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A comparative study of major element rock analyses by argon plasma emission and atomic absorption/emission spectrophotometry.

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UNIVERSITY OF WINDSOR

A COMPARATIVE STUDY OF MAJOR ELEMENT ROCK ANALYSES BY ARGON PLASMA EMISSION AND ATOMIC ABSORPTION/EMISSION SPECTROPHOTOMETRY

By

David Hulse Quirt

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 APPLIED SCIENCE AT
THE UNIVERSITY OF WINDSOR

Windsor, Ontario, Canada

1978

ABSTRACT

A Varian Techron AA-5 atomic absorption unit has been modified for use as an argon plasma emission spectrometer, using a Spectrametrics Inc., SpectraJet II argon plasma arc as the excitation source. This is a simple and reversible modification which extends the capabilities of the atomic absorption instrument. Advantages of this modification include relatively low cost and the ease of analysis for several elements (e.g., Si, Ti and P) that are difficult or impossible to analyse by conventional flame techniques.

A comparison of sensitivity, detection limit, reproducibility and stability for the two methods has been done for the major elements normally determined in rock analysis - Si, Al, Fe, Mn, Ti, Mg, Ca, Na, K and P. The accuracy and precision of the methods for those determinations was verified by analysing various international geochemical standard rocks and an in-house standard rock.

The plasma excitation source showed excellent response for titanium and phosphorus, elements difficult and impossible, respectively, to determine by atomic absorption. This source also gave results as good as or better than did the flame source for silicon, iron and calcium. The other elements studied , manganese, sodium,

potassium, magnesium and aluminum proved to be either more easily, more accurately or more precisely analysed by flame techniques rather than by the plasma emission technique.

It has been shown that the use of an argon plasma jet excitation source as an alternative to the conventional burner assembly on an atomic absorption instrument can improve the precision, accuracy, stability, reproducibility, sensitivity or detection limits for several major elements over that possible by conventional flame methods.

In addition it has been shown that the use of the single solution dissolution with the plasma emission excitation source gives slightly better results than when using the standard multiple solution dissolutions.

ACKNOWLEDGEMENTS

I thank Dr. Andrew Turek for the topic suggestion and I gratefully acknowledge the advice given by him during this study. Thanks are also offered to Dr. Peter Hudec for the use of the Wang mini-computer, without which this study would have taken much longer. The critical assistance, through numerous discussions, of Mr. Daniel Mitchell and Mr. Frank Talerico was very necessary to the completion of this study and was much appreciated. This study has been made possible by an operating grant No. 6055 from Agriculture Canada to Dr. A. Turek.

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INTRODUCTION

Argon Plasma Emission Spectrophotometry has been used in chemical analysis before, however, present instrumentation is expensive ranging from \$28,000.00[1] to \$99,000.00[2] for multi-element instruments.

The cost of adapting a Spectrometrics Model 53000 Spectra Jet II argon plasma jet to a Varian Techron AA-5 spectrophotometer is approximately \$3,500.00. This adaptation allows only single element analyses but it does expand the usefulness of a conventional atomic absorption unit.

The plasma jet can be used in the determination of many elements that are technically difficult or impossible to measure by conventional atomic absorption. An example of the former is silicon, combining with the acetylene in the flame to form a silicon carbide causing partial burner block- and signal loss. An example of the latter is phosphorus which cannot be measured directly by atomic absorption as it exists in aqueous solution as an anion.

An improvement in signal strength when using a plasma excitation source is due to the high temperature of the plasma (10,000°K) causing all chemical bonds to be broken.

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[1] Spectrametrics Inc., 20 elements simultaneously.

[2] Applied Research Laboratories Ltd., 60 elements simultaneously.

Chemical interferences are not significant due to the abundance of accessible energy from the plasma (Spectrametrics Inc., 1975). Both incomplete molecular dissociation, high chemical interferences and matrix effects are common problems with conventional atomic absorption spectrometers.

Optimal plasma parameters are virtually the same for all the 10 elements investigated in this study. This is a distinct advantage over atomic absorption where operating parameters change for every element.

Another advantage of the plasma jet is that both gaseous and solid as well as aqueous samples can be analysed while atomic absorption units can only run aqueous samples. In this study only aqueous samples were run, gaseous and solid samples have not been investigated.

The use of argon as the support gas decreases the chance of oxidation of the sample elements and is both non-toxic and non-explosive as opposed to acetylene, hydrogen, propane, oxygen, nitrous oxide and entrailed gases, that are required when using conventional burners. The low flow rate of 5 liters of argon per minute and the low cost of welders grade argon, which is all that is required, also means reduced operating costs.

This thesis assesses the usefulness of an argon plasma jet as an alternate excitation source to the conventional burner and lamp assembly of atomic absorption units in major element analyses. A typical major element rock analysis usually determines 13 components - SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, TiO_2, MgO, CaO, K_2O, Na_2O, P_2O_5, H_2O, and CO_2. This study determines 10 of these constituents in the sample solutions. The constituents not being determined in this study - FeO, H_2O, and CO_2, are not determined by spectrophotometric methods. Several parameters were experimentally compared. These include elemental detection limits and sensitivity of the two methods and the reproducibility, stability and precision of the analyses using an argon plasma jet and a conventional atomic absorption burner/lamp assembly.

Several geochemical rock standards were analysed to determine the accuracy of the methods.

This was done by comparing the experimentally obtained mean values for each standard with their respective literature values.

The versatility of the argon plasma jet was tested by the determination of optimum working ranges and optimum instrument settings for the various major elements under consideration: Si, Al, Fe, Mn, Ca, K, Na, Ti and P.

THEORETICAL CONSIDERATIONS

ATOMIC ABSORPTION SPECTROSCOPY

In the technique of Atomic Absorption Spectrophotometry the absorption of a specific wavelength of light by the sample is measured. The production of atoms from a molecule requires the absorption of energy, usually supplied in the form of heat. Compounds, when vaporized by heating in a flame, are partially or totally dissociated into their elemental constituents in the gaseous form. Some of these atoms are further excited to a state from which they can emit radiation on returning to the unexcited state. The relation between the number of atoms, N_j, in an excited state and the number, N_o, in the ground state is given by the Boltzmann relationship (Price, 1969):

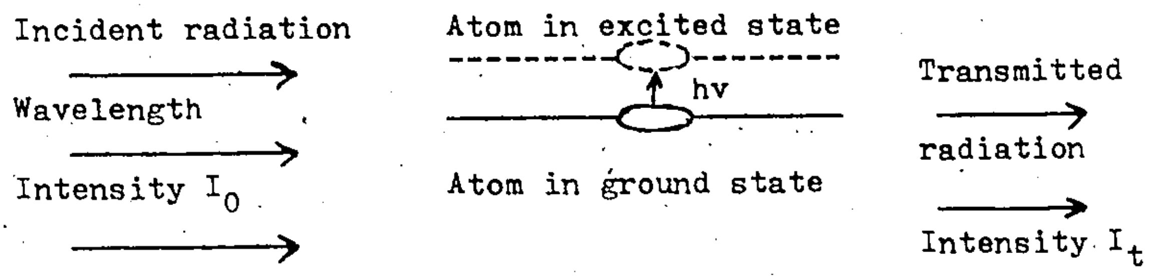
$$\frac{N_j}{N_o} = \frac{P_j}{P_o}\exp\left(\frac{-E_j}{kT}\right)$$

where: P_j and P_o are statistical weights of the two states
E_j is the energy difference between the two states
k is the Boltzman constant
T is the absolute temperature

The higher the value of E_j or the shorter the wavelength of the spectral line corresponding to the transition between the ground and the excited state, the smaller will be the fraction of atoms in the excited state.

Only a small fraction of the atoms are raised above the ground state at the temperatures attainable with conventional flames. If the absorption of light energy by the atoms in the highly populated ground-state is measured, the order of instrumental sensitivity for both difficult to excite atoms like zinc and easily excited atoms like cesium can be comparable.

Atoms in the ground state can only absorb radiation at wavelengths corresponding to their resonance lines. A line spectrum is produced by raising an electron from a lower excitation state, E_1, to a higher state, E_2 (Fig. 1). The first resonance line (wavelength line produced from atomic excitation from ground state to the first excited state) is usually used in atomic absorption as it is usually the most sensitive line. By using a source that emits a narrow wavelength of radiation (hollow cathode lamp) at the appropriate wavelength, the radiation can be directed through the atomic vapor and onto the entrance slit of the monochromator which only has to separate the desired line from any others emitted by the flame. The absorption at the peak of the line is proportional to the concentration of atoms of that element in the vapor.



Absorption of Energy by Atom

FIGURE 1

The intensity of the transmitted radiation is governed by Beer's Law (Price, 1969):

$$I_t = I_o \exp(-abc)$$

where:
- I_o is intensity of incident radiation
- I_t is intensity of transmitted radiation
- a is absorption coefficient at wavelength used
- b is concentration of absorbing atoms
- c is length of the absorption path

This shows that the absorbance is proportional to the concentration for any given absorption path length at any given wavelength In practice, since the relationship between absorbance and concentration is linear, it is not necessary to determine values for the constant 'a' and the path length 'c'.

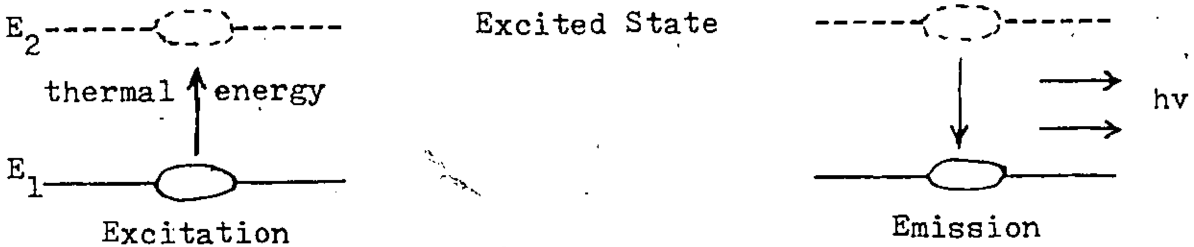
The degree of absorption is related to concentration by the use of calibrating standards. The decrease in intensity, at the resonance line produced by the absorption of the sample, is compared to the absorption produced by a standard of known concentration.

EMISSION SPECTROSCOPY

In emission spectroscopy use is made of lines produced in almost any transition; as compared to atomic absorption which is usually only concerned with lines which involve the ground state atoms.

The emission of a spectrum line is the reverse of absorption of a spectrum line as it is produced by an atom lowering an electron from a higher excitation state, E_2, to a lower state, E_1, (Fig.2) emitting characteristic radiation in the process. Its frequency (v), and therefore its wavelength is directly related to the energy difference between the two excitation states:

$$\Delta E = E_2 - E_1 = hv$$



Emission of Energy by Atom
FIGURE 2

As there are a limited number of such levels, there are a limited number of combinations, therefore a limited number of spectral lines that can be produced.

Flame emission uses sample atoms which are excited in the flame, due to thermal energy, to emit light of the characteristic wavelength. The intensity of the emitted light (transmittance) is then related to the concentration through linear calibration curves. Transmittance is logarithmically related to absorbance.

This technique has two fundamental disadvantages (Varian Techron, 1972 and Ewing, 1969):

(1) Low population of excited atoms, typically less than 1% of the total atom population, are excited at normal flame temperatures.

(2) Spectral interferences caused by the presence of other species emitting in the same spectral region as the element of interest.

The first disadvantage can be corrected by using a flame with a higher energy content, such as a nitrous oxide-acetylene flame, to excite a larger number of atoms. The second disadvantage still remains as this flame still has regions of intense band emission caused by CN^- and OH^- radicals. Spectral interference from emission from other atomic species within the sample can be reduced by isolating the required wavelength. This is done by using a narrow spectral band slit width in the monochromator .

Argon plasma emission operates identically to flame emission, the difference being the source of the thermal energy. Instead of a flame, an argon plasma is used to excite the sample atoms. This gives a temperature of at least twice that of a flame, allowing a much greater number of atoms to become excited and a proportional increase in the amount of emitted radiation. The use of a plasma also eliminates the band emission due to the CN^- radical. Extensive search of tables of spectral lines has been made to locate spectral lines for the analyte elements that are free from spectral interference or to identify any interfering species for interference tests on the spectrophotometer (see Harrison, 1956 and Meggens et al, 1961).

A plasma is generated by imparting enough energy to a gas to cause at least partial ionization. This starts when electrons are accelerated between two electrodes in a gaseous environment, in this case argon. The electrons accelerate toward the anode, colliding with and exciting the atoms in the gas. This excitation can cause complete ionization, electron orbital displacement or increased kinetic energy. The additional electrons freed by this ionization are also accelerated toward the anode, in turn causing more collisions and further ionization. Collisions between electrons and the larger particles become more frequent, transferring the kinetic energy of the electrons to the particles, raising the temperature of the gas. The temperatures within the plasma can vary from 7,000^{o}K to 10,000^{o}K (Gerdeman and Hecht, 1972), and in the excitation region of the D.C. plasma the temperature can reach 8,000^{o}K (Corcoran and Elliot, 1972).

The energy from the plasma is transmitted to the particles in the aspirated sample by means of the energy release from the metastable argon. A characteristic of the inert gases, which include argon, is that when excited, the electrons move into a metastable state. Once in this state they cannot return directly to the ground state. The excited atom must transfer its excess energy to another particle by collision in order to return to the ground state, thus exciting the aspirated element.

INTERFERENCES

Atomic absorption measurements can be subject to the following interferences (Varian Techron, 1972):

(1) Matrix effects influencing the amount of sample reaching the flame.

(2) Chemical interferences affecting the number of atoms formed in the flame.

(3) Non-atomic absorption by undissociated molecules in the flame.

Matrix effects can take one or both of two forms:

(1) Precipitation of the element of interest, such as hydrolysis of silicon and the formation of insoluble chlorides and sulfates.

(2) Differences in the amount of sample aspirated by the nebulizer and in the amount reaching the flame.

The latter effect can be due to variations in viscosity, surface tension, density and vapor pressure between the sample solution and the standard solutions. This effect was not a factor in this study. Matrix effects influence the results obtained by atomic absorption to some extent, however the abundance of accessible energy in the plasma reduces this problem in plasma emission by dissociating the insoluble compounds.

Chemical interferences are caused by two factors:

(1) Incomplete dissociation of compounds, and;

(2) Ionization.

Incomplete dissociation of compounds is usually due to the formation of refractory compounds in the flame, such as calcium phosphate and potassium fluorotantalate (Varian Techron, 1972). These are not completely dissociated at flame temperatures, and therefore inhibit the formation of neutral ground state atoms. The use of the nitrous oxide-acetylene flame can usually supply enough thermal energy to cause complete dissociation; however this extra temperature and energy can cause additional problems such as increased ionization.

Ionization in high temperature flames is usually confined to elements such as potassium, sodium, aluminum and magnesium, which have low ionization potentials. The degree of ionization is reduced when a more concentrated solution is used or when the excitation is done at very high temperatures as is possible using the argon plasma jet.

Ionization becomes important, and a significant concentration of free electrons is present, when the temperature of the flame or plasma is increased. Examples are potassium and sodium where the degree of ionization increases from 0.003 and 0.0003 respectively at 2000°K to 0.66 and 0.26 at 3500°K to 0.99 and 0.98 at 5000°K (ionization in fraction of atoms).

The presence of ionization affects the intensity of the atomic emission lines as the increased temperature causes an increase in the number of excited atoms but, as a result of ionization, there is a decrease in the concentration of neutral atoms. This can cause a decrease in emission intensity at high temperatures.

The degree of ionization of a metal will be strongly influenced by the presence of other ionizable metals in ~~the~~ excitation source. The degree of ionization of a given metal will be decreased by the mass-action effect of the electrons. This effect is useful in suppressing the ionization of potassium, sodium, magnesium and aluminum by the addition of an excess of lanthanium or cesium, which are very easily ionized elements to increase the number of free electrons present. The mass-action effect of electrons produced from the ionization of lanthanium or cesium represses the formation of potassium/sodium/magnesium and aluminum ions.

When the degree of ionization of a sample element is high, resonance lines of the singly charged ion species are used instead of neutral atom resonance lines.

Non-atomic absorption can be caused by the presence of molecules in the optical path. Each molecule absorbs a characteristic band of radiation. Interference will occur when this band coincides with the atomic absorption line under observation. It will decrease as the molecular concentration is reduced. One means of achieving this decrease is to use a high temperature flame to improve the degree of molecular dissociation.

In argon plasma emission the only interferences of note are the spectral interferences. Spectral interference refers to the situation where an interfering line lies close to the resonance line and is not resolved by the monochromator. These are reduced by narrowing the bandwidth allowed to enter the monchromator and by choosing wavelengths that are as free as possible from such interference.

INSTRUMENTATION

VARIAN TECHRON AA-5 ATOMIC ABSORPTION SPECTROPHOTOMETER

The AA-5 unit is a conventional atomic absorption spectrophotometer consisting of four basic components:

(1) A line source emitter (hollow cathode lamp) that produces a sharp line spectrum of the element in question.

(2) An excitation source used to produce an atomic vapor of the sample.

(3) A monochromator or wavelength selector which is used to isolate the spectral resonance line required.

(4) A detector/amplifier/readout system consisting of a photomultiplier connected to a readout panel.

The line source emitter consists of a lamp current supply (Varian type MLS-5) modulated at 285 Hz that supplies a current, variable from 0 mA to 30 mA, to the hollow cathode lamp turret assembly. The turret assembly contains four lamp quadrants and a lens. The lens focuses the light spectrum emitted through the excitation source via the flame region to a second lens which focuses the transmitted light onto the entrance slit of the monochromator

The monochromator serves to isolate a narrow spectral region from the spectrum emitted by the light source. The monochromator used in this study (Varian type AA-5 Si-Ro-Spec Grating Monochromator) is of the Ebert type using a 50 x 50 mm plane grating ruled with 638 lines per millimeter giving a linear dispersion at the exit slit of 3.3 nm/mm in the first order. The focal length of the unit is 50 cm and the wavelength range of the unit is from 0.0 nm to 1015.0 nm. There is however a mechanical limiter which prevents operation of the unit at wavelengths below 186.0 nm.

The width of the wavelength band isolated by the monochromator is determined by the width of the entrance and exit slits, which are continuously variable and are adjusted simultaneously by a single drum control. They open from zero to a maximum width of 300 microns giving a maximum spectral band width of 0.99 nm.

The sample to be analysed is vaporized in the excitation source and the radiation transmitted is focused onto the entrance slit of the monochromator . The wavelength of the most suitable line emitted by the element to be determined is selected and the intensity of the transmitted light is measured. The intensity will be a linear function of the concentration of the element in the sample.

The photomultiplier is a HTV type R213 (Hamamatsu T.V. Co. Ltd.) unit which is recommended for use in the region between 300 nm and 780 nm. This range covers all

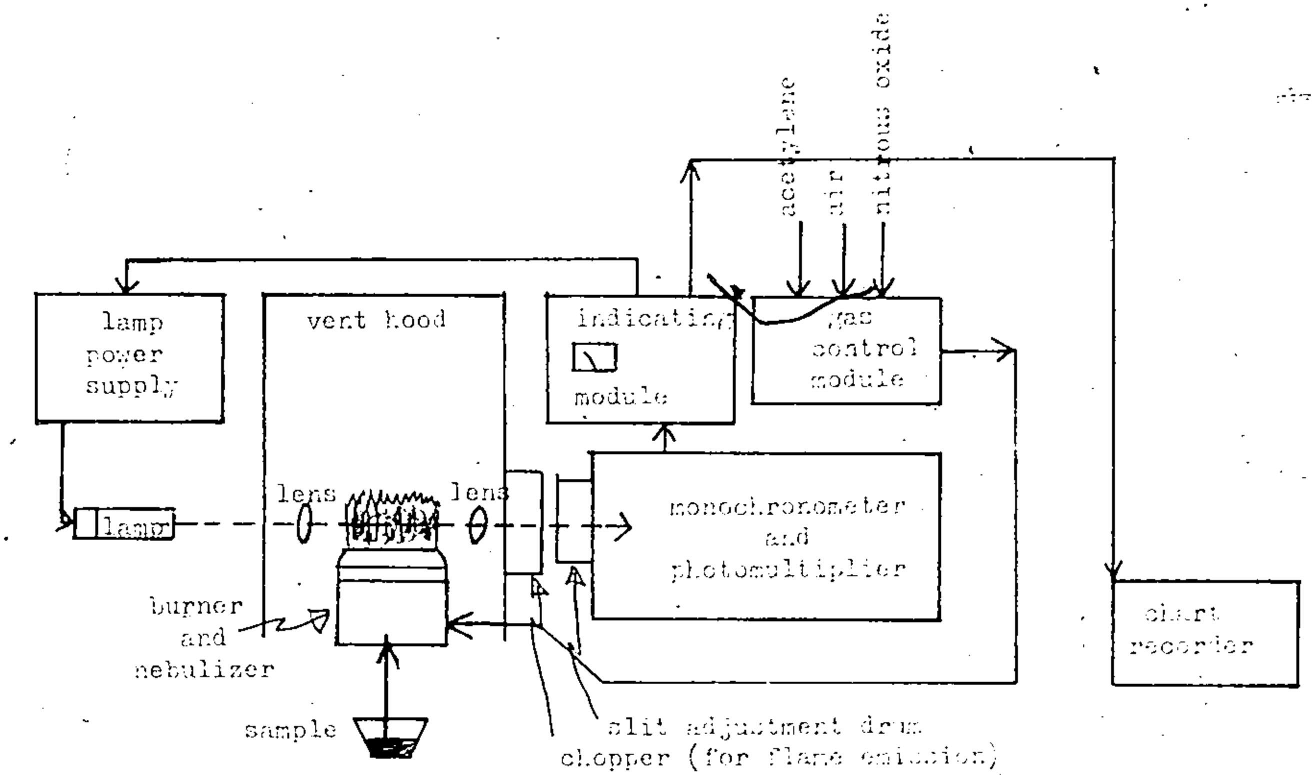


Fig. 3 Schematic diagram of Atomic Absorption setup

elements under study here.

The indicating module is a Varian IM-5 unit which provides a one-channel readout directly in either %-transmittance (%T) or %-absorbance (% Abs). It has an auto-set system which, when used in the absorbance mode, compensates for baseline drift due to lamp fluctuations and drift in the amplifier electronics. It ensures a constant amplifier output level (Varian Techron, 1971).

The excitation source for both atomic absorption and flame emission is a conventional gas burner using acetylene as a fuel gas and either compressed air or nitrous oxide as a support gas. The support gas enters the nebulizer and draws up the solution to be analysed through a capilliary tube, converting it there to a fine aerosol spray. These fine droplets are mixed with the fuel gas, passed through the spray chamber and burned in a flame at a suitable long slit laminar flow burner.

For emission work, the instrumentation is identical to that for atomic absorption except that the line source emitter is not used. As for all emission work, a chopper (Varian type AA-5) is used between the excitation source and the monochromator to provide synchronizing signals to trigger the amplifier system of the IM-5 indicating module.

The only additional instrumentation provided for argon plasma emission is the exchange of the plasma arc assembly for the burner unit and the use of the Spectrametrics power supply (Model 53000) which incorporates the power supply for the D.C. arc and the argon gas supply controls.

ARGON PLASMA EMISSION SET UP AND OPERATION

The D.C. argon plasma arc used in this study is ignited by passing a high voltage spark between two Zirtung electrodes, 0.040 inches (1.0 mm) in diameter, in an argon atmosphere. This spark ionizes the gas making it electrically conductive. When the gas is ionized, the ignition spark is cut off and direct current from the power supply begins to flow. This current heats the plasma up to 10,000°K at the center of the arc and provides between 6,000°K and 7,000°K in the excitation region at the junction of the plasma arc (Spectrametrics Inc., 1975) (see Figure 5).

Ceramic sleeves are used to provide a thermal pinch to contain and direct the structure of the plasma.

The argon supplied from the cylinder flows into the back of the power supply. There the gas supply is split into separate streams to the nebulizer and the electrodes by the use of a "T", mounted on the bottom of the Spectra Jet base. This flow is controlled by the meter marked "plasma" on the front of the power supply.

The sample solutions are fed into the nebulizer by a peristaltic pump (see Figure 6) at a rate of 2.0 m./min. This allows a controlled and even sample uptake. Liquid samples are converted to a fine aerosol (drops from 1 to 5 microns in diameter) by a ceramic nebulizer mounted in a separate spray

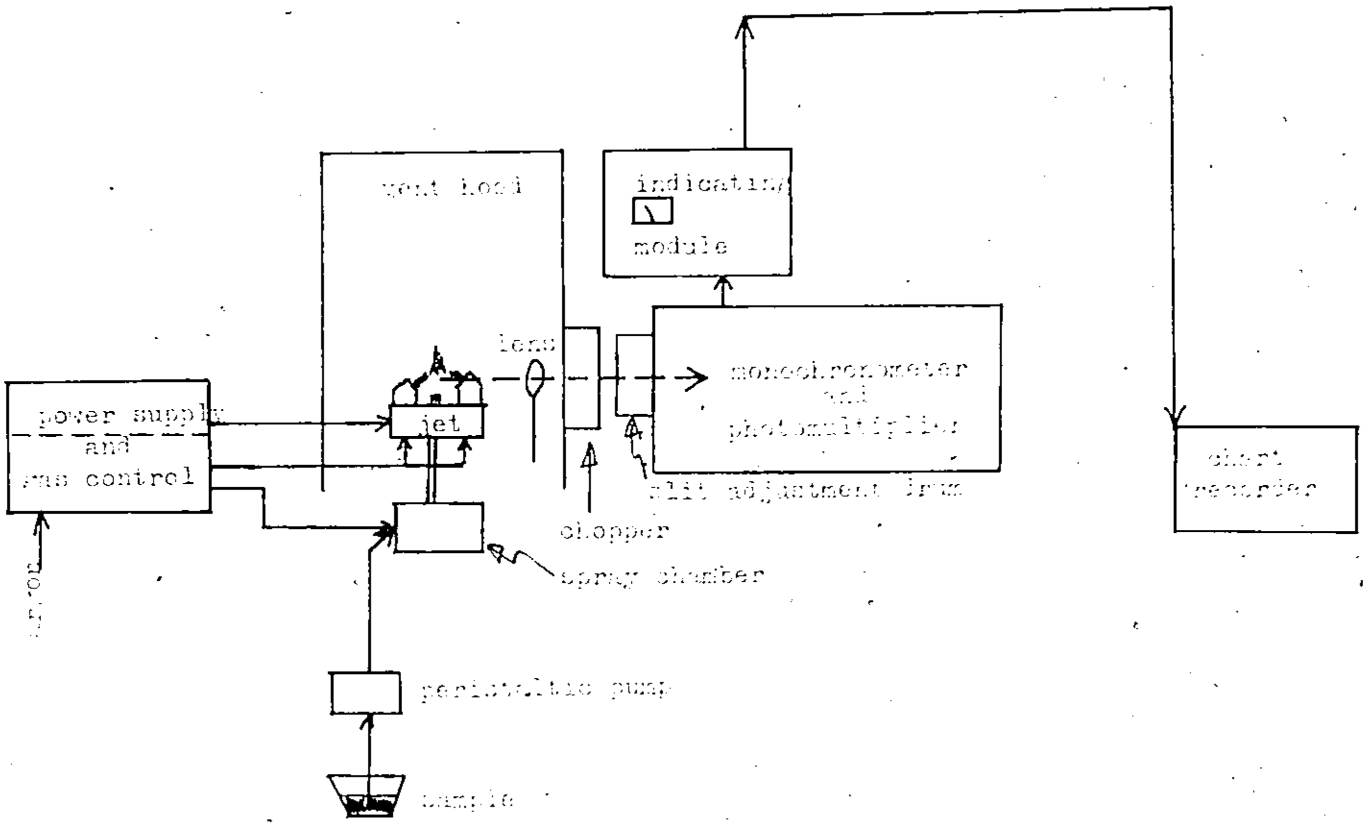


Fig. [illegible] Schematic Diagram of Argon Plasma Emission Set-up

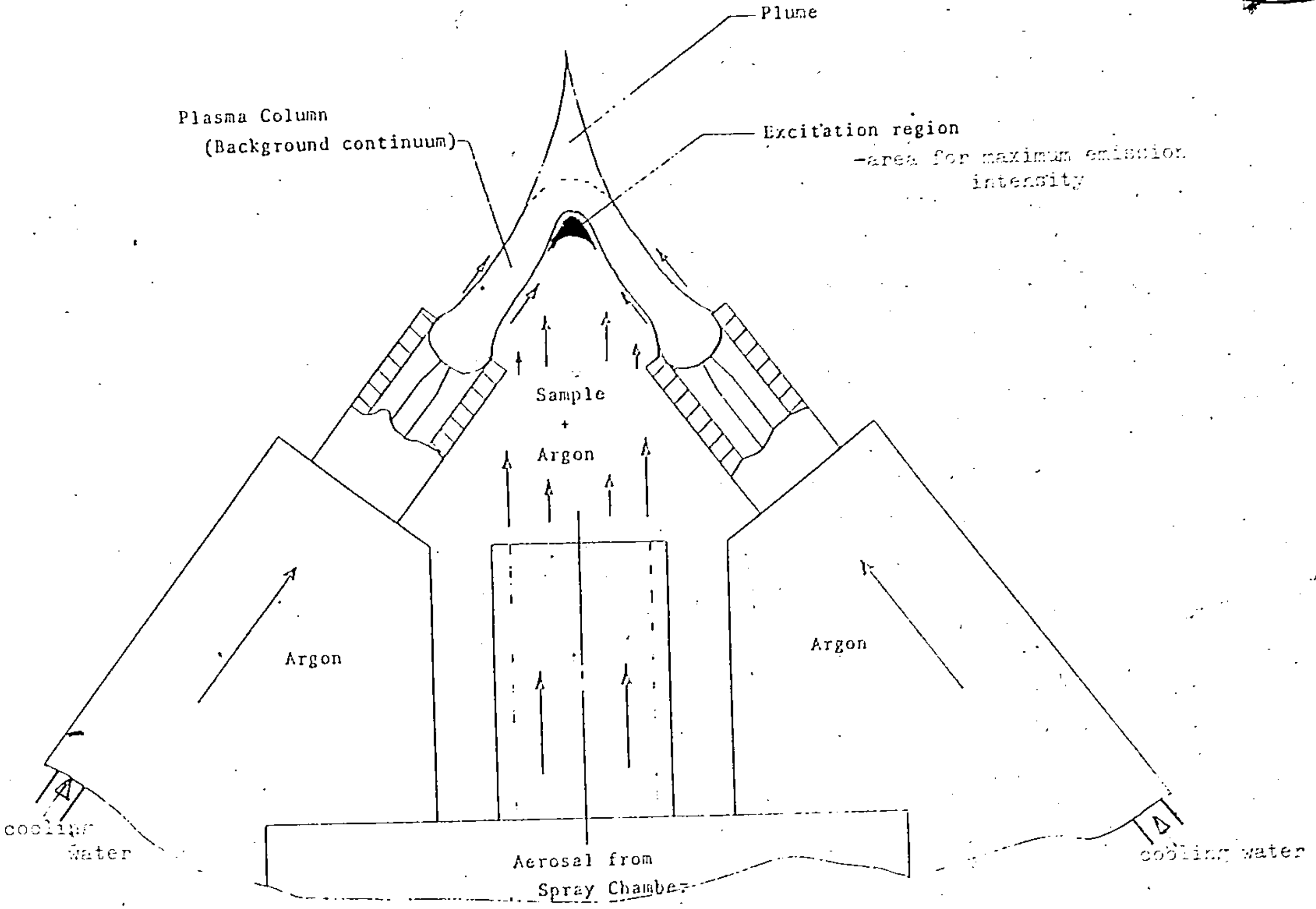


Fig. 5 SpectraJet II argon plasma jet

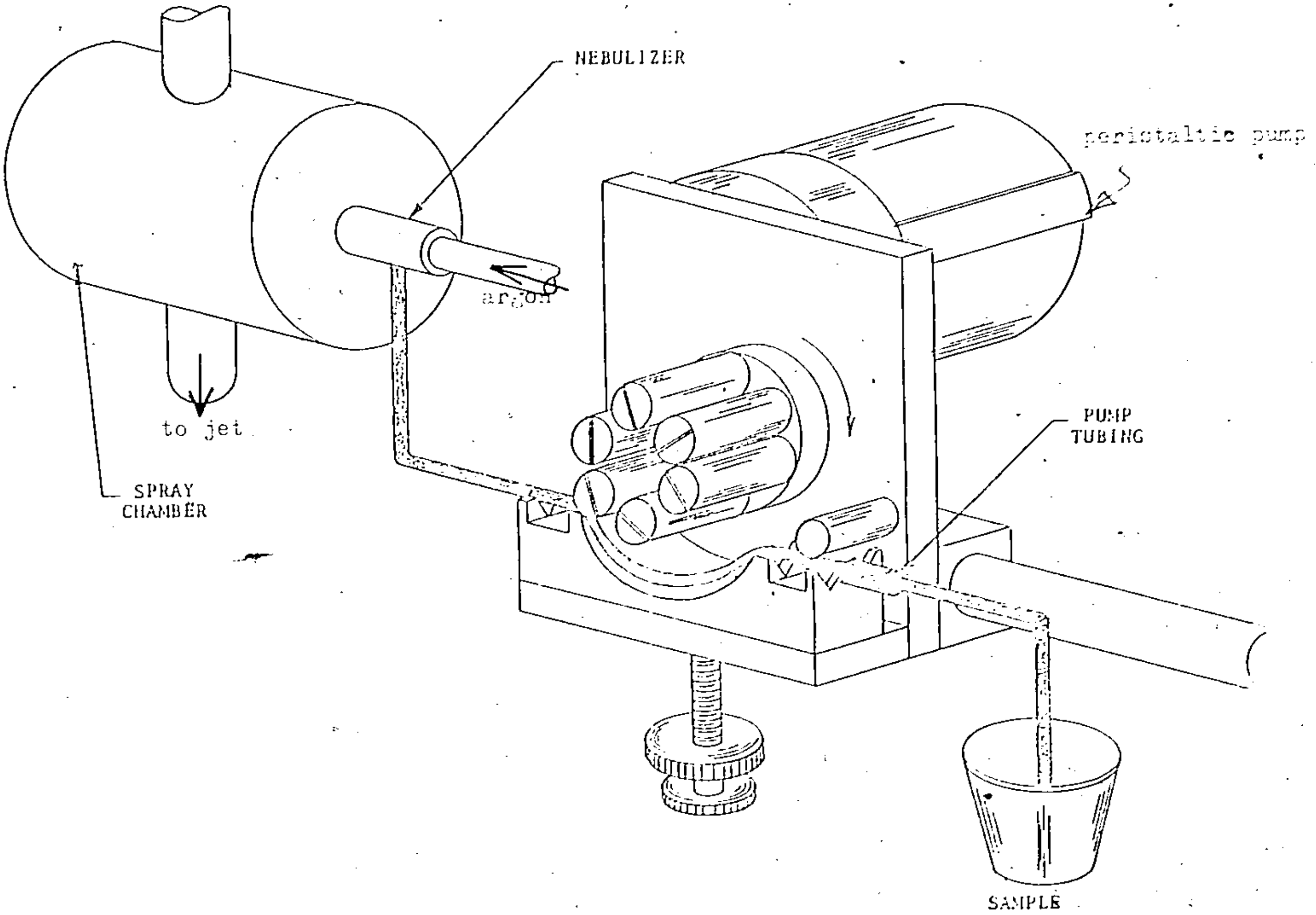


Fig. 6 Peristaltic pump and spray chamber layout

chamber (see Figure 6). This nebulizer has an efficiency of nearly 20% in converting the liquid to an aerosol. An argon stream is used to push the sample through the spray chamber. The stream is then directed upwards at the plasma from immediately below. This argon stream also serves to stabilize the arc as it flows past it. This support gas is welders grade argon supplied at a pressure of approximately 200 kPa regulated by a Purox 2-stage R-2053 regulator.

Three argon streams, one from each electrode and one from the sample delivery tube, create a region of sample concentration just below the junction of the arc, but outside the plasma envelope itself (see Figure 5). This is where the sample atoms are excited, in a region of very little background emission. The complete cycle of desolvation, molecular dissociation and, excitation takes place during the residence time of the sample within the excitation region (Spectrametrics Inc., 1975, 1975).

The cooling of the jet assembly is achieved by circulating cool tap water through cooling blocks in the jet assembly (see Figure 5) at a recommended rate of 0.25 liters per minute. This is necessary to avoid welding of the electrodes to their holders and the ceramic sleeves.

The two major modifications made to the existing Varian Techron atomic absorption spectrophotometer to adapt it to the use of the argon plasma jet were relatively simple.

The first modification involved the use of an extension block between the burner adjustment assembly and the optical rail to move the plasma arc into alignment with the monochronometer. This misalignment is due to the construction of the jet, as the plasma is not produced directly over the neck that fits into the burner adjustment portion of the flame nebulizer assembly (see Figure 8). The use of this portion of the burner assembly allows the use of the vertical, horizontal and rotational adjustment controls for the atomic absorption burner. The second modification called for the replacement of the original flame shade by a sheet aluminum shield incorporating a darker 4.5 x 5.25 inch piece of welders glass (shade 12). This was necessary in order to give sufficient protection to the operator from the intense ultraviolet light emitted by the plasma arc (see Figure 9).

The compressed air, acetylene and nitrous oxide gas supplies for the conventional burner assembly remain connected to the GCU-5 gas control unit of the spectrophotometer, but are not used.

