELATION COEFFICIENT IS 0.99991
Figure 5. Calibration Curves for Arsenic
Figure 6. Recorder plots for Arsenic
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microm)</th>
<th>GAIN</th>
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<td>5</td>
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</table>

(1) OXID. = Oxidizing
BERYLLIUM

Beryllium has a crustal abundance of 2.6 ppm. It is
found in soils derived from rocks containing beryl,
$\text{BeAl}_2\text{Si}_2\text{O}_8$, or other beryllium minerals such as chryso-
beryl, $\text{BeAl}_2\text{O}_4$. These minerals occur as accessories in
wurzite, granite pegmatites, and non schists and
metamorphosed (Hamilton, Colley and Bishop, 1974).

Atomic absorption techniques for the determination
of beryllium in beryl ores are outlined by Angino and
Williams (1972), and colorimetric methods for the deter-
mination of beryllium in soils are discussed by Hessè (1971).

There are several spectral lines available for use
in the determination of beryllium, and many were tested
for use by plasma emission. The line at 234.861 nm,
although not the most sensitive (313.107 nm was more
sensitive) was found to be the best compromise between
signal intensity and noise level. This wavelength is also
recommended for atomic absorption analyses by Varian
Spectrotron (1974) and was therefore used for that method as
well. The working conditions used for both methods are
listed in Table 7.

The ionic standards of beryllium used in this study
ranged from 0.1 $\mu\text{g}/\text{ml}$ to 2.0 $\mu\text{g}/\text{ml}$ Be, and Tables 5 and 6
show the results obtained by the two methods. The data
This is in part due to the use of the 'auto set' mode while in the absorption mode. The signal noise by atomic absorption is much lower than by plasma emission and this is evident from the recorder plots. The values for the signal noise are 19.7083 for absorption and 10.1735 for emission.

The standard deviation for the drift over an extended period of time is 0.3112 by atomic absorption and by plasma emission it is 1.0763, and the variances are significantly different at the 5% level of significance. Therefore, atomic absorption is more stable than plasma emission for beryllium determinations (See Table 47).

For the six repetitions showing repeatability, the standard deviation by argon plasma emission is 1.0106 compared to 0.2560 by absorption. The variances are significantly different at the 5% level of significance, therefore the repeatability by atomic absorption is better than by plasma emission (See Table 48).

Of the eight major element ionic standards tested as possible spectral interferents only iron proved to interfere at the wavelength used in the emission analyses. Iron, therefore, acts as a releasing agent causing strong enhancement of the signal. No interferences were noted by atomic absorption.
Considering the above experimental factors, atomic absorption is considered to be the better method for the determination of beryllium.
Table 5

BERYLLIUM BY ATOMIC ABSORPTION

WORKING CONDITIONS: WAVELENGTH 234.9 nm, GAIN 4,
SLIT WIDTH 100 microns, LAMP CURRENT 5 mA
REDUCING NITROUS OXIDE-ACETYLENE FLAME
ABSORPTION MODE

<table>
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<tr>
<th>CONC. OF STANDARD (µg/ml)</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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THE SLOPE IS 31.5418

THE INTERCEPT IS 0.1161

THE CORRELATION COEFFICIENT IS 0.99987
Table 6

**BERYLLIUM BY ARGON PLASMA EMISSION**

WORKING CONDITIONS: WAVELENGTH 234.9 nm, GAIN 7,
SLIT WIDTH 25 microns, PLASMA CURRENT 7.0 A

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
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<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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</thead>
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<td>15.9</td>
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<td>8.3</td>
<td>0.4</td>
<td>7.9</td>
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**THE SLOPE IS 79.4680**

**THE INTERCEPT IS - 0.0065**

**THE CORRELATION COEFFICIENT IS 0.99992**
BERYLLIUM BY ATOMIC ABSORPTION

BERYLLIUM BY PLASMA EMISSION

Figure 7. Calibration Curves for Beryllium
(a) Atomic Absorption

(b) Argon Plasma Emission

Figure 8. Recorder Plots for Berylliu.
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
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<td>--</td>
<td>---</td>
<td>25</td>
<td>7</td>
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(1) RED. = Reducing
The crustal abundance of boron is 9 ppm. It occurs as the borates; borax, \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \); boracite, \( \text{Sr}_2\text{C}_3\text{Cl} \); colemanite, \( \text{CaB}_6\text{S}_4\text{C}_2 \cdot 5\text{H}_2\text{O} \); kernite, \( \text{Na}_2\text{B}_4\text{O}_3 \); and ulexite, \( \text{NaCaB}_3\text{O}_6 \cdot 8\text{H}_2\text{O} \). It is abundant in arid regions and is precipitated as an evaporite along with halite, sulfates and carbonates, by the evaporation of water from saline lakes (Hesse, 1971 and Hamilton, Woolley and Bishop, 1974).

Boron in soils has a very narrow range between being deficient for plant growth and being toxic. Because of its association with the uptake of calcium by plants, the ratio of boron to calcium is often measured in soil fertility studies. Total boron in a soil is most commonly brought into solution and determined titrimetrically, colorimetrically or spectrographically, however, it is important to note that the total boron present is not all available to plants. Therefore, the water soluble form of boron generally provides the most useful measure of available boron.

The wavelength recommended by Varian Techtron (1974) for boron determinations by conventional atomic absorption techniques was also found to give the best signal by argon plasma emission. That wavelength is 249.7733 nm. The working conditions used for the two methods are listed in
Table 10.

The ionic standards run by atomic absorption ranged from 50 μg/ml to 1000 μg/ml B, and for plasma emission they ranged from 0.5 μg/ml to 5 μg/ml B. Tables 8 and 9 give the results obtained.

The calibration curve for boron by atomic absorption (Figure 9a) shows a slight negative deviation from Beer's law, however, over the range tested by plasma emission the calibration curve is linear (Figure 9b). The respective correlation coefficients are 0.99950 and 0.99995.

The slopes for boron are 0.0256 by atomic absorption and 10.9287 by emission, and the detection limits are 17.2052 μg/ml and 0.0288 μg/ml respectively. Table 45 lists the standards run in determining the detection limits as well as the statistical parameters derived from them.

The recorder plots showing the drift and the repeatability of boron by absorption and emission are illustrated in Figures 10a and 10b respectively. An 800 μg/ml ionic standard was used by both methods. For the test by atomic absorption, a gain of 6 and a slit width of 100 microns were used to obtain the plot shown, whereas by plasma emission, the same peak intensity was obtained using a gain of only 1 and a slit width of 5 microns. A complete list of the instrument parameters used is given
in Table 49.

The standard deviation for the drift by atomic absorption is 0.1345 and by plasma emission it is 0.2426. Therefore both signals are stable, with atomic absorption being more stable. Snedecor's F-test of variances shows the difference between the variances to be significant at the 5% level of significance (Table 47).

The standard deviation for repeatability over six repetitions by atomic absorption is 0.1247 compared to 0.6387 by plasma emission, and the variances for the two are significantly different at the 5% level of significance. Therefore a higher degree of repeatability is obtained by the conventional flame technique over the plasma emission technique.

The base line noise levels for the two methods are very low. They are 0.0040 µg/ml by atomic absorption and 0.0080 µg/ml by plasma emission. The signal noise by atomic absorption (23.1569) is lower than that by plasma emission (10.1212), as indicated by the higher value, and as evident from Figures 10a and 10b.

For the determination of boron, the above factors indicate that argon plasma emission is the better of the two methods. This is primarily based on the much better detection limit by that method, which outweighs the improved drift, repeatability and noise levels by atomic absorption.
Table 8

BORON BY ATOMIC ABSORPTION

WORKING CONDITIONS: WAVELENGTH 249.7 nm, GAIN 6,
SLIT WIDTH 100 microns, LAMP CURRENT 12 mA
REDUCING NITROUS OXIDE-ACETYLENE FLAME
ABSORPTION MODE

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THE SLOPE IS 0.0256

THE INTERCEPT IS 0.0913

THE CORRELATION COEFFICIENT IS 0.99950
Table 9

BORON BY ARGON PLASMA EMISSION

WORKING CONDITIONS; WAVELENGTH 249.7 nm, GAIN 5,
SLIT WIDTH 50 microns, PLASMA CURRENT 7.0 A

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<th>CONC. OF STANDARD µg/ml</th>
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</table>

THE SLOPE IS 10.9287

THE INTERCEPT IS - 0.0992

THE CORRELATION COEFFICIENT IS 0.99995
Figure 9. Calibration Curves for Boron
Figure 10. Recorder Plots for Boron

(a) Atomic Absorption

(b) Argon Plasma Emission
### TABLE 10

**INSTRUMENT PARAMETERS FOR BORON ANALYSIS**

<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)/PLASMA CURRENT (A)</th>
<th>SUPPORT GAS</th>
<th>PLATE (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLAME</td>
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<td>12.0</td>
<td>H₂</td>
<td>RED.</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>PLASMA</td>
<td>249.7</td>
<td>7.0</td>
<td>H₂</td>
<td></td>
<td>50</td>
<td>5</td>
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</tbody>
</table>

(1) RED. = Reducing
CADMIUM

Cadmium has a crustal abundance of 0.16 ppm. It is widely distributed in small amounts in soils and occurs as the mineral greenockite, CdS, which forms as a yellow coating on zinc minerals such as sphalerite, ZnS (Hesse, 1971, and Hamilton, Wooley and Bishop, 1972).

Methods for the determination of cadmium in soils, recommended by Hesse (1971), are described as being "not particularly sensitive" and "subject to interference from other ions". Several classical techniques for the determination of cadmium are outlined by Vogel (1961).

Of the wavelengths tested for cadmium determinations by argon plasma emission, four lines gave useful peaks. These were 214.4382 nm, 226.5017 nm, 228.8016 nm and 361.0150 nm. The most sensitive line for plasma emission, 228.8016 nm, is also recommended by Varian Techtron (1974) for use in atomic absorption analyses and was therefore used for both methods. Table 15 lists the working conditions used by the two methods.

The ionic standards of cadmium which were prepared and used in this study ranged from 0.1 µg/ml to 7.0 µg/ml Cd, and Tables 11 and 12 give the results obtained by each method. The data from these two tables was used to obtain the calibration curves which are presented in Figures 11a
and 11b. Both curves are linear over the ranges tested with correlation coefficients of 0.99989 for atomic absorption and 0.99968 for plasma emission.

The slopes obtained are 21.7264 and 6.6029 for absorption and emission respectively.

The standards and statistical parameters used in determining the detection limits for the two methods of analyses are compiled in Table 45. The detection limits by atomic absorption and plasma emission are 0.0084 µg/ml and 0.0577 µg/ml respectively.

Figures 12a and 12b are recorder plots which show the drift and repeatability of cadmium by atomic absorption and plasma emission. An ionic standard of 1.0 µg/ml Cd was run by both methods to obtain the plots. A gain of 7 and slit width of 50 microns were used for the test by absorption and a gain of 13 and slit width of 10 microns for emission. Table 49 gives a complete list of the instrument parameters used.

Both the base line noise and signal noise levels are greater by plasma emission than by atomic absorption. The base line noise levels are 0.0040 µg/ml by absorption and 0.3640 µg/ml by emission, and the signal noise levels are 31.763 and 19.7573 respectively.

The standard deviation for the drift over an
extended period of time is 0.1549 by atomic absorption and by plasma emission it is 0.6697, and the variances are significantly different at the 5% level of significance. Therefore, atomic absorption is more stable than plasma emission in the determination of cadmium (Table 47).

For the six repetitions showing repeatability, the standard deviation by argon plasma emission is 0.1863 compared to 0.2114 by atomic absorption. The difference between the variances is not significant at the 5% level, therefore, the repeatability by one method is no better than the other (Table 48).

No interferences were noted for determinations by the conventional absorption method, however, silica does produce a strong depression in the signal at the cadmium wavelength by plasma emission.

From this discussion, it is evident that atomic absorption is better for the determination of cadmium than argon plasma emission.
### Table 11

**CADMIUM BY ATOMIC ABSORPTION**

WORKING CONDITIONS: WAVELENGTH 228.8 nm, GAIN 7,
SLIT WIDTH 50 microns, LAMP CURRENT 3 mA,
OXIDIZING AIR-ACETYLENE FLAME

**ABSORPTION MODE**

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
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<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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<td>10.8</td>
<td>11.0</td>
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</table>

THE SLOPE IS 21.7264

THE INTERCEPT IS - 0.0168

THE CORRELATION COEFFICIENT IS 0.99989
Table 12

CADMIUM BY ARGON PLASMA EMISSION

<table>
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<tr>
<th>CONC. OF STANDARD (µg/ml)</th>
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<th>AVERAGE READING</th>
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The slope is 6.6029

The intercept is 0.2561

The correlation coefficient is 0.99968
Figure 11. Calibration Curves for Cadmium.
Figure 12. Recorder plots for Cadmium.
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>PLASMA CURRENT (A)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
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<td>OX10</td>
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<td></td>
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</table>

(1) OX10 = Oxidizing
CHROMIUM

Chromium has a crustal abundance of 122 ppm. The chromium minerals chromite, FeCr₂O₄, and magnesiochromite, MgCr₂O₄, are associated with ultramafic rocks and their derived serpentines. Crocoite, PbCrO₄, is a rare secondary mineral of chromium and it occurs in the oxidized zone of lead mineral veins.

Generally, chromium is present in soils only in very small amounts, and due to its relatively inert nature it has little influence on plant growth.

Recommended methods for the determination of chromium in soils include gravimetric, volumetric and potentiometric techniques (Hesse, 1971).

Measurable signals were obtained for several wavelengths tested by plasma emission and they include 263.5633 nm, 264.3252 nm, 360.533 nm, 425.4346 nm and 520.5436 nm. The two most sensitive lines are at 360.5 nm and 425.4 nm. However, the 425.4 nm line is the least noisy of the two and therefore it was used in the emission analyses. The line at 357.9 nm was recommended by Varian Techtron (1974) for atomic absorption analyses and was therefore used by that method. A complete list of the working conditions used for both methods is given in Table 16.
The standards prepared and run by atomic absorption ranged from 0.5 µg/ml to 50.0 µg/ml Cr. Only those from 0.5 µg/ml to 5.0 µg/ml were run by plasma emission. Tables 14 and 15 give the results obtained by the two methods. The slopes are 3.4603 by absorption and 15.9826 by emission.

The calibration curve for chromium by atomic absorption (Figure 13a) shows a distinct negative deviation from Beer's law but is linear up to 10 µg/ml, for which the correlation coefficient is 0.99727. The curve by plasma emission (Figure 13b) is linear over the range studied, and up to 50 µg/ml, the correlation coefficient is 0.99994.

Table 45 shows the standards and statistical parameters used in determining the detection limits. The detection limit for chromium is better by argon plasma emission than by conventional atomic absorption. The values obtained are 0.0840 µg/ml by absorption and 0.0331 µg/ml by emission.

The drift and repeatability plots for absorption and emission are illustrated in Figures 14a and 14b. They were each obtained by aspirating a 5 µg/ml ionic standard of chromium. The gain and slit width used for the absorption test were 5 and 100 microns respectively, and for emission the gain was 8 and the slit width was 10 microns. A complete list of the working conditions used to obtain
the recorder plots is given in Table 49.

The noise levels are very good for both methods although the signal is slightly quieter by atomic absorption. The values for the base line noise levels are 0.0040 μg/ml and 0.0960 μg/ml for absorption and emission respectively. The signal noise by atomic absorption is 20.9138 and by plasma emission it is 14.3510.

The drift tests show argon plasma emission to be the more stable method of the two with the standard deviation being 0.2968 by absorption compared to 0.0700 by emission. This is substantiated by the fact that the difference between the variances (Table 47) is significant at the 5% level of significance.

The standard deviations for the six repetitions showing repeatability are 0.2671 and 0.3464 by absorption and emission respectively. The variances for the two data sets (Table 46) are not significantly different at the 5% level, therefore the repeatability by one method is no better than the other.

Chemical and spectral interferences in the plasma emission analyses also caused problems by that method. In particular, sodium and aluminum produced slight depressions and silica produced a strong depression when ionic standards of these elements were run at the chromium wavelength.
From the above discussion, it is concluded that argon plasma emission is the better of the two methods for the determination of chromium.
Table 14

CHROMIUM BY ATOMIC ABSORPTION

******************************************************************************
WORKING CONDITIONS; WAVELENGTH 357.9 nm, GAIN 5,
SLIT WIDTH 100 microns, LAMP CURRENT 5 mA
REDUCING AIR-ACETYLENE FLAME
ABSORPTION MODE
******************************************************************************

<table>
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<th>CONC. OF STANDARD µg/ml</th>
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<th>CORRECTED READING</th>
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</tr>
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</table>

THE SLOPE IS 1.5792
THE INTERCEPT IS 3.7994
THE CORRELATION COEFFICIENT IS 0.95207

FOR A LINE FIT THROUGH THE FIRST FOUR POINTS WHICH ARE COLINEAR:

THE SLOPE IS 3.4603
THE INTERCEPT IS 0.4379
THE CORRELATION COEFFICIENT IS 0.99727
Table 15

CHROMIUM BY ARGON PLASMA EMISSION

**************************************************************************************************
WORKING CONDITIONS: WAVELENGTH 425.4 nm, GAIN 10,
SLIT WIDTH 25 microns, PLASMA CURRENT 7.0 A
**************************************************************************************************

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<th>Corrected Reading</th>
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</table>

THE SLOPE IS 15.9826

THE INTERCEPT IS - 0.1430

THE CORRELATION COEFFICIENT IS 0.99994
CHROMIUM BY ATOMIC ABSORPTION

CHROMIUM BY PLASMA EMISSION

Figure 13. Calibration Curves for Chromium
(a) Atomic Absorption

(b) Argon Plasma Emission

Figure 14. Recorder Plots for Chromium
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)/PLASMA CURRENT (A)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
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<td>---</td>
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(1) RED = Reducing
COBALT

Cobalt has a crustal abundance of 29 ppm. It occurs in the minerals cobaltite, (Co,Fe)AsS; skutterudite, (Co,Mn,Fe)AsS; linnaeite, Co3S4; and erythite, Co3(AsS4)2·3H2O. These minerals are found in high-temperature hydrothermal veins and are associated with native silver, arsenopyrite, FeAsS, and calcite, CaCO3 (Hesse, 1971 and Hamilton, Woolley and Bishop, 1974). It has been shown that the cobalt content of many soils is related to the magnesium content of the parent rocks. Therefore, serpentine rocks produce soils with a high cobalt content, and soils derived from granites are low in cobalt.

Cobalt is important in soils because it has a direct effect on the rate of iron uptake and the protein content of plants, and also a deficiency can lead to diseases in cattle and sheep (Hesse, 1971).

Total cobalt in soils is most commonly determined colorimetrically, although a polarographic method is also mentioned by Hesse (1971). Several other classical techniques are outlined by Vogel (1961).

The recommended wavelength (Varian Techtron, 1974) for cobalt determinations by atomic absorption is 240.725 nm and it was therefore used by that method. The
line at 345.3505 nm is the most sensitive for plasma emission analyses. The working conditions used are listed in Table 19.

The ionic standards of cobalt used in this study ranged from 0.5 μg/ml to 10.0 μg/ml Co, and the results obtained by the two methods are given in Tables 17 and 18. Figures 15a and 15b are the calibration curves derived from this data. A slight negative deviation from Beer's law is observed in the curve for atomic absorption and the correlation coefficient is 0.99877. Cobalt by plasma emission is linear over the range tested with a correlation coefficient of 0.99986.

The slopes obtained are 6.3638 by atomic absorption and 7.6346 by plasma emission.

Table 45 gives the standards and statistical parameters used in determining the detection limits for the two methods of analysis. The detection limits by absorption and emission are 0.0961 μg/ml and 0.0385 μg/ml respectively.

Figures 16a and 16b are the recorder plots showing drift and repeatability. Figure 16a is by atomic absorption and Figure 16b is by emission, and both were obtained by aspirating a 2.5 μg/ml ionic standard of cobalt. A gain of 11 was used for both methods while the slit width for atomic absorption was 25 microns and for plasma
emission it was 10 microns. Table 49 gives a more complete list of the instrument parameters used.

The signal by the flame technique is much quieter than by plasma emission as can be seen from the two recorder plots (Figure 16a and 16b). The base line noise levels are 0.0040 μg/ml and 0.3320 μg/ml, and the signal noise levels are 18.1833 and 16.8101 for atomic absorption and plasma emission respectively.

The standard deviation for the drift of the signal over an extended period of time is 0.1345 for atomic absorption and 0.1833 for plasma emission. The variances for the readings (Table 47) are not significantly different at the 5% level of significance, therefore the drift for both methods is similar.

For the six repetitions showing repeatability, the standard deviation by atomic absorption is 0.4297 and by plasma emission it is 0.1674. The variances for the two methods (Table 48) are significantly different at the 5% level of significance, indicating that the plasma emission technique has a higher degree of repeatability than the absorption method.

Minimal interferences were noted by atomic absorption with magnesium and aluminum causing a slight enhancement, and iron, sodium, calcium, potassium and silica
producing slight depressions in the signal. These
elements which caused a depression by atomic absorption
also depress the signal by plasma emission, with silica
producing a strong depression below the zero line.

Taking these factors into account, argon plasma
emission is considered to be the better of the two methods
for the determination of cobalt.
Table 17

COBALT BY ATOMIC ABSORPTION

***************************************************************************
WORKING CONDITIONS: WAVELENGTH 243.7 nm, GAIN 11,
SLIT WIDTH 25 microns, LAMP CURRENT 5 mA
OXIDIZING AIR-ACETYLENE FLAME
ABSORPTION MODE
***************************************************************************

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<th>CONC. OF STANDARD</th>
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<th>AVERAGE READING</th>
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</thead>
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</table>

***************************************************************************

THE SLOPE IS 5.3538
THE INTERCEPT IS 1.5703
THE CORRELATION COEFFICIENT IS 0.99377
**COBALT BY ARGON PLASMA EMISSION**

WORKING CONDITIONS: WAVELENGTH 345.4 nm, GAIN 8,
SLIT WIDTH 25 microns, PLASMA CURRENT 7.0 A

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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</thead>
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<tr>
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THE SLOPE IS 7.6346

THE INTERCEPT IS -0.0992

THE CORRELATION COEFFICIENT IS 0.99986
Figure 15. Calibration Curves for Cobalt
Figure 16. Recorder Plots for Cobalt
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>PLASMA CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
</tr>
</thead>
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<tr>
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<td>25</td>
<td>11</td>
</tr>
<tr>
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<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

(1) Oxid. = Oxidizing
The crustal abundance of copper is 68 ppm. Copper is widely distributed in soils and minerals. Two of the more important copper minerals are chalcocite, Cu₂S, and chalcopyrite, CuFeS₂.

Copper is very important as a plant nutrient. Its uses in plants, which vary greatly depending on the type of plant, include processes such as respiration and photosynthesis. Excess copper, however, can be toxic to plants.

The standard methods for the determination of copper in soils are colorimetric, gravimetric, volumetric, spectrographic and polarographic (Hesse, 1971).

The spectral line at 324.7540 nm is recommended by Varian Electron (1974) for copper determinations by atomic absorption. After testing several other wavelengths by plasma emission, it was found that this line is also the most sensitive by emission, therefore it was used in the analyses by both methods. Table 22 gives a list of the working conditions used by the two methods.

Ionic standards of copper ranging from 0.1 μg/ml to 3.0 μg/ml were analysed by atomic absorption, and from 0.1 μg/ml to 1.0 μg/ml by argon plasma-emission. Tables 20 and 21 show the results obtained by each method, and the data from them was used to develop the calibration
curves which are presented in Figures 17a and 17b. Both calibration curves are linear over the ranges tested with correlation coefficients of 0.99975 for atomic absorption and 0.99980 for plasma emission. The experimental value for the slope is 61.2974 by emission compared to the absorption value of 11.1069.

The standards and statistical parameters used in determining the detection limits for the two methods of analysis are given in Table 45. The detection limit of copper by plasma emission is better than by atomic absorption. The detection limit values obtained are 0.0110 μg/ml by emission and 0.0176 μg/ml by absorption.

The drift and repeatability of the two methods is illustrated by Figures 18a and 18b. Figure 18a is the recorder plot by atomic absorption and Figure 18b is by plasma emission. Both plots were obtained by aspirating an ionic standard of 2.0 μg/ml Cu. A gain of 2 and a slit width of 100 microns were used for the absorption test, and for emission the gain was 5 and the slit width was 10 microns. Table 49 gives a more complete list of the working conditions used in obtaining these recorder plots.

Much less noise is observed in the recorder plot by atomic absorption than by plasma emission. Although the base line noise is very good for both methods, the use of
the 'auto set' mode in the absorption test produced an almost linear base line which is slightly more quiet than the base line by emission. The base line noise levels are 0.0040 µg/ml and 0.1000 µg/ml by absorption and emission respectively. The signal noise by atomic absorption is much better than by plasma emission with their respective values being 23.0328 and 9.5894.

The drift over an extended period of time, and the repeatability of six consecutive repetitions, show atomic absorption to be the more stable and repeatable of the two methods. The standard deviations for the drift values are 0.2100 by absorption and 0.5367 by emission, and the variances for the two data sets are significantly different at the 5% level of significance (Table 47). For the repeatability, the standard deviations are 0.2544 and 0.9267 for atomic absorption and plasma emission respectively. The variances obtained in determining the repeatabilities (Table 48) are significantly different at the 5% level of significance.

No interferences were noted in the determination of copper by the conventional atomic absorption method, however, silica does produce a slight depression in the signal by argon plasma emission.

From the above discussion, it is concluded that atomic absorption is the better method for the determination of copper.
Table 20

COPPER BY ATOMIC ABSORPTION

***************************************************************
WORKING CONDITIONS: WAVELENGTH 324.7 nm, GAIN 2,
SLIT WIDTH 100 microns, LAMP CURRENT 3 mA
OXIDIZING AIR-ACETYLENE FLAME
ABSORPTION MODE
***************************************************************

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
</tr>
</thead>
<tbody>
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<td>0.1</td>
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<td>11.9</td>
</tr>
<tr>
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<td>6.0</td>
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<td>5.8</td>
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<tr>
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<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>5.00</td>
<td>55.4</td>
<td>0.1</td>
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</tr>
<tr>
<td>2.00</td>
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<td>1.1</td>
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<td>11.9</td>
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<td>6.0</td>
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<tr>
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<td>2.5</td>
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<tr>
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<td>1.3</td>
<td>0.1</td>
<td>1.2</td>
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</tr>
</tbody>
</table>

***************************************************************

THE SLOPE IS 11.1069
THE INTERCEPT IS 0.2400
THE CORRELATION COEFFICIENT IS 0.99975
**Table 21**

**COPPER BY ARGON PLASMA EMISSION**

WORKING CONDITIONS; WAVELENGTH 324.7 nm, GAIN 8, SLIT WIDTH 25 microns, PLASMA CURRENT 7.0 A

<table>
<thead>
<tr>
<th>CONC. OF STANDARD (µg/ml)</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
</tr>
</thead>
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<td>0.0</td>
<td>61.0</td>
<td>61.2</td>
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<td>0.50</td>
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<td>0.0</td>
<td>29.4</td>
<td>30.2</td>
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<td>0.20</td>
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<td>0.0</td>
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<td>11.5</td>
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<td>0.0</td>
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<td>11.4</td>
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<td>0.0</td>
<td>5.0</td>
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</table>

THE SLOPE IS 61.2974

THE INTERCEPT IS -0.2981

THE CORRELATION COEFFICIENT IS 0.99980
Figure 17. Calibration Curves for Copper
(a) Atomic Absorption

(b) Argon Plasma Emission

Figure 16. Recorder Blots for Copper
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH ( (\text{nm}) )</th>
<th>LAMP CURRENT ( (\text{mA}) ) \slash PLASMA CURRENT ( (\text{A}) )</th>
<th>SUPPORT GASES</th>
<th>FLAME</th>
<th>SLIT WIDTH ( (\text{microns}) )</th>
<th>GAIN</th>
</tr>
</thead>
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<td>2</td>
</tr>
<tr>
<td>PLASMA</td>
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<td>---</td>
<td>---</td>
<td>25</td>
<td>8</td>
</tr>
</tbody>
</table>

(1) OXID. = Oxidizing;
MOLYBDENUM

Molybdenum has a crustal abundance of 1.2 ppb. It is widely distributed as molybdates such as wulfenite, \( \text{MoO}_4 \), and as the sulfide molybdenite, \( \text{MoS}_2 \). Wulfenite is a secondary mineral that forms in the oxidized zone of ore deposits which contain lead and molybdenum. Molybdenite is an accessory mineral in granites and occurs in association with pegmatites and quartz veins. It can also occur in contact metamorphic deposits.