In addition two minor modifications to the stock Spectra Jet II assembly were required in order to allow continuous operation of the unit. The primary modification relocated the spray chamber, which was originally attached to the jet assembly, to the rear panel of the vent hood. The original position allowed water to build up in the delivery tube leading to the jet. The gas flow in the tube caused this

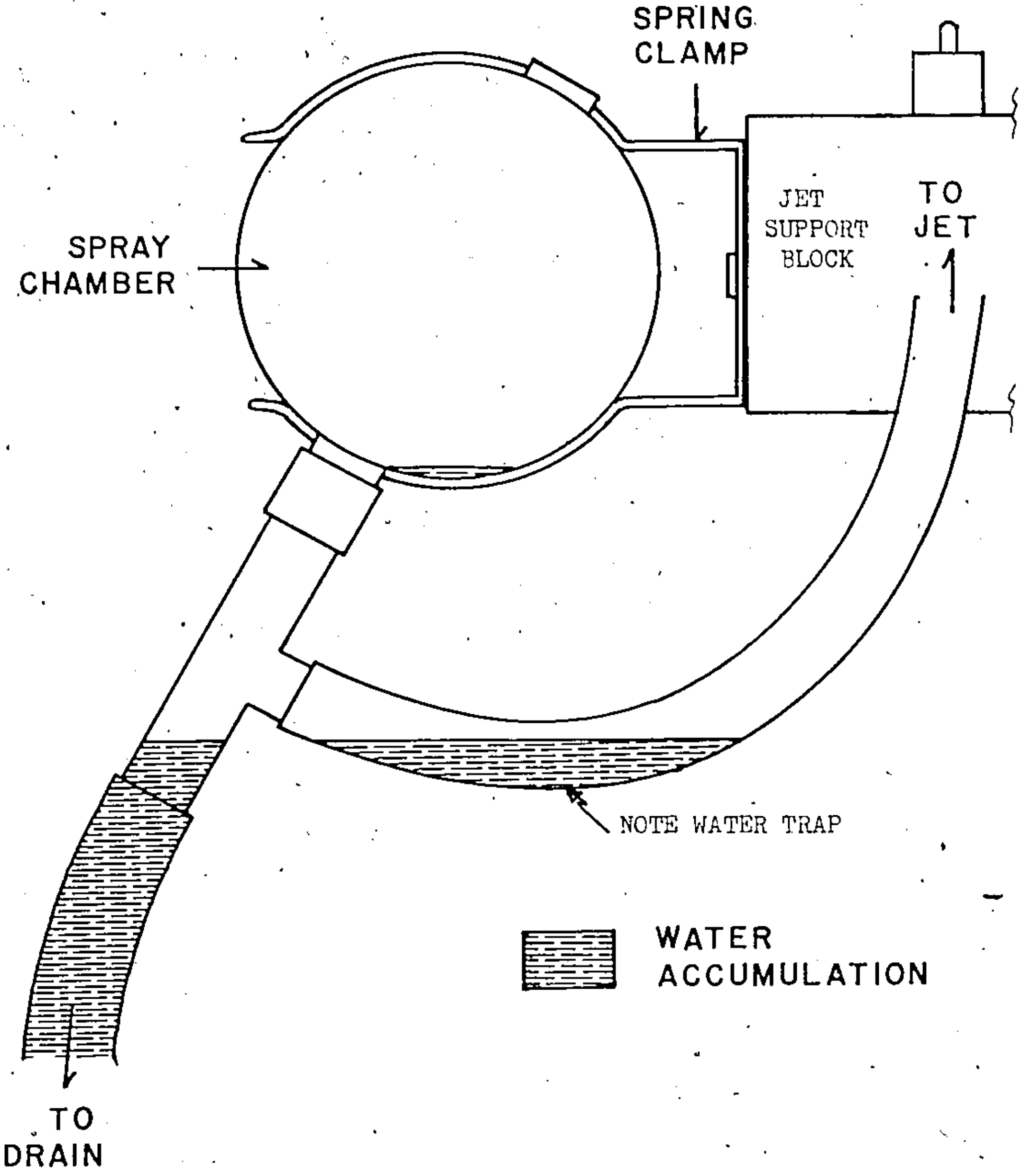
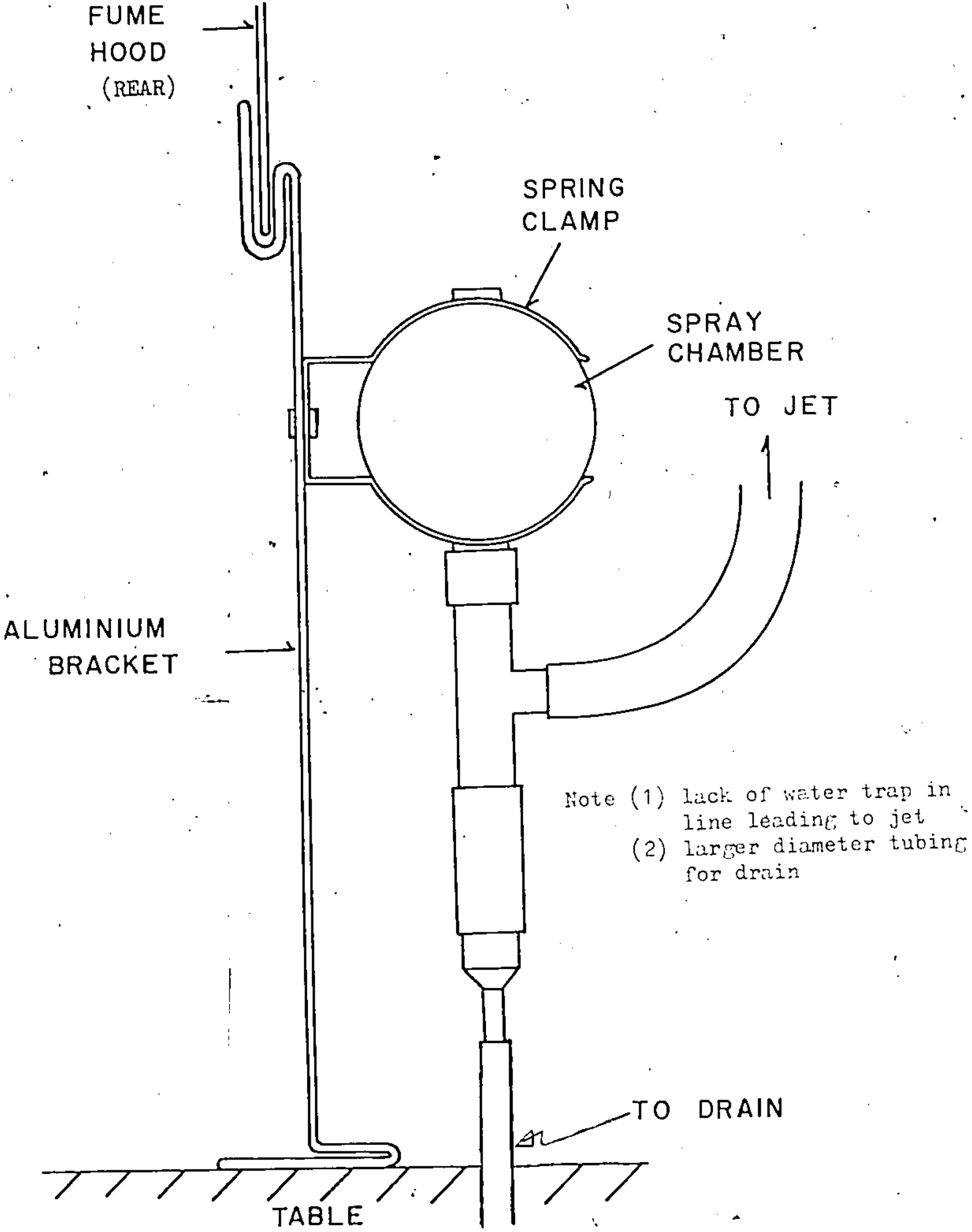


Fig. 7a Original Spray chamber location
(after Mitchell, 1977)



Note (1) lack of water trap in line leading to jet
(2) larger diameter tubing for drain

Fig. 7b Modification to spray chamber location
(after Mitchell, 1977)

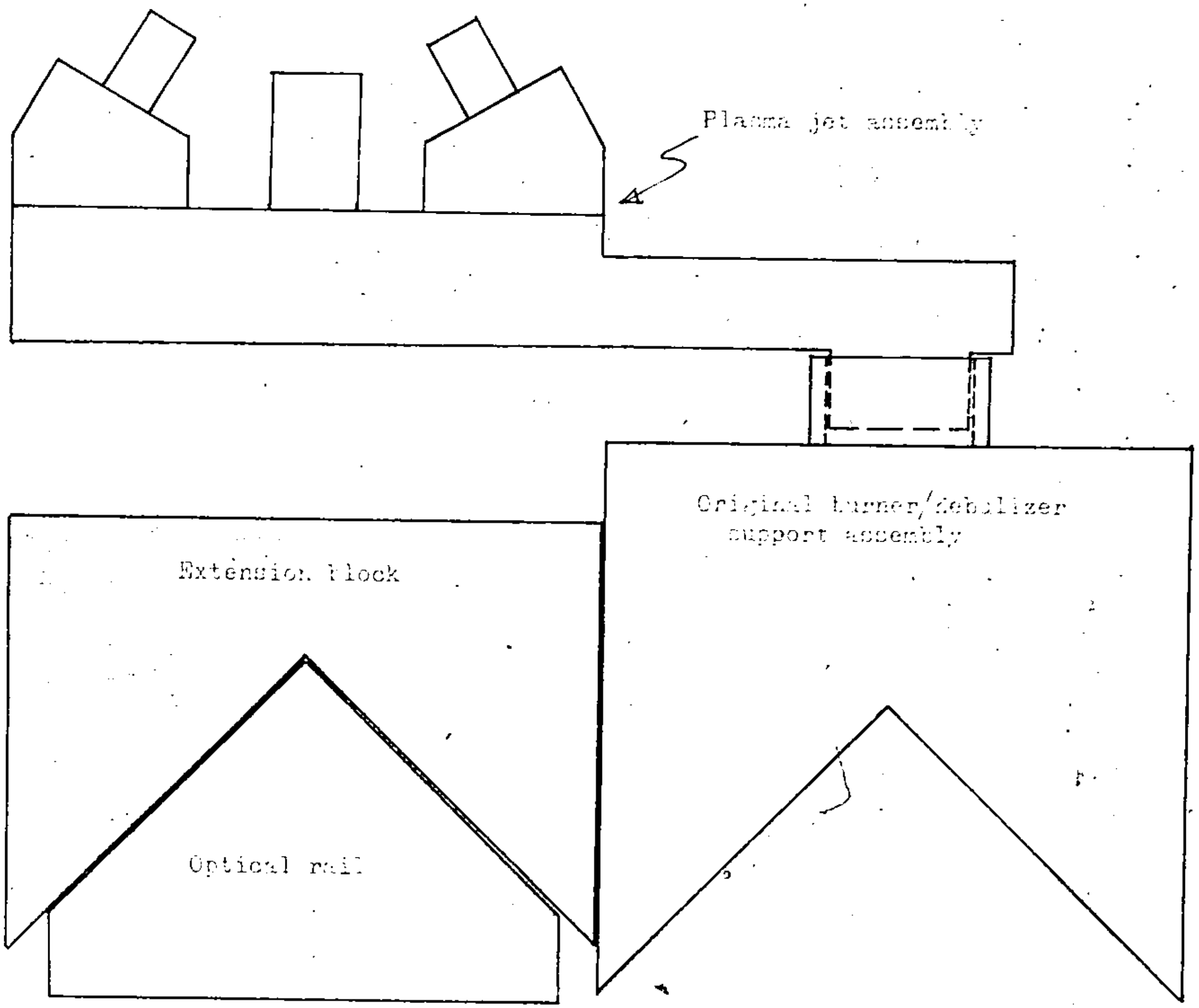
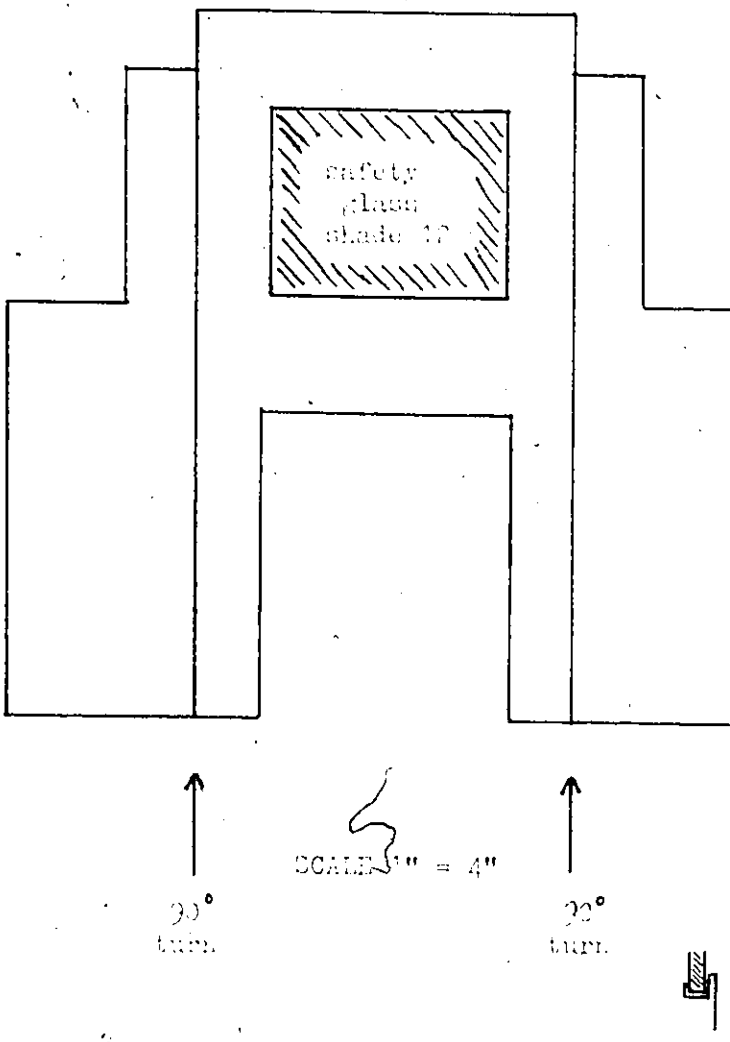


Fig. 9 Extension block modification to support assembly

Fig. 9 Modified view shield



- safety glass retained by three flanges
- metal material is 24 gauge aluminum sheet

water to bubble which in turn extinguished the plasma arc (see Figure 7a, 7b). The second change called for replacing the original spray chamber drain tube with a larger diameter tube. With these two modifications, free and complete drainage of excess water and solution was allowed.

DEFINITIONS

The following sections define the terminology relevant to this study.

SENSITIVITY(1)

Sensitivity is defined here as that concentration of the analyte in aqueous solution (expressed in ug/ml) which will produce a change, compared to pure solvent (water- triple distilled), equivalent to the value of 1/100 of the slope of the calibration curve. This applies when in either the Transmission mode or the Absorption mode.

The definitions of detection limit and noise level used in this study and which are given below are those used by Price (1972).

DETECTION LIMIT

The Detection Limit is defined as the minimum concentration or amount of an element which can be detected with 95% certainty assuming a normal distribution of errors. This is the quantity of the element which gives a reading equal to twice the standard deviation of a series of at least ten determinations at or near blank level.

BLANK NOISE LEVEL

The Blank Noise Level is defined as that concentration

(1) see 'Additional Notes' at end of this section

of the analyte that would give a signal equal to 1/50 the sum of 20 measurements taken as follows:

> The output of an atomic absorption spectrophotometer operating on a <u>blank</u> solution is recorded for 10 time periods, each of the 10 times the time constant of the instrument (in this case taken as 1 second). The <u>maximum</u> displacements that occur to both sides of the median line in each of the 10 periods are measured.

The value returned approximates the standard deviation of the noise, expressed in terms of elemental concentration. All measurements are read in the 'B' damp mode at the same gain setting as for the standard samples.

<u>NOISE</u>

Noise, as distinguished from the Blank Noise Level, is the percentage of the mean signal that the maximum noise oscillation (one-sided) gives. This mean is the mean value of the stability plot.

$$N = \frac{\text{one-sided noise reading}}{\text{mean value of signal}} \times 100$$

<u>SLOPE</u>

The slope (m) of the calibration curves is obtained by least square simple regression with Y regressed on X for no error in X. This curve of the form $Y = mX + b$ is forced through the origin (as for a blank solution) by the addition of extra (0,0) co-ordinates. The formula used is given by:

$$m = \frac{\Sigma(X_i - \overline{X})\ (Y_i - \overline{Y})}{\Sigma(X_i - \overline{X})^2} \quad \text{where } \overline{X} = \frac{X}{n} \quad \overline{Y} = \frac{Y}{n}$$

The intercept (b) is given by:

$$b = \overline{Y} - (m\overline{X})$$

CORRELATION COEFFICIENT (2)

The correlation coefficient (r) is a measure of the degree of correlation between the points on the line of best fit, as defined by 'm' and 'b' in the equation $\overline{Y} = m\overline{X} + b$, 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 formula used is given by (Wine, 1964):

$$r = \frac{\Sigma(X_i - \overline{X})\ (Y_i - \overline{Y})}{\sqrt{\Sigma(X_i - \overline{X})^2 \Sigma(Y_i - \overline{Y})^2}}$$

VARIANCE, STANDARD DEVIATION, MEAN, RELATIVE STANDARD DEVIATION

The variance (σ^2), standard deviation (SD), mean ($\overline{X}$) and the relative standard deviation (RSD), which is also called

---

(2) see 'Additional Notes' at end of this section

the coefficient of variation (CV), are given by the following formulae (Wine, 1964):

$$\sigma^2 = \frac{\Sigma(x_i - \bar{x})^2}{n}$$ where n = number of samples

$$SD = \sqrt{\sigma}$$

$$\bar{X} = \frac{\Sigma x_i}{n}$$

$$RSD = \frac{SD \times 100}{\bar{X}}$$

Additional Notes

1. Sensitivity

The definition of sensitivity as used in this study differs from the conventional definition as accepted for absorption techniques. The definition used here is the accepted definition for use with emission techniques. The commonly used definition used with absorption techniques is as follows:

Sensitivity = slope x 0.0044

The conversion factors for use in converting from the sensitivity figures quoted in this text to figures compatible with the above definition are:

2.27	for sensitivity values < 1.000
0.044	for sensitivity values ≥ 1.000

2. Correlation Coefficient

The slope and correlation coefficient figures used in this study have been derived from curves that have been forced through the origin. This means that the correlation coefficients for the unforced lines through the data points will be slightly greater than the figures quoted. The quoted figures are still acceptable for use as relative as opposed to absolute parameters.

STATISTICS

The statistics involved in this study fall into two sections. The first section contains descriptive statistical parameters generated from the sample data. The second section uses these statistical parameters generated for each standard rock and for each element by each of the two methods. These statistics are used to compare the methods used to each other and to determine if the differences between the methods are significant or not.

SECTION I - Descriptive Statistical Parameters

This first group involves the calculation of slope and intercept for the lines of best fit to the calibration curves using the preceding formulae. From the instrument reading given by the sample solution and the calculated slope value, the concentration of the element in question within the solution can be calculated. The sensitivity of the apparatus to the element is also determined from the slope value at this time. The replicate concentration values for each duplicate of each standard rock sample are compiled, producing mean elemental concentration and variance values for each sample solution. Comparisons of instrumental variability at differing wavelengths and elemental concentrations can be made using these values. A compilation of the values from the duplicate solutions for each standard rock is performed. From this compilation mean elemental concentration, standard deviation, relative standard deviation, standard error and 95% confidence limit values are calculated for each sample. Using replicate readings of solutions at or near blank level, the detection limit for the element in question is determined from the standard deviation of these readings.

SECTION II - Statistical Comparison of Data

This second section uses several statistical tests to compare the mean elemental concentration and variance values obtained for each rock sample by each of the methods used in this study. These tests are as follows:

(1) STUDENT'S t-TEST OF MEANS

The mean values of the elemental concentrations in each standard rock sample, produced by the two methods, are compared using Student's t-test of means. (Kenney and Keeping, 1954). In this test, a 't' value is calculated using the means ($\overline{X}$) and variances (σ^2) produced by the two methods as follows:

$$\text{t-calc} = \frac{\overline{X}_a - \overline{X}_b}{\sqrt{\sigma_a^2 + \sigma_b^2}}$$

where subscripts 'a' and 'b' denote the two methods used

The correct number of degrees of freedom for use in this test is calculated using the number of values (n) used in calculating the means and their respective variances. This calculated degree of freedom (K) is truncated to integer form:

$$K = \frac{(\sigma_a + \sigma_b)^2}{\left(\dfrac{\sigma_a^2}{n_a - 1} + \dfrac{\sigma_b^2}{n_b - 1}\right)}$$

The correct tabulated 't' value for comparison is found in the Tables of 't' corresponding to Given Probabilities (Kenney and Keeping, 1954) under the probability of a deviation greater than 't' equalling 0.025 (the 5% significance level) and using the 'K' value as the value for the number of degrees of freedom. If the calculated value for 't' is greater than the tabulated value, the conclusion is that the two means are significantly different at the 5% significance level.

(2) SNEDECOR'S F-TEST OF VARIANCE

The variance values associated with the above mean values for the two methods are compared using Snedecor's F-test of variance. In this test an 'F' value is calculated using the respective variances.

$$\text{F-calc} = \frac{\sigma_g^2}{\sigma_l^2}$$

where 'σ_g^2' and 'σ_l^2' represents the greater and lesser variance values respectively

The degree of freedom to be used for each of the variances is taken from the following: d.f. = (n - 1), where 'n' is the number of values associated with the respective variance.

The correct tabulated 'F' value is to be found in the tables for Critical values of F, which are extensively tabulated, at the 5% significance level. If the calculated value of 'F' is greater than the tabulated value, the conclusion is that the two variances are significantly different.

The above F-test is also used in the comparison of the reproducibility data of the two methods. In this case the significance of the comparison of the variance values is determined and for each method the relative standard deviation from the mean is calculated.

(3) REJECTION OF VALUES

Before calculating the mean and variance for all the replicate values for each standard rock sample by each method, the values are subjected to a t-test for rejection of values (A. Turek, unpublished report). This is a comparison of a sample value with a standard value (in this case the mean elemental concentration) with the standard deviation being unknown. The formula used to calculate the 't' value is as follows:

$$\text{t-calc} = \frac{\left| X_i - u_o \right| \sqrt{f}}{\sigma}$$

where u_o = std. value (mean)
f = frequency of equal observations
σ = std. deviation of population
x_i = conc. value to be tested

First, all the concentration values are summed, then the mean and variance are calculated. The frequency of occurence of each value is determined and then each different value is tested against the standard value (the mean just produced). If any value fails the t-test (t-calc $>$ t-tables), it is rejected.

This reduces the number of degrees of freedom by the number of values rejected and the whole procedure is repeated (including the recalculation of the mean and variance) until all of the values have been tested. The final output consists of mean, variance and standard deviation values and the 95% confidence limits about the mean for each sample.

All of the above calculations and comparisons, except for (1) the calculation of elemental concentrations from the instrumental readings using the slope factor and (2) the calculation of the percent oxide in the sample, were done using a Wang Corporation mini-computer, Model 2200. The programs used in these calculations are listed in Appendix IV.

RESULTS and DISCUSSION OF EXPERIMENTAL PROCEDURES

SAMPLE PREPARATION

Two methods of sample dissolution were used in this study.

(1) A hydochloric-perchloric-hydrofluoric acid dissolution of the sample rock, given by Turek and Riddle (1977) with some slight modifications was used for most of the samples. This procedure involved placing about 0.5 g (accurately weighed out) of dried rock powder (-105 mesh) into a 30 ml platinum dish, wetting the sample and adding 10 ml HF (48%). This solution was heated to dryness then another 10 ml HF was added and was allowed to go to dryness without heat. At dryness, 5 ml HF and 5 ml $HClO_4$ (72%) was added, heated to dryness and baked for 0.5 hours. This final baking was to vaporize any remaining HF. After allowing the sample to cool, 20 ml 2.5N HCl was added to dissolve the residue. The contents of the dish was transferred quantitatively to a 500 ml volumetric flask, rinsed frequently with 2.5 N HCl and made up to volume with triple distilled water. This dissolution is known as 'solution B'.

(2) A single solution dissolution was used as a check on the previous technique which volatilizes silicon (and some aluminum or titanium) with the fluoride (e.g. as SiF_4) during the baking process. This second dissolution is given by Ward (1977) and has been tailored for use with a Parr acid

digestion bomb. This procedure involved placing about 0.5 g (accurately weighed) of dried rock powder into the teflon liner of the Parr bomb and adding 4 ml HCl, 2 ml HNO_3 (both 6 N) and 10 ml HF (48%). The sealed bomb was then heated at 95°C in an oven for three hours, cooled for 30 minutes and the contents of the bomb quantitatively transferred to a 500 ml nalgene volumetric flask. 914 g. of boric acid crystals were added to the flask to complex the remaining HF and the solution was made up to volume with triple distilled water. This dissolution is referred to as 'solution JA'.

The above dissolution holds two advantages over the HCl-$HClO_4$-HF dissolution. The first is that the sample preparation time is greatly reduced, from over 24 hours for the latter to little over 4 hours for the former. The second advantage is that analyses for silicon can be made on samples digested by the single solution technique, while all of the silicon is baked off when using the other digestion procedure.

Blank solutions from each dissolution were prepared.

Each sample had replicate solutions prepared. For sample BCR-1, 3 replicates were prepared; for sample GA, 4 replicates were prepared, two by single solution dissolution and two by HCl-$HClO_4$-HF dissolution; for sample NBS-70a, 2 replicates were preapred and for sample NSX-RP, 9 replicates were prepared.

STANDARDS PREPARATION

All standard solutions were prepared from Fisher Chemical Co. certified atomic absorption stock solutions of 1000 ug/ml. From these stock solutions, standards were prepared for each element to provide a range that would bracket the samples being analysed and that fell within the optimum working ranges of the analytical methods. The iron standards were acidified using 6 N HCl solution (8 ml for 200 ml final volume).

ANALYTICAL PROCEDURE

The sample, standard and blank solutions were aspirated into the instrument such that the range of standards was run first, followed by the blank and sample solutions. The standard solutions were run again to check for instrumental drift. The mean reading for each standard was used to calculate the calibration curve. Each sample replicate was run six times consecutively and, after three replicates had been run, one standard was aspirated to check on instrumental drift. This pattern was continued until each replicate had been run.

Dilutions of the sample solutions were needed for the analysis of several elements (see Tables in following sections). These dilutions were done by hand as the variable dilutor was not functioning accurately enough to give satisfactory results.

The dilutions were needed to keep the approximate elemental concentration of the solution being analysed within the optimum working range of the instrument. The dilution factors varied for the various elements and for the analytical method used.

The slopes of the calibration curves given by the standard solutions gave the calibration factor, CF = (1/slope), which was used to obtain the concentration of analyte in the solution. The metal-to-oxide conversion factors (see Appendix III) and the dilution factors were calculated and were used to determine the percentage of analyte, in the oxide form, that was present in the original rock sample. The combined conversion equation is as follows:

$$\% \text{ oxide} = \frac{C_s \times V \times D \times C_{mo}}{W} \times 10^{-4}$$

where C_s = concentration of analyte (ug/ml)

V = volume of original solution (ml)

D = dilution factor

C_{mo} = metal/oxide conversion factor

W = weight of sample in volume (g)

SILICON

The wavelength selected for both atomic absorption and plasma emission analysis for silicon was 251.612 nm. No other wavelength tested was as sensitive or as quiet as this line.

Standards were prepared to cover a range from 1 ug Si/ml to 1000 ug Si/ml. In practice, only the lower standards were used with both techniques. This range covered all the samples prepared and allowed a quantitative determination of the detection limit.

The calibration curves to both methods were linear with correlation coefficients from .99991 to 1.00000. There was a slight negative deflection in these curves at high concentrations, from 750 to 1000 ug Si/ml. Even at that low sensitivity the correlation coefficients for plasma emission and atomic absorption were .99989 and .99860 respectively. Typical calibration curves are shown in Figures 11 and 13.

No interferences of any kind were apparent using a ten-fold dilution of the samples although there was some chemical interference evident when using the full strength solutions with plasma emission, and rather more of this problem with atomic absorption.

Tables 1 to 5 illustrate the results obtained for sensitivity and detection limits for the two methods. The detection limit determined for plasma emission (0.062 ug/ml) is over five times lower than that determined for atomic absorption (0.335 ug/ml). This value for atomic absorption is close to the optimum instrument detection limit of 0.300 ug/ml (Varian Techron, 1972), while the reported detection limit for plasma emission of 0.010 ug/ml (Spectrametrics Inc., 1972) is less than a factor of 10 than that determined in this study.

In the course of normal operation, the sensitivity values determined for the two methods are similar with atomic absorption giving a maximum sensitivity of 0.0029 ug/ml. Plasma emission, while running the sample solutions, gave a sensitivity of 0.0019 ug/ml. More importantly, while running a series of standards to get detection limit data, the maximum sensitivity value increased to 0.0265 ug/ml.

This illustrates well the flexibility of the emission technique which allows a greater variation in sensitivity and a greater dymamic range.

The reproducibility and stability of the signals from plasma emission and atomic absorption are illustrated in Figures 12 and 14 and by Table 5. The relative standard deviation, for reproducibility over six repetitions, for atomic absorption is 0.136%, more than an order of magnitude lower than that for plasma emission (1.760%). This indicates a better reproducibility when using atomic absorption than when using the plasma emission technique. This is borne out statistically where the variances of the two reproducibility data sets are significantly different at the 5% significance level.

The figures for stability are similar, with both methods showing minor drift from the mean and both showing fairly low blank level noise (plasma - 0.056 ug/ml and absorption - 0.041 ug/ml). The actual noise on the plot is also greater when using plasma emission, with a slightly greater noise working on a lower mean signal, giving a noise of 2.8% as compared to a quieter value of 0.5% for atomic absorption.

The accuracy of both methods is comparable, showing good agreement with the literature value for sample GA of 69.90% SiO_2, with differences of -1.6% (68.78% SiO_2) for plasma emission. The only sample solutions analysed for silicon were the single solution dissolution replicates of sample GA. The regular 'solution B' solutions have lost silicon during baking as SiF_4. Statistically, there is no significant difference (at the 5% level) between the means obtained by the two methods. A ten-fold dilution was used even though it was possible to run the samples at full strength. The results using the full strength solutions were high due to chemical interferences. The results by atomic absorption were approximately 30% high (95% SiO_2) while the results by plasma emission were only 8.5% high giving 75% SiO_2. The higher temperature of the argon plasma arc is the probable reason for the better results by the plasma method with the full strength solutions.

The precision of the methods was also comparable on this sample at the ten-fold dilution, with relative standard deviations of 1.664% for atomic absorption and 1.420% for plasma emission. The variances associated with the means by the two methods were also not significantly different at the 5% level.

On the basis of accuracy, precision and noise levels there is no significant difference between atomic absorption and plasma emission. The only significant difference between the methods is in the reproducibility of results, where atomic absorption is better. This is not the whole picture however, as the atomic absorption technique has two major disadvantages. First, the silicon in the solution tends to combine with the acetylene in the flame, forming a silicon carbide on the burner slot. This partially blocks the burner and causes a noticable signal loss if not cleared away. This occurs within ten minutes, even when using a freshly cleaned burner. The other disadvantage is the high heat output from the nitrous oxide-acetylene flame which causes operator discomfort.

The advantage of the somewhat better reproducibility by atomic absorption must be balanced against; (1) the two disadvantages mentioned above, which are eliminated by the use of plasma emission, and (2) the greater flexibility and better sensitivity of the emission technique. On this basis, the argon plasma emission technique has a slight advantage, including ease of operation and a greater flexibility and dynamic range, which offsets slight loss in reproducibility.

TABLE 1

Silicon by Plasma Emission

****

Working Conditions

Wavelength 251.612 nm, Gain 3

Slit width 10 microns, Plasma current used = 7.5 Amps.

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
1	3.0	3.0
10	26.5	26.6
1	3.0	
10	26.7	

****

THE SLOPE IS 2.6596

THE INTERCEPT IS 0.0344

THE CORRELATION COEFFICIENT IS .99991

THE SENSITIVITY IS 0.0265 ug/ml

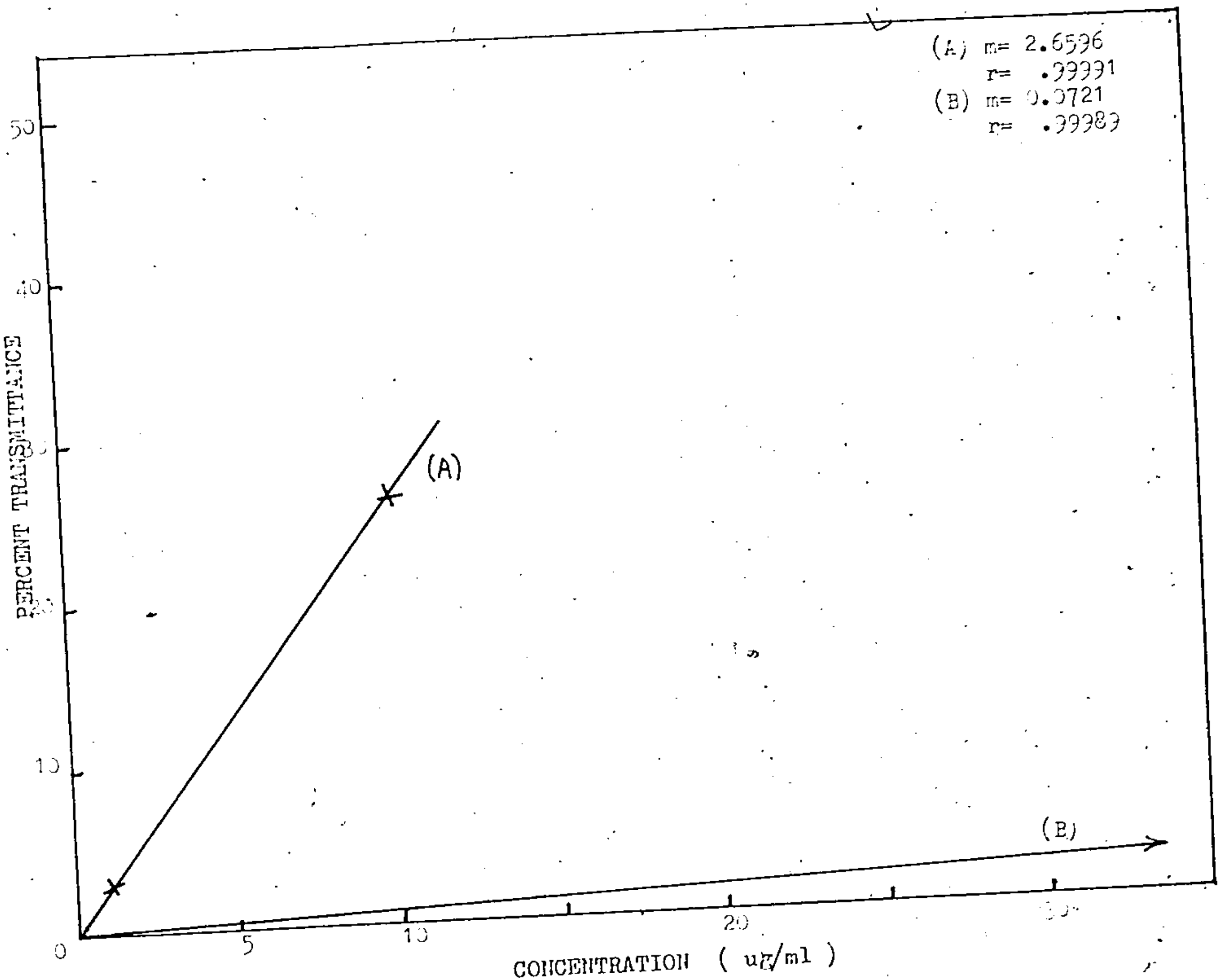


Fig. 11 Typical calibration curves for silicon by plasma emission

TABLE 2

Detection Limit for Silicon by Plasma Emission

Working Conditions

Wavelength 251.612 nm, Gain 3

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
1	3.0
1	3.0
1	3.1
1	3.1
1	3.0
1	3.0
1	3.0
1	2.9
1	2.8
1	3.0

THE MEAN IS 2.99

THE STD. DEVIATION IS 0.083

THE SLOPE IS 2.6596

THE DETECTION LIMIT IS 0.0624 ug/ml

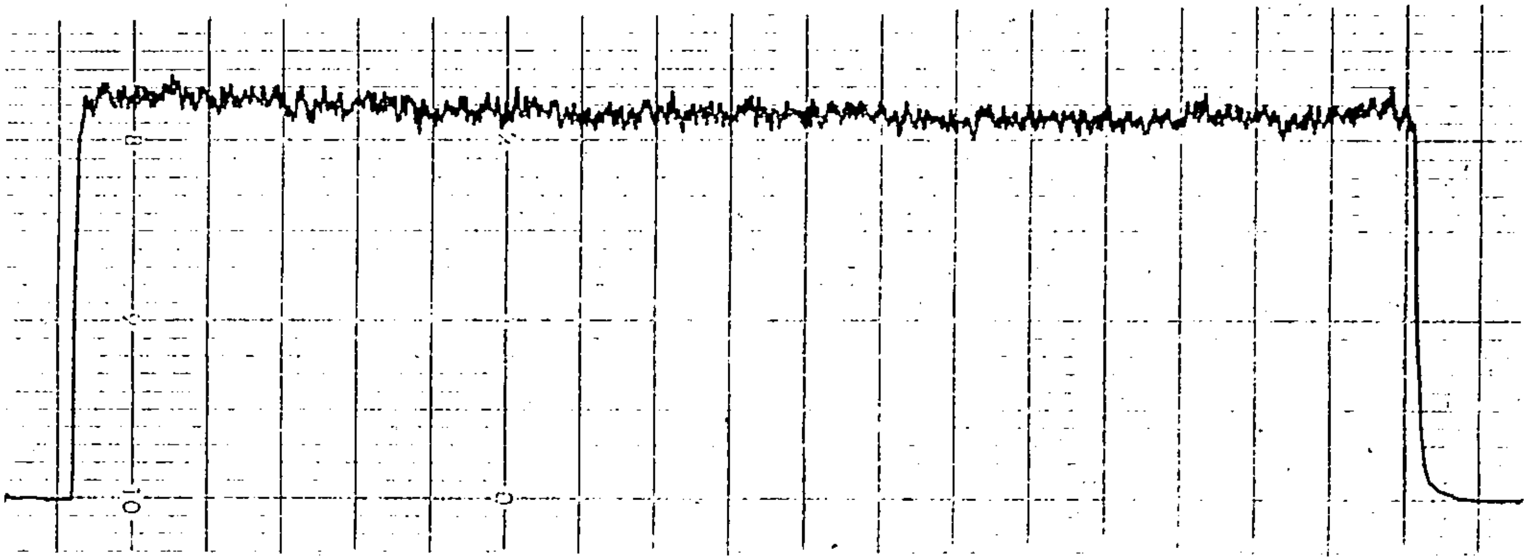


Fig. 12 Stability plot for silicon by plasma emission

TABLE 3

Silicon by Atomic Absorption

****

Working Conditions

Wavelength 251.612 nm, Gain 4

Slit width 50 microns, Lamp current used = 15 mA

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
10	2.8	2.9
50	14.1	14.5
10	3.0	
50	14.9	

****

THE SLOPE IS 0.2900

THE INTERCEPT IS 0.0000

THE CORRELATION COEFFICIENT IS 1.00000

THE SENSITIVITY IS 0.0029 ug/ml

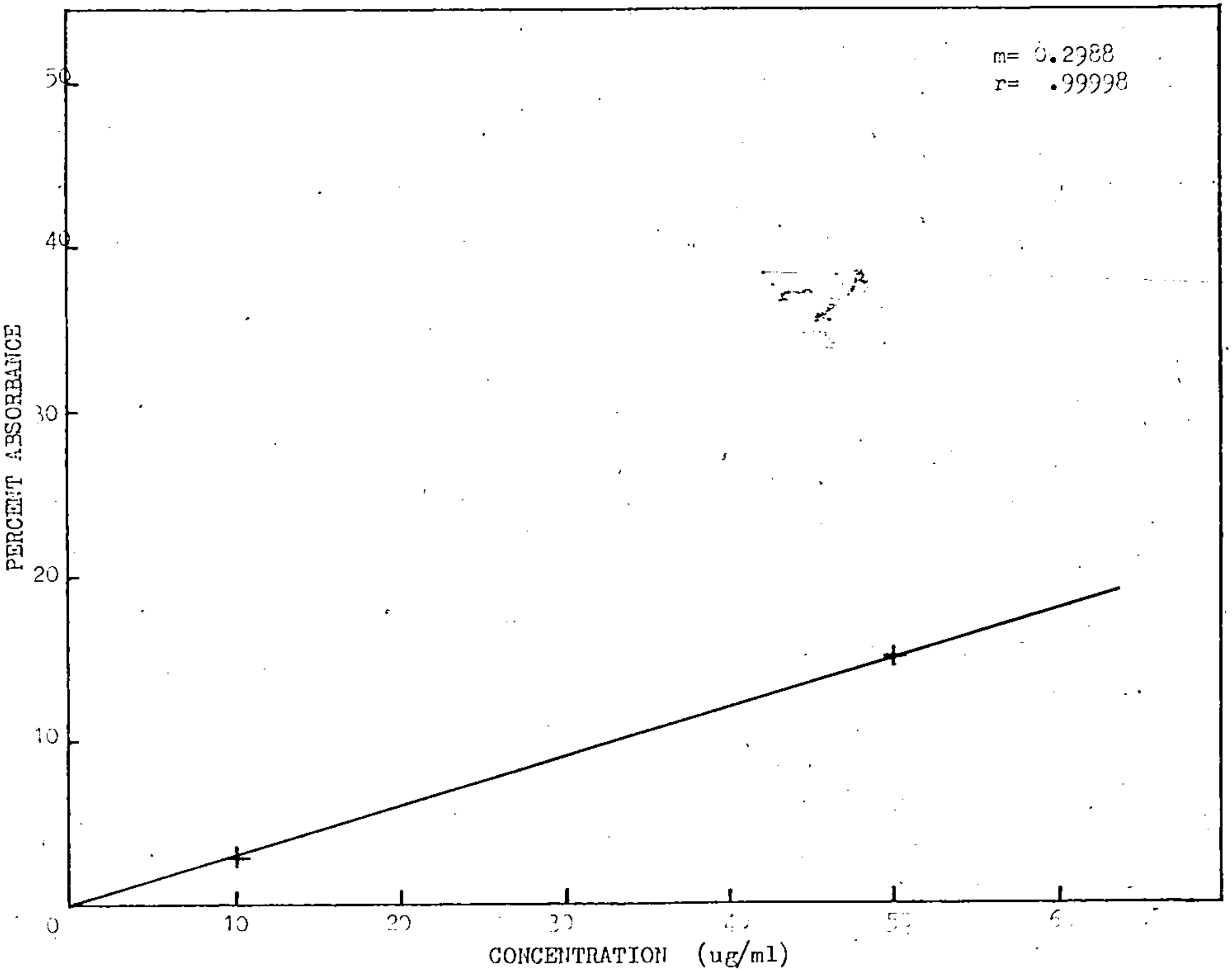


Fig. 13 Typical calibration curve for silicon by atomic absorption

TABLE 4

Detection Limit for Silicon by Atomic Absorption

****

Working Conditions

Wavelength 251.612 nm, Gain 4
Slit width 50 microns, Lamp current used = 15 mA
Support gas used was nitrous oxide
Flame stoichiometry was reducing
Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
Blank	0.2
	0.2
	0.1
	0.1
	0.1
	0.2
	0.2
	0.2
	0.1
	0.1