Molybdenum is important as a pathfinder element in geochemical exploration, particularly in the search for titanium and copper.

It has been observed that plants can develop satisfactorily in the absence of molybdenum as a trace nutrient element in soils, while in excess molybdenum can be toxic.

The spectrographic method of analysis is recommended by Hesse (1971) for molybdenum determinations in soils. Nogel (1961) outlines several other classical techniques for its determination.

The wavelength selected for atomic absorption determinations of molybdenum was 313.259 nm as recommended by Varian Techtron (1974). This line and the one at 290.296 nm both produce useful peaks by argon plasma emission.
However, it was found that the line at 379.825 nm was even more sensitive and therefore it was used for the emission analyses. A complete list of the working conditions used for both methods is given in Table 25.

The ionic standards of molybdenum that were prepared and run by atomic absorption ranged from 1.0 μg/ml to 50.0 μg/ml No. Only those standards from 2.0 μg/ml to 10.0 μg/ml were run by plasma emission. Tables 23 and 24 give the results obtained by the two methods. The slopes are 1.3864 by absorption and 3.8009 by emission.

The calibration curves for molybdenum (Figures 19a and 19b) are linear over the ranges tested by both methods, with correlation coefficients of 0.99983 and 0.99933 for absorption and emission respectively.

The detection limit for molybdenum is better by conventional atomic absorption than by argon plasma emission. The values obtained are 0.2884 μg/ml by absorption and 0.4620 μg/ml by emission. The standards and statistical parameters used in determining the detection limits are given in Table 45.

Figures 20a and 20b are recorder plots by atomic absorption and plasma emission respectively, which show the drift and repeatability of the two methods of analysis. They were each obtained by aspirating a 10 μg/ml ionic
standard of molybdenum. A gain of 4 was used for both methods, however, a slit width of 100 microns was used for atomic absorption compared to a 25 micron slit width for plasma emission. A more complete list of the working conditions used to obtain the recorder plots is given in Table 49.

Noise levels by atomic absorption are much better than by plasma emission. The values for the base line noise levels are 0.0040 µg/ml and 0.0740 µg/ml for absorption and emission respectively. The signal noise by atomic absorption is 20.9138 and by plasma emission it is 14.3510.

The drift tests show that the conventional method of flame analyses is more stable than the plasma emission technique, with standard deviations of 0.1246 by absorption and 0.2993 by emission. This fact is substantiated by applying Snedecor's F-test of variances which shows the variances of the two methods (Table 47) to be significantly different at the 5% level of significance.

The standard deviations for the six repetitions showing repeatability are 0.1462 and 0.4573 by absorption and emission respectively. Only five peaks are shown in Figure 20 because each peak required a considerable length of time to stabilize and to return to zero. The variances for the two data sets (Table 48) are significantly different
at the 5% level of significance, therefore the repeatability by atomic absorption is better than by plasma emission.

In the test for interferences by the eight major elements, iron was found to cause a slight enhancement, while the ionic standard of silica produced a depression below zero.

Taking these factors into account, atomic absorption is favoured over argon plasma emission for the determination of molybdenum.
Table 23

MOLYBDENUM BY ATOMIC ABSORPTION

-----------------------------------------------------------------------------------
WORKING CONDITIONS; WAVELENGTH 313.3 nm, GAIN 4,
SLIT WIDTH 100 microns, LAMP CURRENT 5 mA
REDUCING NITROUS OXIDE-ACETYLENE FLAME
ABSORPTION MODE
-----------------------------------------------------------------------------------
<table>
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<tr>
<th>CONC. OF STANDARD µg/ml</th>
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<th>ZERO READING</th>
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<th>AVERAGE READING</th>
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<td>0.1</td>
<td>7.9</td>
<td>7.6</td>
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</tr>
<tr>
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THE SLOPE IS 1.3884

THE INTERCEPT IS 0.2631

THE CORRELATION COEFFICIENT IS 0.99983
### Table 24

**MOLYBDENUM BY ARGON PLASMA EMISSION**

<table>
<thead>
<tr>
<th>CONC. OF STANDARD, µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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</thead>
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</tr>
<tr>
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<td>0.0</td>
<td>26.0</td>
<td>26.2</td>
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<td>17.0</td>
<td>17.7</td>
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<td>6.9</td>
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<td>38.0</td>
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<td>7.0</td>
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</table>

THE SLOPE IS 3.8009

THE INTERCEPT IS -0.2340

THE CORRELATION COEFFICIENT IS 0.99933
Figure 19. Calibration Curves for Molybdenum.
Figure 20. Recorder Plots for Molybdenum
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>PLANE (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLAME</td>
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<td>H.0</td>
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<td>4</td>
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<tr>
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<td>379.3</td>
<td>7.0</td>
<td></td>
<td>---</td>
<td>25</td>
<td>7</td>
</tr>
</tbody>
</table>

(1) RED. = Reducing
Nickel has a crustal abundance of 99 ppm. The principle sources of nickel in soils are pentlandite, \((\text{Fe, Ni})_2\text{S}_3\), and pyrrhotite \((\text{Fe}_{1-x}\text{S})\), although it is present in other minerals such as garnierite, a nickel-bearing variety of serpentine, niccolite, NiAs, breithauptite, NiSb, and millerite, NiS. When present in greater than minute quantities, nickel is toxic to plant growth.

Spectrographic methods are most commonly used in determining nickel in soils, although photometric and polarographic methods do exist. Vogel (1961) outlines several methods for making nickel determinations.

There are several spectral lines available for use in spectrophotometric determinations of nickel, and many were tested for use by argon plasma emission. The signals obtained using the 305.082 nm and 351.5054 nm wavelengths are satisfactory for analysing solutions with a high nickel content. However, the more sensitive line at 361.959 nm was used in this study.

A wavelength of 232.003 nm is recommended by Larien echtron (1974) for atomic absorption determinations of nickel and it was therefore used for that method of analysis. The working conditions used for both methods are listed in Table 28.
The ionic standards of nickel used in this study ranged from 0.2 μg/ml to 10.0 μg/ml Ni, and Tables 26 and 27 show the results obtained by the two methods. The data from these two tables was used to obtain the calibration curves which are presented in Figures 21a and 21b. The correlation coefficient of 0.99879 for the curve by absorption is due to a slight negative deviation from Beer's law. The calibration curve for emission is linear over the range tested with a correlation coefficient of 0.99997.

The slopes obtained are 4.7868 and 5.6412 by absorption and emission respectively.

The standards and statistical parameters used in determining the detection limits for the two methods of analysis are given in Table 45. The detection limits by atomic absorption and plasma emission are 0.1080 μg/ml and 0.1086 μg/ml respectively.

The results of the drift and repeatability tests by atomic absorption and plasma emission are presented in Figures 22a and 22b. The ionic standard run by both methods was 5.0 μg/ml Ni. A gain of 9 and a slit width of 50 microns were used for the absorption test while by emission the gain and slit width used were 8 and 25 microns. A more complete list of the instrument parameters used in obtaining these recorder plots is given in
Table 49.

The standard deviation for the drift over an extended period of time is 0.0594 by atomic absorption and by plasma emission it is 0.7323, and the variances are significantly different at the 5% level of significance (Table 47). Therefore, absorption is the more stable of the two methods for nickel determinations.

For the six repetitions showing repeatability, the standard deviation by atomic absorption is 0.5408 compared to 0.8091 by argon plasma emission. The variances (Table 48) are significantly different at the 5% level of significance, therefore, the repeatability by absorption is better than by emission.

The noise levels observed in the recorded signals are greater by plasma emission than by atomic absorption for both the base line noise and signal noise levels. The values obtained are 0.0040 μg/ml and 0.1920 μg/ml for the base line noise levels by absorption and emission, and 21.9155 and 29.3882 for the signal noise levels by absorption and emission.

Interferences were noted from six of the eight major elements tested as possible interferents in the plasma emission analyses of nickel. Slight depressions below the base line were produced when aspirating ionic
standards of sodium, magnesium, aluminum and calcium. An even more intense depression was produced by silica, and a strong enhancement was observed when aspirating iron. This behaviour is believed to be the result of chemical and spectral interferences.

Further evidence of these chemical and spectral interferences was obtained by aspirating several samples of pure and mixed ionic standards. To three of five 3 ml aliquots of a 25 μg/ml ionic standard of nickel were added 3 ml of a standard of either 1000 μg/ml Al, 100 μg/ml Fe or 1000 μg/ml Si. To one of the remaining aliquots of nickel standard 3 ml of each of the other standards were added. The solutions were then brought up to a volume of 12 ml each with triple distilled water. The final solutions then contained 6.25 μg/ml Ni, 250 μg/ml Al, 25 μg/ml Fe and/or 250 μg/ml Si where applicable. These five solutions were then run by plasma emission and the recorder plot obtained is given in Figure 23. From Figure 23 it is evident that a peak of approximately 30 units was produced solely by the nickel (6.25 μg/ml). The second solution produced a peak of approximately the same intensity and therefore the 250 μg/ml Al present had no noticeable effect on the signal. As observed from the third peak, the 25 μg/ml Fe present in the Ni–Fe solution strongly enhanced
the original nickel peak of 30 units to read approximately 37.6 units. The presence of 250 μg/ml Si in the Ni-Si solution resulted in a strong depression in the signal. This is observed in the fourth peak which has an intensity of only 22.2 units. The fifth and final peak in Figure 24 was obtained by aspirating the Ni-Si-Fe-Al solution. The signal intensity developed by this solution was a combined result of all four elements present in the solution. It is approximately 34 units, which is the nickel peak enhanced by the iron, but to a lesser extent then in the third peak, due to the presence of the silica. It is this evidence which leads to the belief that in the very highly concentrated samples analysed by plasma emission, chemical and spectral interferences produce varying degrees of enhancement and depression to give the erroneous values obtained.

Minimal interferences were noted in the analyses for nickel by atomic absorption from magnesium, iron, sodium, calcium, silica, aluminum and potassium. In the argon plasma emission analyses, slight depressions were noted while aspirating sodium, magnesium, aluminum and calcium, and a strong depression was produced by silica. A strong enhancement was produced by an ionic standard of iron.

Considering the above factors, atomic absorption appears to have a slight advantage over argon plasma emission in the determination of nickel.
Table 26

NICKEL BY ATOMIC ABSORPTION

*******************************************************************************
WORKING CONDITIONS: WAVELENGTH 232.0 nm, GAIN 3,
SLIT WIDTH: 50 microns, LAMP CURRENT 5 mA
OXIDIZING AIR-AcETYLENE FLAME
ASSUMPTION MODE
*******************************************************************************

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1</td>
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</table>

THE SLOPE IS 1.7333
THE INTERCEPT IS 1.2735
THE CORRELATION COEFFICIENT IS 0.99579
### Table 27

**Nickel by Argon Plasma Emission**

Working conditions: Wavelength 361.9 nm, Gain 8, Slit Width 25 microns, Plasma Current 7.0 A

<table>
<thead>
<tr>
<th>Conc. of Standard (µg/ml)</th>
<th>Actual Reading</th>
<th>Zero Reading</th>
<th>Corrected Reading</th>
<th>Average Reading</th>
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</tr>
<tr>
<td>2.00</td>
<td>11.0</td>
<td>0.0</td>
<td>11.0</td>
<td>10.9</td>
</tr>
<tr>
<td>1.00</td>
<td>5.0</td>
<td>0.0</td>
<td>5.0</td>
<td>5.4</td>
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</tr>
<tr>
<td>5.00</td>
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<td>0.0</td>
<td>10.9</td>
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<td>5.8</td>
<td>0.0</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>

The slope is 5.6412

The intercept is -0.0864

The correlation coefficient is 0.99997
NICKEL BY ATOMIC ABSORPTION

Figure 21. Calibration Curves for Nickel
(a) Atomic Absorption

(b) Argon Plasma Emission

Figure 22. Recorder plots for Nickel
Figure 23. Recorder plot showing interferences in nickel by plasma emission
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA) / PLASMA CURRENT (A)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
</tr>
</thead>
<tbody>
<tr>
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<td>OXID.</td>
<td>59</td>
<td>9</td>
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<td>PLASMA</td>
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<td>---</td>
<td>---</td>
<td>25</td>
<td>8</td>
</tr>
</tbody>
</table>

(1) OXID. = Oxidizing
RUBIDIUM

The crustal abundance of rubidium is 78 ppm. Rubidium never forms its own minerals but instead is always incorporated in potassium minerals. Therefore, rubidium invariably occurs in trace amounts in K-feldspar, KAlSi₃O₈, and biotite, K(Mg,Fe)₃(AlSi₃O₁₀)(OH)₂. It may also be present in concentrations up to several percent in lepidolite, K₂Li₂Al(Si₄O₁₀)(OH)₂, and microcline, KAlSi₃O₈ (Döppel, 1969).

Rubidium occurs in soils derived from pegmatites, and its concentration in soils is generally determined colorimetrically or by flame photometry (Hesse, 1971).

At the time of this study, no hollow cathode lamp was available for rubidium analyses by atomic absorption, therefore a comparison is made between flame emission and plasma emission.

The wavelength recommended by Varian Techtron (1974) for rubidium determinations by flame emission was also found to give the best signal by argon plasma emission. This wavelength is 780.0227 nm. The working conditions used by both methods are listed in Table 31.

Two sets of ionic standards were prepared. Those run by flame emission ranged from 0.1 µg/ml to 0.5 µg/ml Rb, and for plasma emission they ranged from 10.0 µg/ml
to 100 µg/ml Rb. Tables 29 and 30 give the results obtained.

The calibration curves obtained using the values from Tables 29 and 30 are illustrated in Figures 24a and 24b. The graph by flame emission is linear over the range tested, with a correlation coefficient of 0.99969. A very slight negative deviation from Beer's law is noted by plasma emission, with a correlation coefficient by that method of 0.99972.

The slopes obtained are 96.1369 and 0.3952 for flame emission and plasma emission respectively.

The detection limits by flame emission and plasma emission are 0.0034 µg/ml and 1.5548 µg/ml respectively. Table 45 gives the standards and statistical parameters used in determining the detection limits for the two methods of analysis.