****

THE MEAN IS 0.15
THE STD. DEVIATION IS 0.05
THE SLOPE IS 0.2988
THE DETECTION LIMIT IS 0.3346 ug/ml

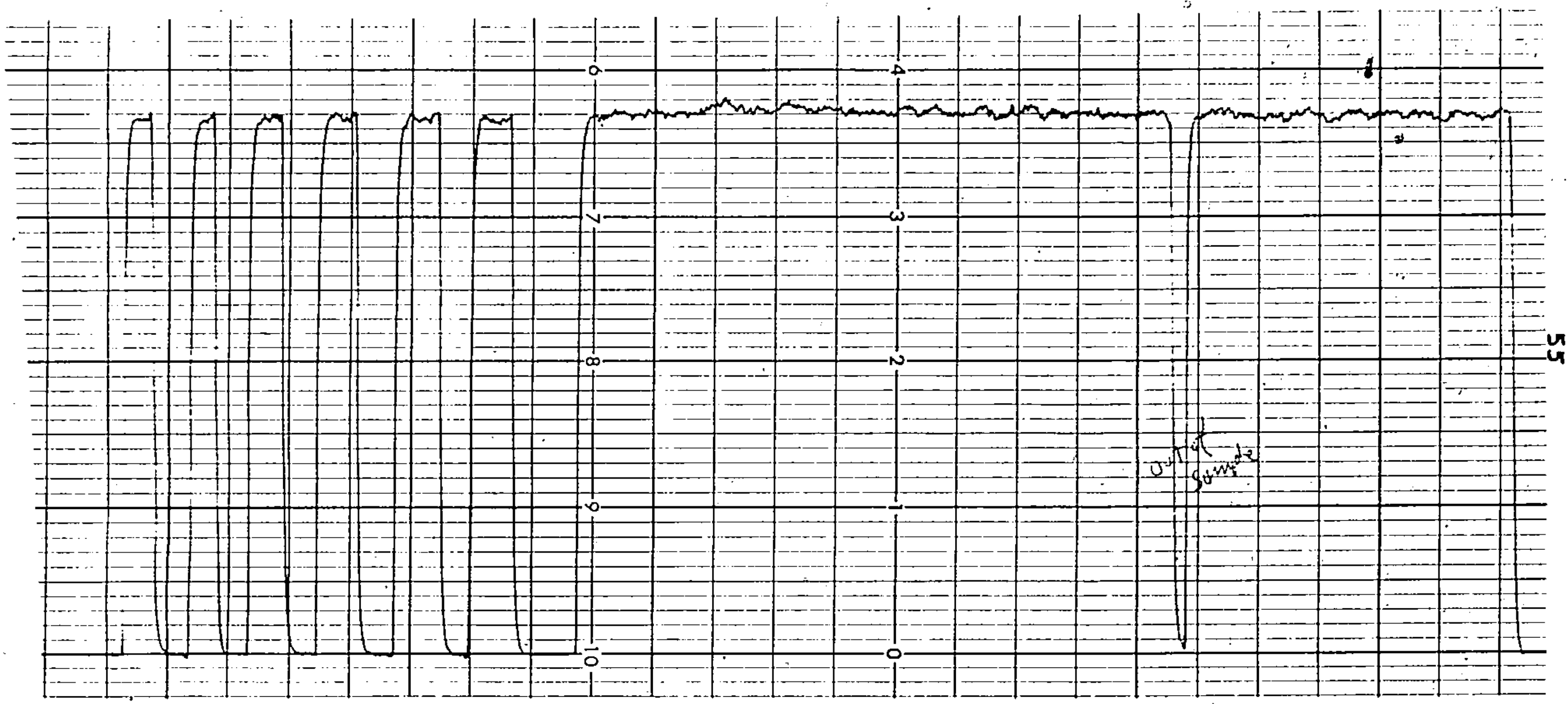


Fig. 14 Reproducibility and Stability plot for silicon by atomic absorption

TABLE 5

Summary of Comparison Parameters - Silicon

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.062	0.010	0.335	0.300
max. Sensitivity (ug/ml)	0.0265	–	0.0029	–
reproducibility				
mean (ug/ml)	11.08	–	36.65	–
standard deviation (ug/ml)	0.195	–	0.050	–
rel. Std. deviation (%)	1.760	–	.1036	–
stability				
drift (analogue units)	-0.8	–	+/- 0.6	–
noise (%)	2.8	–	0.5	–
noise level (ug/ml)	0.0564	–	0.0408	–

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 6

Standard Rock Sample Results - Silicon

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	-	-	70.92	68.78	-	-	-	-
% oxide (lit.)	67.54	67.54	69.90	69.90	67.10	67.10	54.50	54.50
% difference	-	-	1.5	1.6	-	-	-	-
std. dev.	-	-	1.0067	1.1441	-	-	-	-
rel. std. dev.	-	-	1.4195	1.6636	-	-	-	-
repetitions	-	-	12	12	-	-	-	-
dilution	-	-	10	10	-	-	-	-

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 7

Instrumental Parameters for Analysis - Silicon

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	251.612	-	7.5	-	-	10	3	norm	10-300
Atomic Absorp.	251.612	15	-	N_2O	red.	50	4	norm	20-500

(1) red. = reducing or fuel rich

TABLE 8

Wavelength, Dilution Factor and Standard Selection - Silicon

	Plasma Emission	Atomic Absorption
Standards required	10, 50	10, 50
dilution factor required	10	10
alternate wavelengths (in order of decreasing sensitivity)	251.612 nm	251.612 nm

TABLE 9

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Silicon

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	-	NS	-	-	-
F- test on variances of means (2)	-	NS	-	-	S

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level with plasma emission mean closer to rec. value.

(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

ALUMINUM

There are many lines, both ion and neutral atom, available for use in the analysis for aluminum. Several neutral atom lines for atomic absorption analysis, listed by Varian Techron (1972), were tested for relative signal strength, sensitivity and noise levels. Of these lines, 309.271 nm, 237.300 nm, 236.700 nm and 396.155 nm, only the 396 nm line is also recommended for use with argon plasma emission (Spectrametrics Inc., 1972). This line was found to be the most sensitive and least noisy neutral atom line tested. It was, therefore, the line used in this study for plasma emission. The recommended atomic absorption line at 309.271 nm was used with that method. Because of possible ionization of the aluminum in the solution, especially when using the plasma arc, several ion lines, listed in Meggers (1961), were tested. These lines, 226.917 nm, 281.620 nm, 390.068 nm and 466.680 nm all proved to be very insensitive to aluminum at the required concentrations (1-100 ug/ml) and were not used.

The standards prepared ranged from 1 ug Al/ml to 250 ug Al/ml but in practice, the standards used ranged from 1 ug/ml to 50 ug/ml. The calibration curves are linear within this range, with correlation coefficients between .99974 and .99996. This was true for both atomic absorption and plasma emission techniques.

A peculiarity of the line used with plasma emission was the negative reading obtained when air was aspirated between running the sample solutions and triple distilled water. This did not affect the sample readings and was due to the lower emission of air than water at this wavelength. This is probably due to differences in the plasma temperature (Mitchell, 1977).

No measurable spectral interference was noted from the major elements tested, even though there are several low intensity iron lines in the region of 396 nm (396.028 nm, 396.114 nm and 396.311 nm). No interference was found when a standard containing 80 ug Fe/ml was run. Chemical interference was not apparent when using either atomic absorption or plasma emission techniques.

Ionization interference was significant when running the rock sample solutions at full strength. Errors in accuracy were in the range of +35%. A trend appeared where the samples containing the greatest amount of potassium (NBS-70a) had the least error associated with them. This results from the potassium atom being more easily ionized than the aluminum atom, creating an excess of electrons in the arc or flame, suppressing the ionization of the aluminum. For plasma emission analysis, several measures were taken to try to reduce this interference including:

(1) reducing the plasma current from 7.5A

to 7.0A;

(2) using ion lines for the analysis;

(3) diluting the sample solutions by a factor of ten.

The current reduction lessened the ionization only slightly and as mentioned previously, the ion lines were too insensitive for use. The third measure taken, dilution, reduced the errors appreciably from 35% to less than 3%. This is due in part to the increased instrumental sensitivity caused by the higher photomultiplier gain necessary.

This ionization problem also occured, to a lesser extent, in the nitrous oxide-acetylene flame in the atomic absorption analysis, however, as the working range is narrower than with plasma emission, the solutions were being run at a ten-fold dilution from the start. Errors in accuracy were also less than 3%.

Tables 10 to 14 show the results obtained for sensitivity and detection limits for both atomic absorption and plasma emission. Typical calibration curves are shown in Figures 15 and 17. The detection limit determined by plasma emission of 0.086 ug/ml is over an order of magnitude lower than that determined by atomic absorption (0.204 ug/ml). The figure obtained by plasma emission is comparable to that obtained by Mitchell (1977). The optimum detection limit obtained by Spectrametrics Inc. (1972) under ideal operating conditions and using a better monochromator with signal integration is 0.01 ug/ml, less than an order of magnitude lower than that determined experimentally in this study.

The sensitivity values returned by plasma emission and atomic absorption methods are similar, ranging from 0.010 ug/ml to 0.018 ug/ml and 0.003 ug/ml to 0.010 ug/ml respectively. Emission techniques are generally more flexible than absorption as the gain can be varied to give the required sensitivity. This allows a more dynamic range and a closer control on the sensitivity.

Figures 16 and 18 show the stability and reproducibility of the signal for the two techniques. The lower relative standard deviation value for atomic absorption (0.726%) indicates that this method is somewhat more reproducible for aluminum than is plasma emission (2.504%). Statistically, the variance values for the two methods are significantly different at the 5% level. The stability plot shows that the drift is erratic for both methods but it is substantially less for atomic absorption. The noise levels follow the same pattern, with atomic absorption being much quieter (blank noise level = 0.0095 ug/ml and noise = 0.7%) than plasma emission (blank noise level = 0.3743 ug/ml and noise = 4.8%). In both cases the drift of the zero was negligible.

The accuracy of both methods is comparable with the greatest error being -3.1% for atomic absorption and -2.9%

for plasma emission (Table 15). All sample means showed good agreement with the literature values. BCR-1 has a recommended value of 13.61% Al_2O_3 while analysis by plasma emission returned a value of 13.81% and atomic absorption a value of 13.18%. GA gave values of 14.26% and 14.88% Al_2O_3 respectively against the recommended figure of 14.50% Al_2O_3. The analysis of NBS-70a gave excellent agreement with the literature value of 17.90% with 17.81% returned by plasma emission and 17.82% by atomic absorption. This sample also contained the greatest amount of potassium. The results for NSX-RP were identical by plasma emission and atomic absorption at 14.82% Al_2O_3 against a recommended figure of 15.27%. There is no clear significant difference between the means produced by the two methods (at the 5% level) as, of the four data sets, two sets had significantly different means while two sets gave means that were not significantly different. Because of this, neither technique proved to be significantly more accurate than the other.

The precision of these methods is also quite close, with relative standard deviations ranging from 0.5900% to 4.1400%. The tests on the variances of the means for the four sets of standard rocks indicated no clear difference between the two methods while the variances for the other set were not significantly different. Of those three data sets, plasma emission had the lower variance twice. As for the accuracy of the mean values, neither technique proved to be significantly more accurate than the other.

The remaining criteria for judging these methods is ease of analysis which includes:

(1) dilution factor required;
(2) linear working range available;
(3) noise;
(4) reproducibility.

In this respect, the number of dilutions required for each method was identical, both being diluted by a factor of ten; however the working range by plasma emission is greater, allowing a wider range of sample concentrations to be analysed without changing instrumental parameters. Plasma emission falls behind atomic absorption for aluminum analysis in both noise levels and reproducibility. The noise level for atomic absorption is nearly two orders of magnitude lower than that for plasma emission. This allows much easier reading of the analogue output and less error in interpreting the readings. The relative standard deviation of the readings over six repetitions for atomic absorption is three times less than that for plasma emission. This is significant as any one reading obtained by atomic absorption will probably be closer to the actual value than any one reading obtained by plasma emission.

On the basis of accuracy and precision, there is no significant difference between the two methods, however on the basis of ease of operation, noise and reproducibility, the use of the atomic absorption technique shows some advantages over the use of plasma emission in the routine analysis of rock samples for aluminum.

TABLE 10

Aluminum by Plasma Emission

Working Conditions

Wavelength 396.155 nm, Gain 12

Slit width 10 microns, Plasma Current used = 7.0 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
1	2.3	2.25
5	9.3	9.45
10	18.4	18.45
1	2.2	
5	9.6	
10	18.5	

THE SLOPE IS 1.8509

THE INTERCEPT IS 0.0485

THE CORRELATION COEFFICIENT IS .99975

THE SENSITIVITY IS 0.0185 ug/ml

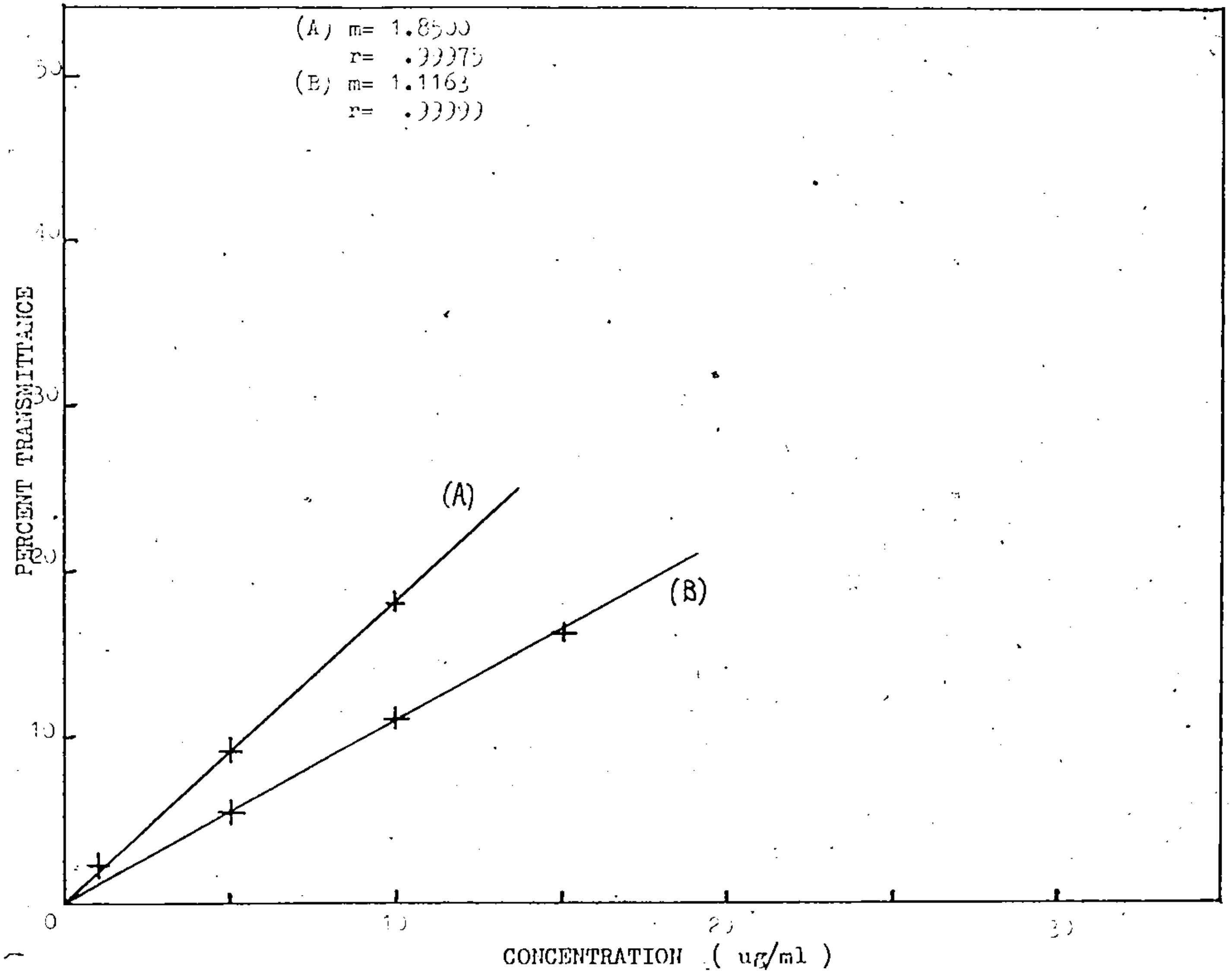


Fig. 15 Typical calibration curves for aluminum by plasma emission

TABLE 11

Detection Limit for Aluminum by Plasma Emission

****

Working Conditions

Wavelength 396.155 nm, Gain 12

Slit width 10 microns, Plasma current used = 7.0 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T
1	2.4
1	2.2
1	2.3
1	2.3
1	2.2
1	2.1
1	2.2
1	2.2
1	2.2
1	2.3

****

THE MEAN IS 2.24

THE STD. DEVIATION IS 0.08

THE SLOPE IS 1.8509

THE DETECTION LIMIT IS 0.0864 ug/ml

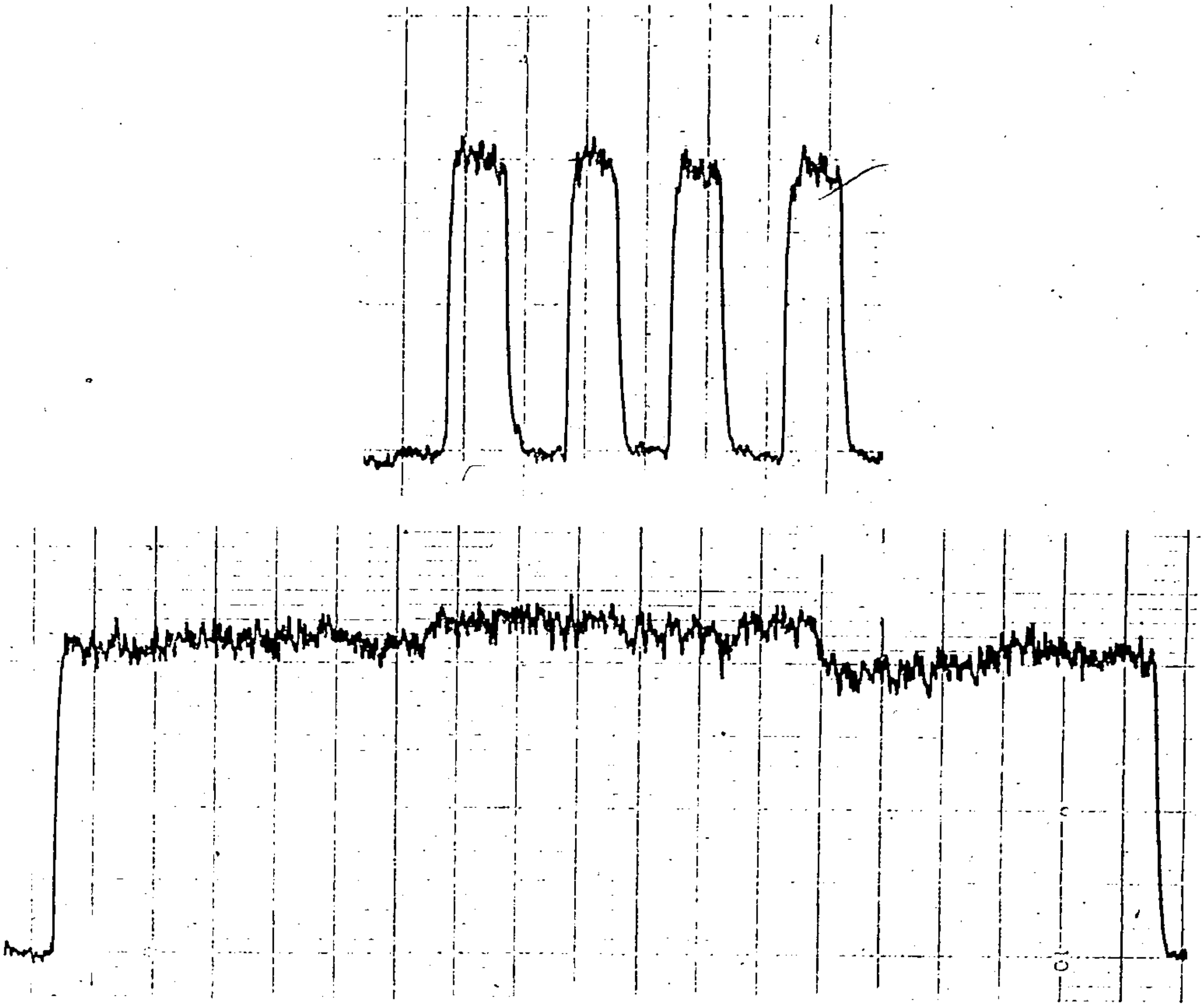


Fig. 16 Reproducibility and Stability plots for aluminum by plasma emission

TABLE 12

Aluminum by Atomic Absorption

****

Working Conditions

Wavelength 309.271 nm, Gain 1

Slit width 50 microns, Lamp current used = 10 mA

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
1	0.8	0.8
5	3.3	3.3
10	6.4	6.25
15	9.6	9.45
1	0.8	
5	3.3	
10	6.1	
15	9.3	

****

THE SLOPE IS 0.6289

THE INTERCEPT IS 0.0251

THE CORRELATION COEFFICIENT IS .99977

THE SENSITIVITY IS 0.0063 ug/ml

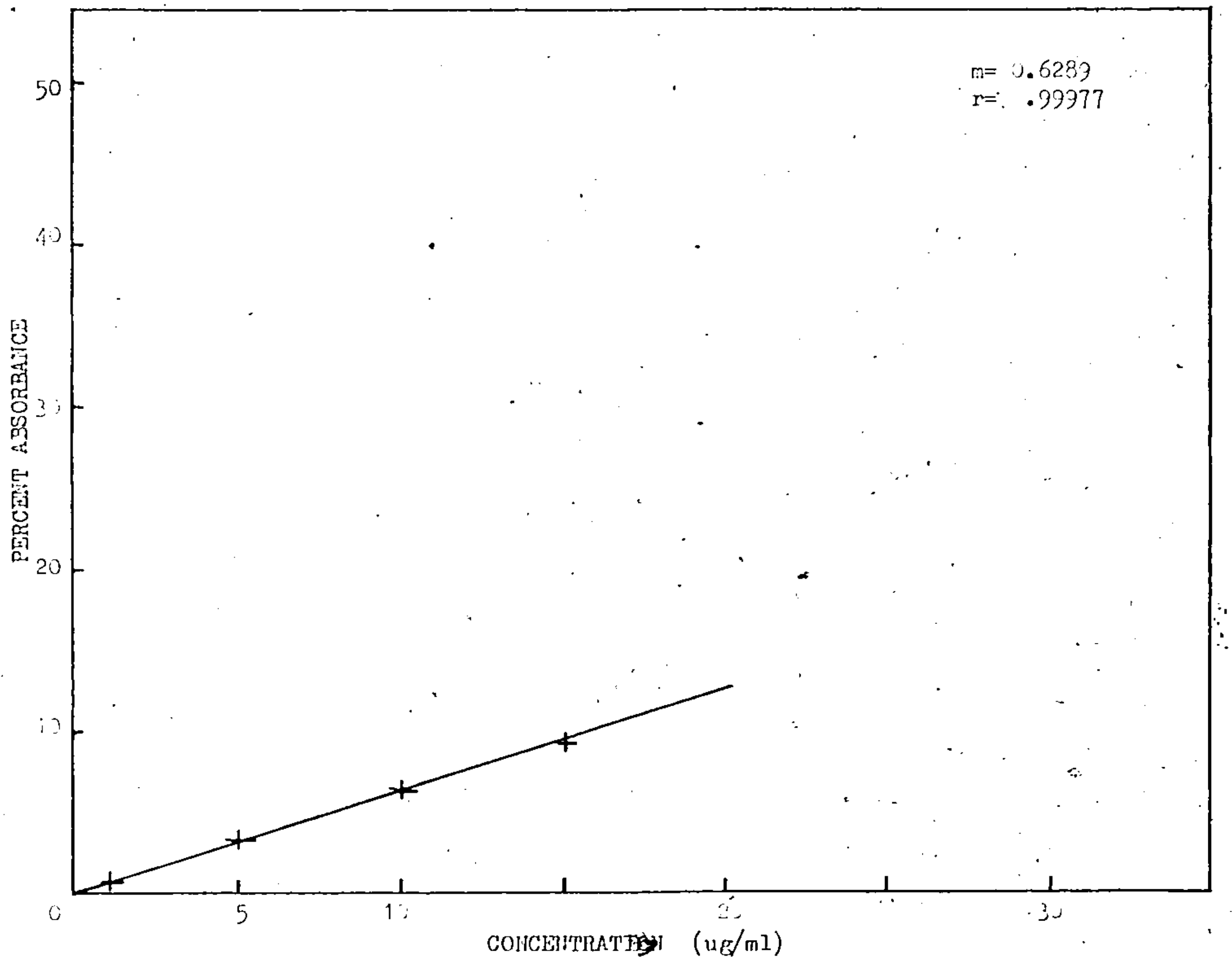


Fig. 17 Typical calibration curve for aluminum by atomic absorption

TABLE 13

Detection Limit for Aluminum by Atomic Absorption
****

Working Conditions

Wavelength 309.271 nm, Gain 1

Slit width 50 microns, Lamp current used = 10 mA

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
1	0.4
1	0.4
1	0.4
1	0.4
1	0.5
1	0.4
1	0.5
1	0.4
1	0.4
1	0.4

****

THE MEAN IS 0.42

THE STD. DEVIATION IS 0.040

THE SLOPE IS 0.3922

THE DETECTION LIMIT IS 0.2039 ug/ml

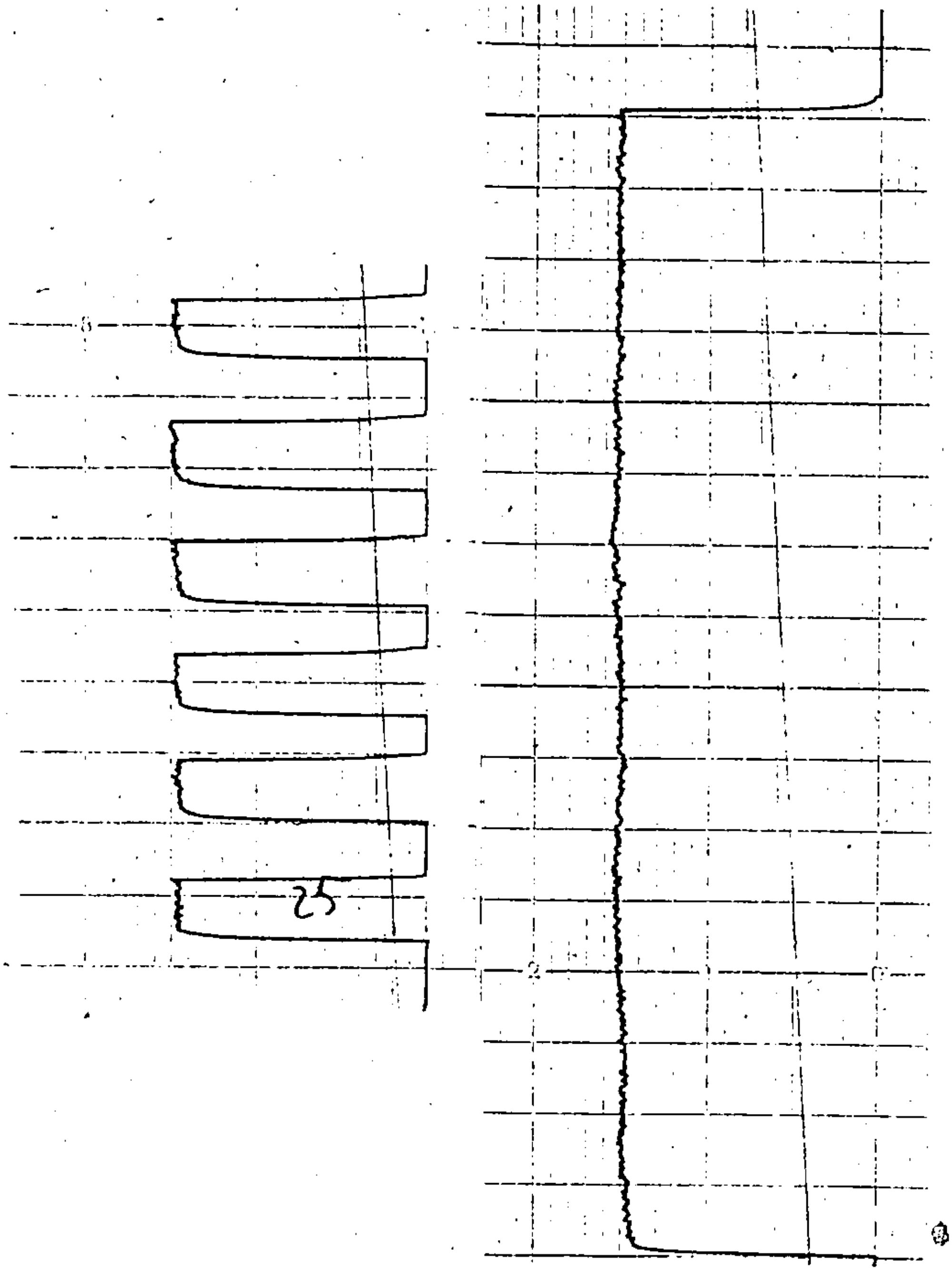


Fig. 18 Reproducibility and Stability plots for aluminum by atomic absorption

TABLE 14

Summary of Comparison Parameters - Aluminum

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.086	0.010	0.204	0.040
max. Sensitivity (ug/ml)	0.018	-	0.010	-
reproducibility				
mean (ug/ml)	20.41	-	14.68	-
standard deviation (ug/ml)	0.511	-	0.106	-
rel. std. deviation (%)	2.504	-	0.726	-
stability				
drift (analogue units)	+/-2.0	-	+/-0.3	-
noise (%)	4.8	-	0.7	-
noise level (ug/ml)	0.3743	-	0.0095	-

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 15

Standard Rock Sample Results - Aluminum

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	14.82	14.82	14.26	14.88	17.81	17.82	13.81	13.18
% oxide (lit.)	15.27	15.27	14.50	14.50	17.90	17.90	13.61	13.61
% difference	2.9	3.0	1.6	2.6	0.5	0.5	1.4	3.1
std. dev.	0.4791	0.6128	0.1430	0.2275	0.1059	0.1913	0.2176	0.1002
rel. std. dev.	3.2321	4.1364	1.0027	1.5288	0.5949	1.0738	1.5769	0.7600
repetitions	49	54	11	12	10	12	12	11
dilution	10	10	10	10	10	10	10	5

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA NBS-70a and BCR-1. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 16

Instrumental Parameters for Analysis - Aluminum

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	396.155	-	7.0	-	-	10	12	high	5-25
Atomic Absorp.	309.271	10	-	N_2O	red.	50	1	norm	10-100

(1) red. = reducing or fuel rich

TABLE 17

Wavelength, Dilution Factor and Standard Selection - Aluminum

	Plasma Emission	Atomic Absorption
standards required	5, 10, 15 ug/ml	5, 10, 15 ug/ml
dilution factor required	10	5, 10
alternate wavelengths (in order of decreasing sensitivity)	396.155 nm 394.403 309.271 308.216	309.271 nm 309.155 232.300 236.700

TABLE 18

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Aluminum

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	NS	S*	NS	S*	-
F- test on variances of means (2)	S*	NS	S*	S	S

(1) NS - means are <u>not</u> significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level, with plasma emission mean closer to rec. value.

(2) NS - variances are <u>not</u> significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

IRON

There are many resonance lines for iron due to its position in the periodic table as a transition element. Of these, only some of the neutral atom lines were practical to use with the plasma emission technique. These include lines at 371.994 nm and 373.713 nm. of which the 371 nm line was used. The 373 nm line was found to be less sensitive but would be excellent for solutions with high iron content. Several ion lines were tested but were found to be relatively insensitive at the concentrations of iron required (0.5 - 100 ug Fe/ml). These lines were 259.940 nm and 238.207 nm. The neutral atom line, 248.330 nm, was also tested and was found to be unsatisfactory for use with the plasma emission technique. That line, however, is the recommended line for use with atomic absorption (Varian Techron and was the one used for that purpose.

Iron standards were prepared ranging from 0.5 ug Fe/ml to 80 ug Fe/ml. These solutions were acidified as explained under experimental procedure. For use with atomic absorption, low concentration standards were used (0.5 - 4 ug/ml) while the higher concentration standards were used with plasma emission (20 - 80 ug/ml).

The calibration curves (Figures 19 and 21) are linear with correlation coefficients between .99984 and .99994 for both methods. No negative deflections at high concentrations were noted.

No interferences of any sort were noted except for a possibly chemical interference by the boric acid in the solution 'JA' dissolutions using plasma emission. This showed up in the blank that was also run and the appropriate corrections were made.

The results for sensitivity and detection limits are represented in Tables 19 to 23. The detection limit determined by atomic absorption was somewhat lower than that for plasma emission (0.013 ug/ml vs. 0.078 ug/ml respectively). Neither of these values were close to the optimum reported values of 0.005 ug/ml and 0.006 ug/ml (Varian Techron, 1972 and Spectrametrics, 1972).

This trend is evident in the values obtained for maximum sensitivity by the two methods. The figure by atomic absorption (0.0719 ug/ml) is about five times higher than that for plasma emission (0.0192 ug/ml). The range of sensitivities obtained using plasma emission was greater than that for atomic absorption, however, the maximum value did not approach that of atomic absorption.

The reproducibility data for the two methods are similar with respective relative standard deviations of 0.266% and 0.185%. Statistically, the variances of the means were not significantly different. In effect, the reproducibilities are identical with each data set having five identical readings and one reading 0.1 unit lower. This is shown by identical standard deviations, the low value of which indicates excellent reproducibility over six repetitions (Figures 20 and 22).

The plots for the stability runs (Figures 20 and 22) indicate near identical traces with noise of 0.9% and 0.5% for atomic absorption and plasma emission. Both traces had some erratic drift but show good stability. The blank noise levels are rather different, with atomic absorption being much quieter with a noise level of 0.0060 ug/ml against 0.1359 ug/ml for plasma emission. This is characteristic of emission analysis as both methods were run at the same gain.

The accuracy of both methods is comparable except at low concentrations of iron. The greatest difference from the literature values (with the preceding exception for NBS-70a) for atomic absorption was 5.0% for BCR-1 and 5.1% for plasma emission also for BCR-1. The literature value (Flanagan, 1973) is 13.40% Fe_2O_3 with atomic absorption and plasma emission values of 12.73% and 14.09%. All other values were closer to their respective recommended values. The results for GA for atomic absorption and plasma emission were both 2.80% Fe_2O_3 against the recommended 2.83% (or 1.1%). The results for NSX-RP were more spread out with an atomic absorption value of 3.89% Fe_2O_3 (-4.3%) and a plasma emission value of 4.17% (+2.5%) with a recommended figure of 4.07% Fe_2O_3: The results for NBS-70a were the furthest from the recommended value , however this is due to the very low concentration of iron in that sample (0.075% Fe_2O_3). Plasma emission was in good agreement with this figure returning 0.079% Fe_2O_3 (+5.3%) while the atomic absorption value was substantially higher than the recommended at 0.091% Fe_2O_3 or +21.3% high. This result is not unacceptable at this low concentration.

Statistically, plasma emission was a slightly more accurate method. Of the four data sets, two means were not significantly different (GA and NBS-70a) while the other two were significantly different. This is a bit misleading as the means by plasma emission and atomic absorption bracketed by the recommended value and were, in fact, not much different in absolute difference from that value (e.g., BCR-1). In view of this neither method proved to be significantly more accurate than the other.

The precision of the two methods is also quite close but the variances of the means for all data sets by atomic absorption were lower than those for plasma emission, with relative standard deviations ranging from 0.7725% to 2.7702% and 1.0401% to 6.9154% respectively (Table 24). This is borne out statistically with the variances for BCR-1 and GA by two techniques being not significantly different (at the 5% level). The variances for NBS-70a and NSX-RP for the two techniques were significantly different, with the atomic absorption variances being lower. This indicates that the atomic absorption technique is somewhat more precise than plasma emission in the analysis for iron.

The analysis for iron by plasma emission was more easily done than by atomic absorption as the wider dynamic range of the emission technique allowed all samples, with iron contents ranging from 0.075-13.40% Fe_2O_3, to be analysed without dilution. On the other hand, various dilutions had to be made when using atomic absorption (25X for BCR-1, 10X for GA and NSX-RP and nil for NBS-70a). Another problem when using atomic absorption was the erratic jump of the reading, on triple distilled water, from the 'auto-zero' zero reading prior to introducing the sample. This jump would vary from +1.0% Abs. to -0.7% Abs., creating difficulty in interpretation and some annoyance to the operator when running the samples. Apart from these factors, no other problems occured when running iron by either method.

This comparison of the two methods brought out three points for iron analysis. First, that atomic absorption has a greater maximum sensitivity and a lower detection limit but less flexibility than plasma emission, with little difference in stability and reproducibility. Second, that despite the above advantages for atomic absorption, the results by plasma emission at low concentrations of iron were better than those by atomic absorption. Third, that atomic absorption suffers from some minor but annoying problems affecting the ease of of analysis. Taking into account these factors, there is no no clear advantage for either method except that plasma emission can be favored by a slight margin due to its superior performance at low concentrations of iron.