The recorder plots showing the drift and repeatability of rubidium by the two techniques are illustrated in Figures 25a and 25b. An ionic standard of 0.2 µg/ml Rb was run by flame emission to obtain the recorder plot in Figure 25a, and the recorder plot by plasma emission (Figure 25b) was obtained by running a standard of 50.0 µg/ml Rb. The slit width used in both cases was 150 microns, but the gain used by the conventional flame
method was 10 compared to 5 by plasma emission. A complete list of the instrument parameters used is given in Table 49.

The standard deviation for the drift of rubidium by flame emission is 0.2135 and by plasma emission it is 0.4548. This suggests that flame emission is more stable and it is substantiated by Snedecor's F-test of variances which shows the difference between the variances (Table 47) to be significant at the 5% level of significance.

The standard deviation for the repeatability over six repetitions by flame emission was 0.1825 compared to 0.3496 by plasma emission. The difference between the variances (Table 48) is not significant at the 5% level of significance. Therefore, one method is no more repeatable than the other.

The noise levels observed in the base line and signal by plasma emission are much greater than those by flame emission (Figures 25a and 25b). The base line noise levels for the two methods are 0.1400 μg/ml by flame and 0.2260 μg/ml by plasma, and the signal noise levels are 39.9231 and 23.4632 respectively.

Interferences observed by plasma emission included slight depressions by sodium and aluminum and a strong depression by silica, as well as a strong enhancement by
iron.

For the determination of rubidium, the preceding factors indicate that flame emission is the better of the two methods of analysis.
Table 29

RUBIDIUM BY FLAME EMISSION

WORKING CONDITIONS; WAVELENGTH 780.0 nm, GAIN 10,
SLIT WIDTH 150 microns, LAMP CURRENT 0 mA
OXIDIZING AIR-ACETYLENE FLAME
TRANSMISSION MODE

<table>
<thead>
<tr>
<th>CONC. OF STANDARD ( \mu g/ml )</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
</tr>
</thead>
<tbody>
<tr>
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<td>48.7</td>
<td>0.7</td>
<td>48.0</td>
<td>48.2</td>
</tr>
<tr>
<td>0.20</td>
<td>18.9</td>
<td>0.3</td>
<td>18.6</td>
<td>18.5</td>
</tr>
<tr>
<td>0.10</td>
<td>11.0</td>
<td>0.5</td>
<td>10.5</td>
<td>10.4</td>
</tr>
<tr>
<td>0.50</td>
<td>48.5</td>
<td>0.0</td>
<td>48.5</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>18.6</td>
<td>0.1</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>10.5</td>
<td>0.1</td>
<td>10.4</td>
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</tr>
</tbody>
</table>

THE SLOPE IS 96.1369

THE INTERCEPT IS 0.0486

THE CORRELATION COEFFICIENT IS 0.99969
Table 30

RUBIDIUM BY ARGON PLASMA EMISSION

******************************************************************************
WORKING CONDITIONS: WAVELENGTH 780.0 nm, GAIN 5,
SLIT WIDTH 150 microns, PLASMA CURRENT 7.0 A
******************************************************************************

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>50.00</td>
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<td>0.0</td>
<td>20.8</td>
<td>20.5</td>
</tr>
<tr>
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<td>0.0</td>
<td>8.5</td>
<td>8.3</td>
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<td>0.0</td>
<td>4.0</td>
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<td>50.00</td>
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<td>3.6</td>
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</tr>
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</table>

******************************************************************************

THE SLOPE IS 0.3952

THE INTERCEPT IS 0.0949

THE CORRELATION COEFFICIENT IS 0.99972
Figure 24. Calibration Curves for Rubidium
(a) Plane Emission

(b) Argon Plasma Emission

Figure 25  Recorder plots for Kubicium.
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)/PLASMA CURRENT (A)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLAME</td>
<td>730.0</td>
<td>---</td>
<td>AIR</td>
<td>OXI</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td>PLASMA</td>
<td>730.0</td>
<td>7.0</td>
<td>---</td>
<td>---</td>
<td>150</td>
<td>5</td>
</tr>
</tbody>
</table>

(1) OXI = Oxidizing
SELENIUM

The crustal abundance of Selenium is 0.05 ppm. In soils it is most commonly derived from metallic selenides, or selenium minerals such as crookesite, \((\text{Cu, Tl, Ag})_2\text{Se}\). It is believed that selenium is an essential micro-nutrient for plant growth, although in excess it can be toxic to both plants and animals.

Analyses for selenium are generally done colorimetrically or volumetrically (Hesse, 1971). Two volumetric methods as well as a gravimetric method are outlined by Vogel (1961).

The recommended wavelength (Varian Techtron, 1974) for the determination of selenium by atomic absorption is 196.026 nm, and it was therefore used by that method. This wavelength was also found to be the most useful for selenium determinations by argon plasma emission. The working conditions used by the two methods are given in Table 34.

The ionic standards of selenium which were prepared and used in this study ranged from 1.0 \(\mu\text{g/ml}\) to 100.0 \(\mu\text{g/ml}\) \(\text{Se}\), and Tables 32 and 33 give the results obtained by each method. The data from these two tables was used to obtain the calibration curves which are presented in Figures 26a and 26b. The calibration curve by atomic absorption is
characterized by a slight negative deviation from Beer's law and has a correlation coefficient of 0.99689. By plasma emission, the curve is linear over the range tested with a correlation coefficient of 0.99961. The slopes are 0.5941 by flame and 0.4816 by plasma emission.

The standards and statistical parameters used in determining the detection limits for the two methods of analysis are compiled in Table 45. The detection limits by absorption and emission are 0.4376 µg/ml and 1.8553 µg/ml respectively.

Figures 27a and 27b are recorder plots which show the drift and repeatability of selenium by atomic absorption and plasma emission. An ionic standard of 25.0 µg/ml Se was run by both methods to obtain the plots. A gain of 14 and a slit width of 300 microns was used for the test by absorption and a gain of 8 and a slit width of 150 microns for emission. Table 49 gives a complete list of the instrument parameters used.

Both the base line noise and signal noise levels are greater by plasma emission than by atomic absorption. The base line noise levels are 0.3540 µg/ml by absorption and 0.8080 µg/ml by emission, and the signal noise levels are 14.2698 and 28.9806 respectively.

The standard deviation for the drift over an
extended period of time is 0.1846 by atomic absorption and
by plasma emission it is 0.4387, and the variances (Table
47) are significantly different at the 5% level of signifi-
cance. Therefore, atomic absorption is more stable than
plasma emission in the determination of selenium.

For the six repetitions showing the repeatability,
the standard deviation by atomic absorption is 0.1105
compared to 0.3554 by argon plasma emission. The difference
between the variances (Table 48) is significant at the 5%
level of significance, therefore the repeatability by
absorption is better than by emission.

No interferences were noted by the eight major
element ionic standards when run at the selenium wave-
length by atomic absorption. However, silica did produce
a slight depression below zero by plasma emission.

Taking these factors into account, it is evident
that atomic absorption is better for the determination of
selenium than argon plasma emission.
### Table 32

**SELENIUM BY ATOMIC ABSORPTION**

<table>
<thead>
<tr>
<th>CONC. OF STANDARD (µg/ml)</th>
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<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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<td>17.5</td>
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</tr>
<tr>
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<td>2.2</td>
<td>9.7</td>
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<td>4.2</td>
</tr>
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</table>

**THE SLOPE IS 1.3911**

**THE INTERCEPT IS 1.3753**

**THE CORRELATION COEFFICIENT IS 0.9999**
<table>
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<tr>
<th>CONC. OF STANDARD µg/ml</th>
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<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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<td>6.0</td>
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<td>6.0</td>
<td>5.7</td>
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</table>

**THE SLOPE IS 0.4816**

**THE INTERCEPT IS 0.2125**

**THE CORRELATION COEFFICIENT IS 0.99961**
Figure 26. Calibration Curves for Selenium.
Figure 27: Recorder Plots for Selenium
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>PLATE (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>GAIN</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>PLASMA</td>
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<td></td>
<td>150</td>
<td>5</td>
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</table>

(1) RED. = Reducing
SILVER

Silver has a crustal abundance of 0.08 ppm. The best known silver mineral is argentite, Ag₂S, which is found in association with native silver, galena, PbS, sphalerite, ZnS, and ores of copper. When in soils, silver has been known to accumulate in mushrooms, however, it is generally toxic to plant growth.

After extraction from soil by acid digestion, silver is classically determined nephelometrically as the chloride (Hesse, 1971). Other alternate methods of determination are outlined by Vogel (1967) including gravimetric as AgCl, electrolysis, and an indirect method using potassium nickelocyanide, (K₂[CN]₄)⁻².

Several wavelengths were tested for use by argon plasma emission for the determination of silver and two were found to produce useful peaks. These wavelengths are 328.0683 nm and 338.2891 nm. Of the two, the first line is the most sensitive and was therefore used in the analyses by plasma emission. The 328.1 nm wavelength is also recommended by Varian Techtron (1974) for absorption analyses and was therefore used by that method as well. A complete list of the working conditions used by both methods is given in Table 37.

The ionic standards prepared and run by atomic
absorption ranged from 0.1 µg/ml to 7.0 µg/ml Ag. Those standards used for the emission analyses ranged from 1.0 µg/ml to 10.0 µg/ml Ag. Tables 35 and 36 give the results obtained by the two methods. The slopes are 10.2629 by absorption and 6.4312 by emission.

The calibration curve for silver by atomic absorption (Figure 28a) shows a slight negative deviation from Beer's law and has a correlation coefficient of 0.99916. The curve by plasma emission (Figure 28b) is linear over the range studied with a correlation coefficient of 0.99969.

Table 45 shows the standards and statistical parameters used in determining the detection limits. The detection limit for silver is better by conventional atomic absorption than by argon plasma emission. The values obtained are 0.0276 µg/ml by absorption and 0.0751 µg/ml by emission.

The drift and repeatability plots for absorption and emission are illustrated in Figures 29a and 29b. They were each obtained by aspirating a 2.0 µg/ml ionic standard of silver. The slit width used by both methods was 25 microns, and the gains used were 3 and 7 by flame and plasma respectively. A complete list of the working conditions used to obtain the recorder plots is given in Table 49.
Much greater noise levels were noted in the baseline and signal peaks by plasma emission than by atomic absorption. The values for the baseline noise levels are 0.0040 \( \mu g/ml \) and 0.3260 \( \mu g/ml \) for absorption and emission respectively. The signal noise by atomic absorption is 24.0847 and by plasma emission it is 14.0000.

The drift tests show atomic absorption to be the more stable of the two methods, with the standard deviation being 0.1486 by absorption compared to 0.4011 by emission. This is substantiated by the fact that the difference between the two variances (Table 47) is significant at the 5\% level of significance.

The standard deviations for the six repetitions showing repeatability are 0.1572 and 0.3144 by absorption and emission respectively. The variances for the two data sets (Table 48) are not significantly different at the 5\% level of significance, therefore the repeatability of silver by one method is no better than the other. Only five peaks are shown in Figure 29b because of the time required for the signal to stabilize and then return to zero.

No interferences were noted in the atomic absorption analyses for silver, however both iron and silica produced interferences by plasma emission. A strong enhancement
was noted when aspirating an ionic standard of iron at the silver wavelength and silice caused a strong depression.

Considering the above factors, atomic absorption is clearly the best method of the two for the determination of silver.
<table>
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<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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</table>

THE SLOPE IS 10.2822

THE INTERCEPT IS 2.9592

THE CORRELATION COEFFICIENT IS 0.99910
Table 36

SILVER BY ARGON PLASMA EMISION

Working Conditions: Wavelength 328.1 nm, Gain 4, Slit Width 50 microns, Plasma Current 7.5 A

<table>
<thead>
<tr>
<th>Concentration (μg/ml)</th>
<th>Actual Reading</th>
<th>Zero Reading</th>
<th>Corrected Reading</th>
<th>Average Reading</th>
</tr>
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<tbody>
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<td>12.4</td>
<td>11.8</td>
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<tr>
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<td>5.2</td>
<td>0.0</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>

The slope is 6.4312

The intercept is -0.3756

The correlation coefficient is 0.99969
Figure 26 Calibration Curves for Silver
Figure 29  Recorder plots for Silver
### Table 37

Electrolysis Parameters for Silver Anode

<table>
<thead>
<tr>
<th>METHOD</th>
<th>CATHODE LENGTH (mm)</th>
<th>LAP CURRENT (mA)</th>
<th>LAP ANODE CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>PLACE (1)</th>
<th>CLAY ALK (mL)</th>
<th>SALT (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLANO</td>
<td>325.1</td>
<td>3.0</td>
<td></td>
<td>AIR</td>
<td>OXID.</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>PLATIN</td>
<td>325.1</td>
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<td></td>
<td></td>
<td>20</td>
<td>4</td>
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</table>

(1) OXID. = Oxidation
STRONTIUM.

Strontium has a crustal abundance of 364 ppm, and it occurs as the sulfate in celestite, SrSO₄, and the carbonate in strontianite, SrCO₃. Both minerals occur in hydrothermal veins and in sedimentary rocks, particularly celestite and limestone. Strontium is also found in various minerals substituting for calcium.

Strontium is widely distributed in soils in small quantities. However, it is not essential to plant growth and can be toxic. Calcium can be replaced, to some extent, by strontium in plants, although complete substitution is harmful to plant growth (Hesse, 1971).

Accepted methods for determination of strontium include X-ray fluorescence, spectrographic techniques, atomic absorption and flame photometry. Vogel (1961) outlines three methods of gravimetric determinations.

The comparison of strontium analyses is made between flame emission and plasma emission because at the time of this study there was no hollow cathode lamp available for strontium determinations by atomic absorption.

The recommended wavelength (Varian Techtron, 1974) for strontium determinations by flame emission is 460.7331 nm, and it was found that this line also produced the best signal for determinations by argon plasma
emission. The working conditions used by the two methods are listed in Table 40.

The ionic standards of strontium used in this study ranged from 0.1 µg/ml to 1.0 µg/ml Sr, and the results obtained by the two methods are given in Tables 38 and 39. Figures 30a and 30b are the calibration curves derived from this data. Both curves are linear over the ranges tested with correlation coefficients of 0.99985 by flame emission and 0.99907 by argon plasma emission. The slopes obtained are 0.0237 µg/ml by flame emission and 0.0211 µg/ml by plasma emission.

Table 45 gives the standards and statistical parameters used in determining the detection limits for the two methods of analyses. The detection limits by flame emission and plasma emission are 0.0071 µg/ml and 0.0283 µg/ml respectively.

Figures 31a and 31b are the recorder plots showing drift and repeatability. Figure 31a is by flame emission and Figure 31b is by plasma emission, and both were obtained by aspirating a 0.5 µg/ml ionic standard of strontium. A gain of 7 and a slit width of 25 microns was used for the flame emission test and by plasma emission a gain of 8 and a slit width of 50 microns was used. Table 49 gives a more complete list of the instrument parameters used.
The signal by the flame technique is much quieter than by plasma emission, as can be seen from the two recorder plots (Figures 31a and 31b). The base line noise levels are 0.0400 μg/ml and 0.5780 μg/ml, and the signal noise levels are 12.2762 and 61.6867 for flame emission and plasma emission respectively. The very high signal noise level by plasma is a result of the noisy base line which when subtracted from the signal noise gives a very high signal-to-noise ratio.

The standard deviation for the drift of the signal over an extended period of time is 0.1907 for flame emission and 0.5752 for plasma emission. The variances for the readings (Table 47) are significantly different at the 5% level of significance, therefore flame emission is the more stable of the two methods.

For the six repetitions showing repeatability, the standard deviation by flame emission is 0.1707 and by plasma emission it is 0.4898. The variances for the two methods (Table 48) are significantly different at the 5% level of significance, indicating that the flame emission technique has a higher degree of repeatability than the plasma emission method.

Of the eight major elements tested as possible interferents, only silica caused an interference. At the
strontium wavelength, silica produced a strong depression in the signal.

It is evident from these factors that flame emission is considerably better than argon plasma emission for the determination of strontium.
### Table 38

**STRONTIUM BY FLAME EMISSION**

**WORKING CONDITIONS:** WAVELENGTH 460.7 nm, GAIN 7,
SLIT WIDTH 25 microns, LAMP CURRENT 0 mA
OXIDIZING NITROUS OXIDE-ACETYLENE FLAME
TRANSMISSION MODE

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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</thead>
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<td>42.0</td>
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<tr>
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<td>20.9</td>
<td>20.9</td>
</tr>
<tr>
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<tr>
<td>0.10</td>
<td>3.7</td>
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<td>0.50</td>
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<td>0.0</td>
<td>21.0</td>
<td></td>
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<tr>
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<td>0.0</td>
<td>3.8</td>
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</tbody>
</table>

THE SLOPE IS 42.1089

THE INTERCEPT IS - 0.1620

THE CORRELATION COEFFICIENT IS 0.99985
Table 39

STRONTIUM BY ARGON PLASMA EMISSION

*********************************************************************************************
WORKING CONDITIONS: WAVELENGTH 460.7 nm, GAIN 11,
SLIT WIDTH 25 microns, PLASMA CURRENT 7.5 A
*********************************************************************************************

<table>
<thead>
<tr>
<th>CONC. OF STANDARD (µg/ml)</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
</tr>
</thead>
<tbody>
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<td>46.5</td>
<td>0.0</td>
<td>46.5</td>
<td>46.6</td>
</tr>
<tr>
<td>0.70</td>
<td>34.3</td>
<td>0.0</td>
<td>34.3</td>
<td>34.6</td>
</tr>
<tr>
<td>0.50</td>
<td>22.8</td>
<td>0.0</td>
<td>22.8</td>
<td>22.5</td>
</tr>
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<td>8.7</td>
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<td>8.7</td>
<td>8.7</td>
</tr>
<tr>
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<td>8.8</td>
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</table>

THE SLOPE IS 47.3113

THE INTERCEPT IS - 0.1183

THE CORRELATION COEFFICIENT IS 0.99907
Figure 30. Calibration Curves for Strontium
Figure 31. Recorder Plots for Strontium
<table>
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<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>SUPPORT GAS</th>
<th>FLAME</th>
<th>FLAME WIDTH (microns)</th>
<th>GAIN</th>
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<td>H₂O</td>
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<td>25</td>
<td>7</td>
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<tr>
<td>PLASMA</td>
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<td>7.5</td>
<td>---</td>
<td>25</td>
<td>11</td>
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</table>

(1) OXID. = Oxidizing
Hinc has a crustal abundance of 76 ppm. It is
widely distributed as the sulfide sphalerite, InS, the
carbonate smithsonite, InCO3, and the silicate hemihydrate
(calcineine), In8(CO3)5(S)2·H2O. All three minerals
are associated with galena and pyrite, and occur in hydro-
thermal veins and limestones (Hamilton, Woolley and Bishop,
1980).

Any methods exist for the determination of zinc
including gravimetric, electrogravimetric, volumetric tri-
colorimetric methods, and they are discussed by Kosco
(1971) and Vogel (1961).

The spectral line at 213.856 nm is recommended by
Varian spectrotron (1974) for zinc determinations by atomic
absorption. Of the wavelengths tested by plasma emission
three produced useful signals. These wavelengths are
202.551 nm, 213.856 nm and 234.502 nm. The most sensitive
of these lines is the 213.856 nm line and it was therefore
used for zinc analyses by plasma emission as well as atomic
absorption. Table 43 gives a list of the working condi-
tions used by the two methods.

Ionic standards of zinc used in this study ranged
from 0.1 µg/ml to 2.0 µg/ml. Tables 41 and 42 show the
results obtained by each method and the data from these was
used to develop the calibration curves which are presented in Figures 32a and 32b. Both calibration curves are linear over the ranges tested with correlation coefficients of 0.99976 for atomic absorption and 0.99997 for plasma emission. The experimental values for the slopes are 29.6849 by absorption and 15.6245 by emission.

The standards and statistical parameters used in determining the detection limits for the two methods of analysis are given in Table 45. The detection limit of zinc by atomic absorption is better than by plasma emission. The detection limit values obtained are 0.0141 µg/ml by absorption and 0.0344 µg/ml by emission.

The drift and repeatability of the two methods is illustrated by Figures 33a and 33b. Figure 33a is the recorder plot by atomic absorption and Figure 33b is by plasma emission. Both plots were obtained by aspirating an ionic standard of 0.5 µg/ml Zn. A gain of 7 and a slit width of 100 microns was used for the absorption test, and for emission the gain was 9 and the slit width was 25 microns. Table 49 gives a more complete list of the working conditions used in obtaining these recorder plots.

Both the baseline noise and the signal noise levels are greater by plasma emission than by atomic absorption. The baseline noise levels are 0.0040 µg/ml by absorption.
and 0.2660 µg/ml by emission, and the signal noise levels are 13.6429 and 9.8058 respectively.

The drift by atomic absorption shows a marked increase in the peak height with time. Initially it might appear as though the instrument was not fully warmed up, however this plot was made near the end of the analysis and more than enough time for warming up had elapsed. It is also interesting to note that even after the peak height had increased from approximately 15 units to 20 units the signal did return to zero when aspirating triple distilled water, and the six peaks which show the repeatability are each approximately the same height as the peak at the start of the drift test. The standard deviations for absorption and emission are 0.7085 and 0.1268. This indicates that the signal by emission is more stable than that by absorption and it is substantiated by Snedecor’s F-test of variances which shows that the difference between the variances (Table 47) is significant at the 5% level of significance.

The standard deviations for the six repeatability peaks by absorption and emission are 0.1795 and 0.0942. The variances for the two data sets (Table 48) are not significantly different at the 5% level of significance, and therefore one method is no more repeatable than the
other in the determination of zinc.

In the zinc analyses by atomic absorption, silica produced a slight enhancement in the signal, and calcium caused a slight depression. No interferences were noted by the other major elements tested. Only silica caused an interference in the form of a depression in the plasma emission analyses.

From the preceding discussion, it is concluded that atomic absorption is the better of the two methods for the determination of zinc.
Table 41

ZINC BY ATOMIC ABSORPTION

***********************
WORKING CONDITIONS; WAVELENGTH 213.9 nm, GAIN 7,
SLIT WIDTH 100 microns, LAMP CURRENT 5 mA
OXIDIZING AIR-ACETYLENE FLAME
ABSORPTION NODE
***********************

<table>
<thead>
<tr>
<th>CONC. OF STANDARD µg/ml</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
<th>AVERAGE READING</th>
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<td>15.7</td>
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<td>7.0</td>
<td>7.0</td>
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<td>2.9</td>
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<td>7.0</td>
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<tr>
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<td>3.2</td>
<td>0.0</td>
<td>3.2</td>
<td>3.2</td>
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</tbody>
</table>

***********************
THE SLOPE IS 29.3849
THE INTERCEPT IS 2.1435
THE CORRELATION COEFFICIENT IS 0.99976
***********************
### Table 42

**ZINC BY ARGON PLASMA EMISSION**

*Working Conditions: Wavelength 213.9 nm, Gain 11, Slit Width 25 microns, Plasma Current 7.5 A*

<table>
<thead>
<tr>
<th>Conc. of Standard (µg/ml)</th>
<th>Actual Reading</th>
<th>Zero Reading</th>
<th>Corrected Reading</th>
<th>Average Reading</th>
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<tbody>
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</tr>
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<td>3.0</td>
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</tr>
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<td>3.1</td>
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</tbody>
</table>

**The slope is 15.6245**

**The intercept is - 0.0388**

**The correlation coefficient is 0.99997**
Figure 32. Calibration Curves for Zinc
Figure 33. Recorder plots for Zinc
<table>
<thead>
<tr>
<th>METHOD</th>
<th>WAVELENGTH (nm)</th>
<th>LAMP CURRENT (mA)</th>
<th>PLASMA CURRENT (A)</th>
<th>SUPPORT GAS</th>
<th>FLAME (1)</th>
<th>SLIT WIDTH (microns)</th>
<th>CALIBRANT</th>
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<tr>
<td>FLAME</td>
<td>213.9</td>
<td>5.9</td>
<td></td>
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<td>OXID.</td>
<td>100</td>
<td>7</td>
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<td>7.5</td>
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<td></td>
<td></td>
<td>25</td>
<td>11</td>
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(1) OXID. = Oxidizing
APPLICATIONS

In assessing the feasibility of argon plasma emission in the determination of the elements studied, in rocks and soils, it was found that many forms of interferences exist which greatly influence the concentrations obtained.

Of the fourteen elements studied, only five (Cr, Cu, Rb, Sr and Zn) were detectable by the conventional flame technique and therefore can be useful for comparing the experimental results of the two methods of analyses. Copper, rubidium, strontium and zinc each gave acceptable results by the flame analyses. However, by plasma emission, chemical and spectral interferences caused the results to be up to several orders of magnitude greater than the literature values. For this reason, it is concluded that the flame technique is the better of the two for determining these elements in geological samples.

The chromium results by atomic absorption are approximately ten times the accepted values, and therefore, the results by plasma emission are also many times greater, or less than the recommended values. This suggests that neither method is acceptable for the determination of chromium. Therefore, for chromium and the other nine remaining elements studied,
for which no experimental values by flame analyses are available, comparisons were drawn from the statistical parameters obtained by the tests made.

Table 44 gives the literature values and experimental values obtained for each element by both flame and plasma methods.

The temperatures produced by the argon plasma jet reduce matrix effects and chemical interferences, and interelement interferences, to the extent where they have little or no influence on the analyses of standard rock solutions made to the recommended concentration of 0.5 grams to 500 ml. However, in the highly concentrated solutions used in the determination of trace elements (1.5 grams to 50 ml) it was found that these interferences do exist, and they greatly influence the results obtained.

The effects of these interferences are observed in the results obtained for the rock standards as significant enhancements in the signal, which caused the results to be several times the recommended value, for twelve of the fourteen elements studied. The other two elements, cobalt and silver, produced signals below the zero obtained while aspirating triple distilled water, also due to chemical interferences.