TABLE 19

Iron by Plasma Emission

Working Conditions

Wavelength 371.994 nm, Gain 12

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	1.0	1.15
1	1.8	2.05
4	7.5	7.70
0.5	1.3	
1	2.3	
4	7.9	

THE SLOPE IS 1.9293

THE INTERCEPT IS 0.0262

THE CORRELATION COEFFICIENT IS .99961

THE SENSITIVITY IS 0.0192 ug/ml

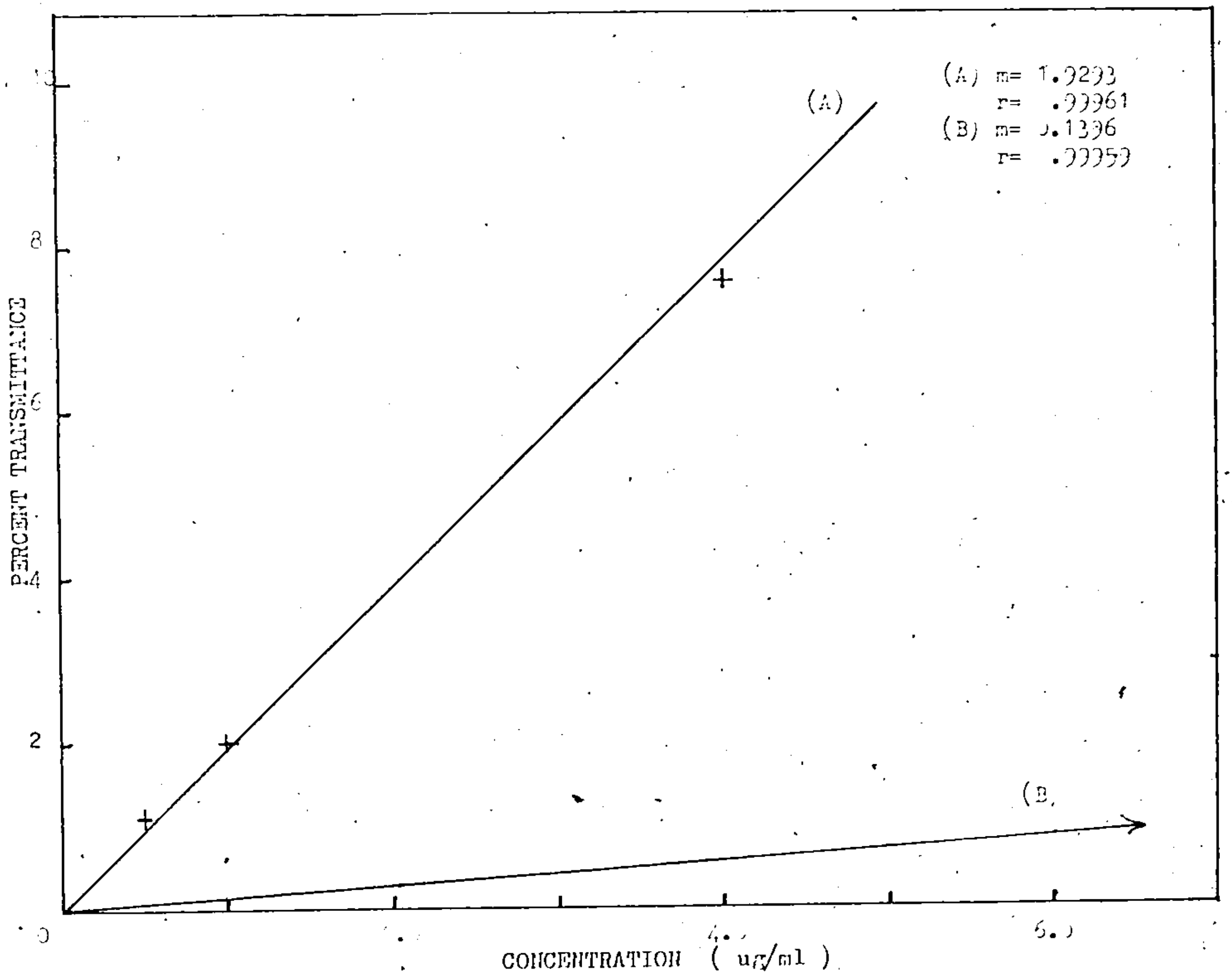


Fig. 19 Typical calibration curves for iron by plasma emission

TABLE 20

Detection Limit for Iron by Plasma Emission

Working Conditions

Wavelength 371.994 nm, Gain 12

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
Blank	0.3
	0.3
	0.2
	0.2
	0.1
	0.1
	0.3
	0.3
	0.2
	0.2

THE MEAN IS 0.22

THE STD. DEVIATION IS 0.0748

THE SLOPE IS 1.92993

THE DETECTION LIMIT IS 0.0775 ug/ml

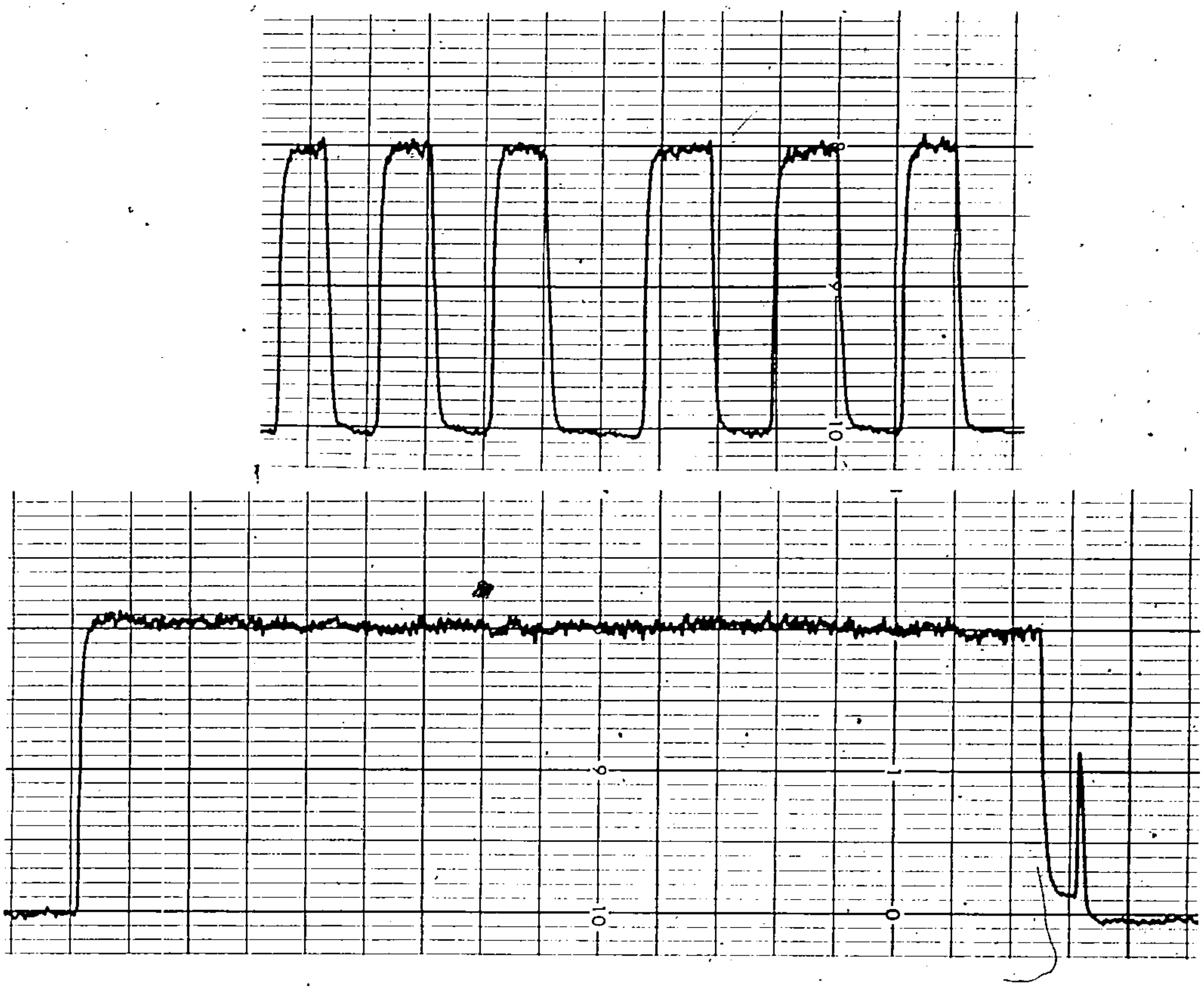


Fig. 20 Reproducibility and Stability plots for iron by plasma emission

TABLE 21

Iron by Atomic Absorption

Working Conditions

Wavelength 248.330 nm, Gain 13

Slit width 50 microns, Lamp current used 6 mA

Support gas used was air

Flame stoichiometry was oxidizing

Absorption mode

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
0.5	3.7	3.55
1	7.8	7.60
2	15.0	14.60
3	21.8	21.40
0.5	3.4	
1	7.2	
2	14.2	
3	21.0	

THE SLOPE IS 7.1943

THE INTERCEPT IS 0.0238

THE CORRELATION COEFFICIENT IS .99984

THE SENSITIVITY IS 0.0719 ug/ml

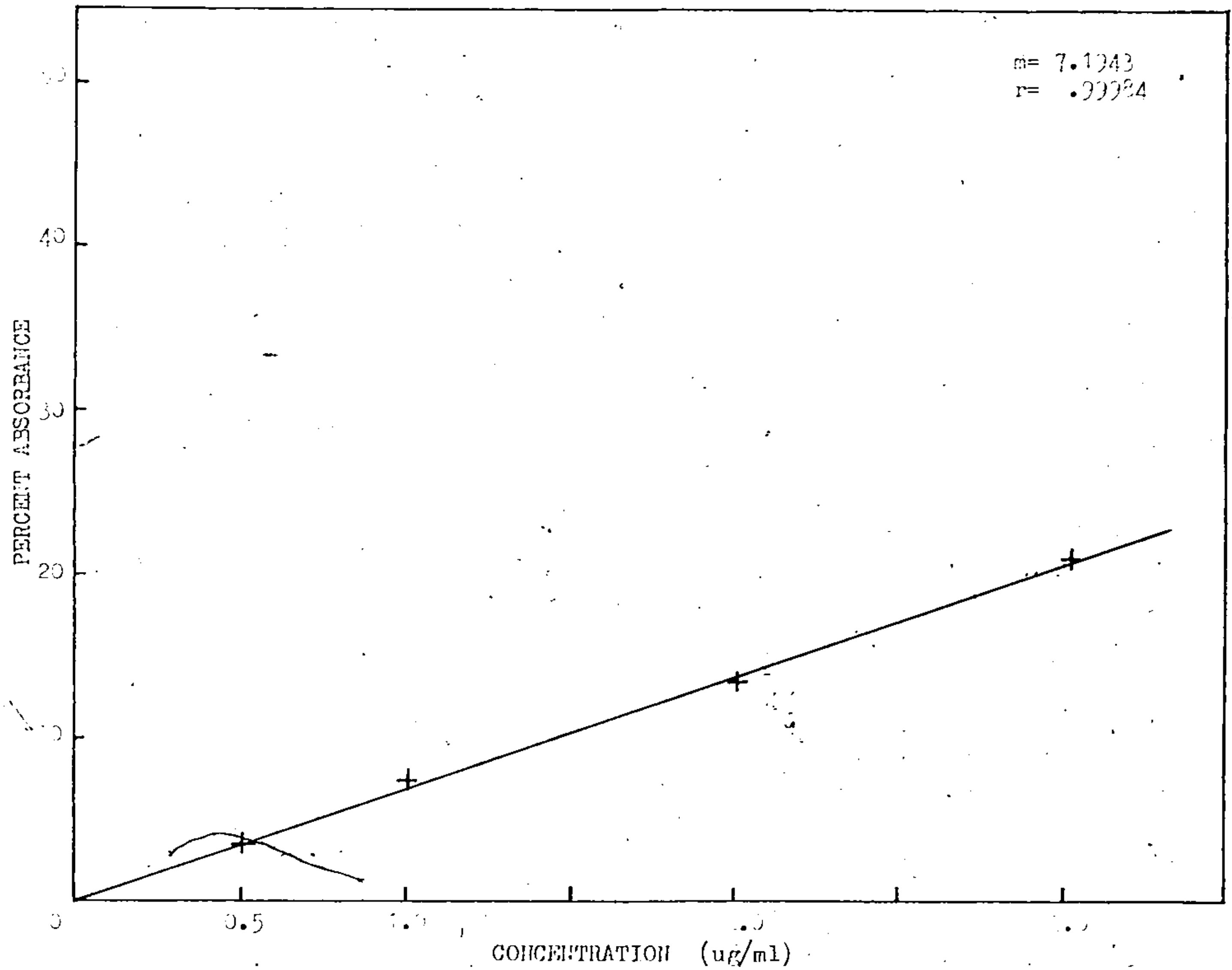


Fig. 21 Typical calibration curve for iron by atomic absorption.

TABLE 22

Detection Limit for Iron by Atomic Absorption

Working Conditions

Wavelength 248.330 nm, Gain 13

Slit width 50 microns, Lamp current used = 6 mA

Support gas used was air

Flame stoichiometry was oxidizing

Absorption mode

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
0.5	3.8
0.5	3.8
0.5	3.7
0.5	3.9
0.5	3.8
0.5	3.8
0.5	3.8
0.5	3.8
0.5	3.8
0.5	3.8

THE MEAN IS 3.80

THE STD. DEVIATION IS 0.0447

THE SLOPE IS 7.0382

THE DETECTION LIMIT IS 0.0127 ug/ml

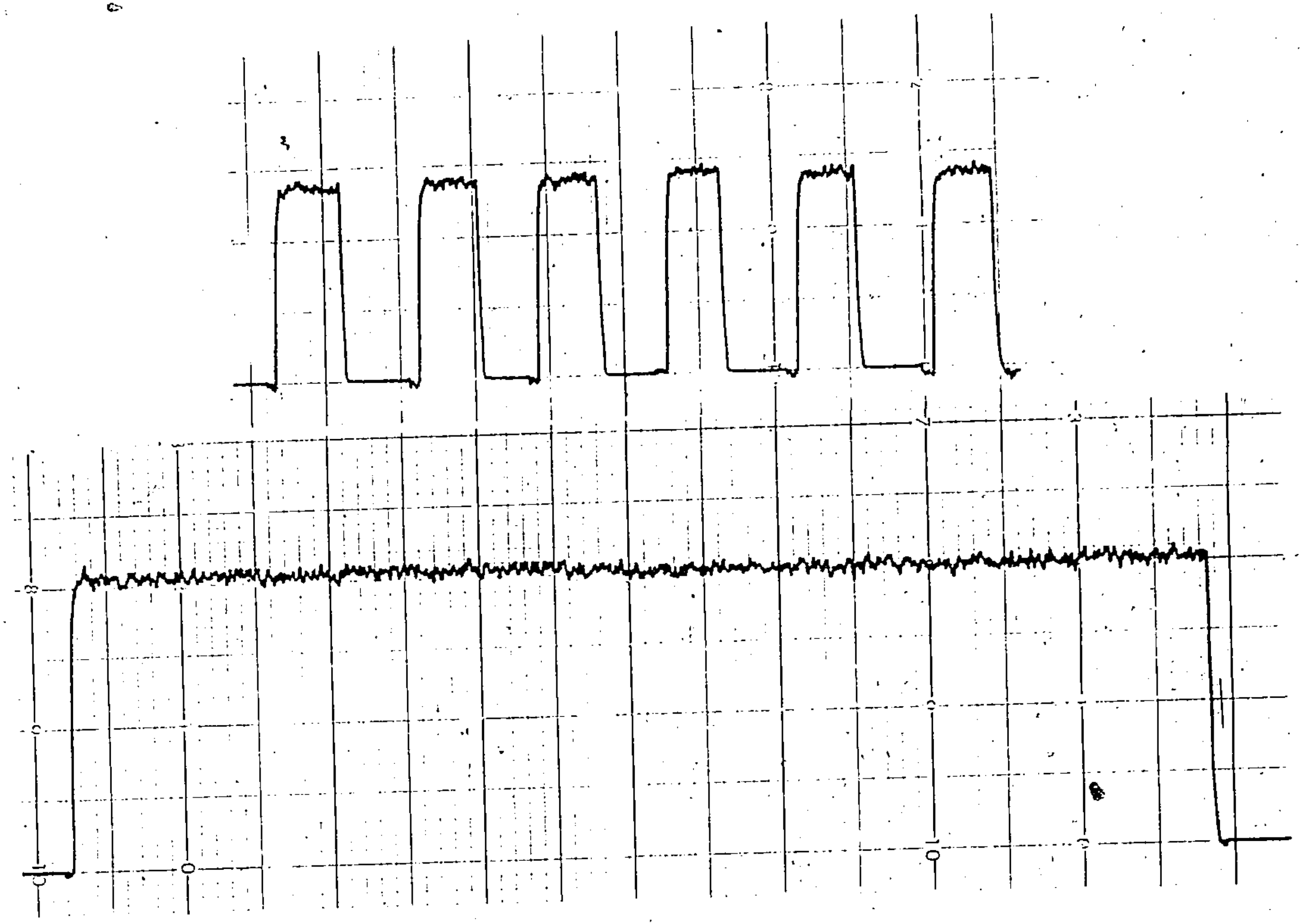


Fig. 22 Reproducibility and Stability plots for iron by atomic absorption

TABLE 23

Summary of Comparison Parameters - Iron

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.0775	0.006	0.0127	0.005
max. Sensitivity (ug/ml)	0.0192	-	0.0719	-
reproducibility				
mean (ug/ml)	20.08	-	13.98	-
standard deviation (ug/ml)	0.037	-	0.037	-
rel. std. deviation (%)	0.185	-	0.261	-
stability				
drift (analogue units)	+/-0.6	-	-0.4	-
noise (%)	1.5	-	1.9	-
noise level (ug/ml)	0.1359	-	0.0060	-

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 24 *

Standard Rock Samples Results - Iron

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	3.89	4.17	2.80	2.80	0.091	0.079	12.73	14.07
% oxide (lit.)	4.07	4.07	2.83	2.83	0.075	0.075	13.40	13.40
% difference	4.3	2.5	1.1	1.1	21.3	5.3	5.0	5.1
std. dev.	0.0310	0.0681	0.0222	0.0311	0.0025	0.0054	0.0983	0.1465
rel. std. dev.	0.7970	1.6347	0.7968	1.1149	2.7702	6.9154	0.7725	1.0401
repetitions	44	52	12	12	12	12	11	12
dilutions	10	nil	10	nil	nil	nil	25	nil

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA. NBS-70a and BCR-1. NSX-RP values are from A. Turek, personal communication, 1978.

* note that the headings 'Plasma' and 'Absorp.' are reversed in this table

TABLE 25

Instrumental Parameters for Analysis - Iron

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	371.994	-	7.5	-	-	10	12	high	1-40
Atomic Absorp.	249.330	6	-	air	oxid.	50	13	norm	2.5-10

(1) oxid. = oxidizing or fuel lean

TABLE 26

Wavelength, Dilution Factor and Standard Selection - Iron

	Plasma Emission	Atomic Absorption
standards required	0.5, 1, 4, 10, 20, 40	0.5, 1, 2, 3, 4
dilution factor required	nil	nil
alternate wavelengths (in order of decreasing sensitivity)	371.994 nm 373.713 259.940 238.207	248.330 nm

TABLE 27

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Iron

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	S*	NS	NS	S*	-
F- test on variances of means (2)	S	NS	S	NS	NS

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level with plasma emission mean closer to rec. value.

(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% level, with plasma emission variance lowest.

MANGANESE

There are only a few suitable wavelengths for use in the analysis for manganese by either atomic absorption or plasma emission. There is a choice of two lines using atomic absorption, 279.480 nm and 403.076 nm. Of these the 279 nm line is much more sensitive and was used in this study. For plasma emission, there are three suitable wavelengths, the two above and 403.449 nm. All these lines have similar sensitivities so the selection was based on noise levels. On this basis, the wavelength used with the plasma emission technique was 403.076 nm.

The standards, both prepared and used, ranged from 0.25 ug Mn/ml to 3.0 ug Mn/ml. This was sufficient to bracket all samples being run in this study. Using these standards, the calibration curves that were produced fitted the data points well with correlation coefficients between .99993 and .99999 for both methods. Typical calibration curves are given in Figures 23 and 25.

The only interferences noted using either atomic absorption or plasma emission were spectral. The most sensitive atomic absorption line (279.48 nm) is very close to a major magnesium ion line at 279.553 nm, as well as many low intensity iron lines in that region. The samples with a significant iron and magnesium content (BCR-1 with 13.40% Fe_2O_3 and 3.46% MgO) gave results that had a greater difference from the recommended value than did the other samples (+15% vs. +5%). This problem also occured using plasma emission at the 403.049 nm line as there is a major iron neutral atom line close by at 403.049 nm as well as several low intensity iron lines. This is apparent from the results for the two samples with the greatest iron content (BCR-1, 13.40% and NSX-RP, 4.07% Fe_2O_3), as they gave much greater differences from the recommended values than did the other samples (+52.8% and +36.6% vs. +15.6%). The 403.449 nm and the 279.48 nm lines also had iron lines nearby. The boric acid in the solution 'JA' again interfered as it did in the iron analysis, but to a greater extent.

The results obtained for detection limits are listed in Tables 29 and 31. The values for both atomic absorption (0.008 ug/ml) and for plasma emission (0.013 ug/ml) are approximately three times greater than the optimum reported values of 0.003 ug/ml and 0.005 ug/ml respectively. As indicated, the detection limit for atomic absorption is somewhat lower than for plasma emission. That trend is similar for the sensitivity values. The maximum sensitivity obtained by atomic absorption (0.1488 ug/ml) is about twice that by plasma emission (0.0719 ug/ml). Tables 28 and 30 illustrate these results.

As in the iron analysis, the reproducibility data for the two methods are similar with relative standard deviations of 0.662% for atomic absorption and 0.400% for plasma emission. The variances are not significantly different at the 5% significance level. Figures 24 and 26 are plots used in the reproducibility runs for manganese.

The data from the stability runs (Table 32) shows that the run by atomic absorption was more stable than that by plasma emission, with no drift, lower noise (2.1%) and a very low blank noise level of 0.0018 ug/ml. The result for plasma emission showed some erratic drift of +/-0.8 units, a mediochre blank noise level of 0.0563 ug/ml and a relatively high noise of 5.2%. Figures 24 and 26 indicate these results.

The atomic absorption method was significantly more accurate than the plasma emission method with two of the four data sets showing that the mean values by each method are significantly different and atomic absorption being closer to the recommended value. One sample (NBS-70a) contained negligible manganese and did not return any comparison data while the last data set (GA) indicated that the means were not significantly different. Even in this case the value by atomic absorption was 10% closer to the recommended value (5.6% vs. 15.6% by plasma emission). Atomic absorption returned a figure of 0.095% MnO on a recommended figure of 0.090% while the figure by plasma emission was 0.104% MnO. The results for BCR-1 were poor using either method due to the interferences mentioned earlier, with atomic absorption indicating

0.207% MnO (+15% difference) and plasma emission 0.275% (+52.8% difference) on a recommended value of 0.180%. Plasma emission did not detect any manganese at all in NBS-70a, however when using atomic absorption, one replicate gave a value of 0.002% MnO, while the other replicate did not indicate any. The results fo NSX-RP were good by atomic absorption but poor by plasma emission. Against a recommended value of 0.082% MnO, atomic absorption returned a value of 0.086% (4.9% difference) while plasma emission indicated 0.112% MnO or a 36.6% difference.

In all cases in this study, the precision in manganese analysis by the atomic absorption method was significantly different at the 5% level (and better) than that by the plasma emission method. The relative standard deviations (Table 33) for atomic absorption range from 0.5724% to 0.9692%, excepting the 104.4% value for NBS-70a which was due to the trace level of manganese in that sample. Values for plasma emission are all greater than the largest value by atomic absorption, ranging from 1.7255% to 4.5508%.

No problems occured using either method, except for the interferences that plagued both methods. The analysis for manganese by atomic absorption gave significantly more accurate and more precise results than did the analysis by plasma emission. The signal, using atomic absorption, was also more stable, less noisy and less prone to spectral interferences. Both the detection limit and maximum sensitivity values by atomic absorption were better than those delivered by plasma emission. As a result of the preceding, the analysis for manganese by atomic absorption is to be recommended over the use of the plasma emission technique.

TABLE 28

Manganese by Plasma Emission

****

Working Conditions

Wavelength 403.076 nm, Gain 8

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	3.6	3.55
1	7.5	7.20
2	14.2	14.40
0.5	3.5	
1	6.9	
2	14.6	

****

THE SLOPE IS 7.1978

THE INTERCEPT IS -0.0038

THE CORRELATION COEFFICIENT IS .99999

THE SENSITIVITY IS 0.0719 ug/ml

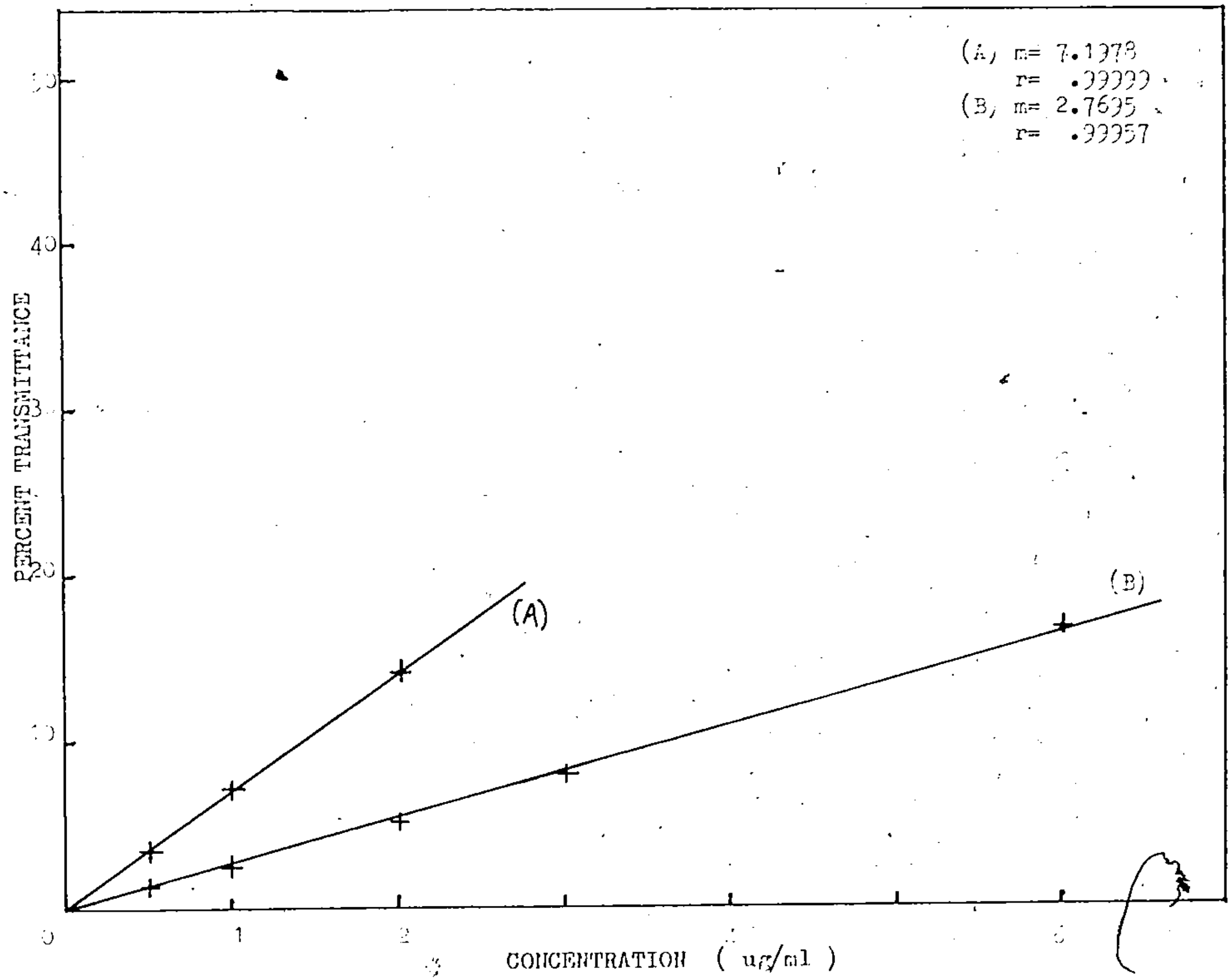


Fig. 23 Typical calibration curves for manganese by plasma emission

TABLE 29

Detection Limit for Manganese by Plasma Emission

****

Working Conditions

Wavelength 403.076 nm, Gain 8

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T
0.5	3.6
0.5	3.5
0.5	3.6
0.5	3.5
0.5	3.5
0.5	3.5
0.5	3.5
0.5	3.6
0.5	3.5
0.5	3.5

****

THE MEAN IS 3.53

THE STD. DEVIATION IS 0.0458

THE SLOPE IS 7.1978

THE DETECTION LIMIT IS 0.0127 ug/ml

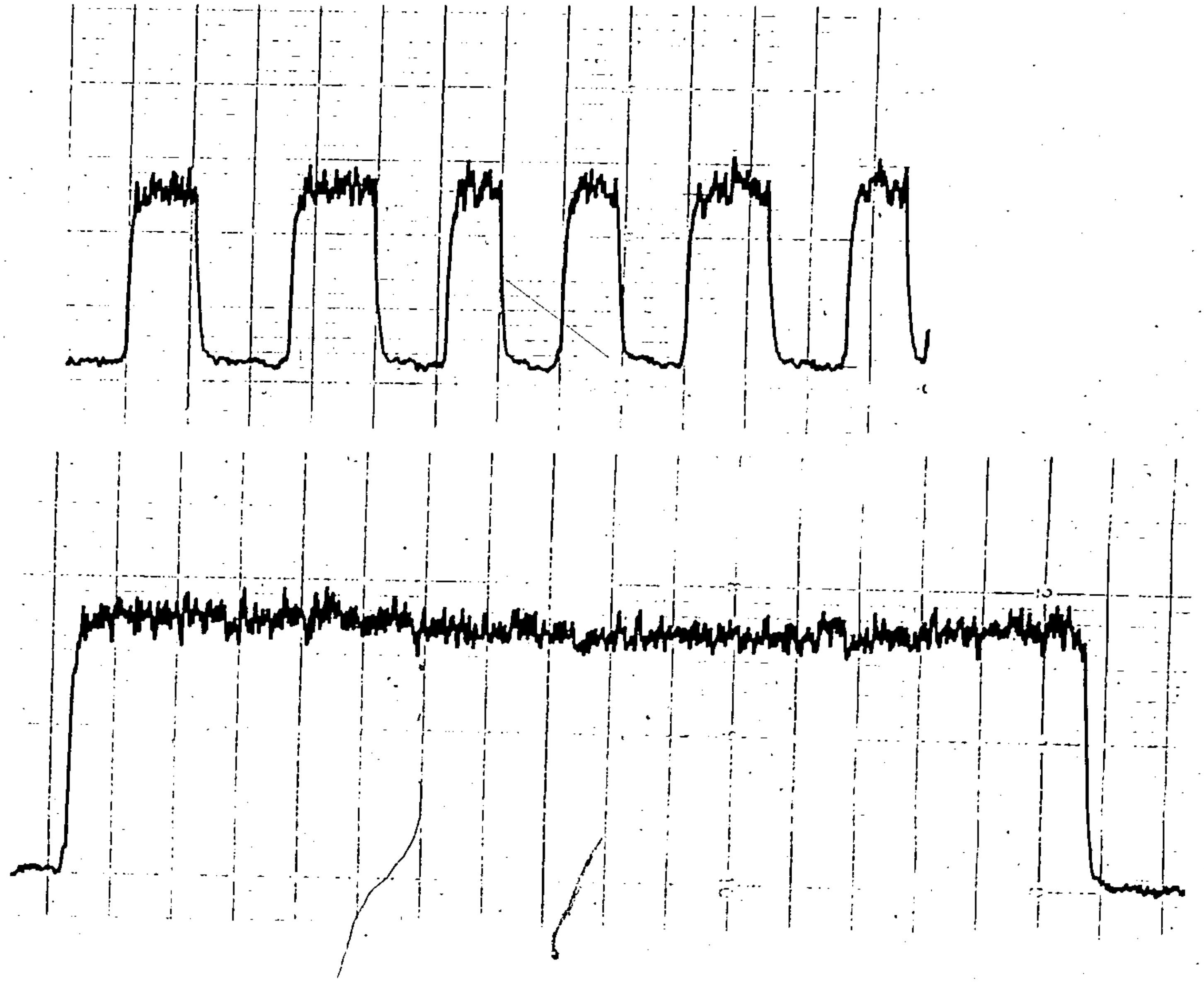


Fig. 24 Reproducibility and Stability plots for manganese by plasma emission

TABLE 30

Manganese by Atomic Absorption

****

Working Conditions

Wavelength 279.480 nm, Gain 6

Slit width 50 microns, Lamp current used = 5 mA

Support gas used was air

Flame stoichiometry was oxidizing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
0.25	4.0	3.95
0.50	7.6	7.45
1.0	15.1	14.90
0.25	3.9	
0.50	7.3	
1.0	14.7	

****

THE SLOPE IS 14.9197

THE INTERCEPT IS 0.0173

THE CORRELATION COEFFICIENT IS .99990

THE SENSITIVITY IS 0.1492 ug/ml

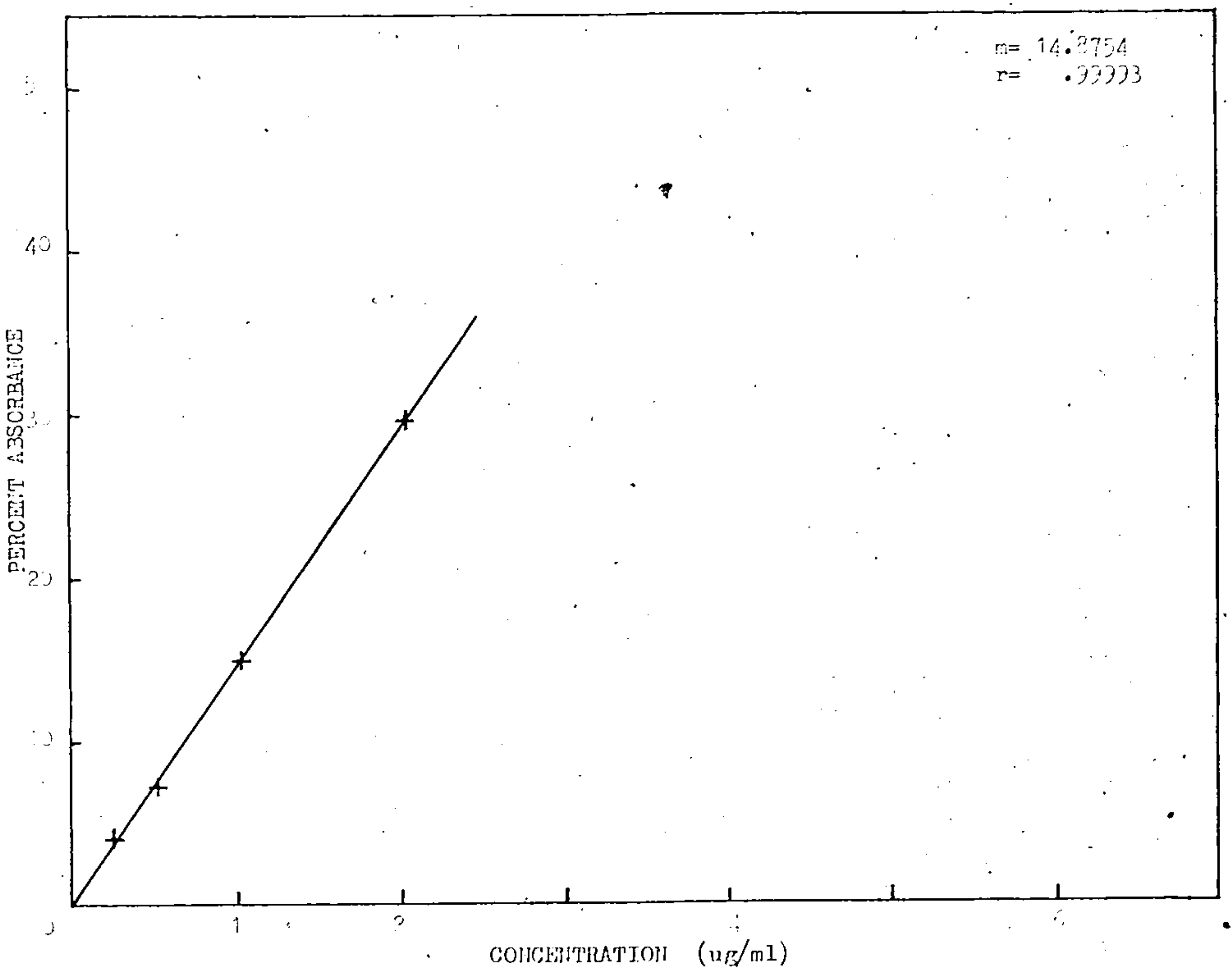


Fig. 25 Typical calibration curve for manganese by atomic absorption

TABLE 31

Detection Limit for Manganese by Atomic Absorption

Working Conditions

Wavelength 279.480 nm, Gain 6

Slit width 50 microns, Lamp current used = 5 mA

Support gas used was air

Flame stoichiometry was oxidizing

Absorption mode

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
0.25	4.0
0.25	3.8
0.25	3.9
0.25	3.9
0.25	3.8
0.25	3.9
0.25	3.9
0.25	3.9
0.25	3.8
0.25	3.9

THE MEAN IS 3.88

THE STD. DEVIATION IS 0.0600

THE SLOPE IS 14.4472

THE DETECTION LIMIT IS 0.0083 ug/ml

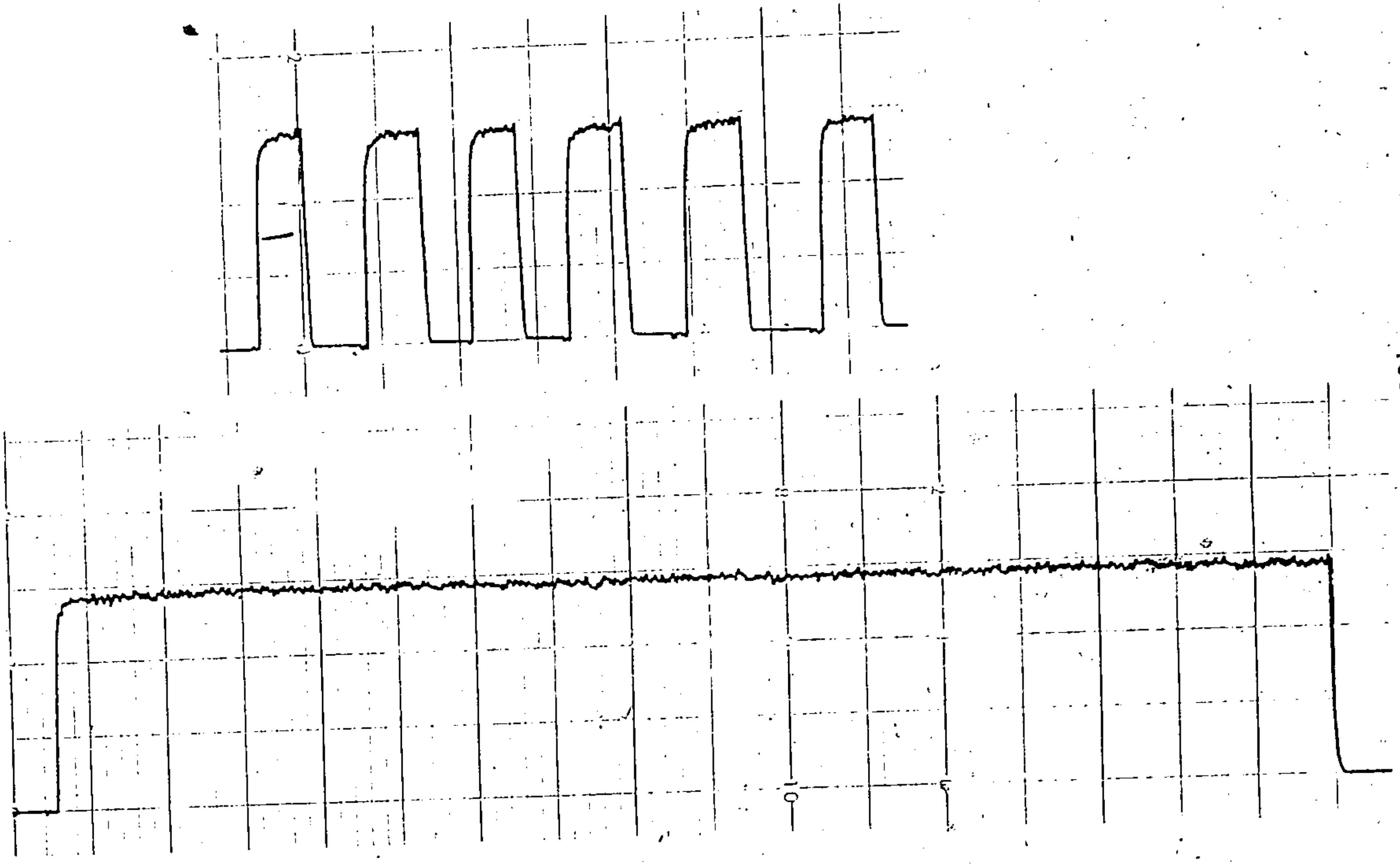


Fig. 26 Reproducibility and Stability plots for manganese by atomic absorption.