Several attempts were made to identify and overcome
<table>
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<th>ELEMENT</th>
<th>METHOD</th>
<th>BCR-1 (Sol'n B) ppm</th>
<th>G-2 (Sol'n B) ppm</th>
<th>GRX-5 (Sol'n B) ppm</th>
<th>SGW-D1050 (Sol'n B) ppm</th>
<th>SGW-D1050 (Sol'n JA) ppm</th>
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<tr>
<td>Ag</td>
<td>L</td>
<td>0.036</td>
<td>0.049</td>
<td>1.71</td>
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<tr>
<td></td>
<td>F</td>
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<td></td>
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<tr>
<td>As</td>
<td>L</td>
<td>0.7</td>
<td>0.25</td>
<td>40.0</td>
<td></td>
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<tr>
<td></td>
<td>F</td>
<td>2802.6 ± 130.7</td>
<td></td>
<td>849.6 ± 15.7</td>
<td>3019.7 ± 57.3</td>
<td>4669.9 ± 25.4</td>
</tr>
<tr>
<td>B</td>
<td>L</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>F(1)</td>
<td>23.3 ± 0.6</td>
<td>15.3 ± 0.5</td>
<td>28.6 ± 4.7</td>
<td>23.4 ± 2.1</td>
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<tr>
<td>Be</td>
<td>L</td>
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<td>2.6</td>
<td>1.1</td>
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</tr>
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<td></td>
<td>F</td>
<td>338.5 ± 0.8</td>
<td>60.6 ± 0.8</td>
<td>9.6 ± 0.4</td>
<td>380.8 ± 3.4</td>
<td>322.4 ± 16.4</td>
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<td>0.039</td>
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<td></td>
<td>F</td>
<td>130.1 ± 3.8</td>
<td></td>
<td>46.7 ± 2.2</td>
<td>195.0 ± 4.3</td>
<td>290.4 ± 3.7</td>
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<td>38</td>
<td>5.5</td>
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<tr>
<td>Cr</td>
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<td>F</td>
<td>183.4 ± 45.8</td>
<td>77.6 ± 28.6</td>
<td>145.7 ± 2.0</td>
<td>294.0 ± 41.4</td>
<td>45.9 ± 2.5</td>
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<td>ELEMENT</td>
<td>METHOD</td>
<td>BCR-1 (Sol'n B) ppm</td>
<td>G-2 (Sol'n B) ppm</td>
<td>GRX-5 (Sol'n B) ppm</td>
<td>SGM-D1050 (Sol'n B) ppm</td>
<td>SGM-D1050 (Sol'n JA) ppm</td>
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<td>---------------------</td>
<td>-------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Cu</td>
<td>L</td>
<td>18.4</td>
<td>11.7</td>
<td>359.79</td>
<td>88.29</td>
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<td>F</td>
<td>18.5 ± 1.3</td>
<td>9.6 ± 1.7</td>
<td>359.0 ± 10.0</td>
<td>98.4 ± 5.0</td>
<td>15.3 ± 0.2</td>
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<td>P(1)</td>
<td>8.7 ± 0.4</td>
<td>0.8 ± 0.01</td>
<td>37.6 ± 0.7</td>
<td>19.1 ± 4.3</td>
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<td>Mo</td>
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<td>0.36</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
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<td>F</td>
<td></td>
<td></td>
<td>39.6</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>1350.5 ± 34.2</td>
<td>50.3 ± 0.7</td>
<td>378.1 ± 8.0</td>
<td>1537.7 ± 28.8</td>
<td>1172.7 ± 15.2</td>
</tr>
<tr>
<td>Ni</td>
<td>L</td>
<td>15.8</td>
<td>5.1</td>
<td>77.17</td>
<td>26.85</td>
<td>26.85</td>
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<td></td>
<td>F</td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>4379.2 ± 26.8</td>
<td>939.5 ± 0.7</td>
<td>1945.6 ± 42.4</td>
<td>4957.2 ± 107.3</td>
<td>3828.4 ± 42.0</td>
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<td>Rb</td>
<td>L</td>
<td>46.6</td>
<td>168.0</td>
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<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>F(1)</td>
<td>67.1 ± 1.5</td>
<td>169.6 ± 2.5</td>
<td>45.2 ± 1.0</td>
<td>—</td>
<td>—</td>
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<tr>
<td></td>
<td>P</td>
<td>622.9 ± 20.7</td>
<td>194.4 ± 3.4</td>
<td>721.5 ± 18.6</td>
<td>48.1 ± 0.7</td>
<td>—</td>
</tr>
<tr>
<td>Se</td>
<td>L</td>
<td>0.1</td>
<td>0.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>2748.1 ± 373.8</td>
<td>1127.8 ± 29.2</td>
<td>3546.7 ± 191.6</td>
<td>4241.5 ± 310.1</td>
<td>—</td>
</tr>
<tr>
<td>Sr</td>
<td>L</td>
<td>330</td>
<td>479</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>302.9 ± 15.4</td>
<td>450.3 ± 8.4</td>
<td>99.0 ± 2.8</td>
<td>190.3 ± 4.5</td>
<td>239.5 ± 13.5</td>
</tr>
<tr>
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<td>P</td>
<td>734.1 ± 20.6</td>
<td>901.4 ± 3.0</td>
<td>177.1 ± 6.1</td>
<td>491.9 ± 8.2</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>L</td>
<td>120</td>
<td>85</td>
<td>49.19</td>
<td>112.42</td>
<td>112.42</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>138.7 ± 3.1</td>
<td>88.8 ± 4.7</td>
<td>56.8 ± 5.0</td>
<td>142.8 ± 18.7</td>
<td>254.0 ± 1.9</td>
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<tr>
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<td>P</td>
<td>209.4 ± 1.2</td>
<td>101.5 ± 1.0</td>
<td>85.3 ± 13.7</td>
<td>186.6 ± 1.3</td>
<td></td>
</tr>
</tbody>
</table>

(1) Method of Standard Addition
L Literature Values
F Flame Analyses
P Plasma Emission Analyses
the interferences in plasma emission analyses. The cause of the enhancements and depressions of the signal is believed to be chemical and spectral interferences. This was shown to be the case by analysing ionic standards of nickel spiked with aluminum, silica and iron. As explained in the section on nickel, the spikes caused significant enhancement and depression of the nickel peaks, similar to that seen in the rock sample analyses.

In dilute solutions, Quirt (1978) has shown that argon plasma emission is a satisfactory method for the determination of titanium. By analysing reference sample SGX-D1050 for titanium, the effects of chemical and spectral interferences in plasma emission analyses are further exemplified. Unfortunately, there is no recommended value for the concentration of titanium in SGX-D1050, however this is not important for this purpose. For this analysis, the sample was diluted to fall within the range of the ionic standards used, and since dilutions of 10 times and 100 times both were within the standards, titanium results were calculated for each. The fact that a linear calibration curve was obtained for the ionic standards run would suggest that a sample, diluted by 10, would give a peak height 10 times that produced by the same sample diluted by 100. This, however, was not the
case. Instead, the peak for the more concentrated solution was approximately thirteen times the height of the peak for the more dilute solution. This resulted in an experimental value of 4696.3 ppm Ti in the more dilute solution compared to 6038.3 ppm Ti for the more concentrated solution.

The method of standard addition (Appendix VII), which proved useful in the determination of strontium by flame emission, was attempted for the determination of boron and copper by plasma emission. This method produced results which are better than those by direct analysis.

A further attempt to overcome these interferences involved the plotting of calibration curves for boron and copper using several standard reference samples. Boron and copper concentrations in sample \( \text{V-1} \) are taken from Maxwell, 1968. The results of this, which are illustrated in Figures 34 and 35, indicate that the interferences are dependent on the concentrations of other elements present and therefore vary from rock type to rock type. Correlation coefficients for the two figures are 0.98531 for copper and -0.20657 for boron.

In trying to determine the elements studied in actual rock and soil solutions by argon plasma emission, the
Figure 34. Calibration Curve for Boron in Rock Standards by Plasma Emission
Figure 35. Calibration Curve for Copper in Rock Standards by Flame Emission
results are generally erroneously high, although silver and cobalt are low. The use of the method of standard addition for boron and copper did improve the results, indicating that matrix effects are a component of the problem. That similar problems have not been encountered by Quirt (1976), who reported on the data of 10 major elements in 30-fold more dilute solutions, suggests that the total ion strength must be another component of the problem.

Interferences due to background matrix effects are believed to be another factor contributing to the problems encountered in rock and soil analyses. By aspirating an ionic standard of strontium and reference sample G-2, at wavelength settings starting 2.0 nm below the strontium wavelength and increasing by increments of 0.2 nm to 2.0 nm above the strontium wavelength, curves are developed which illustrate the presence of background interferences. However, improvements in the results, by making background corrections using these curves, were only minimal. Furthermore, attempts to generate calibration curves for boron and copper, using reference rock samples, showed that the individual composition is also a contributing factor.
DISCUSSION AND CONCLUSIONS

All experimental methods have their own specific limitations for which improvements are continually being sought. In past studies (Mitchell, 1977 and Quirt, 1978), it has been shown that the use of an argon plasma jet, as an alternative to the conventional flame excitation source, can reduce these limitations and expend the capabilities of an atomic absorption instrument at the low cost of approximately $3,500.00.

The objective of this study was to make a comparison between the two methods of analysis in the determination of the following trace elements: Ag, As, B, Be, Cd, Co, Cr, Cu, Fo, Ni, Rb, Se, Sr and Zn. Another purpose was to assess the feasibility of argon plasma emission in the determination of the above elements in rocks and soils.

The statistical parameters used in the comparison include the detection limit, slope of the line, noise levels, drift and repeatability. The working conditions used in determining the slopes are given in the tables listing the experimental data for the calibration curves which are presented in the sections on each element. These working conditions are also the ones used in determining the detection limits, and the values obtained for the average reading, variance and standard deviation, as
well as the concentrations of the solutions run are given in Table 45.

A complete list of the base line noise and signal noise levels for the two methods of analysis is given in Table 46.

Tables 47 and 48 give the concentrations of the solutions run, along with the average readings, variances, standard deviations and relative standard deviations obtained for each element by both the flame and plasma analyses, for the drift and repeatability tests. The working conditions used during the drift and repeatability tests are listed in Table 49.

A general summary of the performance of the two methods of analysis is made in Table 50. This table shows, by the use of an asterisk (*) representing the argon plasma emission technique and a zero (0) for atomic absorption/flame emission methods, which method of analysis is considered superior under the categories given. Where there is no clear advantage by one method over the other, a dash (-) is used. From this table, it is inferred that argon plasma emission is superior for the determination of arsenic, boron, cobalt and chromium; and the conventional flame techniques are considered to be better for the remaining ten elements studied. However,
severe problems, which are spectral and chemical in nature, remain unsolved in the application of this to trace element determinations in complex materials such as rocks and soils. From this study, it is concluded that this method of analysis has significant advantages over conventional flame techniques, although it is limited in its application to trace analyses in geological samples.
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>METHOD</th>
<th>CONC. OF STANDARD (µg/mL)</th>
<th>AVERAGE READING</th>
<th>VARIANCE</th>
<th>STANDARD DEVIATION</th>
<th>DETECTION LIMIT ppm</th>
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</thead>
<tbody>
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<td>1.67</td>
<td>0.0201</td>
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<td>0.0584</td>
<td>0.2416</td>
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<td>AA</td>
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<td>1.15</td>
<td>0.0495</td>
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<td>3.04</td>
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(1) AA = ATOMIC ABSORPTION  
APE = ARGON PLASMA EMISSION  
FE = FLAME EMISSION
Table 46

BASE LINE NOISE AND SIGNAL NOISE
BY ELEMENT AND METHOD

<table>
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<th>ELEMENT</th>
<th>FLAME</th>
<th>PLASMA</th>
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<td>BASE LINE NOISE</td>
<td>SIGNAL NOISE</td>
</tr>
<tr>
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<td>µg/ml</td>
<td>µg/ml</td>
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<tr>
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<td>0.0040</td>
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FE = FLAME EMISSION
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(1) AA = ATOMIC ABSORPTION  
APE = ARGON PLASMA EMISSION  
FL = FLAME EMISSION
### Working Conditions for Stability and Reproducibility Plots

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* Atomic Absorption/Flame Emission

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APPENDIX 1

Start Up and Shut Down Procedure for Plasma Jet

1. Turn on coolant water and exhaust fan.
2. Turn on argon and set flow rates:
3. Extend cathode 10 mm (0.4") beyond ceramic sleeve.
4. Set plasma current to 7.0 A and turn on power source.
5. Push plasma switch.
6. Retract cathode approximately 1/2 (1"")
7. Aspirate distilled water and let run for 5–10 minutes.
8. Aspirate standard solution.
9. Set wavelength.
10. Optimize parameters.
11. Analyse samples.
12. Aspirate distilled water for several minutes.
13. Turn off pump.
15. Allow argon to flow for one minute.
16. Turn off argon and power source.
17. Turn off coolant water and exhaust fan.
APPENDIX II

Start Up and Shut Down Procedure for Atomic Absorption Unit

1. Turn on the instrument.

2. Set lamp at desired current.

3. Allow 10-15 minutes to warm up.

4. Set indicator unit to 'Transmission' mode and select switch to 'normal'.

5. Set monochromator to desired wavelength and slit width to desired opening.

6. Adjust gain to give 0.1 T and adjust 'x' set to give the maximum reading.

7. Select 'Acetylene' with fuel selector.

8. Adjust fuel flow valve to read 3 on the flow gauge.

9. Rotate 'Selector Switch' to 'Cif'.

10. Turn 'Support Selector' to 'N₂O'.

11. Adjust valve to read 10-124 kPa (15-18 psi) on the gauge.

12. Rotate 'Support Selector' to 'Cif'.

13. Turn 'Support Selector' to 'Acetylene'.

14. Wait 5-10 seconds and ignite.

15. Adjust fuel to desired flow rate.

16. Rotate 'Support Selector' to 'N₂O' if an Acetylene-Nitrous Oxide flame is desired.

17. Adjust acetylene flow to give desired flame stoichiometry.

18. Optimize parameters to give 100% T.

19. Select desired mode.
20. Aspirate samples.

21. If using "C₂C", increase acetylene flow to produce a luminous flame and then rapidly rotate 'Support Selector' to 'Air' and leave for 5 seconds.

22. Turn off 'Fuel Selector' and wait for flame to go out.

23. Turn off 'Support Selector'.

24. Turn off instrument.
Wang 2200 Program for Sensitivity and Detection Limit Tables

10 SELECT PRINT 005
20 INPUT "HALT/STEP; INPUT A PRINT STATEMENT No. 610 WITH THE TITLE OF THE TABLE IN QUOTES CENTERED OVER 59 SPACES WHICH START 5 SPACES FROM THE LEFT MARGIN; RUN; INPUT '1'".B
30 DIM A(20),C(20),D(20),E(20),F(20),G(20),H(20)
40 PRINT "IF THE TABLE IS FOR A CALIBRATION GRAPH INPUT '1'"
50 INPUT "IF THE TABLE IS FOR DETERMINING THE DETECTION LIMIT IN "
   "PUT '2'".Z1
60 PRINT "IF THE TABLE IS FOR PLASMA EMISSION INPUT '1'"
70 INPUT "IF THE TABLE IS FOR ATOMIC ABSORPTION INPUT '2'".I
80 INPUT "WAVELENGTH USED =",A1
90 INPUT "GAIN USED =",B1
100 INPUT "SLIT WIDTH USED =",C1
110 IF I=1 THEN 140
120 IF I=2 THEN 160
130 GOTO 60
140 INPUT "PLASMA CURRENT USED =",D1
150 GOTO 270
160 INPUT "LAMP CURRENT USED =",D1
170 PRINT "INPUT THE TYPE OF FLAME USED"
180 PRINT "INPUT '1' FOR OXIDIZING AIR-ACETYLENE"
190 PRINT "INPUT '2' FOR NEUTRAL AIR-ACETYLENE"
200 PRINT "INPUT '3' FOR REDUCING AIR-ACETYLENE"
210 PRINT "INPUT '4' FOR OXIDIZING NITROUS OXIDE-ACETYLENE"
220 PRINT "INPUT '5' FOR NEUTRAL NITROUS OXIDE-ACETYLENE"
230 PRINT "INPUT '6' FOR REDUCING NITROUS OXIDE-ACETYLENE"
240 INPUT "THE TYPE OF FLAME USED WAS",X7
250 PRINT "IF TRANSMISSION MODE WAS USED INPUT '1'"
260 INPUT "IF ABSORPTION MODE WAS USED INPUT '2'".L3
270 INPUT "NUMBER OF READINGS =",K
280 PRINT "STANDARD CONCENTRATIONS"
290 R1=1
300 FOR B=1 TO K
310 INPUT A(B)
320 NEXT B
330 J=0
340 INPUT "ROW TO BE CORRECTED =",J
350 IF J=0 THEN 380
360 GOSUB '1 (R1,A(J))
370 GOTO 340
380 PRINT "ACTUAL READING"
390 R1=2
400 FOR B=1 TO K
410 INPUT C(B)
420 NEXT B
430 J=0
440 INPUT "ROW TO BE CORRECTED =",J
450 IF J=0 THEN 480
460 GOSUB '1 (R1,C(J))
470 GOTO 440
480 PRINT "ZERO READING"
490 R1=3
500 FOR B=1 TO K
510 INPUT D(B)
520 NEXT B
530 J=0
540 INPUT "ROW TO BE CORRECTED =",J
550 IF J=0 THEN 580
560 GOSUB '1 (J,D(J))
570 GOTO 540
580 IF ZI=1 THEN 600
590 INPUT "THE SLOPE IS ",T1
600 SELECT PRINT 211
610 PRINT " EXAMPLE"
620 PRINT
630 PRINT "*****************************************************************************