TABLE 32

Summary of Comparison Parameters - Manganese

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.0127	0.005	0.0083	0.003
max. Sensitivity (ug/ml)	0.0719	–	0.1492	–
reproducibility				
mean (ug/ml)	11.76	–	14.45	–
standard deviation (ug/ml)	0.047	–	0.095	–
rel. std. deviation (%)	0.400	–	0.662	–
stability				
drift (analogue units)	+/-0.8	–	nil	–
noise (%)	5.2	–	2.1	–
noise level (ug/ml)	0.0563	–	0.0018	–

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 33

Standard Rock Sample Results - Manganese

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	0.112	0.086	0.104	0.095	N/A	0.001	0.28	0.21
% oxide (lit.)	0.082	0.082	0.090	0.090	-	-	0.18	0.18
% difference	36.6	4.9	15.6	5.6	-	N/A	52.8	15.0
std. dev.	0.0026	0.0008	0.0047	0.0007	-	0.0010	0.0047	0.0011
rel. std. dev.	2.3681	0.9692	4.5508	0.8065	-	104.4000	1.7255	0.5724
repetitions	46	41	12	11	12	12	11	12
dilutions	nil	nil	nil	nil	nil	nil	nil	nil

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 34

Instrumental Parameters for Analysis - Manganese

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	403.076	-	7.5	-	-	10	8	high	0.25-10
Atomic Absorp.	279.480	5	-	air	oxid.	50	6	norm	1-4

(1) oxid. = oxidizing or fuel lean

TABLE 35

Wavelength, Dilution Factor and Standard Selection - Manganese

	Plasma Emission	Atomic Absorption
standards required	0.25, 0.5, 1, 2	0.25, 0.5, 1, 2
dilution factor required	nil	nil
alternate wavelengths (in order of decreasing sensitivity)	403.076 nm 279.480 403.449	279.480 nm 403.076

TABLE 36

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Manganese

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	S	NS	-	S	-
F- test on variances of means (2)	S	S	-	S	NS

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level, with plasma emission mean closer to rec. value.

(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% level, with plasma emission variance lowest.

TITANIUM

The recommended wavelength (Varian Techron, 1972) for titanium analysis by atomic absorption is 364.300 nm, and the strongest titanium line available for plasma emission (Spectrametrics, 1972) being 334.904 nm. The line at 337.280 nm can also be used with plasma emission when higher concentrations are to be measured (greater than 20 ug/ml). The response, using atomic absorption, at 364 nm was poor, not allowing samples with low concentrations of titanium to be analysed at all.

The standards prepared ranged from 1 to 30 ug Ti/ml. The response by atomic absorption was very poor as indicated by the calibration curve obtained from the standard solutions. The line of best fit did not fit the data points well with a correlation coefficient of only .99690 due to the slight flattening of the curve.. The standard containing 30 ug Ti/ml produced a maximum reading of only 4.8% Abs resulting in a low slope of 0.16. On the other hand, the response using the plasma arc was excellent. The correlation coefficient of this calibration curve was .99988, with a slope of nearly 5.0. This allowed the peaks given by a 10ug Ti/ml solution to be easily read (6.5% T). Typical calibration curves are represented in Figures 27 and 29.

Spectral interferences by all the major elements were checked for and no interference was noted. This is despite the presence of minor iron, calcium and manganese lines in the vicinity of 364 nm. There were also no apparent chemical or ionization interferences present.

Tables 37 to 41 show the results obtained for sensitivity and detection limits for both atomic absorption and plasma emission. The detection limit obtained by using the plasma arc is 1.5 orders of magnitude lower than that for atomic absorption (0.020 ug/ml vs. 0.667 ug/ml). Both of these values are approximately five times greater than their respective optimum values of 0.005 ug/ml and 0.100 ug/ml (Spectrametrics Inc., 1972 and Varian Techron, 1972).

The sensitivity values are similarily much different, with the maximum figure returned by atomic absorption being 0.0016 ug/ml as compared to the 0.0495 ug/ml figure of plasma emission; again a difference of 1.5 orders of magnitude. The lowest sensitivity for plasma emission, at low gain, was 0.0068 ug/ml which is still four times that of the maximum value given by atomic absorption. The flexibility, due to the better gain control, when using the emission method has much to do with this advantage. The main factor is the high arc temperature which allows the excitation of enough titanium atoms to produce sufficient emitted radiation, as they return to the ground state, to realize a relatively high sensitivity.

The stability of the signal using plasma emission was fair with noise in the region of 5.1%, with the noise using atomic absorption being lower at 1.0%. This is due to the very low response by atomic absorption where a stability run using a 30 ug/ml standard averaged only 4.8% Abs (Figure 30). At this level, little noise is expected and the blank noise levels are comparable but with plasma emission being somewhat quieter (0.0597 ug/ml vs. 0.0653 ug/ml). This can be attributed to the relatively high gain necessary, using atomic absorption, to give a sufficiently strong signal.

Results by plasma emission were also somewhat more reproducible than those by atomic absorption over six repetitions with respective relative standard deviations of 0.5870% and 0.8787%. These results were not significantly different statistically at the 5% significance level. The higher figure for atomic absorption can be explained by the high gain necessary to get the readings. This tends to accentuate any fluctuations present in the input to the amplifier.

In terms of accuracy, there is little comparison between the results. No dilutions were required by either technique but the atomic absorption method did not have sufficient energy intensity to produce enough signal to give accurate readings (very low sensitivity). These results ranged from 105% to 145% high as compared to the recommended values. This was partially due to the low peak height giving difficulty in interpretation. A change in peak height of 0.1% Abs resulted in a very much greater change in the value for the concentration of titanium in the solution (about 6.3 ug/ml). In contrast to this, the results by plasma emission were quite accurate with a maximum difference, from the literature values, of 7.9%, which for a minor element is excellent. The statistics for the four sets of standard samples show that the means by the plasma emission method are all significantly different than those by atomic absorption (at the 5% level).

For the same reasons as above, the precision of the atomic absorption results was poor, with relative standard deviations ranging from 6.52% to 10.35%. The precision by plasma emission was good, especially as compared to atomic absorption, with relative standard deviations from 1.69% to 2.60%. Statistically, all four sets of data showed that the variance values generated by the plasma emission technique were significantly different (at the 5% level) and more precise than those generated by the atomic absorption method.

Normally in rapid rock analysis schemes titanium is determined spectrophotometrically with rocks dissolved in the usual manner (0.5 g to 500 ml) containing approximately 3 to 10 ug/ml Ti in solution, while by atomic absorption at the most sensitive line, the optimum titanium concentration for analysis is between 60 to 240 ug/ml (Varian Techron, 1972). Some laboratories do determine titanium by atomic absorption, however the solutions have to be concentrated by evaporation, a tedious procedure.

In summary, the atomic absorption method is too insensitive to be useful for analysis at these low concentrations of titanium. As the reproducibility statistics indicate that the two techniques are not significantly different in that regard, the atomic absorption method would probably be more useful at higher concentrations of titanium than indicated here. At the low levels required in most major element rock analysis, the argon plasma emission technique gives reliable results and must be recommended.

TABLE 37

Titanium by Plasma Emission

Working Conditions

Wavelength 334.903 nm, Gain 9

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
1	6.4	6.45
5	24.2	24.65
1	6.5	
5	25.1	

THE SLOPE IS 4.9571

THE INTERCEPT IS 0.1357

THE CORRELATION COEFFICIENT IS .99813

THE SENSITIVITY IS 0.0495 ug/ml

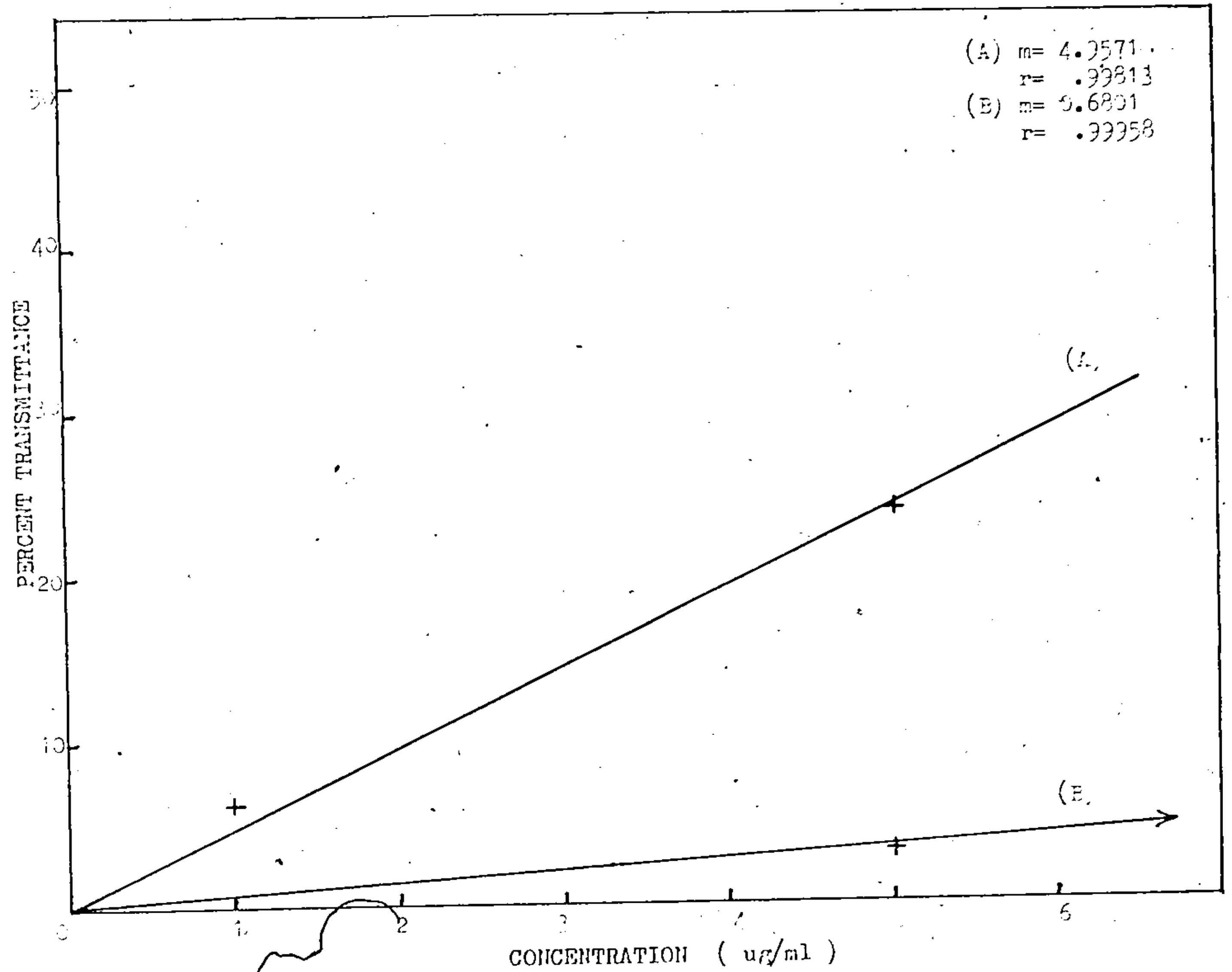


Fig. 27 Typical calibration curves for titanium by plasma emission

TABLE 38

Detection Limit for Titanium by Plasma Emission

****

Working Conditions

Wavelength 334.903 nm, Gain 9

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T
1	6.5
1	6.5
1	6.4
1	6.5
1	6.5
1	6.5
1	6.4
1	6.4
1	6.5
1	6.4

****

THE MEAN IS 6.46

THE STD. DEVIATION IS 0.0489

THE SLOPE IS 4.9571

THE DETECTION LIMIT IS 0.0197 ug/ml

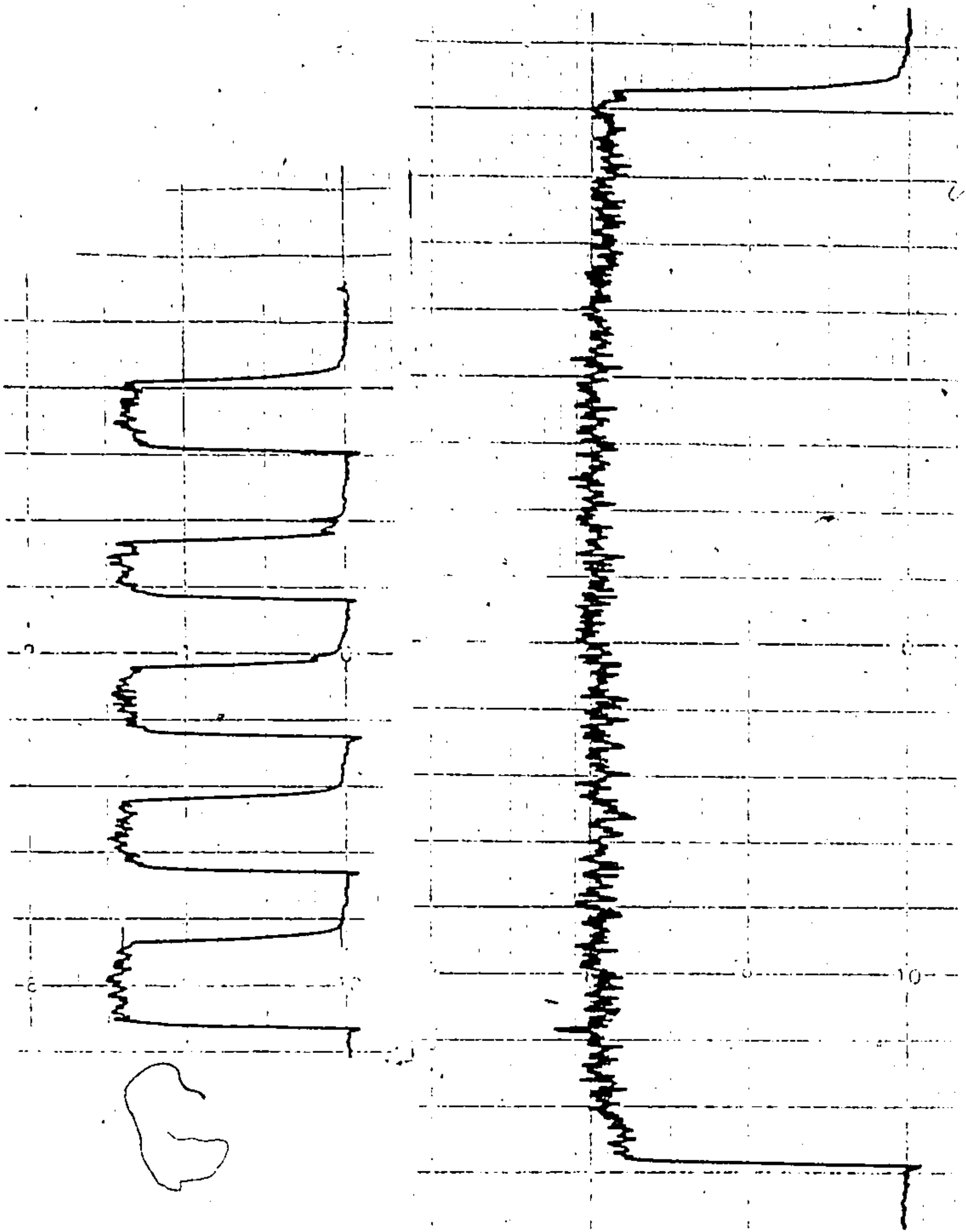


Fig. 28 Reproducibility and Stability plots for titanium by plasma emission

TABLE 39

Titanium by Atomic Absorption

Working Conditions

Wavelength 363.300 nm, Gain 1

Slit width 50 microns, Lamp current used = 18 mA

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Absorption mode

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
1	0.2	0.2
5	1.1	1.15
10	1.8	1.9
20	3.3	3.3
30	4.7	4.75
1	0.2	
5	1.2	
10	2.0	
20	3.3	
30	4.8	

THE SLOPE IS 0.1614

THE INTERCEPT IS 0.0497

THE CORRELATION COEFFICIENT IS .99680

THE SENSITIVITY IS 0.0016 ug/ml

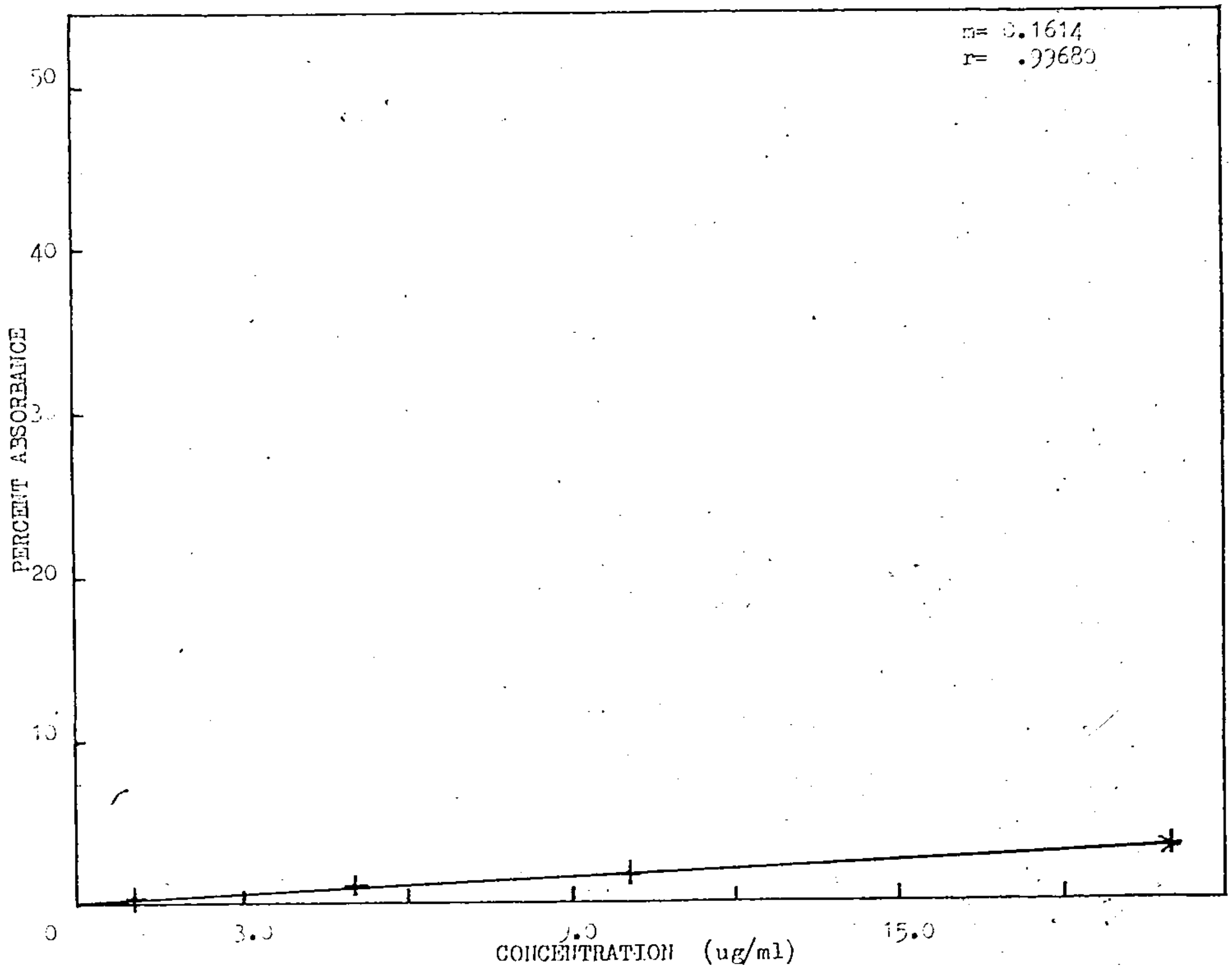


Fig. 29 Typical calibration curve for titanium by atomic absorption

TABLE 40

Detection Limit for Titanium by Atomic Absorption

****

Working Conditions

Wavelength 363.300 nm, Gain 1

Slit width 50 microns, Lamp current used = 18mA

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
1	0.1
1	0.3
1	0.2
1	0.2
1	0.2
1	0.3
1	0.2
1	0.2
1	0.2
1	0.2

****

THE MEAN IS 0.21

THE STD. DEVIATION IS 0.0538

THE SLOPE IS 0.1614

THE DETECTION LIMIT IS 0.6673 ug/ml

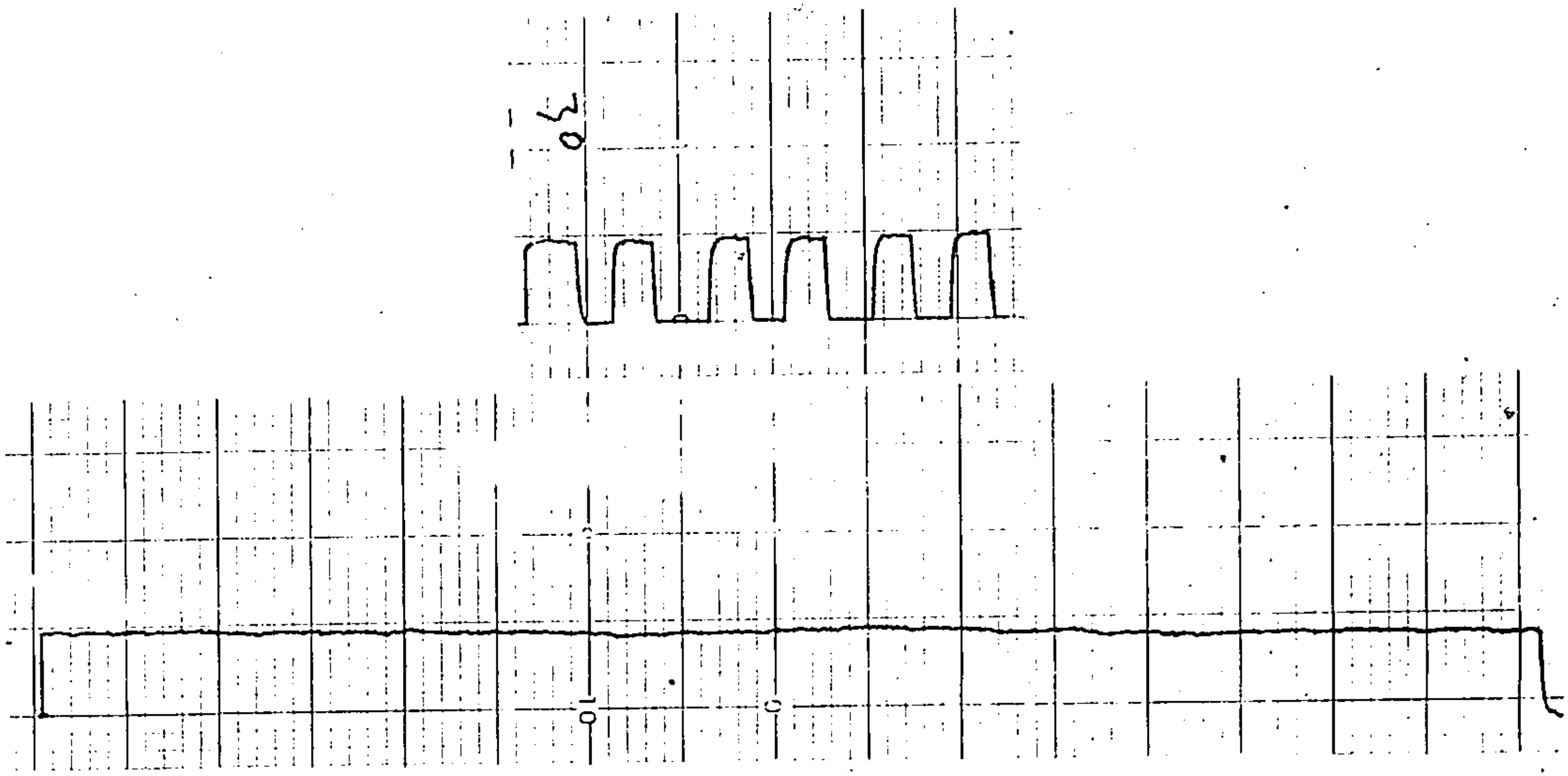


Fig. 30 Reproducibility and Stability plots for titanium by atomic absorption

TABLE 41

Summary of Comparison Parameters - Titanium

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.0197	0.005	0.6673	0.1000
max. Sensitivity (ug/ml)	0.0144	−	0.0016	−
reproducibility				
mean (ug/ml)	13.80	−	4.78	−
standard deviation (ug/ml)	0.081	−	0.037	−
rel. std. deviation (%)	0.591	−	0.779	−
stability				
drift (analogue units)	+/-1.0	−	+/-0.1	−
noise (%)	5.1	−	1.0	−
noise level (ug/ml)	0.0597	−	0.0653	−

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 42

Standard Rock Sample Results - Titanium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	0.615	1.301	0.407	0.778	ND	ND	2.095	4.615
% oxide (lit.)	0.57	0.57	0.38	0.38	0.01	0.01	2.20	2.20
% difference	7.9	128.2	7.1	104.7	-	-	4.8	109.8
std. dev.	0.0131	0.0849	0.0087	0.0719	-	-	0.0354	0.3488
rel. std. dev.	2.1329	6.5273	2.1555	9.2350	-	-	1.6937	7.5585
repetitions	51	52	12	13	12	12	12	12
dilution	nil	nil	nil	nil	nil	nil	nil	nil

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 43

Instrumental Parameters for Analysis - Titanium

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	334.903	-	7.5	-	-	10	9	high	0.5-100
Atomic Absorp.	363.300	18	-	N_2O	red.	50	1	norm	35-150

(1) red. = reducing or fuel rich

TABLE 44

Wavelength, Dilution Factor and Standard Selection - Titanium

	Plasma Emission	Atomic Absorption
standards required	1, 5, 10 ug/ml	1, 5, 10, 20, 30+ ug/ml
dilution factor required	nil	nil
alternate wavelengths (in order of decreasing sensitivity)	334.903nm 334.941 337.280 361.213	364.300nm 365.400 399.000

TABLE 45

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Titanium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t-test on means (1)	S*	S*	-	S*	-
F-test on variances of means (2)	S*	S*	-	S*	NS

(1) NS - means are not significantly different at 5% significance level.

S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.

S* - means are significantly different at 5% significance level with plasma emission mean closer to rec. value.

(2) NS - variances are not significantly different at 5% significance level.

S - variances are significantly different at 5% significance level, with atomic absorption variance lowest.

S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

CALCIUM

Calcium has been determined by three methods - atomic absorption, atomic or flame emission and plasma emission. The first two use a flame as the excitation source while the third uses the argon plasma arc. The instrumentation for atomic absorption and atomic emission is nearly identical and only requires the removal of the lamp turret from use and the addition of a chopper to change to atomic emission. The neutral atom wavelength recommended for both flame techniques is 422.700 nm with a less sensitive alternate for absorption at 239.900 nm. There are three wavelengths available for use with the plasma emission technique - 422.700 nm plus two ion lines - 393.367 nm and 396.847 nm. All three were similar in sensitivity, however, the 422 nm line showed a strong negative deviation on its calibration curve past 40 ug Ca/ml. Both the ion lines gave excellent linear curves past 100 ug/ml, with the 393 nm line being slightly more sensitive than the other and therefore the line used with the plasma emission technique.

Standards were prepared to test the working ranges of the methods. These standards ranged from 0.5 ug Ca/ml to 100 ug Ca/ml. In practice, while full strength solutions could be used with both emission methods, the best results were obtained when running the solutions diluted to between 0.5 ug Ca/ml and 3.0 ug Ca/ml. Correlation coefficients were numerically a little lower for atomic absorption than for the other methods, at .99959 as compared to .99999 for plasma emission and .99982 for atomic emission. These curves are illustrated in Figures 31, 33 and 35.

Interferences were noticable when using all three methods. Aluminum, sodium and potassium were common major interferants for these methods. This was very apparent in the results for sample NBS-70a. This sample has the highest aluminum and potassium content and the lowest calcium content of all the samples tested. These interferences caused differences between the experimental value and the recommended value to range from +39.1% to +194.5%. This trend was further documented by the results for BCR-1, with the lowest aluminum and potassium and the highest calcium content, which showed the lowest difference from the literature values. The only other interference occured when using the atomic absorption method where iron caused a slight signal enhancement.

The results for detection limits, illustrated in Tables 47, 49 and 51, show that the emission techniques have lower detection limits (by a factor of 10) than for atomic absorption. The flame emission method was the lowest at 0.0011 ug/ml with plasma emission close at 0.0019 ug/ml. Atomic absorption was rather higher at 0.0176 ug/ml. The optimum detection limits for these methods are 0.0005 ug/ml for the flame methods (Varian Techron, 1972), and 0.0007 ug/ml for plasma emission (Spectrametrics Inc., 1972). Only the emission experimental values are within a factor of five of the reported optimum values.

This trend is also true for the sensitivity figures (Tables 46, 48 and 50) with the emission maximum sensitivities in the region around 1.0 ug/ml (flame, 1.5219 ug/ml and plasma, 0.9359 ug/ml) and the figure for atomic absorption being much lower at 0.1140 ug/ml.

The reproducibility data for the three techniques are similar, with relative standard deviations for flame and plasma emission and atomic absorption data being 0.482%, 0.698% and 0.471%. Statistically, there is no significant difference, at the 5% level, between any of the variances on the mean values obtained by these methods. Sample plots are illustrated in Figures 32, 34 and 36.

This trend is true also for the stability data, with none of the methods having much drift from the mean over 6-8 minutes and little noise. The noise values for these methods are 1.2%, 2.7% and 2.2% for atomic and plasma emission and atomic absorption. The blank noise levels by the emission techniques are similar with 0.0015 ug/ml for flame and 0.0040 for plasma. The figure for atomic absorption is lower (0.0005 ug/ml) due to the low gain needed to get a maximum signal. All these noise values are low and indicate that all the methods tested are quiet with very good stability.

In terms of accuracy, values obtained by all three methods were poor. The samples with the greatest calcium content with respect to the interfering elements, aluminum, sodium and potassium, gave the closest results to the recommended figures. The results by these methods are listed in Tables 53a to 53c and summarized here. BCR-1 gave 7.56% CaO, 6.98% and 7.43% for flame and plasma emission and atomic absorption against a recommended value of 6.92% CaO. This corresponds to +9.2%, +0.9% and +7.4% differences from that value. The results for both GA and NSX-RP are intermediate in accuracy with respect to BCR-1 and NBS-70a. The experimental CaO contents for GA, against a recommended value of 2.45% CaO, were 3.17% (+29.6% difference), 2.80% (+14.3%) and 2.99% (+22.0%). CaO contents for NSX-RP, against a recommended figure of 2.10% CaO, were 2.56% (+21.9% difference), 2.53% (+20.5%) and 2.65% (+26.2%). The rather poor results for the CaO content of NBS-70a by flame and plasma emission and atomic absorption were as follows; 0.17% CaO (+50.9% difference), 0.32% (+194.5%) and 0.15% (+39.1%). In general, the plasma emission values were closer to the literature values for these samples, with the exception of NBS-70a, than were the results by either of the flame methods. The values by atomic absorption were usually closer than the atomic emission values by several percent. Statistically, neither atomic absorption proved to be significantly different (more accurate) than plasma emission (Table 56a, b, c). In both cases (plasma emission vs. atomic absorption and vs. atomic emission) the means of two data sets were not significantly different at the 5% level while two were. Of these two, plasma emission was closer to the recommended value than the flame in one case while the flame method was the closer on the other. There was a more apparent difference between the flame methods. Again the means of two of the four data sets were not significantly different but of the other two, both means by atomic absorption were closer to the recommended value. On this basis, the atomic absorption methods proved to be a fraction more accurate than the flame emission method. The results by plasma emission tended to be closer to the recommended figure except for sample NBS-70a. This sample had a much lower CaO content than the other samples. As no clear difference in accuracy could be proved between atomic absorption and plasma emission, this extreme inaccuracy (+194.5%) at low concentrations of calcium by plasma emission becomes an important factor. Because of this, the recommended method for use when dealing with low concentrations of calcium (less than 0.75 ug Ca/ml) must be atomic absorption while plasma emission is recommended only at higher conentrations.

In general, precision by these methods was not very good either with relative standard deviations ranging from

0.6061% to 10.7874% for atomic emission, 1.3553% to 4.5333% for plasma emission and from 1.9242% to 4.7381% for atomic absorption. Statistically, the variances from the means of the data sets by atomic absorption and by plasma emission were not clearly different (Table 56a, b, c). Two sets were not significantly different while the other two sets went one each way. This was not the case between atomic emission and plasma emission or atomic absorption. In both cases atomic emission was clearly, but not overwhelmingly, more precise (see Tables 56a, b, c). There was no apparent correlation between the relative standard deviation figures and the calcium contents of the samples.

The only problem encountered, and which was common to all three techniques, was an erratic instability in the observed readings. This was not apparent in the short term as illustrated by the good reproducibility results, but only over a longer time span. This resulted in rather poor precision figures for NSX-RP, where there were many more repetitions made than for the other samples. The instability took the form of erratic and occasional increases in the observed peaks, not of sufficient size to merit immediate rejection, which lasted up to ten minutes followed by a return to the original state. This caused a greater variation in the calculated results than would ordinarily be expected. Apart from this, none of these techniques offer much advantage over each other in any respect except for the better operator comfort from the use of the 'cooler' plasma arc and the ease of operation of both emission methods.

On the whole, the plasma emission method is somewhat more useful than the flame methods so long as the calcium content of the sample solution is greater than 0.75-1.0 ug/ml. For concentrations less than that, either of the flame methods would be satisfactory for use.

TABLE 46

Calcium by Plasma Emission

****

Working Conditions

Wavelength 393.367 nm, Gain 14

Slit width 6 microns, Plasma current used = 7.5 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	48.0	46.8
0.5	45.6	

****

THE SLOPE IS 93.5999

THE INTERCEPT IS 0.0000

THE CORRELATION COEFFICIENT IS .99999

THE SENSITIVITY IS 0.9359 ug/ml

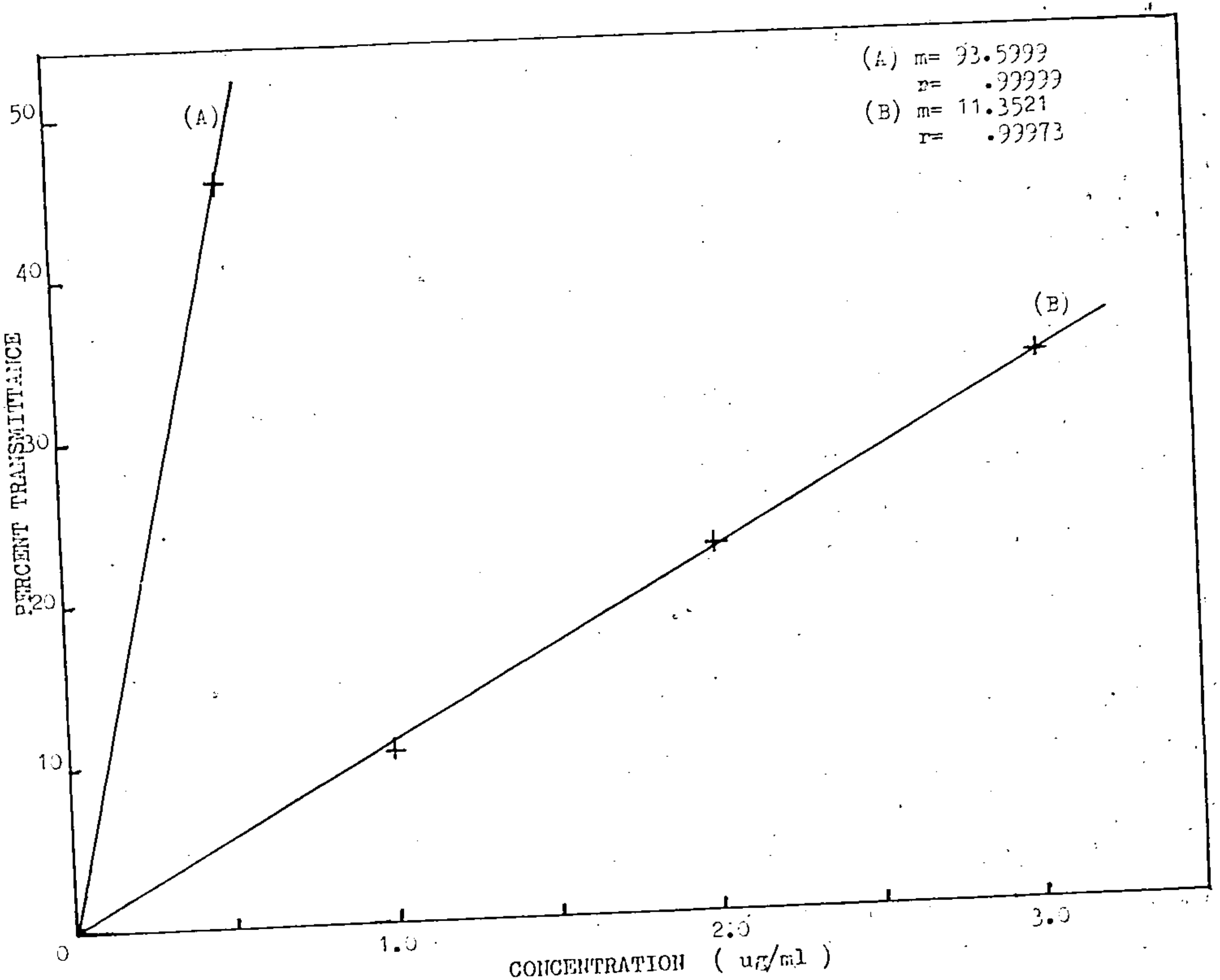


Fig. 3/ Typical calibration curves for calcium by plasma emission

TABLE 47

Detection Limit for Calcium by Plasma Emission

Working Conditions

Wavelength 393.367 nm, Gain 14

Slit width 6 microns, Plasma current used = 7.5 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
Blank	0.0
	0.1
	0.1
	0.2
	0.1
	-0.1
	-0.1
	0.1
	0.1
	0.0

THE MEAN IS 0.05

THE STD. DEVIATION IS 0.0921

THE SLOPE IS 93.5999

THE DETECTION LIMIT IS 0.0019 ug/ml

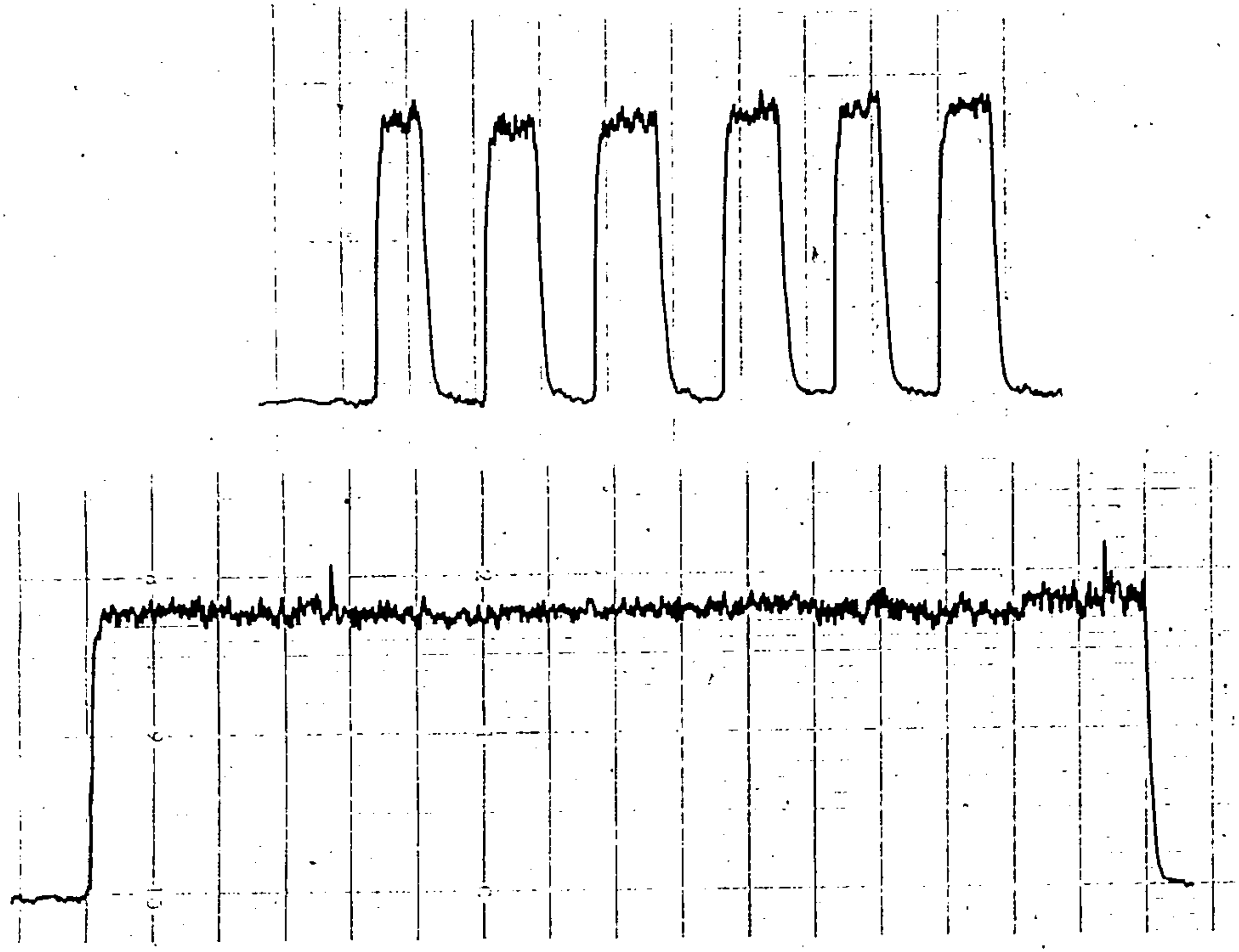


Fig. 32 Reproducibility and Stability plots for calcium by plasma emission

TABLE 48

Calcium by Atomic Emission

****

Working Conditions

Wavelength 422.700 nm, Gain 7

Slit width 25 microns

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	77.0	76.1
0.5	75.2	

THE SLOPE IS 152.1999

THE INTERCEPT IS 0.0000

THE CORRELATION COEFFICIENT IS 1.00000

THE SENSITIVITY IS 1.5219 ug/ml

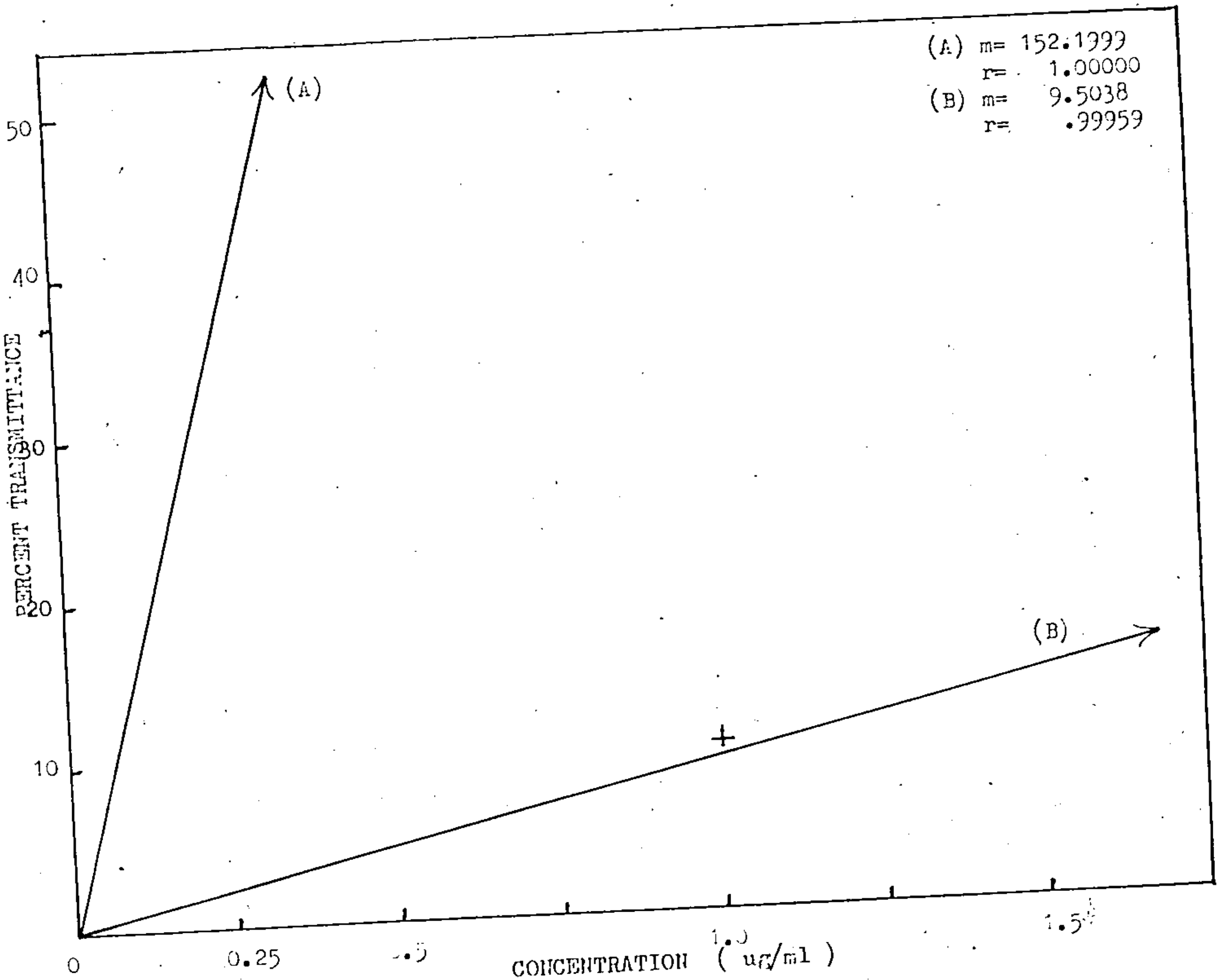


Fig. 33 Typical calibration curves for calcium by flame emission

TABLE 49

Detection Limit for Calcium by Atomic Emission

Working Conditions

Wavelength 422.700 nm, Gain 7

Slit width 25 microns

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
Blank	9.4
	9.6
	9.5
	9.4
	9.5
	9.4
	9.6
	9.3
	9.5
	9.5

THE MEAN IS 9.47

THE STD. DEVIATION IS 0.0900

THE SLOPE IS 152.1999

THE DETECTION LIMIT IS 0.0011 ug/ml

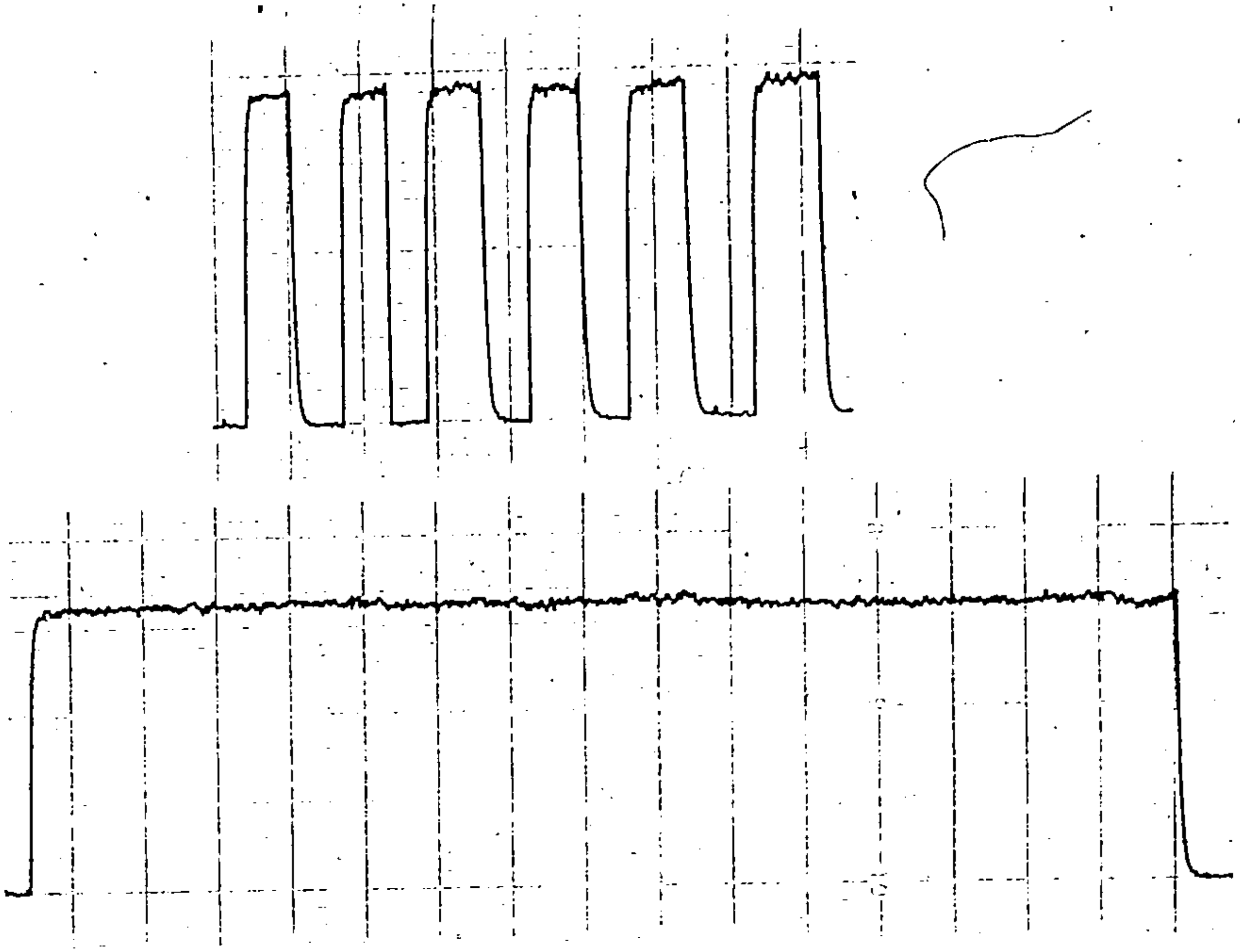


Fig. 34 Reproducibility and Stability plots for calcium by flame emission

TABLE 50

Calcium by Atomic Absorption

```
*************************************************

               Working Conditions
Wavelength 422.700 nm, Gain
Slit width 50 microns, Lamp current used = 8 mA
Support gas used was nitrous oxide
Flame stoichiometry was reducing
Absorption mode
*************************************************
```

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
0.5	5.3	5.3
1	11.9	11.9
2	22.9	23.0
3	34.1	34.0
0.5	5.3	
1	11.9	
2	23.1	
3	33.9	

```
*************************************************

          THE SLOPE IS  11.4042
          THE INTERCEPT IS  0.0060
          THE CORRELATION COEFFICIENT IS  .99982
          THE SENSITIVITY IS  0.1140 ug/ml
```

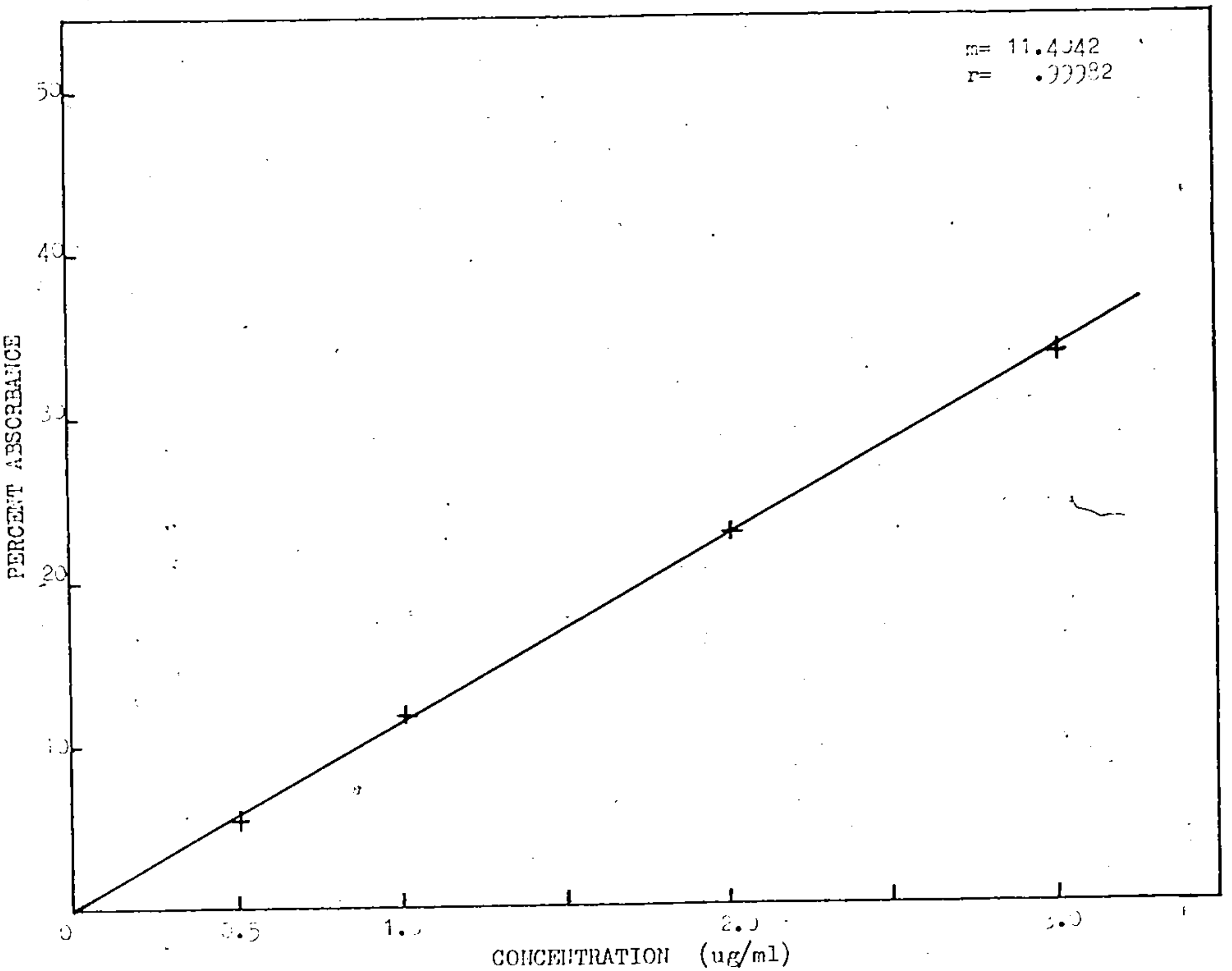


Fig. 35 Typical calibration curve for calcium by atomic absorption

TABLE 51

Detection Limit for Calcium by Atomic Absorption

****

Working Conditions

Wavelength 422.700 nm, Gain 1

Slit width 50 microns, Lamp current used = 8 mA

Support gas used was nitrous oxide

Flame stoichiometry was reducing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
Blank	0.9
	0.8
	0.8
	0.9
	0.8
	1.0
	1.0
	1.0
	1.1
	1.0

****

THE MEAN IS 0.93

THE STD. DEVIATION IS 0.1004

THE SLOPE IS 11.4042

THE DETECTION LIMIT IS 0.0176 ug/ml

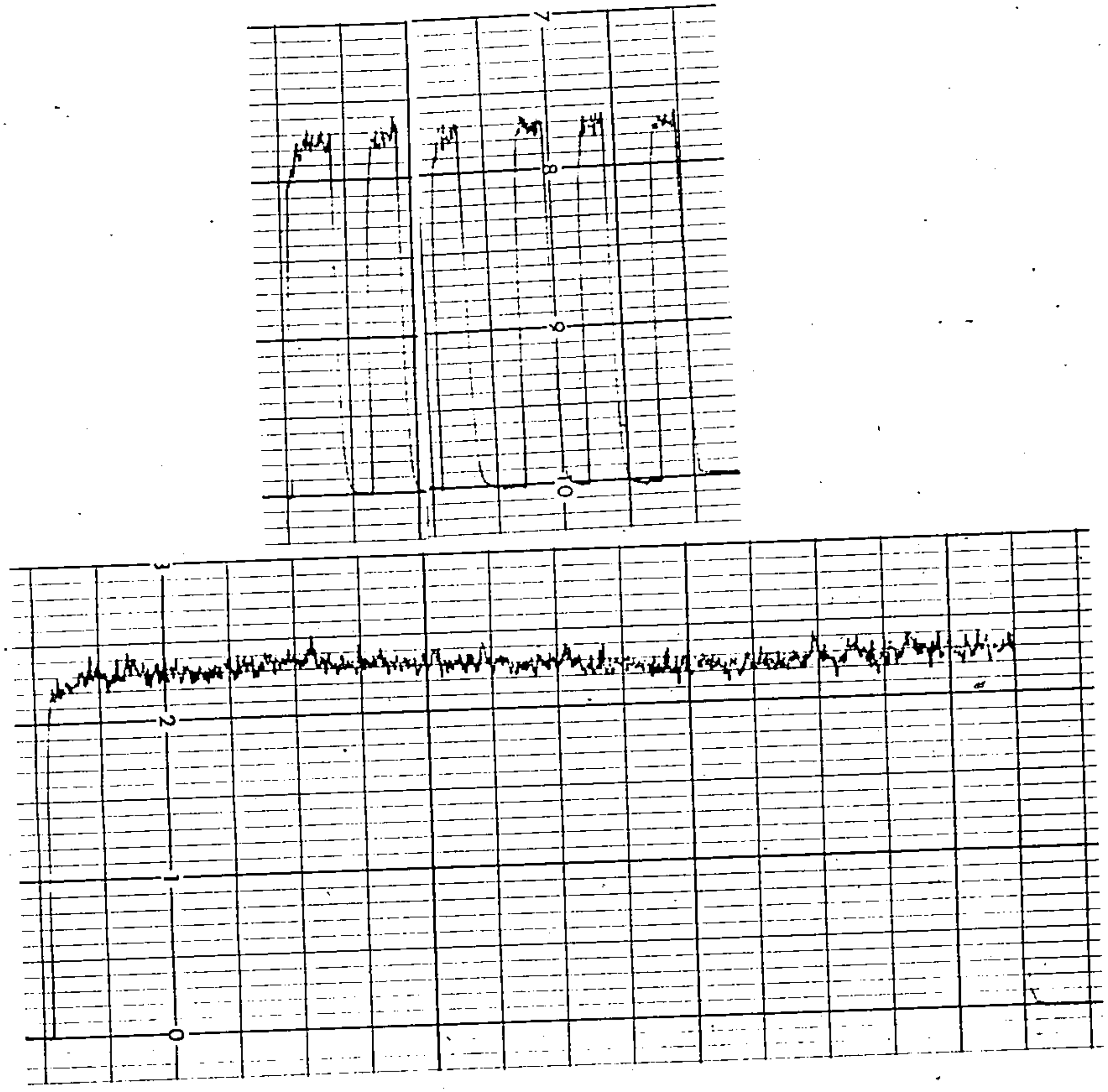


Fig. **36** Reproducibility and Stability plots for calcium by atomic absorption

TABLE 52a

Summary of Comparison Parameters - Calcium

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (1)
Detection Limit (ug/ml)	0.0019	0.0007	0.0176	0.0005
max. Sensitivity (ug/ml)	0.9359	—	0.1140	—
reproducibility				
mean (ug/ml)	17.86	—	22.61	—
standard deviation (ug/ml)	0.124	—	0.106	—
rel. std. deviation (%)	0.698	—	0.471	—
stability				
drift (analogue units)	+/-0.3	—	+/-0.5	—
noise (%)	2.7	—	2.2	—
noise level (ug/ml)	0.0040	—	0.0005	—

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 52b

Summary of Comparison Parameters - Calcium

	Plasma Emission	Literature (1)	Atomic Absorption	Literature ( )
Detection Limit (ug/ml)	0.0019	0.0007	0.0011	0.0005
max. Sensitivity (ug/ml)	0.9359	—	1.5219	—
reproducibility				
mean (ug/ml)	17.86	—	18.61	—
standard deviation (ug/ml)	0.124	—	0.089	—
rel. std. deviation (%)	0.698	—	0.482	—
stability				
drift (analogue units)	+/-0.3	—	0.2	—
noise (%)	2.7	—	1.2	—
noise level (ug/ml)	0.0040	—	0.0015	—

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 52c

Summary of Comparison Parameters - Calcium

	Atomic Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.0011	0.0005	0.0176	0.0005
max. Sensitivity (ug/ml)	1.5219	—	0.1140	—
reproducibility				
mean (ug/ml)	18.61	—	22.61	—
standard deviation (ug/ml)	0.089	—	0.106	—
rel. std. deviation (%)	0.482	—	0.471	—
stability				
drift (analogue units)	0.2	—	+/-0.5	—
noise (%)	1.2	—	2.2	—
noise level (ug/ml)	0.0015	—	0.0005	—

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 53a

Standard Rock Sample Analysis - Calcium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	2.53	2.65	2.80	2.99	0.32	0.15	6.98	7.43
% oxide (lit.)	2.10	2.10	2.45	2.45	0.11	0.11	6.92	6.92
% difference	20.5	26.2	14.3	22.0	194.5	39.1	0.9	7.4
std. dev.	0.0623	0.1257	0.0379	0.0575	0.0068	0.0046	0.3165	0.1435
rel. std. dev.	2.4621	4.7381	1.3553	1.9242	2.1074	0.0172	4.5333	1.9331
repetitions	39	42	12	12	12	12	12	12
dilution	10	10	10	10	10	nil	25	25

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 53b

Standard Rock Sample Results - Calcium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Flame	Plasma	Flame	Plasma	Flame	Plasma	Flame
% oxide	2.53	2.56	2.80	3.17	0.32	0.17	6.98	7.56
% oxide (lit.)	2.10	2.10	2.45	2.45	0.11	0.11	6.92	6.92
% difference	20.5	21.9	14.3	29.6	194.5	50.9	0.9	9.2
std. dev.	0.0623	0.2761	0.0379	0.0192	0.0068	0.0036	0.3165	0.0694
rel. std. dev.	2.4621	10.7874	1.3553	0.6061	2.1074	2.2186	4.5333	0.9186
repetitions	39	30	12	11	12	12	12	12
dilution	10	10	10	10	10	nil	25	25

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 53c

Standard Rock Sample Results - Calcium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Emission	Absorp.	Emission	Absorp.	Emission	Absorp.	Emission	Absorp.
% oxide	2.56	2.65	3.17	2.99	0.17	0.15	7.56	7.43
% oxide (lit.)	2.10	2.10	2.45	2.45	0.11	0.11	6.92	6.92
% difference	21.9	26.2	29.6	22.0	50.9	39.1	9.2	7.4
std. dev.	0.2761	0.1257	0.0192	0.0575	0.0036	0.0046	0.0694	0.1435
rel. std. dev.	10.7874	4.1381	0.6061	1.9242	2.2186	3.0172	0.9186	1.9331
repetitions	30	42	11	12	12	12	12	12
dilution	10	10	10	10	nil	nil	25	25

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 54

Instrumental Parameters for Analysis - Calcium

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	393.367	-	7.5	-	-	6	9	high	0.5-5
Atomic Absorp.	422.700	8	-	N_2O	red.	50	1	norm	1-4
Atomic Emission	422.700	-	-	N_2O	red.	25	1	high	0.5-4

(1) red. = reducing or fuel rich

TABLE 55

Wavelength, Dilution Factor and Standard Selection - Calcium

	Plasma Emission	Atomic Absorption	Atomic Emission
standards required	1, 2, 3	0.5, 1, 2, 3	0.5, 1, 2, 3
dilution factors required	10, 25	0, 10, 25	0, 10, 25
alternate wavelengths (in order of decreasing sensitivity)	393.367nm 396.847 422.700	422.700nm 239.900	422.700nm 239.900

TABLE 56a

Statistical Comparisons

Atomic Emission vs. Plasma Emission - Calcium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	NS	S*	S	NS	-
F- test on variances of means (2)	S*	S	S	S	NS

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic emission mean closer to rec. value.
S* - means are significantly different at 5% significance level, with plasma emission mean closer to rec. value.

(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic emission variance lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

TABLE 56b

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Calcium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	NS	S*	S	NS	-
F- test on variances of means (2)	S*	NS	NS	S	NS

TABLE 56c

Statistical Comparisons

Atomic Absorption vs. Atomic Emission - Calcium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t- test on means (1)	NS	S	S	NS	-
F- test on variances of means (2)	S	S*	NS	S*	NS

(1) NS - means are <u>not</u> significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level, with atomic emission mean closer to rec. value.

(2) NS - variances are <u>not</u> significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% significance level, with atomic emission variance lowest.

MAGNESIUM

The wavelength selection for magnesium analysis by atomic absorption is not extensive with only one very sensitive line, 285.213 nm, and another less sensitive line at 383.826 nm. The most sensitive line was used in this study. There is a greater selection available for use with the plasma emission technique. Both neutral atom and ion lines tested, 279.553 nm and 280.270 nm, were both substantially more sensitive than were the neutral atom lines tested, 285.213 nm and 393.826 nm. The 279 nm line was used in this study but the 280 nm line can be recommended as an alternate for use with more highly concentrated solutions.

The calibration curves for both techniques show a good fit with the data points, with correlation coefficients ranging from .99976 to .99997 for both. The standards prepared ranged from 0.1 ug Mg/ml through 30 ug Mg/ml. A lower range (up to 1 ug/ml) was used for the atomic absorption analysis where a ten-fold dilution was normally used while the high range (from 5 - 35 ug/ml) was used with the plasma emission where no dilutions were necessary.

There were no apparent chemical interferences when using the plasma emission technique but, at the 279 nm wavelength, there was some spectral interferences from iron and manganese. The most sensitive manganese line is at 279.482 nm, too close to the magnesium 279.553 nm line to be resolved separately. There are also many minor iron lines in that region as well as a relatively strong line at 279.555 nm. The same problem occurs when using atomic absorption at 285.213 nm as there are many minor iron lines there plus relatively strong iron and sodium lines at 285.180 nm and 285.281 nm. The iron interference was substantial but the sodium line did not affect the results. Aluminum caused some interference through ionization. This was not very substantial however.

Detection limit data (Tables 58 and 60) show that the plasma emission technique has a slightly lower detection limit than that of atomic absorption (0.0035 ug/ml vs. 0.0052 ug/ml). This value for plasma emission is approximately one-half of the optimum value (0.007 ug/ml) listed by Spectrametrics (1972). The figure obtained by atomic absorption is roughly one order of magnitude higher than the optimum value of 0.0003 ug/ml (Varian Techron, 1972). The sensitivity values follow a similar trend with the maximum figure obtained by plasma emission, 0.8475 ug/ml, being somewhat better than that obtained by atomic absorption (0.3188 ug/ml). This is due to the greater flexibility of the emission technique with respect to the gain control.

The reproducibility data (Figures 38 and 40) for the two methods were similar, with the atomic absorption data indicating slightly better reproducibility than that for plasma emission. The respective relative standard deviations were 0.481% and 0.815%. The variances of the means over six repetitions were not significantly different at the 5% level indicating that neither method gives clearly more reproducible results than the other.

The data from the stability plots (Figures 38 and 40) show that the signal is considerably noisier when using plasma emission; the noise on the signal being 4.5% versus 2.0% for atomic absorption. These figures point out that both methods are relatively noisy. The blank noise levels of 0.0229 ug/ml and 0.0010 ug/ml more clearly illustrate the difference in noise between these methods. .The value for atomic absorption is quite low with a high signal-to-noise ratio but the figure for plasma emission is only fair. Drift was not signficant using atomic absorption (+/- 0.3 units) but the signal tended to drop off (-0.9 units) when using plasma emission. This was mostly due to the electrode geometry being off rather than an actual flaw in the method.

The atomic absorption method proved to be significantly more accurate than plasma emission (Tables 62 and 65) in all cases. Neither method was very accurate but the plasma emission results were much further from the recommended values than were the results by atomic absorption. This was due to the relative effect of the interferences on each method. The values obtained and their differences from the recommended figures are listed in Table 62. The sample containing the highest concentration of iron and manganese (BCR-1) proved to be the one most affected by these interferences with both methods. The differences from the recommended value were great, with +55.8% for plasma emission and +21.1% for atomic absorption. The sample, with the next highest concentrations of iron and manganese (NSX-RP), gave correspondingly high results (+40.0% and +14.1% high). Sample NBS-70a should not have given any results at all as the magnesium content in this sample, according to Flanagan (1976), is negligible. Definite peaks were recorded for this sample by both methods. The value obtained by plasma emission, 0.052% MgO, was higher than that by atomic absorption, 0.043% MgO, illustrating the relative effect of the interferences on the magnesium results.

The results of the precision comparisons were similar to the preceding as the variances of the means by atomic absorption were significantly different (less) at the 5% level than those associated with the plasma emission technique. The one exception to this was sample BCR-1 where there was no significant difference between the variances With both methods, the relative standard deviations were only fair to good, ranging from 1.8430% to 3.8440% for plasma emission and from 0.9873% to 2.7097 for atomic absorption.

The plasma emission technique had one advantage over atomic absorption, that no dilutions were necessary, for any of the samples, to keep within the working range of the method. Dilution factors for atomic absorption varied from zero (NBS-70a) to one hundred (BCR-1). This caused delays in analysis as the proper dilution factor was determined. As for manganese, no problems occured with either method with the notable exception of the interferences. Both the accuracy and the precision by atomic absorption were significantly better than by plasma emission due to the combined effects of the increased noise and greater interference problem on the plasma emission method. The detection limit and sensitivity values by plasma emission were better than those by atomic absorption but this does not counterbalance the grave inaccuracy of the results obtained by plasma emission. As a result, the atomic absorption method must be preferred over plasma emission in the analysis for magnesium because of the accuracy and precision errors found when using the plasma emission tehcnique.

TABLE 57

Magnesium by Plasma Emission

Working Conditions

Wavelength 279.553 nm, Gain 16

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.1	9.3	9.20
0.4	33.6	33.80
0.1	9.1	
0.4	34.0	

THE SLOPE IS 84.7586

THE INTERCEPT IS 0.0620

THE CORRELATION COEFFICIENT IS .99976

THE SENSITIVITY IS 0.8475 ug/ml

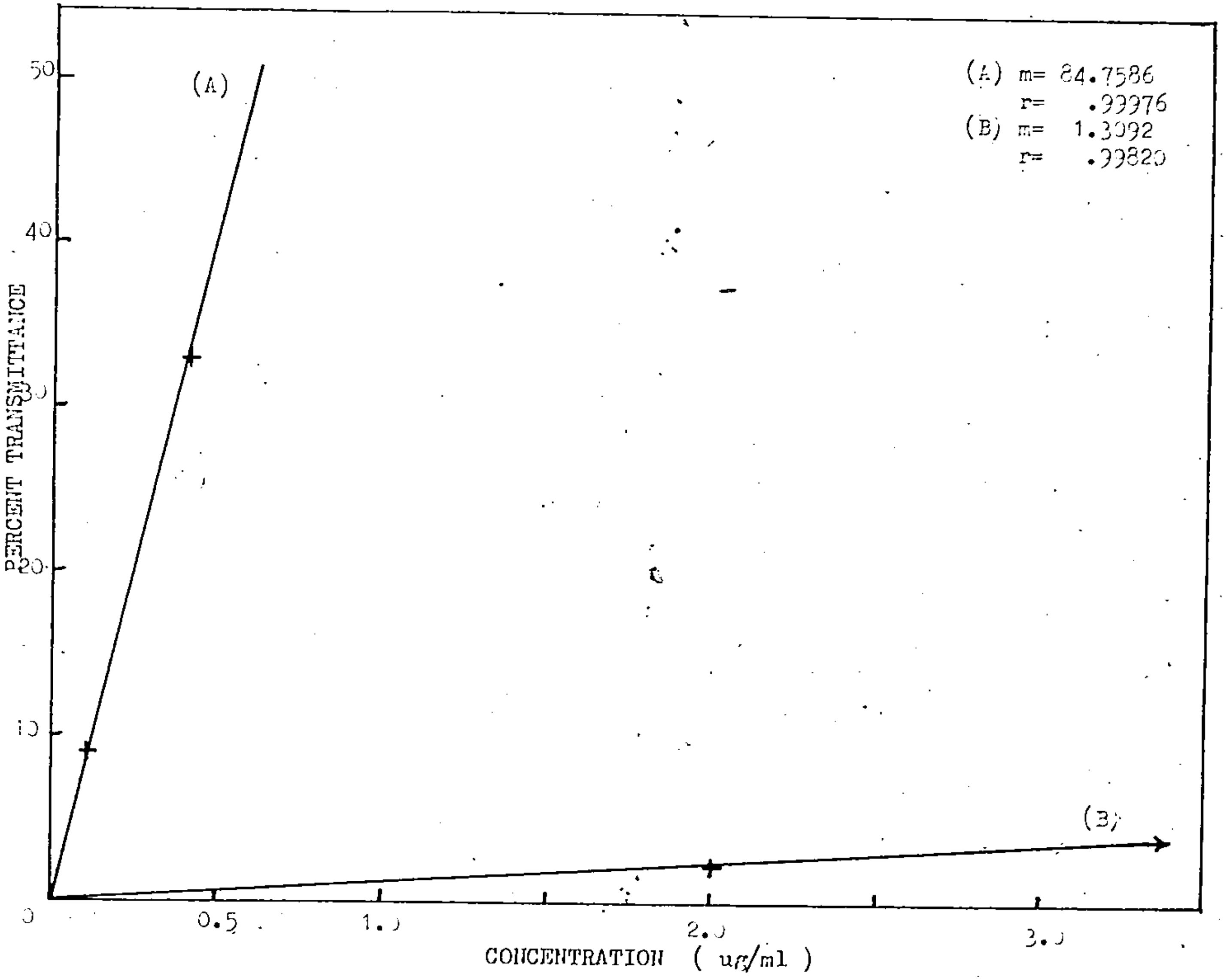


Fig. 37 Typical calibration curves for magnesium by plasma emission

TABLE 58

Detection Limit for Magnesium by Plasma Emission

Working Conditions

Wavelength 279.553 nm, Gain 16
Slit width 10 microns, Plasma current used = 7.5 Amps
Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
Blank	0.1
	0.2
	0.0
	0.4
	0.2
	0.1
	0.4
	0.4
	0.3
	0.0

THE MEAN IS 0.21
THE STD. DEVIATION IS 0.1513
THE SLOPE IS 84.7586
THE DETECTION LIMIT IS 0.0035 ug/ml

Fig. 38 Reproducibility and Stability plots for magnesium by plasma emission

TABLE 59

Magnesium by Atomic Absorption

****

Working Conditions

Wavelength 285.213 nm, Gain 3

Slit width 100 microns, Lamp current used = 3 mA

Support gas used was nitrous oxide

Flame stoichiometry was oxidizing

Absorption mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs	AVERAGE READING %Abs
0.1	3.3	3.35
0.2	6.2	6.35
0.3	9.4	9.50
0.4	12.7	12.80
0.1	3.4	
0.2	6.5	
0.3	9.6	
0.4	12.9	

****

THE SLOPE IS 31.8846

THE INTERCEPT IS 0.0096

THE CORRELATION COEFFICIENT IS .99992

THE SENSITIVITY IS 0.3188 ug/ml

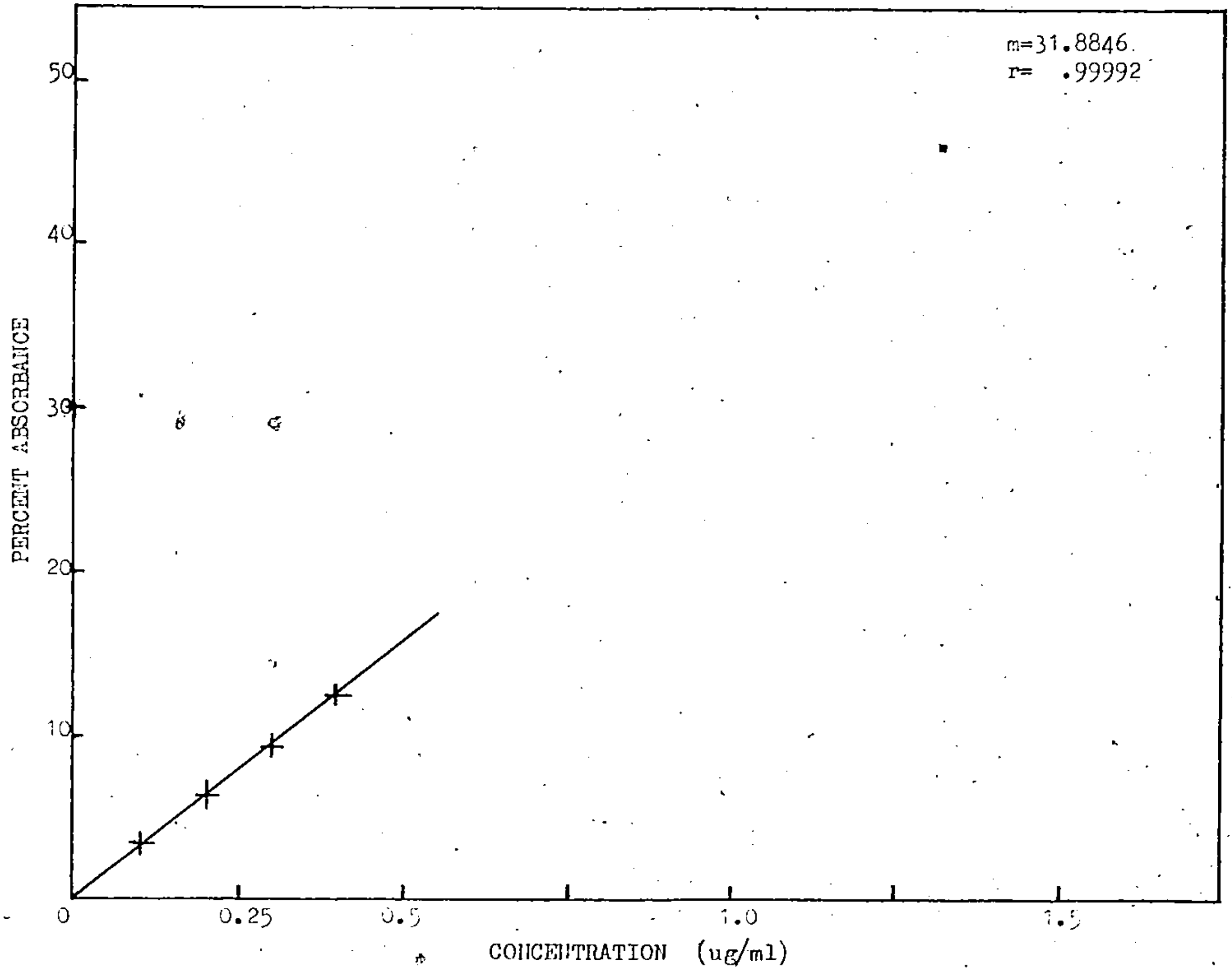


Fig. 39 Typical calibration curve for magnesium by atomic absorption

TABLE 60

Detection Limit for Magnesium by Atomic Absorption

Working Conditions

Wavelength 285.213 nm, Gain 3
Slit width 100 microns, Lamp current used = 3 mA
Support gas used was nitrous oxide
Flame stoichiometry was oxidizing
Absorption mode