**********
640 PRINT USING 650,A1,B1
650 % WORKING CONDITIONS; WAVELENGTH #.# nm, GAIN #,
660 IF I=1 THEN 680
670 IF I=2 THEN 710
680 PRINT USING 690,C1,D1
690 % SLIT WIDTH # microns, PLASMA CURRENT # A
700 GOTO 950
710 PRINT USING 720,C1,D1
720 % SLIT WIDTH # # microns, LAMP CURRENT # mA
730 IF X7=1 THEN 790
740 IF X7=2 THEN 810
750 IF X7=3 THEN 830
760 IF X7=4 THEN 850
770 IF X7=5 THEN 870
780 IF X7=6 THEN 890
790 PRINT " OXIDIZING AIR-ACETYLENE FLAME"
800 GOTO 900
810 PRINT " NEUTRAL AIR-ACETYLENE FLAME"
820 GOTO 900
830 PRINT " REDUCING AIR-ACETYLENE FLAME"
840 GOTO 900
850 PRINT " OXIDIZING NITROUS OXIDE-ACETYLENE FLAME"
860 GOTO 900
870 PRINT " NEUTRAL NITROUS OXIDE-ACETYLENE FLAME"
880 GOTO 900
890 PRINT " REDUCING NITROUS OXIDE-ACETYLENE FLAME"
900 IF L3=1 THEN 920
910 IF L3=2 THEN 940
920 PRINT " TRANSMISSION MODE"
930 GOTO 950
940 PRINT "ABSORPTION MODE"
950 PRINT "******************************************************************

***************

960 IF Z1=1 THEN 980
970 IF Z1=2 THEN 1560
980 PRINT "CONC. OF ACTUAL ZERO CORRECTED AVERAGE"
990 PRINT "STANDARD READING READING READING READING"

***************

1000 IF L3=1 THEN 1020
1010 IF L3=2 THEN 1040
1020 PRINT "ppm %T %T %T"
1030 GOTO 1050
1040 PRINT "ppm %ABS %ABS %ABS %ABS"
1050 PRINT "******************************************************************

***************

1060 FOR B=1 TO K
1070 E(B)=C(B)-D(B)
1080 NEXT B
1090 Y=K/2
1100 FOR B=1 TO Y
1110 F(B)=((E(B)+E(B+Y))/2
1120 G(B)=A(B)
1130 NEXT B
1140 Z=Y+4
1150 FOR B=1 TO Z
1160 L=L+G(B)
1170 M=M+F(B)
1180 NEXT B
1190 N=L/Z
1200 P=M/Z
1210 FOR B=1 TO Z
1220 Q=Q+((G(B)-N)*(F(B)-P))
1230 R=R+((G(B)-N)/2)
1240 U=U+((F(B)-P)/2)
1250 NEXT B
1260 S=Q/R
1270 T=P-(S*N)
1280 V=Q/SQR(R*U)
1290 FOR B=1 TO Y
1300 PRINT USING 1310, A(B), C(B), D(B), E(B), F(B)
1310 % ****## ### ##.

***************

1320 NEXT B
1330 Y=Y+1
1350 FOR B=Y TO K
1360 PRINT USING 1320, A(B), C(B), D(B), E(B)
1370 NEXT B
1380 PRINT "*************************************************************"
1390 PRINT USING 1400, S
1400 % THE SLOPE IS ####
1410 PRINT
1420 PRINT USING 1430, T
1430 % THE INTERCEPT IS ####
1440 PRINT
1450 PRINT USING 1460, Y
1460 % THE CORRELATION COEFFICIENT IS ####
1470 PRINT
1480 P1=(I/S)+.00005
1490 PRINT USING 1500, P1
1500 % THE SENSITIVITY IS #### ppm
1510 GOTO 1980
1520 FOR B=1 TO K
1530 E(B)=C(B)-D(B)
1540 W=W+E(B)
1550 V=V+(E(B)^2)
1560 NEXT B
1570 X=W/K
1580 L=(V/K)-(X^2)
1590 M=SQR(L)
1600 N1=2*M/T1
1610 PRINT " CONC. OF ACTUAL ZERO"
1620 PRINT " CORRECTED"
1630 IF L<=1 THEN 1650
1640 IF L=2 THEN 1670
1650 PRINT " STANDARD READING READING"
1660 GOTO 1680
1670 PRINT " ppm %T %T"
1680 PRINT " %ABS %ABS"
1690 FOR B=1 TO K
1700 PRINT USING 1710, A(B), C(B), D(B), E(B)
1710 %       #.# # # # # #
.#
1720 NEXT B
1730 PRINT "#" # # # # # # # # #
1740 PRINT USING 1750,X
1750 %       THE MEAN IS #.####
1760 PRINT
1770 PRINT USING 1780,L
1780 %       THE VARIANCE IS #.####
1790 PRINT
1800 PRINT USING 1810,M
1810 %       THE STANDARD DEVIATION IS #.####
1820 PRINT
1830 PRINT USING 1840,N1
1840 %       THE DETECTION LIMIT IS #.#### ppm
1850 GOTO 1880
1860 DEFFN'1(N,H(N))
1870 PRINT "INCORRECT VALUE =",H(N)
1880 INPUT "CORRECT VALUE =",H(N)
1890 IF R1=1 THEN 1920
1900 IF R1=2 THEN 1940
1910 IF R1=3 THEN 1960
1920 A(J)=H(N)
1930 GOTO 1970
1940 C(J)=H(N)
1950 GOTO 1970
1960 D(J)=H(N)
1970 RETURN
1980 STOP
1990 END
Table 51
Detection Limit Table (Example)

BERYLLIUM BY ARGON PLASMA EMISSION

*WORKING CONDITIONS: WAVELENGTH 234.9 nm, GAIN 7, SLIT WIDTH 25 microns, PLASMA CURRENT 7.0 A*

<table>
<thead>
<tr>
<th>CONC. OF STANDARD (µg/ml)</th>
<th>ACTUAL READING</th>
<th>ZERO READING</th>
<th>CORRECTED READING</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>6.6</td>
<td>0.0</td>
<td>6.6</td>
</tr>
<tr>
<td>0.10</td>
<td>6.8</td>
<td>0.1</td>
<td>6.7</td>
</tr>
<tr>
<td>0.10</td>
<td>6.9</td>
<td>0.2</td>
<td>6.7</td>
</tr>
<tr>
<td>0.10</td>
<td>7.0</td>
<td>0.3</td>
<td>6.7</td>
</tr>
<tr>
<td>0.10</td>
<td>7.1</td>
<td>0.5</td>
<td>6.6</td>
</tr>
<tr>
<td>0.10</td>
<td>7.2</td>
<td>0.5</td>
<td>6.7</td>
</tr>
<tr>
<td>0.10</td>
<td>7.1</td>
<td>0.4</td>
<td>6.7</td>
</tr>
<tr>
<td>0.10</td>
<td>7.0</td>
<td>0.5</td>
<td>6.5</td>
</tr>
<tr>
<td>0.10</td>
<td>7.2</td>
<td>0.6</td>
<td>6.6</td>
</tr>
<tr>
<td>0.10</td>
<td>6.5</td>
<td>0.0</td>
<td>6.5</td>
</tr>
</tbody>
</table>

THE MEAN IS 6.6300

THE VARIANCE IS 0.0061

THE STANDARD DEVIATION IS 0.0781

THE DETECTION LIMIT IS 0.0019 µg/ml
APPENDIX I:  

WANG 2200 Program for F-test and T-test

10 REM ***** T-test AND F-test, KDM, 30/3/78 *****
20 SELECT PRINT 005
30 PRINT HEX(03)
40 INPUT "HALT/STEP; INPUT A PRINT STATEMENT NO. 330 WITH THE TITLE CENTERED OVER 43 SPACES STARTING 5 SPACES FROM THE LEFT, RUN; INPUT '1'",F8
50 DIM B(20),D(20),R(10),W(10),H(10),X(20),Z(20)
60 PRINT HEX(03)
70 INPUT "THE NUMBER OF READINGS BY PLASMA EMISSION IS",E
80 PRINT HEX(03)
90 INPUT "THE NUMBER OF READINGS BY ATOMIC ABSORPTION IS",F
100 E1=E
110 F7=F
120 PRINT HEX(03)
130 PRINT "INPUT THE PLASMA EMISSION READINGS"
140 H1=1
150 FOR G=1 TO E
160 INPUT B(G)
170 NEXT G
180 PRINT "ROW TO BE CORRECTED=",I
190 IF I=0 THEN 220
200 GOSUB '1 (H1,B(I))
210 GOTO 180
220 PRINT "ATOMIC ABSORPTION READINGS"
230 H1=2
240 FOR G=1 TO F
250 INPUT D(G)
260 NEXT G
270 PRINT "ROW TO BE CORRECTED=",I
280 IF I=0 THEN 310
290 GOSUB '1 (H1,D(I))
300 GOTO 270
310 SELECT PRINT 211
320 PRINT "F-test AND T-test"
330 PRINT 
340 PRINT "ELEMENT" BY "METHOD"
350 PRINT "***********************************************************
360 PRINT "PLASMA FLAME"
370 PRINT "***********************************************************
380 PRINT "CONC. CONC." 
390 PRINT "ppm ppm"
400 PRINT "***********************************************************
410 IF E1>F7 THEN 540
420 R7=F7
430 FOR G=1 TO R7
440 PRINT USING 450,B(G),D(G)
450 % #.##
460 NEXT G
470 IF E1=F7 THEN 630
480 R7=R7+1
490 FOR G=R7 TO E1
500 PRINT USING 510,B(G)
510 *** ***
520 NEXT G
530 GOTO 630
540 R7=E1
550 FOR G=1 TO R7
560 PRINT USING .450,B(G),D(G)
570 NEXT G
580 R7=R7+1
590 FOR G=R7 TO F7
600 PRINT USING 610,D(G)
610 *** ***
620 NEXT G
630 PRINT "..............................
640 S=0
650 J=0
660 K=0
670 Y=0
680 FOR G=1 TO E
690 IF B(G)=9999 THEN 740
700 Y=Y+1
710 X(Y)=B(G)
720 J=J+X(Y)
730 K=K+(X(Y)*2)
740 NEXT G
750 M1=J/Y
760 S1=SQR((K/Y)-(M1^2))
770 Q1=Y-0.85
780 T4=1.96-.00554568/SQR(Q1)+2.4059333/Q1+.671777/(Q1^2)-.38312
14/(Q1^3)
790 Q6=0
800 FOR G=1 TO E
810 IF B(G)=9999 THEN 890
820 IF B(G)=M1 THEN 850
830 Q5=B(G)-M1
840 GOTO 860
850 Q5=M1-B(G)
860 IF Q5=Q6 THEN 890
870 Q6=Q5
880 T9=G
890 NEXT G
900 N=0
910 FOR G=1 TO E
920 IF B(G)!18(T9) THEN 940
930 N=N+1
940 NEXT G
950 P=M1-B(T9)
960 IF P<10 THEN 980
970 P=P*(-1)
980 T1=(P*SQR(N))/S1
990 IF T1<T4 THEN 1010
1000 GOTO 1070
1010 S=S+1
1020 R(S)=B(T9)
1030 B(T9)=9999
1040 Y=0
1050 GOTO 650
1060 Y1=0
1070 K=0
1080 J=0
1090 FOR G=1 TO F
1100 IF D(G)=9999 THEN 1150
1110 Y1=Y1+1
1120 Z(Y1)=D(G)
1130 J=J+Z(Y1)
1140 K=K+(Z(Y1))^2
1150 NEXT G
1160 M2=J/Y1
1170 S2=SQR((K/Y1)-(M2^2))
1180 Q2=Y1-0.85
1190 T5=1.96-.00554568/SQR(Q2)+2.40593333/Q2+.671777/(Q2^2)-.3831
214/(Q2^3)
1200 Q8=0
1210 FOR G=1 TO F
1220 IF D(G)=9999 THEN 1300
1230 IF D(G)!M2 THEN 1260
1240 Q7=D(G)-M2
1250 GOTO 1270
1260 Q7=M2-D(G)
1270 IF Q7!Q3 THEN 1300
1280 Q8=Q7
1290 T8=G
1300 NEXT G
1310 N=0
1320 FOR G=1 TO F
1330 IF D(G)!1D(T8) THEN 1350
1340 N=N+1
1350 NEXT G
1360 P=M2-D(T8)
1370 IF P<10 THEN 1390
1380 P=P*(-1)
1390 T2=(P*SQR(N))/S2
1400 IF T2>75 THEN 1420
1410 GOTO 1470
1420 L1=L1+1
1430 W[L1]=D(T8)
1440 D(T8)=9999
1450 Y1=0
1460 GOTO 1070
1470 FOR S=1 TO 10
1480 IF R(1)=0 THEN 1550
1490 IF R(S)=0 THEN 1540
1500 P7=1
1510 PRINT USING 1520,R(S)
1520 /* REJECTED VALUE FOR PLASMA EMISSION IS ##.##
1530 NEXT S
1540 IF P7>10 THEN 1570
1550 PRINT "NONE OF THE PLASMA EMISSION VALUES ARE REJECTED"
1560 P7=0
1570 FOR L1=1 TO 10
1580 IF W(1)=0 THEN 1650
1590 IF W(L1)=0 THEN 1640
1600 P7=1
1610 PRINT USING 1620,W(L1)
1620 /* REJECTED VALUE FOR ATOMIC ABSORPTION IS ##.##
1630 NEXT L1
1640 IF P7>10 THEN 1680
1650 PRINT "NONE OF THE ATOMIC ABSORPTION VALUES ARE REJECTED"
1660 G6=(S1/M1)*100
1670 G7=(S2/M2)*100
1680 PRINT HEX(0AOA)
1690 PRINT USING 1700,M1,M2
1700 /* MEAN ##.##
1710 PRINT USING 1720,S1,S2
1720 /* STANDARD DEVIATION ##.##
1730 PRINT USING 1740,G6,G7
1740 /* RELATIVE STD. DEV. ##.##
1750 PRINT HEX(0AOA)
1760 IF (S2/S2)**2*(S1/S2) THEN 1790
1770 F1=(S1/S2)/(S2/S2)
1780 GOTO 1850
1790 F1=(S2/S2)/(S1/S2)
1800 L=(S1/S2)/(Y-1)
1810 R=(S2/S2)/(Y1-1)
1820 K=(((S1/S2)+(S2/S2))/2)/(L+R)
1830 \( w = k - 0.85 \)
1840 \( T = 1.96 - 0.00554568 / \text{SQR}(w) + 2.4059333 / w + 0.671777 / (w^2) - 0.3831214 \)
1850 \( Y_1 = Y_1 - 1 \)
1860 \( Y = Y - 1 \)
1870 IF \( (S_2^2)^2 < (S_1^2)^2 \) THEN 1900
1880 PRINT USING 1910, F1, Y1, Y
1890 GOTO 1920
1900 PRINT USING 1910, F1, Y, Y1
1910 " F-cal = ###.## WITH ## AND ## DEGREES OF FREEDOM
1920 INPUT "F-table = ", F7
1930 IF (S2^2)!<(S1^2) THEN 1960
1940 PRINT USING 1970, F7, Y1, Y
1950 GOTO 1980
1960 PRINT USING 1970, F7, Y, Y1
1970 IF F1!=F7 THEN 1990
1980 " THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL"
1990 GOTO 2020
2000 PRINT " THE DIFFERENCE BETWEEN THE VARIANCES IS NOT SIGNIFICANT AT THE 5% LEVEL"
2010 PRINT HEX(0AOA)
2020 PRINT USING 2040, T1, K
2030 PRINT USING 2050, T7, K
2040 " T-cal = ###.### WITH ## DEGREES OF FREEDOM
2050 PRINT USING 2060, T7, K
2060 " T-table = ###.### FOR ## DEGREES OF FREEDOM
2070 IF T1=T7 THEN 2100
2080 PRINT " THE DIFFERENCE BETWEEN THE MEANS IS NOT SIGNIFICANT AT THE 5% LEVEL"
2090 GOTO 2200
2100 PRINT " THE DIFFERENCE BETWEEN THE MEANS IS SIGNIFICANT AT THE 5% LEVEL"
2110 GOTO 2200
2120 DEFN '1' '(N,H(N))
2130 PRINT "INCORRECT VALUE =", H(N)
2140 INPUT "CORRECT VALUE =", H(N)
2150 IF N=1 THEN 2180
2160 D(I)=H(N)
2170 GOTO 2190
2180 B(I)=H(N)
2190 RETURN
2200 STOP
2210 END
Table 52
Output for F-test and T-test Program (Example)