CONC. OF STANDARD ug/ml	ACTUAL READING %Abs
Blank	0.7
	0.7
	0.5
	0.7
	0.6
	0.6
	0.6
	0.6
	0.7
	0.6

THE MEAN IS 0.63
THE STD. DEVIATION IS 0.0640
THE SLOPE IS 24.3923
THE DETECTION LIMIT IS 0.0052 ug/ml

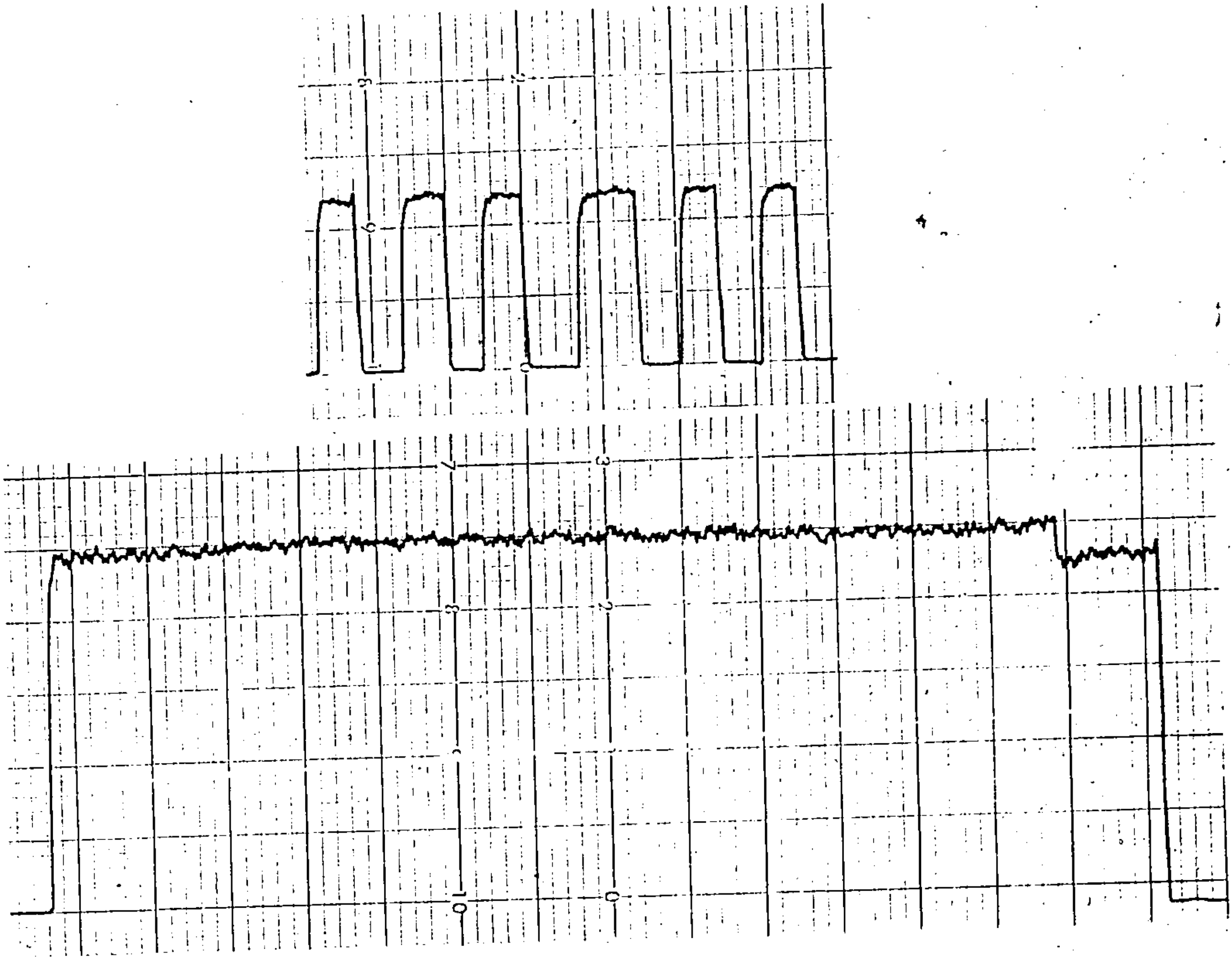


Fig. 40 Reproducibility and Stability plots for magnesium by atomic absorption

TABLE 61

Summary of Comparison Parameters - Magnesium

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.0035	0.0070	0.0052	0.0003
max. Sensitivity (ug/ml)	0.8475	–	0.3188	–
reproducibility				
mean (ug/ml)	11.56	–	12.00	–
standard deviation (ug/ml)	0.094	–	0.057	–
rel. std. deviation (ug/ml)	0.815	–	0.481	–
stability				
drift (analogue units)	-0.9	–	+/-0.3	–
noise (%)	4.5	–	2.0	–
noise level (ug/ml)	0.0229	–	0.0010	–

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 62

Standard Rock Sample Results - Magnesium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	1.61	1.31	1.14	1.05	0.052	0.043	5.39	4.19
% oxide (lit.)	1.15	1.15	0.95	0.95	-	-	3.46	3.46
% difference	40.0	14.1	20.0	10.5	NA	NA	55.8	21.1
std. dev.	0.0616	0.0253	0.0209	0.0103	0.0024	0.0011	0.1057	0.1134
rel. std. dev.	3.8440	1.9332	1.8430	0.9873	4.7607	2.5387	1.9608	2.7097
repetitions	54	51	12	12	12	12	12	24
dilution	nil	10	nil	10	nil	nil	nil	100

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976

TABLE 63

Instrumental Parameters for Analysis - Magnesium

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	279.553	-	7.5	-	-	10	12	high	0.2-10
Atomic Absorp.	285.213	3.0	-	N_2O	oxid.	100	3	norm	0.1-0.75

(1) oxid. = oxidizing or fuel lean

TABLE 64

Wavelength, Dilution Factor and Standard Selection - Magnesium

	Plasma Emission	Atomic Absorption
standards required	5, 10, 35	0.2, 0.3, 0.5, 1.0
dilution factor required	nil	0, 10, 100
alternate wavelengths (in order of decreasing sensitivity)	279.553nm 280.270 285.213 383.826	285.213nm 383.826

TABLE 65

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Magnesium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t-test on means (1)	S	S	S	S	-
F-test on variances of means (2)	S	S	S	NS	NS

(1) NS - means are <u>not</u> significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level, with plasma emission mean closer to rec. value.

(2) NS - variances are <u>not</u> significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

POTASSIUM

Atomic absorption was not used in the analysis for potassium as the best and most often used flame method is atomic flame emission. There are two useful wavelengths available in the analysis for potassium by emission techniques. The most sensitive of these, 766.490 nm, is the recommended flame emission line (Varian Techron, 1972) and was so used. The other line at 769.896 nm, proved to be slightly less sensitive but is the recommended line for plasma emission (Spectrametrics Inc., 1972). The 766 nm line, when used with the plasma technique, showed a severe negative deflection in the calibration curve at potassium concentrations greater than 40 ug/ml. The 769 nm line was linear through concentrations up to 129 ug/ml. Both lines were used with plasma emission depending on the potassium content of the sample.

Neither emission technique gave very high correlation coefficients for their calibration curves; flame ranging from .99387 to .99679 and plasma ranging from .99425 to .99790. This is due to the tendency of these lines to flatten due to ionization at higher concentrations of potassium. The standards prepared were from 0.5 ug K/ml to 129 ug K/ml, with one series (0.5-4 ug/ml) being used with the flame method and another series, 12.9 - 129 ug/ml, with the plasma method.

Interferences were minor when using the flame excitation source. No chemical interferences were noted and the only spectral interferant was sodium, and that was only to a minor degree. This did not pose any problem as all the solutions used with flame emission were diluted by a factor of at least five. Plasma emission, on the other hand, while not having any chemical interferences, did show a substantial interference by magnesium which has a low intensity line in the 766 nm region. This interference by a 35 ug Mg/ml solution was equivalent to a potassium concentration of approximately 4 ug/ml, or roughly 12% of the results on a typical sample. Iron also showed a slight interference but it was not substantial. These spectral interferences were important as none of the solutions used with plasma emission were diluted.

Ionization was also a problem when using the plasma source but this was slightly reduced by lowering the plasma current to 6.5 - 7.0 amperes. This interference was most apparent in the samples with the least potassium content (BCR-1) and was not as evident in the samples with higher potassium contents (NVS-70a). This trend was apparent when a ten-fold dilution of sample NBS-70a was run. The results of those solutions were higher than the undiluted solutions by 2.1% K_2O on a recommended content of 11.80% K_2O (15.5% vs. 13.4%).

Detection limit data (Tables 67 and 69) demonstrate clearly the better response by the flame method to potassium. The figure obtained using flame emission was 0.0012 ug/ml which compares very favorably with the optimum figure of 0.003 ug/ml for atomic absorption (Varian Techron, 1972). No optimum detection limit data was available for atomic emission. On the other hand, plasma emission gave very poor results with a detection limit of only 0.1968 ug/ml which does not compare favorably with the optimum figure of 0.0007 ug/ml (Spectrametrics Inc., 1972). This is due to the poor sensitivity to potassium shown by the plasma source in this study.

This problem is evident when the values for sensitivity are compared. Using flame emission, an excellent maximum sensitivity of 1.4009 ug/ml was obtained. This is about two orders of magnitude greater than that by plasma emission, which gave a maximum sensitivity of only 0.0189 ug/ml. This lack of sensitivity could be due to extreme ionization of the potassium and unfortunately there is no strong ion line available. The ion line at 404.414 nm was tested and was found to be very insensitive as expected, having a low intensity figure of 40 as compared to an intensity of 1800 for the 766 nm neutral atom line (Zaidel et al, 1970). The addition of lanthanium to the sample solutions and standard solutions would reduce the ionization of the potassium and could increase the sensitivity by plasma emission.

The reproducibility of these emission methods over six repetitions was good with low relative standard deviation values. The flame method gave slightly lower values but statistically, there was no significant difference between the variances about the means for these two techniques. The low relative standard deviations by the atomic and plasma emission methods (0.491% and 0.710%) indicate good reproducibility.

The stability data (Table 70 and Figures 42 and 44) show that, as for magnesium, the signal is considerably noisier when using plasma emission, with noise on the signal being 3.1% compared to 1.2% for the flame source. The blank noise levels show the same pattern with a very quiet 0.0004 ug/ml for flame emission and a noisy 0.4560 ug/ml using plasma emission. Drift was not important in either case but the flame method showed a smaller drift (0.2 units) than did plasma emission (-0.7 units). On the whole, both techniques showed good stability but the plasma technique produced greater noise levels than did the flame method.

As for magnesium, the flame method proved to be significantly more accurate than plasma emission in all cases with one exception. This exception was sample NBS-70a where the means were statistically not different at the 5% level. This was due to the high variance values of the flame method. These high values were caused by one poor forty-fold dilution probably in error, which naturally increased the variance values. The accuracy was good at 11.83% K_2O or +0.3% different from the recommended value of 11.80%. This is much closer than the plasma value of 13.42% K_2O (+13.7%). All other mean values for the sample data sets were significantly different at the 5% level, indicating that the flame method is significantly more accurate than the plasma technique. See Tables 71 and 74 for the results.

The comparison with respect to precision is similar with the same exception. In this case plasma emission is significantly more precise but as mentioned earlier, this was due to the dilution error rather than being due to analytical method. All other comparisons show that the atomic emission technique is significantly more precise (significantly different at the 5% level) than the plasma emission technique. The results are summarized in Tables 71 and 74 with relative standard deviations ranging from 0.2400% to 0.8788% for flame emission (NBS-70a: R.S.D. = 9.3860%) and from 0.5107% to 3.1161% for plasma emission.

The only advantages that the plasma emission technique has over the flame method are cooler operation for operator comfort and the fact that no dilutions are necessary. Even this last point is not necessarily valid as the samples could have been run undiluted by flame emission without problems. It is apparent, then, that the use of atomic emission is to be preferred when analysing for potassium instead of using plasma emission. This observation is based on the superior sensitivity, detection limit, accuracy, precision and lower noise levels available with atomic emission.

TABLE 66

Potassium by Plasma Emission

****

Working Conditions

Wavelength 766.940 nm, Gain 13

Slit width 12 microns, Plasma current used = 7.0 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
1	2.4	2.35
4	9.4	9.55
12.9	24.6	25.10
1	2.3	
4	9.7	
12.9	23.6	

****

THE SLOPE IS 1.8982

THE INTERCEPT IS 0.1832

THE CORRELATION COEFFICIENT IS .99658

THE SENSITIVITY IS 0.0189 ug/ml

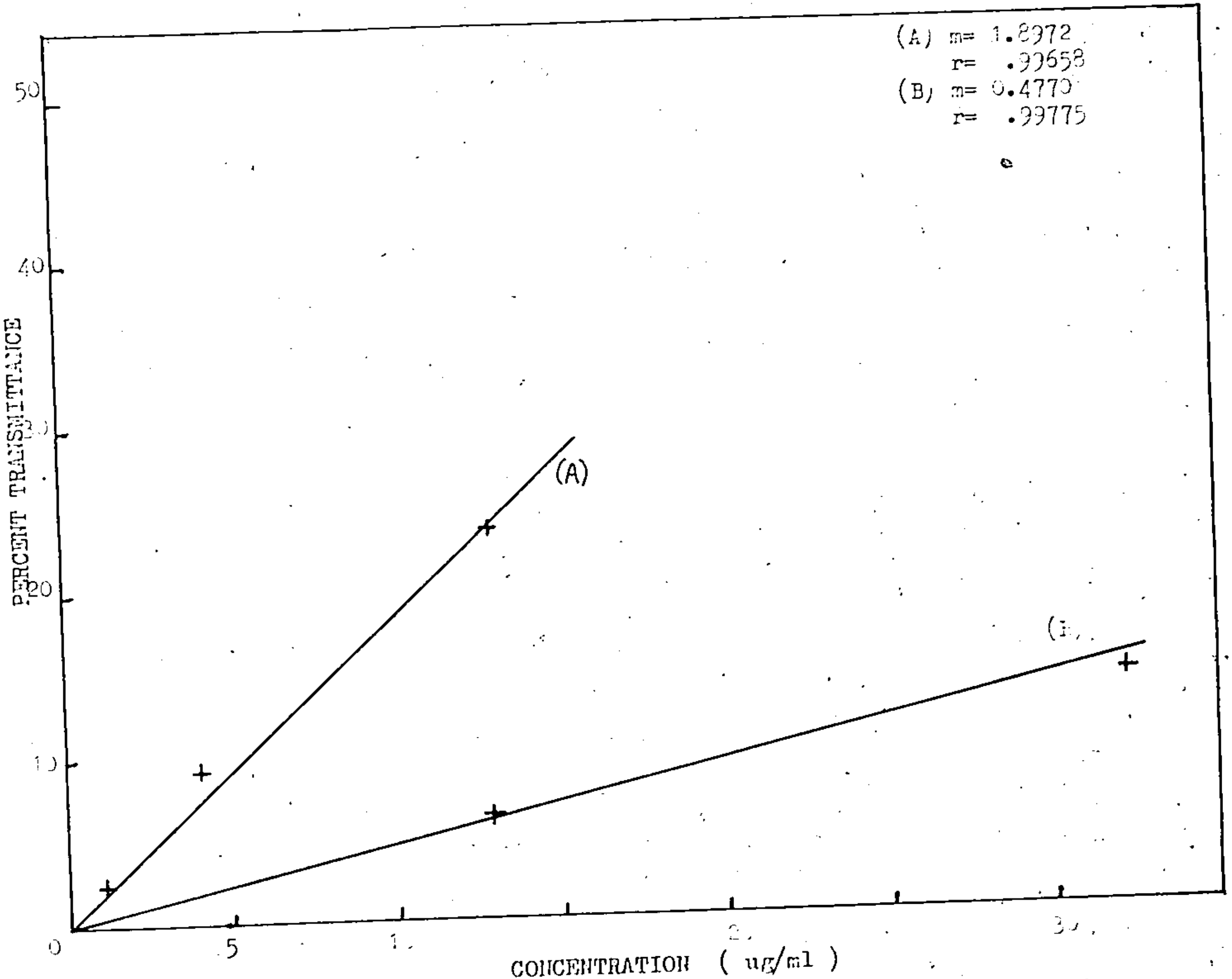


Fig. 4 Typical calibration curves for potassium by plasma emission

TABLE 67

Detection Limit for Potassium by Plasma Emission

****

Working Conditions

Wavelength 766.940 nm, Gain 13

Slit width 12 microns, Plasma current used = 7.0 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T
1	2.4
1	2.0
1	2.0
1	2.2
1	2.2
1	2.5
1	2.3
1	2.6
1	2.4
1	2.3

****

THE MEAN IS 2.29

THE STD. DEVIATION IS 0.1868

THE SLOPE IS 1.8982

THE DETECTION LIMIT IS 0.1968 ug/ml

Fig. 42 Reproducibility and Stability plots for potassium by plasma emission

TABLE 68.

Potassium by Atomic Emission

****

Working Conditions

Wavelength 766.940 nm, Gain 1

Slit width 50 microns

Support gas used was air

Flame stoichiometry was oxidizing

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	70.0	70.05
0.5	70.1	

****

THE SLOPE IS 140.0999

THE INTERCEPT IS 0.0000

THE CORRELATION COEFFICIENT IS .99999

THE SENSITIVITY IS 1.4009 ug/ml

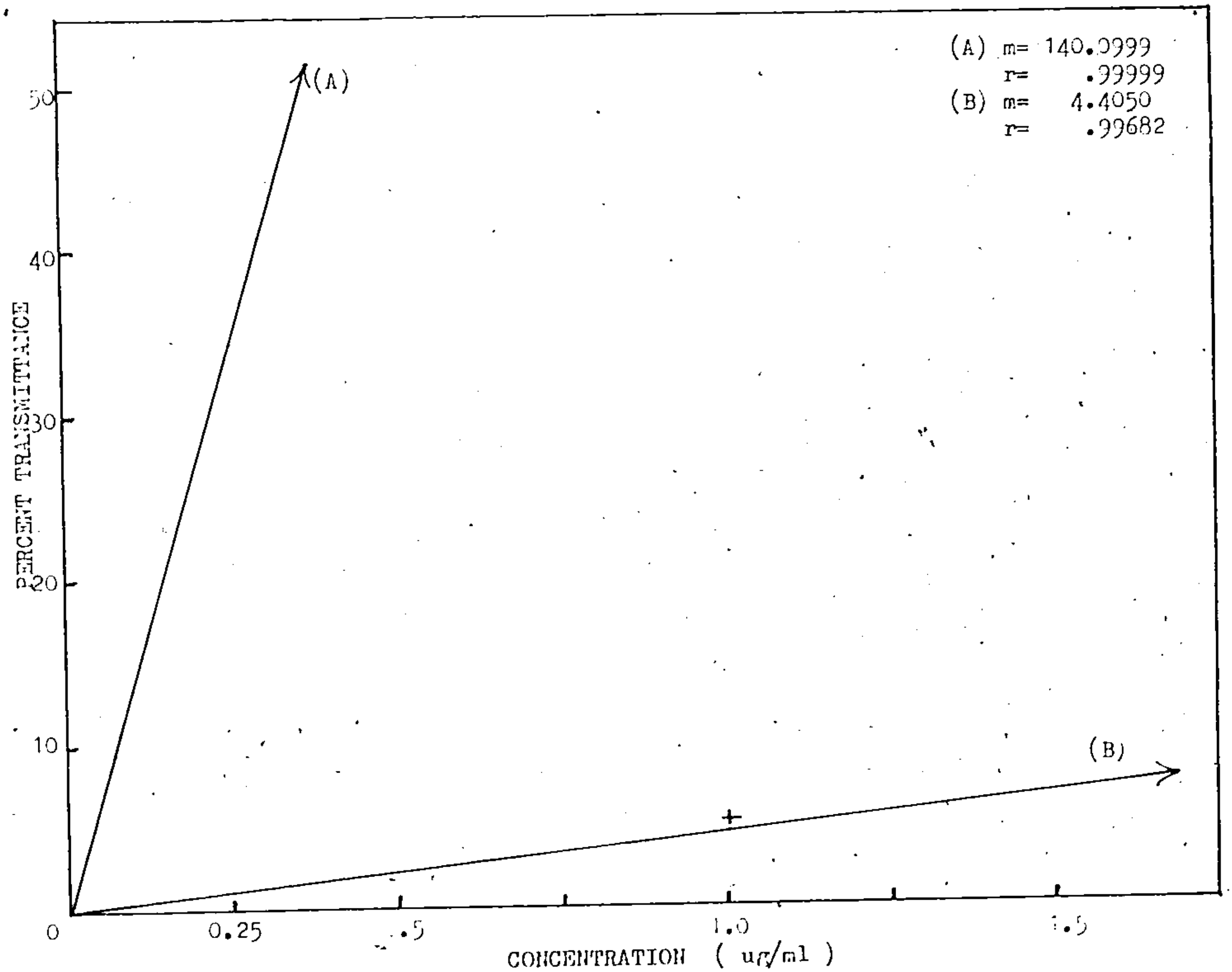


Fig. 43 Typical calibration curves for potassium by flame emission

TABLE 69

Detection Limit for Potassium by Atomic Emission

Working Conditions

Wavelength 766.940 nm, Gain 1

Slit width 50 microns

Support gas used was air

Flame stoichiometry was oxidizing

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
Blank	1.6
	1.6
	1.5
	1.6
	1.8
	1.6
	1.5
	1.6
	1.7
	1.5

THE MEAN IS 1.60

THE STD. DEVIATION IS 0.0894

THE SLOPE IS 140.0999

THE DETECTION LIMIT IS 0.0012 ug/ml

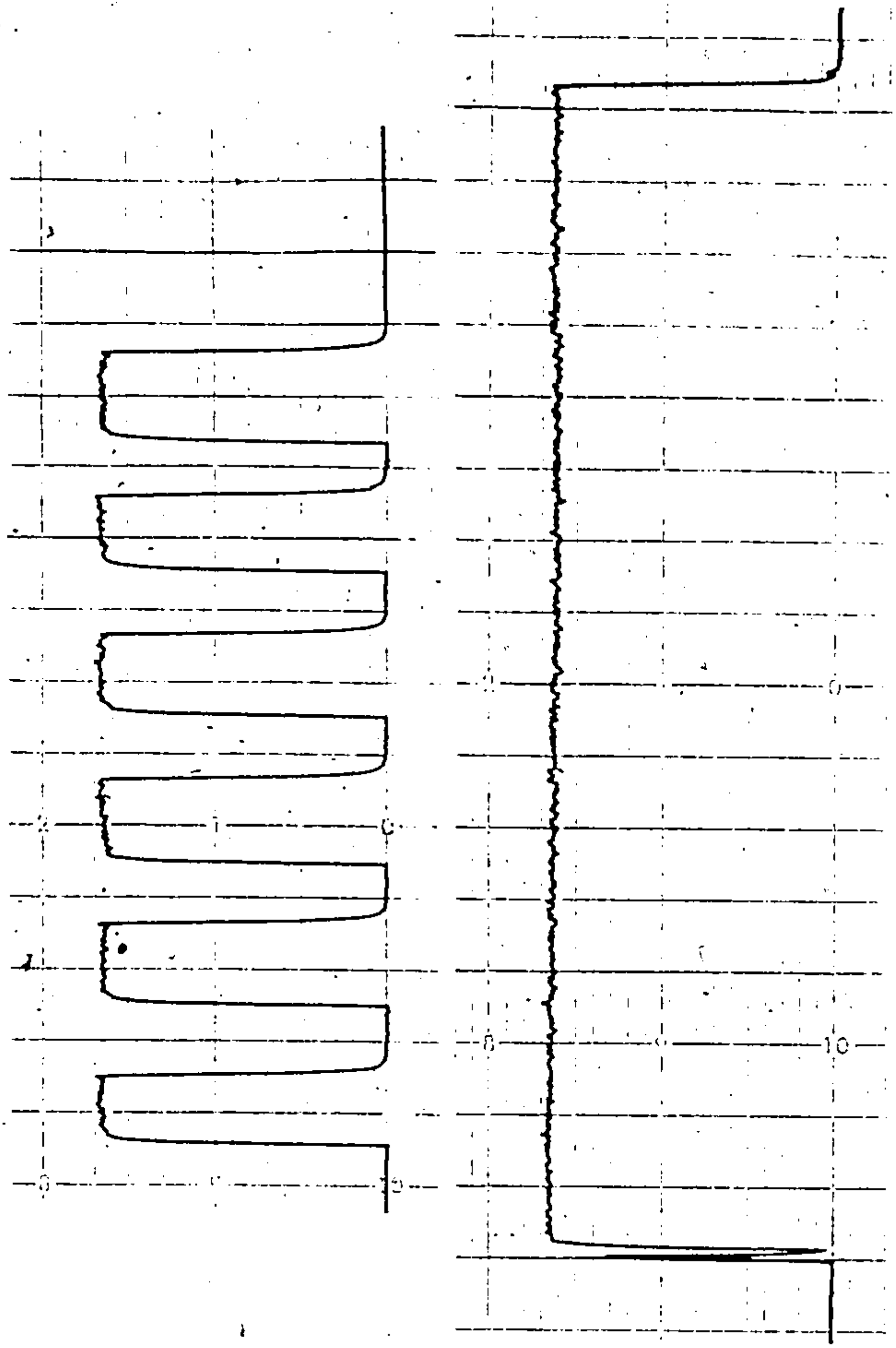


Fig. 44 Reproducibility and Stability plots for potassium by flame emission

TABLE 70

Summary of Comparison Parameters - Potassium

	Plasma Emission	Literature (1)	Atomic Emission	Literature (2)
Detection Limit (ug/ml)	0.1968	0.0007	0.0012	0.003
max. Sensitivity (ug/ml)	0.0189	—	1.4009	—
reproducibility				
mean (ug/ml)	19.90	—	16.60	—
standard deviation (ug/ml)	0.141	—	0.081	—
rel std. deviation (%)	0.710	—	0.491	—
stability				
drift (analogue units)	-0.7	—	0.2	—
noise (%)	3.1	—	1.2	—
noise level (ug/ml)	0.4560	—	0.0004	—

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 71

Standard Rock Sample Results - Potassium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Flame	Plasma	Flame	Plasma	Flame	Plasma	Flame
% oxide	5.58	3.99	5.56	4.01	13.42	11.83	3.61	1.81
% oxide (lit.)	3.93	3.93	4.03	4.03	11.80	11.80	1.70	1.70
% difference	42.0	1.5	38.0	0.6	13.7	0.3	115.3	6.2
std. dev.	0.1739	0.0350	0.0284	0.0096	0.0894	1.1106	0.0447	0.138
rel. std. dev.	3.1161	0.8788	0.5107	0.2400	0.6664	9.3855	1.2233	0.7652
repetitions	42	41	12	11	12	12	12	12
dilution	nil	10	nil	10	nil	40	nil	5

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communitcation, 1978.

TABLE 72

Instrumental Parameters for Analysis - Potassium

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	766.940	-	7.0	-	-	12	12	high	1-25
Atomic Emission	766.940	-	-	air	oxid.	50	1	high	0.5-5.0

(1) oxid. = oxidizing or fuel lean

TABLE 73

Wavelength, Dilution Factor and Standard Selection - Potassium

	Plasma Emission	Atomic Emission
standards required	12.9, 32.3, 51.6	1, 2, 3, 4
dilution factor required	nil	10
alternate wavelengths (in order of decreasing sensitivity)	766.940nm 769.896	766.940nm 769.896

TABLE 74

Statistical Comparisons

Atomic Emission vs. Plasma Emission - Potassium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t-test on means (1)	S	S	NS	S	-
F-test on variances of means (2)	S	S	S*	S	NS

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic emission mean closer to rec. value.
S* - means are significantly different at 5% significance level, with plasma emission mean closer to rec. value.
(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic emission variance lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

SODIUM

The two methods of analysis for sodium used were flame emission and plasma emission. The reasons for this are mentioned in the discussion for potassium. There are several neutral lines available but no strong ion lines available for use with emission analysis. The wavelength couplet at 330.299 nm and 330.232 nm proved to be very insensitive as did the line at 819.482 nm. The other two lines tested, 588.995 nm and 589.592 nm, were both useful with the latter being slightly less sensitive and better for use with higher sodium concentrations and the former being extremely sensitive. The only drawback of the 588 nm line is a negative deflection to the calibration curve that limits its use to low sodium concentrations of less than 30 ug/ml.

The lines of best fit on the calibration graphs were, relative to other elements, fair fits with both methods having correlation coefficients ranging from .99956 to .99991. The standards prepared were from 0.3 ug Na/ml to 30 ug Na/ml. The series of 0.3 - 3 ug/ml was used with flame emission and the plasma emission method used the series of from 15 - 30 ug/ml.

The major interference noted with the use of plasma emission was due to ionization. This required the sample solutions to be run at full strength as the results using dilutions were much higher than the undiluted solutions.

Potassium was a major interferant with both the flame and plasma methods. This became insignificant when running diluted samples as was done in this case with the flame excitation source. No other interferences were noted.

The detection limits obtained using these two techniques were fairly low with neither being close to the optimum figures. The lowest, 0.0018 ug/ml, was given by the flame source and was six times greater than the optimum value of 0.0003 ug/ml listed by Varian Techron (1972). The figure obtained by plasma emission of 0.0101 ug/ml was somewhat higher than that by flame emission and did not compare as favorably with the optimum figure of 0.0004 ug/ml as given by Spectrametrics Inc. (1972). This data is listed in Tables 76, 78 and 79.

As for potassium, this trend continues with the sensitivity figures, with 1.5009 ug/ml being obtained by flame and a maximum of 0.4984 ug/ml being obtained using the plasma arc. The high noise at high gain is the cause of the poor results by plasma emission.

The plasma technique was also significantly less reproducible over six repetitions with a relative standard deviation of 0.657% against 0.310% for the flame source. This was confirmed statistically as the variances were significantly different at the 5% level. This is rather arbitrary as both methods showed excellent reproducibility

(Figures 46 and 48). This remark also holds true for the results for stability of the signal. Both methods had low noise on the signal, with the flame method (0.7%) being quieter than the plasma method (0.1%). Blank noise levels were similarly quiet (0.0013 ug/ml and 0.0106 ug/ml) and drift was not significant. The atomic emission data plot shows a slightly more stable signal however, both methods show good stability.

The remarks concerning the relative accuracies of these methods with respect to potassium are generally true for sodium as well. In all cases, the means of the sample data sets by atomic emission were significantly different at the 5% level from those obtained by plasma emission. These values were also much closer to the recommended values (see Table 80). The differences from the recommended values ranged from +1.5% to +16.5% by flame and from +11.9% to +32.9% by plasma. These differences reflect the relative potassium contents in the samples, with the greatest differences being for sample NBS-70a which has the highest potassium content and the least differences being with the samples with the lowest potassium content (BCR-1 and GA).

This trend was not followed in the precision comparisons. These methods are essentially no different in this respect. Statistically, three sets showed variances for each method that were not significantly different while the other two were significantly different. Of these two, one showed plasma emission with the lowest variance and the other showed flame emission to have the lowest. The relative standard deviation figures, 0.6006% to 2.8495% and 0.09732% to 4.3903% respectively, show that the precision by plasma emission is slightly better than that by atomic emission.

As mentioned for potassium, the dilutions used with the atomic emission technique were not strictly necessary as the samples could have been analysed using full strength solutions. This negates one of the two advantages that plasma emission had over the flame method. The other: cooler, more comfortable operation is still true.

From the preceding discussion it is evident that, concerning detection limits, sensitivity, reproducibility and accuracy, the use of the flame emission technique is to be preferred over the use of plasma emission. In no area in the analysis for sodium did the plasma emission technique prove to be substantially better or more useful than flame emission.

TABLE 75

Sodium by Plasma Emission

****

Working Conditions

Wavelength 588.995 nm, Gain 14

Slit width 10 microns, Plasma current used = 7.5 Amps

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	24.3	24.3
1.0	50.1	50.1
0.5	24.3	
1.0	50.1	

****

THE SLOPE IS 49.8439

THE INTERCEPT IS -0.0365

THE CORRELATION COEFFICIENT IS .99991

THE SENSITIVITY IS 0.4984 ug/ml

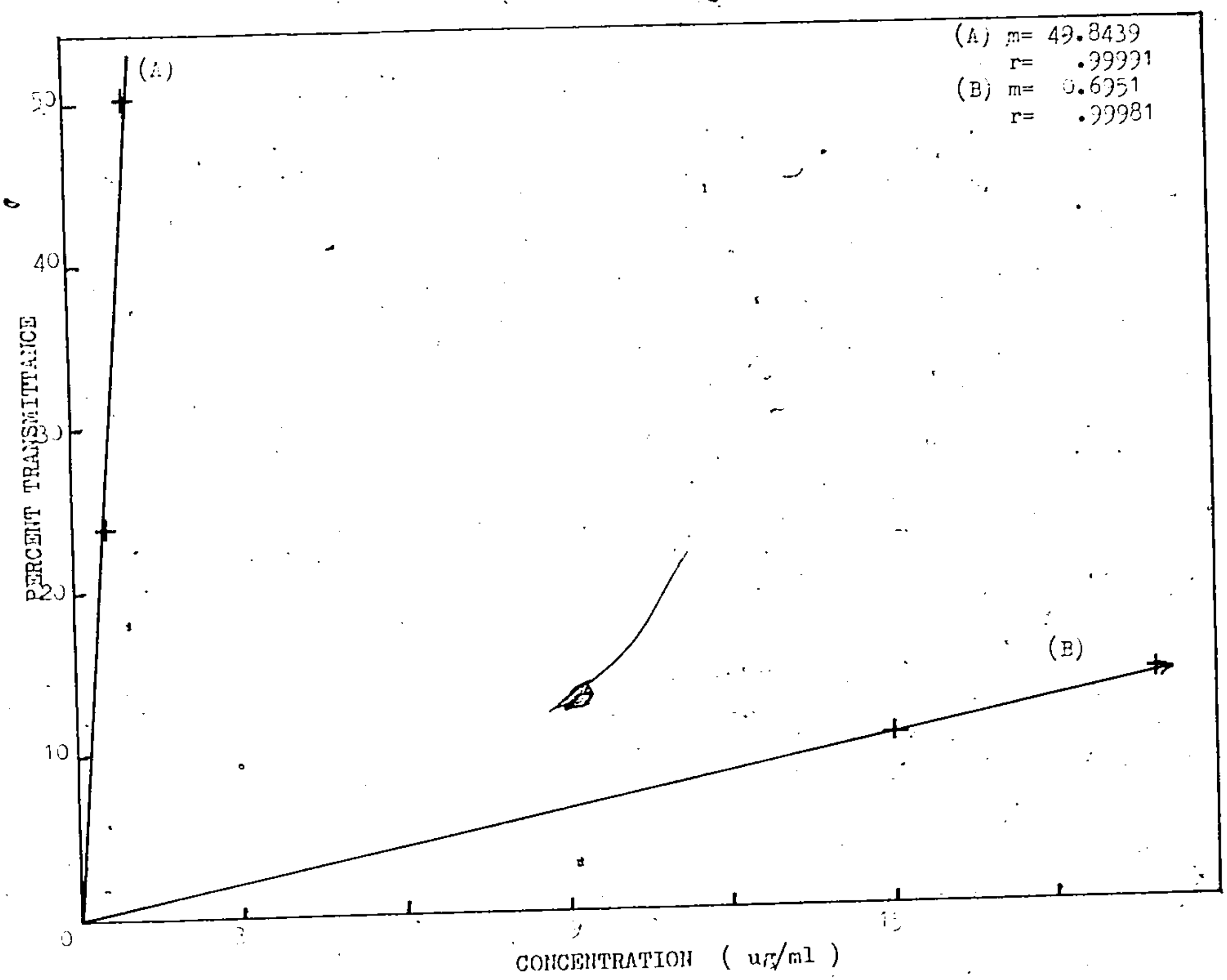


Fig. 45 Typical calibration curves for sodium by plasma emission

TABLE 76

Detection Limit for Sodium by Plasma Emission

****

Working Conditions

Wavelength 588.995 nm, Gain 14
Slit width 10 microns, Plasma current used = 7.5 Amps
Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T
Blank	0.0
	0.2
	0.4
	0.3
	0.1
	-0.1
	0.6
	0.0
	0.5
	-0.2