F-test AND T-test
STABILITY OF BORON

<table>
<thead>
<tr>
<th>FLAME</th>
<th>PLASMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>READING</td>
<td>READING</td>
</tr>
<tr>
<td>20.60</td>
<td>23.00</td>
</tr>
<tr>
<td>20.50</td>
<td>23.10</td>
</tr>
<tr>
<td>20.90</td>
<td>23.00</td>
</tr>
<tr>
<td>20.90</td>
<td>23.00</td>
</tr>
<tr>
<td>20.70</td>
<td>23.00</td>
</tr>
<tr>
<td>20.90</td>
<td>22.80</td>
</tr>
<tr>
<td>20.70</td>
<td>22.80</td>
</tr>
<tr>
<td>20.60</td>
<td>22.50</td>
</tr>
<tr>
<td>20.70</td>
<td>22.40</td>
</tr>
<tr>
<td>20.80</td>
<td>22.50</td>
</tr>
</tbody>
</table>

NONE OF THE ATOMIC ABSORPTION VALUES ARE REJECTED
NONE OF THE PLASMA EMISSION VALUES ARE REJECTED

<table>
<thead>
<tr>
<th>20.73</th>
<th>MEAN</th>
<th>22.81</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>STANDARD DEVIATION</td>
<td>0.24</td>
</tr>
<tr>
<td>0.64</td>
<td>RELATIVE STD. DEV.</td>
<td>1.06</td>
</tr>
</tbody>
</table>

F-calc = 3.25 WITH 9 AND 9-DEGREES OF FREEDOM
F-table = 3.18 FOR 9 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT
AT THE 5% LEVEL

T-calc = 1.709 WITH 14 DEGREES OF FREEDOM
T-table = 2.144 FOR 14 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS IS NOT SIGNIFICANT
AT THE 5% LEVEL
APPENDIX V

Lang 2200 Program for Rejection Test

10 REM ***** REJECTION TEST, KDM, 29/3/78 *****
20 SELECT PRINT 005
30 DIM B(60),R(20),X(60)
40 PRINT HEX(03)
50 INPUT "IF ONLY THE RESULTS ARE REQUIRED, AND NOT THE TABLE, I";
51 INPUT 'I"","Z6"
60 IF Z6=1 THEN 120
70 PRINT HEX(03)
80 PRINT "HALT/STEP; INPUT A PRINT STATEMENT No. 220 WITH THE TI"
81 PRINT "TLE CENTERED OVER 31 SPACES STARTING 5 SPACES FROM THE LEF"
82 PRINT "; RUN; INPUT 'I"","P8"
90 PRINT HEX(03)
100 INPUT "INPUT THE NUMBER OF VALUES";E
110 PRINT HEX(03)
120 PRINT "INPUT THE VALUES"
130 FOR G=1 TO E
140 INPUT B(G)
150 NEXT G
160 INPUT " INPUT THE INCORRECT VALUE";I
170 IF I=0 THEN 200
180 GOSUB '1(I,E)
190 GOTO 160
200 IF Z6=1 THEN 330
201 SELECT PRINT 211
210 PRINT " REJECTION TEST"
220 PRINT " EXAMPLE"
230 PRINT "***************
240 PRINT " CONC."
250 PRINT " ppm"
260 PRINT "***************
270 PRINT " FOR G=1 TO E
280 PRINT USING 300,B(G)
290 PRINT USING 300,"##.##
300 NEXT G
310 PRINT "***************
320 PRINT " S=G
330 PRINT " J=G
340 PRINT " K=G
350 PRINT " Y=G
360 PRINT " FOR G=1 TO E
370 PRINT " IF B(G)=9999 THEN 430
380 Y=Y+1
390 PRINT " X(Y)=B(G)
400 PRINT " J=J+X(Y)
410 PRINT " K=K+(X(Y)^2)
420 NEXT G
440 M1=J/Y
450 S1=SQR((K/Y)-(M1^2))
460 Q1=Y-0.95
470 T4=1.96-.00554568/SQR(Q1)+2.4059333/Q1+.671777/(Q1^2)-.38312
14/(Q1^2)
480 Q6=0
490 FOR G=1 TO E
500 IF B(G)=9999 THEN 580
510 IF B(G)*M1 THEN 540
520 Q5=B(G)-M1
530 GOTO 550
540 Q5=M1-B(G)
550 IF Q5*Q6 THEN 580
560 Q6=Q5
570 T9=G
580 NEXT G
590 N=0
600 FOR G=1 TO E
610 IF B(G)*I1B(T9) THEN 630
620 N=N+1
630 NEXT G
640 P=M1-B(T9)
650 IF P10 THEN 670
660 P=P*(-1)
670 T1=(P*SQR(N))/S1
680 IF T1*T4 THEN 700
690 GOTO 750
700 S=S+1
710 R(S)=B(T9)
720 B(T9)=9999.
730 Y=0
740 GOTO 340
750 P7=0
760 PRINT " REJECTED VALUE(S)"
770 FOR S=1 TO 15
780 IF R(S)=0 THEN 820
790 P7=1
800 PRINT USING 300,R(S)
810 NEXT S
820 IF P7=1 THEN 840
830 PRINT " NONE OF THE VALUES ARE REJECTED"
840 PRINT HEX(DAA)
850 PRINT USING 860,M1,S1
860 " THE MEAN IS #.###
870 " THE STANDARD DEVIATION IS #.##
880 GOTO 970
380 DEFFN '1(H,E4)
890 PRINT "INCORRECT VALUE IS",H
900 INPUT "CORRECT VALUE IS",H1
910 FOR G=1 TO 4
920 IF B(G)=H THEN 950
930 NEXT G
940 GOTO 960
950 B(G)=H1
960 RETURN
970 STOP
980 END
APPENDIX VI.

Wang 2200 Plotter Program

10 REM ***** PLOTTER II, KUM, 6/4/78 *****
20 DIM C(30), D(30), XS20, YS20, TS32
30 SELECT PRINT 413
40 X, Y=200
50 REM ***** DRAW BORDER *****
60 PLOT 6!X,,D1,!(X/2),,D1,4!,Y,D1,!,!(Y/2),,D1
70 PLOT !(X/2),,D1,6!-X,,D1,!,-(Y/2),,D1,4!,-Y,D1,!,!,R1
80 SELECT PRINT 005
90 PRINT HEX(03)
100 REM ***** INPUT LABELS *****
110 INPUT "INPUT THE TITLE",TS
120 INPUT "X-AXIS LABEL",XS
130 INPUT "Y-AXIS LABEL",YS
140 C=2
150 S=13*C
160 X2=(6*X-LEN(XS)*42)/2
170 Y2=(4*Y-(LEN(YS)*42))/2
180 SELECT PRINT 413
190 PLOT !C,,C1,!,S,,S1
200 PLOT !,-5*S,U1,!,X2,,U1
210 PRINT XS
220 PLOT !,!,R1
230 STOP "CHANGE AXIS ORIENTATION"
240 PLOT !C,,C1,!,S,,S1
250 PLOT !Y2,,U1,!,10*S,U1
260 PRINT YS
270 PLOT !,!,R1
280 STOP "CHANGE AXIS ORIENTATION TO NORMAL"
290 REM ***** INPUT DATA *****
300 SELECT PRINT 005
310 PRINT HEX(03)
320 INPUT "INPUT THE NUMBER OF DATA POINTS",A
330 PRINT "INPUT THE DATA POINTS"
340 FOR G=1 TO A
350 INPUT C(G), D(G)
360 NEXT G
370 INPUT "INPUT THE MAXIMUM LIMIT OF THE X-AXIS",E
380 INPUT "INPUT THE MAXIMUM LIMIT OF THE Y-AXIS",F
390 REM ***** CALCULATE SLOPE *****
400 L,H,I,V=0
410 FOR G=1 TO A
420 L=L+C(G)
430 !="M+D(G)
440 NEXT G
450 N=L/A
V=\frac{1}{A} \\
\text{FOR } G=1 \text{ TO } A \\
Q=Q+((C(G)-N)\times(U(G)-V)) \\
R=R+((C(G)-N)^2) \\
\text{NEXT } G \\
J=J/R \\
\text{REM ***** PLOT DIVISIONS ON AXIS *****} \\
I1=(6*X/10) \\
I2=(4*Y/10) \\
\text{SELECT PRINT 413} \\
\text{FOR } G=1 \text{ TO } 10 \\
PLOT !1,,C1,!,0,,S1 \\
PLOT !1,,U1,!,,"+"1 \\
\text{NEXT } G \\
PLOT !,,R1 \\
\text{FOR } G=1 \text{ TO } 10 \\
PLOT !1,I2,U1,!,1,,C1,!,0,,S1,!,,"+"1 \\
\text{NEXT } G \\
PLOT !,,R1 \\
I1=(6*X/5) \\
I2=(4*Y/5) \\
\text{SELECT PRINT 305} \\
\text{PRINT Hex(03)} \\
\text{SELECT PRINT 413} \\
\text{REM ***** NUMBER X-AXIS DIVISIONS *****} \\
\text{FOR } G=1 \text{ TO } 5 \\
PLOT !,,-50,U1 \\
E1=G*((E/5))+0.005 \\
I1=5*X/5 \\
PLOT !1,,C1,!,13,,S1 \\
PLOT G!1,,U1,!,-(4*5),,U1 \\
\text{PRINT USING 780,E1} \\
\text{###} \\
PLOT !,,R1 \\
\text{NEXT } G \\
\text{REM ***** LABEL THE Y-AXIS DIVISIONS *****} \\
\text{FOR } G=1 \text{ TO } 5 \\
PLOT !-200,,U1,!,-10,(4*Y/5)*G,,U1 \\
PLOT !1,,C1,!,13,,S1 \\
F1=G*((F/5))+0.005 \\
\text{PRINT USING 780,F1} \\
PLOT !,,R1 \\
\text{NEXT } G \\
\text{REM ***** PLOT POINTS *****} \\
\text{SELECT PRINT 413}
910 FOR G=1 TO A
920 T=((C(G)*5*X)/E)/3
930 P=((D(G)*4*Y)/F)/3
940 PLOT 3!T,P,U1,!1,,C1,!0,,S1,,,"x"1.
950 PLOT !,,R1
960 NEXT G
970 H=(((F/J)*X*5/E)/3
980 F=4*Y/3
990 PLOT 3!H,F,D1
1000 PLOT !,,R1
1010 REM ***** TITLE *****
1020 PLOT 4!,Y,U1,,!210,U1,,!-275,,U1
1030 SELECT PRINT 005
1040 SELECT PRINT 413
1050 PLOT !2,,C1,!25,,S1
1060 R=((G*X)-LEN(TS)*50)/2
1070 PLOT !R,,U1
1080 PRINT TS
1090 STOP
1100 END
APPENDIX VII

STANDARD ADDITION TECHNIQUE

Single Addition Method

To one of two aliquots of sample solution add an aliquot of a standard such that the analyte concentration is approximately 10-50% higher. To the other aliquot add an equal volume of blank (triple distilled water). Analyze both solutions.

The concentration is calculated from the following equation:

\[ \frac{Cs}{Cs + a} = \frac{As}{Aa} \]

where:  
Cs = weight of element in sample aliquot.  
As = %ABS. or %T of aliquot having only a blank addition.  
a = weight of added element.  
Aa = %ABS. or %T of sample aliquot having the addition a.

(Varian Techtron, 1974)
REFERENCES


REFERENCES (Cont'd)


REFERENCES (Cont'd)


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