****

THE MEAN IS 0.18
THE STD. DEVIATION IS 0.2521
THE SLOPE IS 49.8439
THE DETECTION LIMIT IS 0.0101 ug/ml

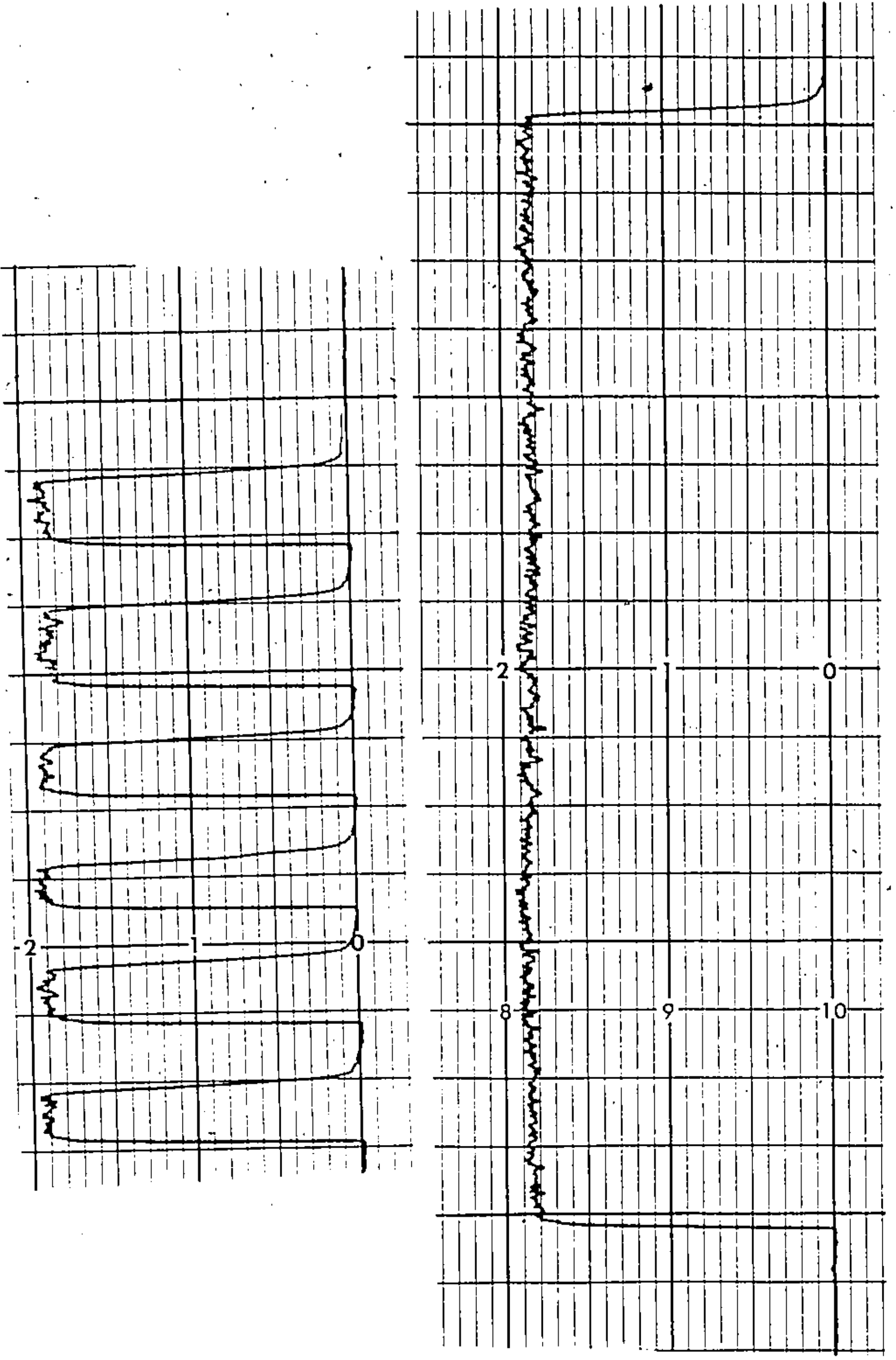


Fig. 46 Reproducibility and Stability plots for sodium by plasma emission

TABLE 77

Sodium by Atomic Emission

****

Working Conditions

Wavelength 588.995 nm, Gain 3

Slit width 50 microns

Support gas used was air

Flame sotichiometry was oxidizing

Transmission mode

****

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
0.5	74.9	75.05
0.5	75.2	

****

THE SLOPE IS 150.0999

THE INTERCEPT IS 0.0000

THE CORRELATION COEFFICIENT IS .99999

THE SENSITIVITY IS 1.5009 ug/ml

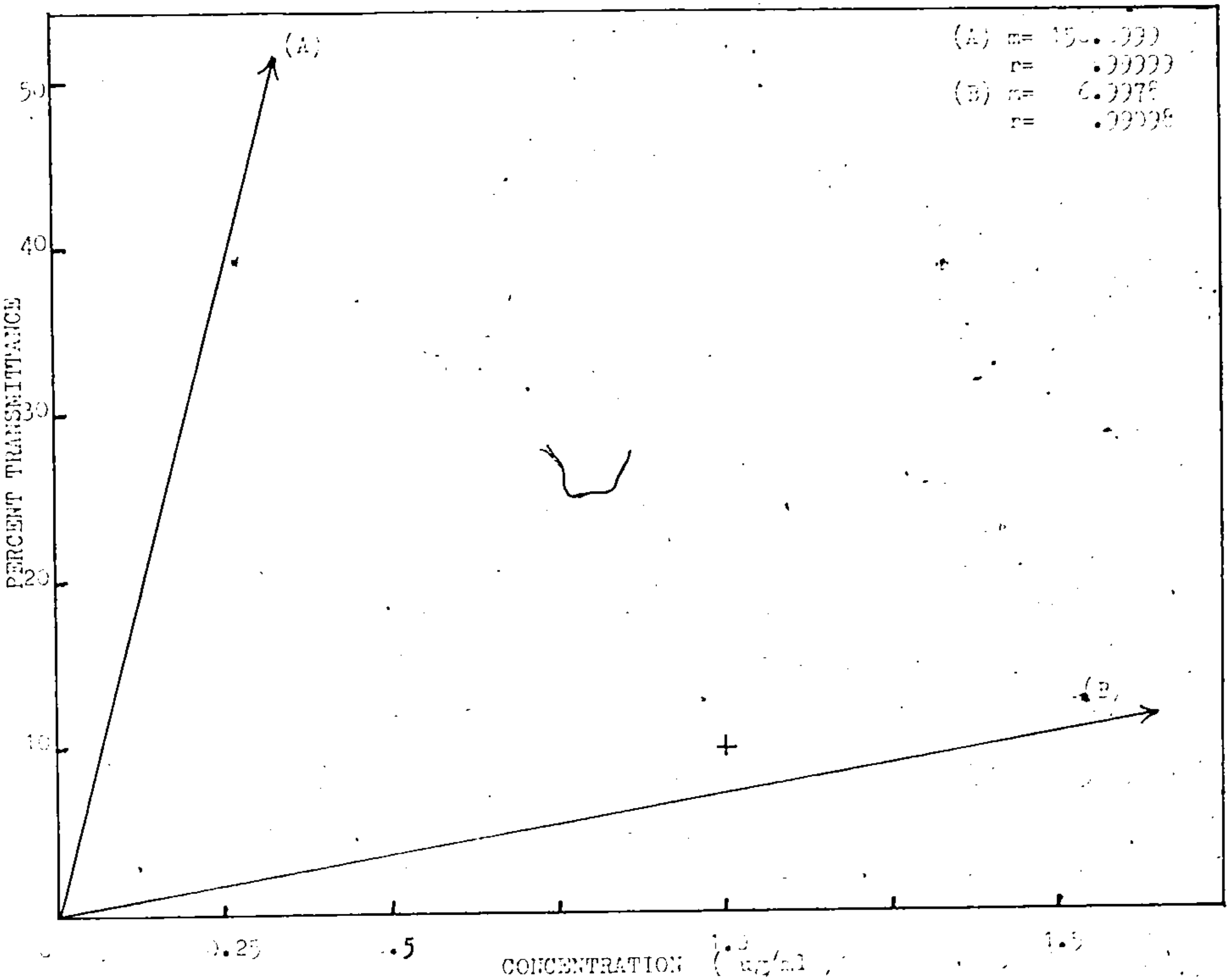


Fig. 47 Typical calibration curves for sodium by flame emission

TABLE 78

Detection Limit for Sodium by Atomic Emission

Working Conditions

Wavelength 588.995 nm, Gain 3
Slit width 50 microns
Support gas used was air
Flame stoichiometry was oxidizing
Transmission mode

CONC. OF STANDARD ug//ml	ACTUAL READING %T
Blank	6.5
	6.6
	6.1
	6.3
	6.4
	6.4
	6.5
	6.3
	6.2
	6.4

THE MEAN IS 6.37
THE STD. DEVIATION IS 0.1417
THE SLOPE IS 150.0999
THE DETECTION LIMIT IS 0.0018 ug/ml

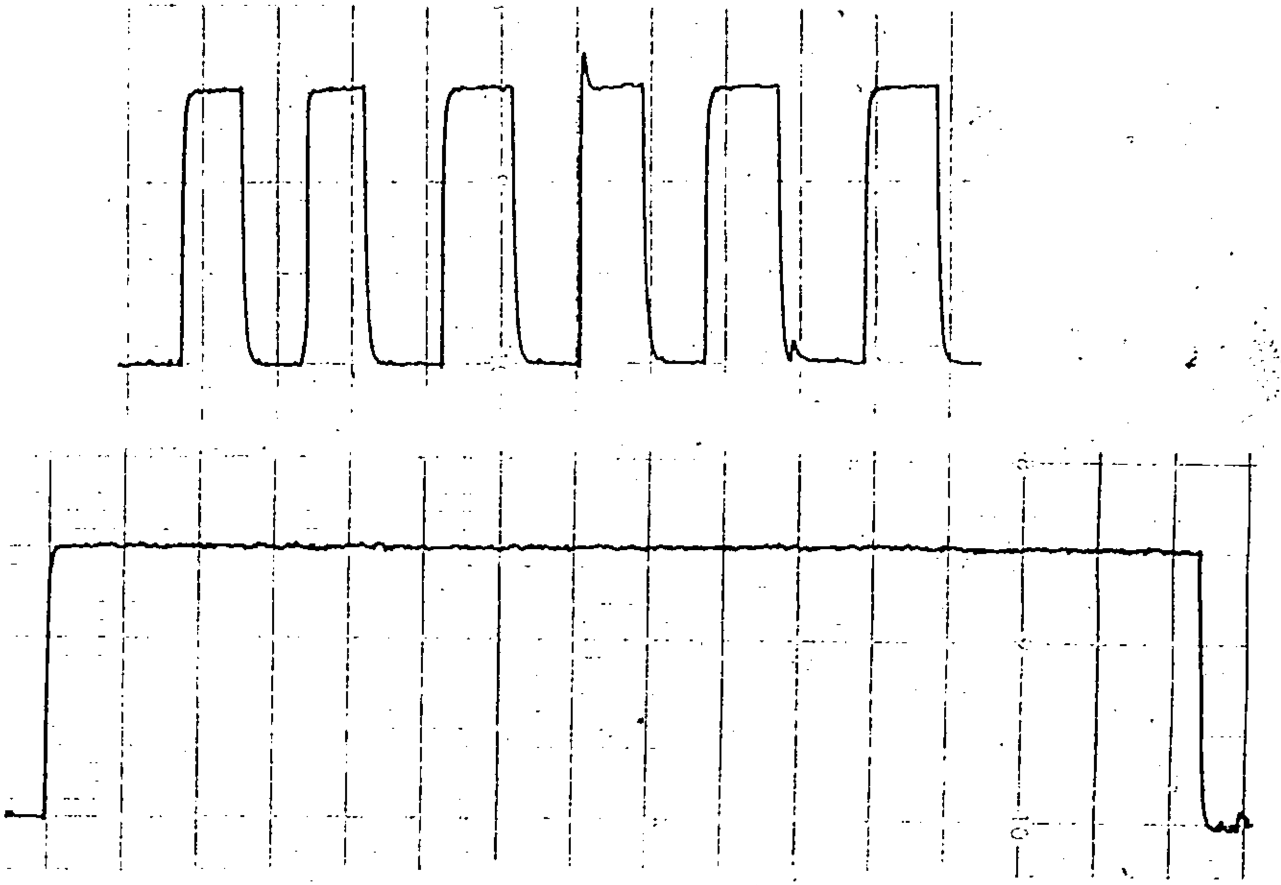


Fig. 48 Reproducibility and Stability plots for sodium by flame emission

TABLE 79

Summary of Comparison Parameters - Sodium

	Plasma Emission	Literature (1)	Atomic Emission	Literature (2)
Detection Limit (ug/ml)	0.0101	0.0004	0.0018	0.0003
max. sensitivity (ug/ml)	0.4984	–	1.5009	–
reproducibility				
mean (ug/ml)	18.96	–	15.16	–
standard deviation (ug/ml)	0.124	–	0.054	–
rel. std. deviation (%)	0.657	–	0.310	–
stability				
drift (analogue units)	+/-0.3	–	+0.1	–
noise (%)	1.1	–	0.7	–
noise level (ug/ml)	0.0106	–	0.0013	–

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 80

Standard Rock Sample Results - Sodium

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Flame	Plasma	Flame	Plasma	Flame	Plasma	Flame
% oxide	3.90	3.51	4.13	3.50	3.39	2.97	3.66	3.38
% oxide (lit.)	3.35	3.35	3.55	3.55	2.55	2.55	3.27	3.27
% difference	16.4	4.8	16.3	1.5	32.9	16.5	11.9	3.3
std. dev.	0.1109	0.1541	0.0569	0.0340	0.0660	0.0348	0.0219	0.0371
rel. std. dev.	2.8495	4.3903	1.3787	0.9732	1.9496	1.1724	0.6006	1.0998
repetitions	21	52	12	12	12	12	12	12
dilution	nil	10	nil	10	nil	10	nil	10

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 81

Instrumental Parameters for Analysis - Sodium

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	588.995	-	7.5	-	-	10	4	high	2-60
Atomic Emission	588.995	-	-	air	oxid.	20	1	high	0.3-5

(1) oxid. = oxidizing or fuel lean

TABLE 82

Wavelength, Dilution Factor and Standard Selection - Sodium

	Plasma Emission	Atomic Emission
standards required	15, 20,30	0.5, 1, 2, 3
dilution factor required	nil	10
alternate wavelengths (in order of decreasing sensitivity)	588.995nm 589.592	588.995nm 589.592

TABLE 83

Statistical Comparisons

Atomic Emission vs. Plasma Emission - Sodium

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t-test on means (1)	S	S	S	S	-
F-test on variances of means (2)	NS	NS	S	S*	S

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic emission mean closer to rec. value.
S* - means are significantly different at 5% significance level with plasma emission mean closer to rec. value.
(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic emission variances lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variances lowest.

PHOSPHORUS

Phosphorus is an element that cannot be determined directly from aqueous solution by atomic absorption techniques. This is due to the presence of phosphorus in solution as anions. In rock analysis, phosphorus is normally determined spectrophotometrically as the molybdenum blue complex. This method is good but very tedious. Particularly disadvantageous is the need to wait 24 hours for colour development as well as the narrow concentration range of the method. Therefore, the development of an emission technique is very promising. Emission techniques can then be used, however the energy contained in a flame, even a nitrous oxide-acetylene flame, is insufficient to excite enough atoms to give an instrumental reading. The use of the argon plasma excitation source did provide sufficient energy to allow analysis for phosphorus.

There are several wavelengths available for use in the analysis for phosphorus by emission spectroscopy. The wavelength recommended for phosphorus using the plasma arc is 253.565 nm (Spectrametrics Inc., 1972) however several other wavelengths are available including 255.325 nm, 255.490 nm and 650.797 nm (Meggers et al, 1956). Another wavelength at 214.980 nm has been used previously with the plasma arc by Mitchell (1977). All of these wavelengths were tested and it was found that the 214 nm line gave the strongest response and was accordingly the one that was used in this study.

The range of standards prepared was from 1 ug P/ml to 200 ug P/ml. No calibration changes, excepting gain control, were required to run this range of standards at the wavelength of 214.980 nm.

No measurable spectral interference was noted from any of the major elements tested on this wavelength. No ionization or chemical interferences were noted.

Tables 84 to 86 show the results obtained for sensitivity and detection limits, run on the most suitable wavelength of 214.980 nm. Figure 44 is a plot of typical calibration curves with correlation coefficients of .99936 and .99972 respectively. These curves show good agreement of the line of best fit with the data points. The detection limit for phosphorus by plasma emission of 0.2356 ug/ml is slightly better than the 0.4765 ug/ml obtained by Mitchell (1977) and reported by Turek et al, 1977 and than the reported optimum value of 0.500 ug/ml (Spectrametrics Inc., 1972). The values obtained for sensitivity ranged from 0.0011 ug/ml to 0.0059 ug/ml depending on the gain used.

Figure 50 is a recorder analogue output showing the results of the reproducibility and stability runs. These plots were obtained using a 200 ug P/ml standard at a gain of 5, slit width 10 u and a plasma current of 7.0A. The low relative standard deviation of 0.656% for the reproducibility readings indicate good reproducibility over six repetitions. The stability plot shows that the signal is fairly noisy with a blank noise level of 0.4937 ug/ml and noise on the peak of 3.8% but the drift from the mean is small and the zero is very stable.

Few measurable peaks were obtained when analysing the standard rock solutions as the phosphorus contents of these solutions were approximately at the level of the detection limit.

The approximate phosphorus content of the BCR-1 solutions was 1.5 ug/ml. This amount did produce measurable peaks, between 1.1 - 1.3% T. These returned a figure of 0.40% P_2O_5 as opposed to the literature figure of 0.36 % P_2O_5 (Flanagan, 1976).

The approximate phosphorus contents of the NSX-RP and GA solutions were 0.7 ug/ml and 0.5 ug/ml respectively, while sample NBS-70a contained negligible phosphorus. None of these solutions gave measurable peaks. The blank solution also did not register.

No problems occured when analysing for phosphorous but the low sensitivity made readings under 1 ug/ml unreliable. At high gain, the C-damp mode was used to further dampen the noise oscillations. The evidence is that phosphorus can be readily determined by argon plasma emission, but rock solutions, at least for some rocks, should be more concentrated. This concentration can be done by evaporation or better still, the solutions 'B' and 'JA' should be prepared to 200 ml instead of 500 ml volume.

TABLE 84

Phosphorus by Plasma Emission

Working Conditions

Wavelength 214.980 nm, Gain 10

Slit width 10 microns, Plasma current used = 7.1 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T	AVERAGE READING %T
2	1.3	1.25
5	3.3	3.2
10	6.0	5.6
20	12.0	12.0
2	1.2	
5	3.1	
10	5.2	
20	12.0	

THE SLOPE IS 0.5941

THE INTERCEPT IS 0.0056

THE CORRELATION COEFFICIENT IS .99936

THE SENSITIVITY IS 0.0059 ug/ml

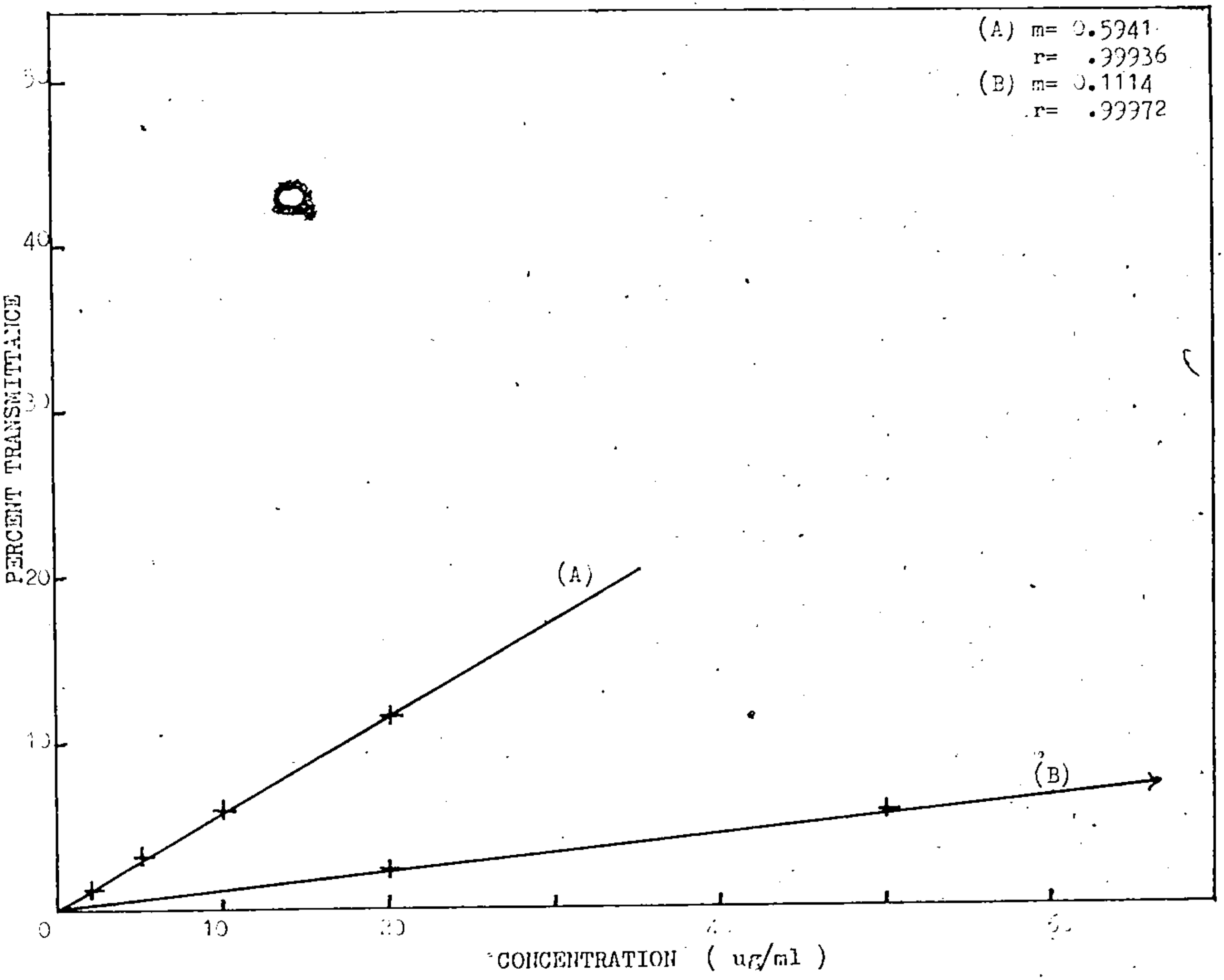


Fig. 49 Typical calibration curves for phosphorus by plasma emission

TABLE 85

Detection Limit for Phosphorus by Plasma Emission

****

Working Conditions

Wavelength 214.980 nm, Gain 10

Slit width 10 microns, Plasma current used = 7.1 Amps

Transmission mode

CONC. OF STANDARD ug/ml	ACTUAL READING %T
5	3.3
5	3.2
5	3.2
5	3.1
5	3.2
5	3.3
5	3.2
5	3.1
5	3.2
5	3.1

THE MEAN IS 3.19

THE STD. DEVIATION IS 0.070

THE SLOPE IS 0.5941

THE DETECTION LIMIT IS 0.2356 ug/ml

Fig. 50 Reproducibility and Stability plots for phosphorus by plasma emission

TABLE 86

Summary of Comparison Parameters - Phosphorus

	Plasma Emission	Literature (1)	Atomic Absorption	Literature (2)
Detection Limit (ug/ml)	0.236	0.500	N/A	N/A
max. Sensitivity (ug/ml)	0.006	–	N/A	–
reproducibility				
mean (ug/ml)	16.46	–	N/A	–
standard deviation (ug/ml)	0.094	–	N/A	–
rel. std. deviation (%)	0.656	–	N/A	–
stability				
drift (analogue units)	+/-0.4	–	N/A	–
noise (%)	3.8	–	N/A	–
noise level (ug/ml)	0.494	–	N/A	–

(1) Spectrametrics Inc., 1972

(2) Varian Techron Ltd., 1972

TABLE 87

Standard Rock Sample Results - Phosphorus

Sample	NSX-RP		GA		NBS-70a		BCR-1	
	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.	Plasma	Absorp.
% oxide	ND	N/A	ND	N/A	ND	N/A	0.40	N/A
% oxide (lit.)	0.16	0.16	0.12	0.12	-	-	0.36	0.36
% difference	-	-	-	-	-	-	11.1	-
std. dev.	-	-	-	-	-	-	0.0146	-
rel. std. dev.	-	-	-	-	-	-	3.6596	-
repetitions	18	0	4	0	4	0	10	0
dilution	nil	N/A	nil	N/A	nil	N/A	nil	N/A

N.B. The % oxide (lit.) values are from F. J. Flanagan, 1973 and 1976, for GA, BCR-1 and NBS-70a. NSX-RP values are from A. Turek, personal communication, 1978.

TABLE 88

Instrumental Parameters for Analysis - Phosphorus

method	wavelength (nm)	lamp current (mA)	plasma current (A)	support gas	flame (1)	slit width (u)	gain	type	range (ug/ml)
Plasma Emission	214.980	-	7.1	-	-	10	10	high	1-100
Atomic Absorp.	N/A	N/A	-	N/A	N/A	N/A	N/A	N/A	N/A

TABLE 89

Wavelength, Dilution Factor and Standard Selection - Phosphorus

	Plasma Emission	Atomic Emission
standards required	1, 2, 5, 10 ug/ml	N/A
dilution factor required	nil	N/A
alternate wavelengths (in order of decreasing sensitivity)	214.980nm 253.565 255.325 255.490 650.797	N/A

TABLE 90

Statistical Comparisons

Atomic Absorption vs. Plasma Emission - Phosphorus

Sample	NSX-RP	GA	NBS-70a	BCR-1	Reproducibility data
t-test on means (1)	-	-	-	-	-
F-test on variances of means (2)	-	-	-	-	-

(1) NS - means are not significantly different at 5% significance level.
S - means are significantly different at 5% significance level, with atomic absorption mean closer to rec. value.
S* - means are significantly different at 5% significance level, with plasma emission mean closer to rec. value.
(2) NS - variances are not significantly different at 5% significance level.
S - variances are significantly different at 5% significance level, with atomic absorption variance lowest.
S* - variances are significantly different at 5% significance level, with plasma emission variance lowest.

SINGLE SOLUTION DISSOLUTION versus STANDARD $HF-HClO_3-HCl$ DISSOLUTION

The single solution (HF) pressure bomb dissolution, or 'solution JA' was compared with the standard $HF-HClO_3-HCl$ multiple solution dissolution, or 'solution B', using a common standard rock sample (GA). Each solution was analysed for all ten major elements by both plasma and flame techniques. Each pair of results for variance and mean values were compared using the 't' and 'F' tests described earlier. A summary of the findings of the tests can be found in Table 91. A total of seventeen comparisons were computed.

The variances did not prove to be substantially different. Statistically, of the seventeen comparisons, nine variance pairs (or 52.9%) were not significantly different at the 5% significance level. The remaining eight pairs were significantly different and for all eight, the variance values for the 'solution B' dissolution were the lowest. Not one variance from the 'solution JA' dissolution was significantly lower than the corresponding variance from 'solution B'. Of these significantly different pairs, only one pair showed extremely different variances (manganese). This was due to the low concentration of the metal in the solution.

The results of the comparisons of the mean values obtained were not as conclusive. Of the seventeen comparisons, the means of eleven (or 64.7%) were not significantly different.

The remaining six comparisons showed means that were significantly different, however the split was three for 'solution JA' with means closer to the recommended value and three for 'solution B'. In most of these cases there was a substantial difference between the means (see Table 91) but the trend was for the 'JA' solutions to give more accurate results when using the plasma emission technique while with the flame method, the 'B' solutions gave the more accurate results. The most dramatic improvements in accuracy were obtained by using solution 'JA' in the analysis for sodium, potassium and calcium by plasma emission. The differences from the recommended values were much lower; sodium, 4.5% vs. 16.3%; potassium, 5% vs. 38%; and, calcium, 6.9% vs. 14.3%. This is possibly due to the suppression of ionization of these metals by the boric acid-hydrofluoric acid complex in the solution.

The advantages of the 'solution JA' are:

(1) the silicon is not lost during dissolution as with 'solution B';

(2) for silicon analysis, this dissolution is much quicker than a fusion method (see Turek and Riddle, 1977, for details of this procedure);

(3) this dissolution appears to give better results using the plasma emission technique for the more easily ionized metals.

With respect to accuracy , 'solution JA' gives results that are as close if not closer than the results of 'solution B' As a result of this, the use of 'solution JA' in major element rock analysis can be recommended, as much for the accuracy and precision results as for the much easier and quicker sample preparation time.

TABLE 91

Comparison of results obtained using solutions 'B' and 'JA' on sample GA

element	Mean Values				Significance (1)	Variance Values		Significance (1)
	Solution 'B'		Solution 'JA'			Solution 'B' Std. Dev.	solution 'JA' Std. Dev.	
	% oxide	% diff. from rec.	% oxide	% diff. from rec.				
Si	-	-	-	-	-	-	-	-
Al-plasma	14.26	-1.6	14.81	+2.1	NS	0.1430	0.3235	S*
-A.A.	14.88	+2.6	14.80	+2.6	NS	0.2275	0.3310	NS
Fe-plasma	2.80	-1.1	2.99	+5.7	NS	0.0311	0.0922	S*
-A.A.	2.80	-1.1	2.75	-2.8	NS	0.0222	0.0289	NS
Mn-plasma	0.104	+15.6	0.125	+38.9	NS	0.0047	0.0091	S*
-A.A.	0.095	+5.6	0.084	-6.7	S*	0.0007	0.0012	NS
Ti-plasma	0.407	+7.1	0.394	+3.7	NS	0.0087	0.0102	NS
-A.A.	0.778	+104.7	0.931	+145.0	NS	0.0719	0.0963	NS
Ca-plasma	2.80	+14.3	2.62	+6.9	S	0.0379	0.0750	S*
-A.E.	3.17	+29.6	3.81	+30.1	NS	0.0192	0.0100	S*
-A.A.	2.99	+22.0	3.07	+25.3	NS	0.0575	0.0225	S*
Mg-plasma	1.14	+20.0	1.32	+38.9	S*	0.0209	0.0251	NS
-A.A.	1.05	+10.5	1.05	+10.1	NS	0.0103	0.0062	NS
K-plasma	5.56	+38.0	4.23	+5.0	S	0.0284	0.1116	S*
-A.E.	4.01	-0.6	3.61	-10.4	S*	0.0096	0.0201	S*
Na-plasma	4.13	+16.3	3.71	+4.5	S	0.0569	0.0708	NS
-A.E.	3.50	-1.5	3.53	-0.6	NS	0.0340	0.0564	NS

(1) NS - results not significantly different

S*- results significantly different - solution 'B' results better

S - results significantly different - Solution 'JA' results better

DISCUSSION AND CONCLUSIONS

This study involved a comparison of the argon plasma jet excitation source with the traditional atomic absorption/ emission flame excitation source in major and minor element analysis of rocks and soils. The cost of the conversion was approximately $3,500.00 and the goal of the study was to show that an investment of this amount could lead to substantial improvements in the performance of the basic Varian Techron AA-5 atomic absorption spectrophotometer.

The high temperature of the plasma dissociates nearly all molecular bonds, eliminating many matrix effects and the interelement interferences generally are diminished.

This was apparent when analysing for refractory elements such as titanium and for non-metals such as phosphorus. The sensitivities for these elements were much higher than when using the flame source. Further advantages of the argon plasma jet are the safety features and low cost of the non-explosive inert argon and the operating comfort due to the low heat output of the plasma arc.

The addition of this source to the atomic absorption unit has been shown to improve the sensitivity and lower the detection limits for several of the ten major elements. These include silicon, aluminum, titanium, magnesium and phosphorus (Table 94). Stability and reproducibility of the signal did not deteriorate with the use of the plasma arc. Several elements that are difficult to determine by flame methods, silicon and titanium, were determined more easily and more accurately by plasma emission (Tables 92, 93 and 96, Fig. 51). Phosphorus, an element that cannot be determined by atomic absorption and extremely poorly by flame emission, was easily determined by plasma emission.

The addition of the plasma source also has additional advantages over the flame system. The optical parameters are similar for all the elements tested with the only adjustments necessary being gain and wavelength selection. No burner, fuel or flame stoichiometry changes are necessary as with the flame source and no hollow cathode lamps are needed as with atomic absorption. The operator comfort is also improved as the heat dissipation is better with the plasma source, radiating only several hundred watts of power, with the resultant low heat transfer to the room. No flashbacks are possible using the inert argon as is possible when using a nitrous oxide-acetylene flame. The use of a peristaltic pump allows a controlled and even sample uptake, with less sample consumption than with a burner/nebulizer setup.

In general the plasma arc source showed a greater linear dynamic range over either atomic absorption or flame emission, without adjustments in the optical parameters or sample manipulation (dilution/concentration). This greater range is an asset when samples containing varying concentrations

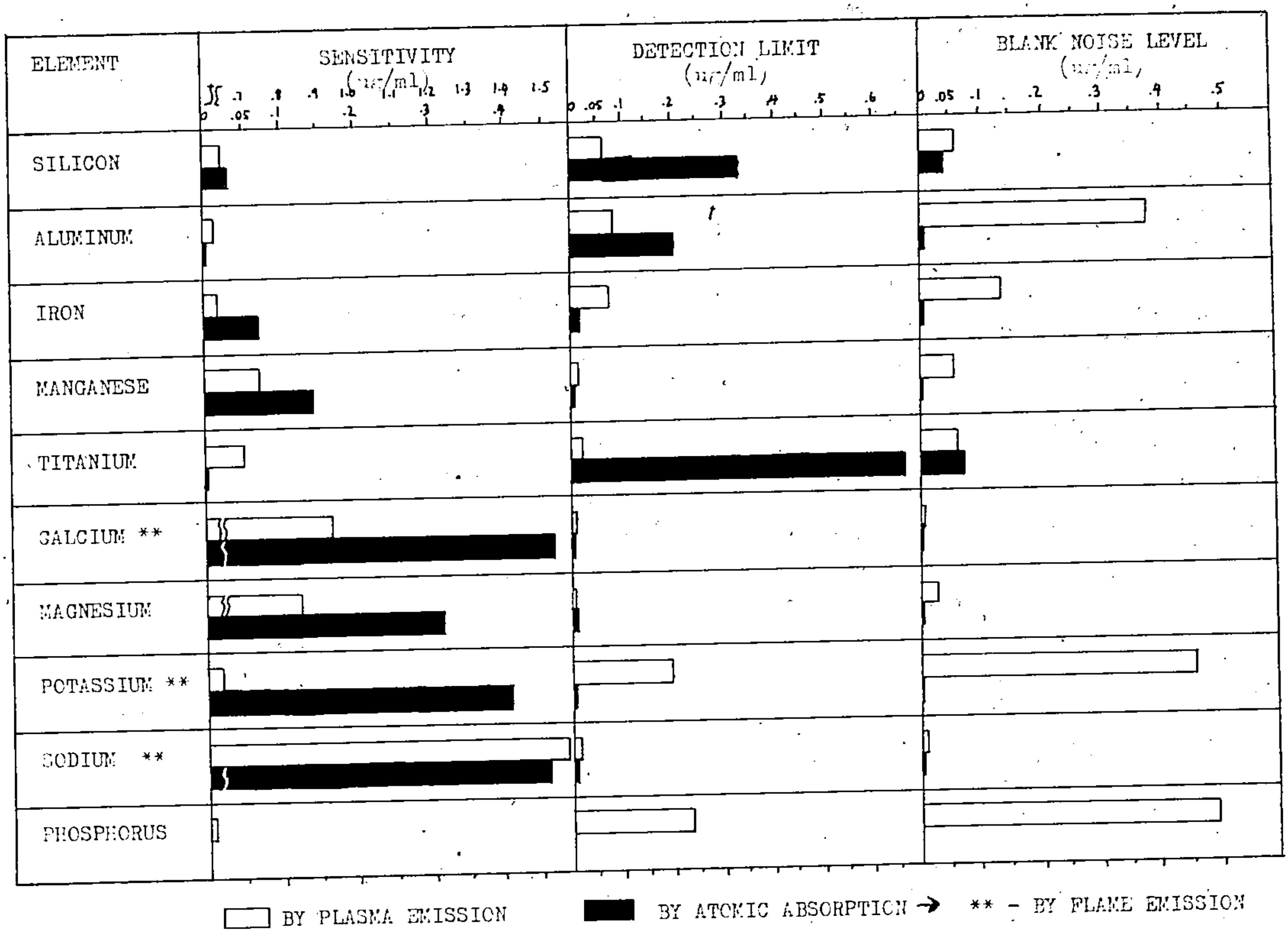


Fig. 51 Sensitivities, Detection Limits and Blank Noise Levels

of an element have to be analysed together.

The advantages of the plasma technique can be seen in the preceding discussions. Only by choosing an alternate wavelength can the sensitivity of the atomic absorption technique be substantially changed. When this occurs, the instrument must be set up again (gain, etc.) to show 100% T. This means that the slit width and lamp current can not be used as variables. The use of the emission technique allows the use of slit width as variable and eliminates the lamp current as a parameter. When changing to an alternate line, the instrument does not have to be reset, only the backing must be corrected.

The main problem with flame emission is that it is not significantly better than atomic absorption except when analysing for sodium or potassium. In the other cases, the flexibility gained is lost to the reduced sensitivity and detection limits obtained. By using the plasma emission method, the flexibility is retained and the sensitivity and detection limits are as good if not better than for atomic absorption for most elements.

The deciding factor in this study was the accuracy, precision, reproducibility and stability of the analyses by plasma emission, on the standard rock samples, as compared to the appropriate flame method (Tables 92, 93 and 96). In this sense, plasma emission does not appear to be as good as described above. Of the five elements mentioned earlier as being better with respect to sensitivity and detection limit; one, magnesium, must now be regarded as an element to be analysed by atomic absorption rather than by plasma emission due to the grave inaccuracies and low precision shown by plasma emission. Another, aluminum, loses most of the advantage gained with detection limit and sensitivity by plasma emission to the lesser noise and better reproducibility available by using atomic absorption. On the other hand, analysis for an element that has better sensitivity and detection limit by atomic absorption, iron, becomes more attractive by plasma emission due to the greater flexibility and higher accuracy at low concentrations possible by that method. Phosphorus and titanium, as before, are difficult if not impossible to do by flame methods and are easily done by plasma emission. Three other element analyses, sodium, potassium and manganese, proved to be much more accurate and precise by flame methods as well as having lower detection limits and better sensitivities. The reproducibility, stability and noise levels by the flame methods were also better than that possible using plasma emission for these elements.

Plasma emission is the recommended method for silicon. The problems when using the flame, such as burner blockage and excessive heat output, outweighed the better reproducibility obtained by atomic absorption and left plasma emission as the recommended method.

The only element remaining is calcium. This element was analysed by three methods; plasma and flame emission as well as atomic absorption. The sensitivities and detection limits by the emission methods are similar with the flame method being somewhat better, however, with regards to accuracy and precision there was little difference. The plasma method appeared to be less precise and less accurate at low calcium concentrations than was atomic emission and the opposite occured at higher concentrations. Atomic absorption was not far off in any of these categories. Because of this, any of these three methods, but especially either of the emission methods, could be used with reliability in the analysis for calcium.

[illegible]

From the preceding summary, it can be seen that the plasma emission technique proved to be much better than either flame method for two elements, titanium and phosphorus, and was only somewhat better than the flame methods for two others, silicon and iron. Both flame and plasma methods appeared to work equally well in the analysis for calcium while atomic absorption appeared to work somewhat better for aluminum. On the other hand the flame methods worked substantially better in the analyses for magnesium, potassium, sodium and manganese.

From this, the financial costs involved can be seen to expand the analytical capabilities absorption instrument. The point that must be emphasized is that the addition of the plasma arc improved the results *substantially* for only two elements, titanium and phosphorus and only slightly better results were obtained for two other elements, silicon and iron. The latter two elements can be analysed almost as well by atomic absorption however, the former two elements cannot. The other main advantage of the plasma technique is the capability of running a series of elements rapidly without shutting down or resetting the instrument. The investment of this money must be weighed against the demand for phosphorus and titanium analyses to be done, and the trouble of longer analysis time through analysis by optical spectrophotometer. For major element rock analysis involving only these ten elements, the added expense of installing the plasma arc to the atomic absorption unit can be justified if a large number of samples are to be analysed for titanium and phosphorus or if a large number of elements are to be analysed for in the samples.

This cost, $3,500.00, is very reasonable for the results obtained, as an investment of $1,000.00 per extra element is not excessive. Alternative methods such as spectrophotometry and potentiometric and photometric titrations are also expensive. The larger dynamic range of the plasma source makes it highly suitable for geochemical exploration sample analyses. The range of elemental concentrations in these rock samples are extremely variable and often require numerous dilutions when analysed by the conventional atomic absorption method.

It has been shown that for the 10 elements in this study, the plasma source has advantages in the analysis of elements that are difficult by flame methods. Although this study is restricted to 10 of the 13 elements normally determined in major rock analyses (the other three are FeO, H_2O and CO_2), there are other 'minor' elements that are in some cases found in greater concentrations than Mn and Ti, for instance. Examples of these are barium and boron, both of which are not usually analysed for because of analytical difficulties. With the availability of the plasma emission technique, , such elements could be included in major element analysis.

With regard to the dissolution comparison, it has been shown that the single solution dissolution is not significantly less accurate than the standard HF-$HClO_3$-HCl multiple solution dissolution. It does show, however, slightly poorer precision. The main advantages of using this solution are:

(1) quicker dissolution time;

(2) the ability to analyse for silicon.

An additional advantage to this dissolution is the use of pressure bombs in the process. This requires less expenditure than for the platinum dishes required by 'solution B', if numerous samples are to be prepared simultaneously. On top of this there is no question that the use of 'solution JA' is much faster and easier to prepare than a standard fusion dissolution for the analysis for silicon.

In short, this single solution dissolution becomes ideal when small batches of samples must be analysed for silicon by either flame or plasma methods or for sodium, potassium or calcium by plasma emission. For larger batches, if Si is not being determined, the 'solution B' dissolution is better despite the longer preparation time as less apparatus is required.

TABLE 92

Summary of Results - Plasma Emission Method

Sample		$\%S_iO_2$	$\%Al_2O_3$	$\%Fe_2O_3$[3]	$\%M_nO$	$\%T_iO_2$	$\%CaO$	$\%M_gO$	$\%K_2O$	$\%Na_2O$	$\%P_2O_5$
BCR-1	ref value (1)	54.50	13.61	13.40	0.18	2.20	6.92	3.46	1.70	3.27	0.36
	exp value (2)	N/A	13.81	14.09	0.28	2.10	6.98	5.39	3.66	3.66	0.40
GA	ref value (1)	69.90	14.50	2.83	0.09	0.38	2.45	0.95	4.03	3.55	0.12
	exp value (2)	70.92*	14.26	2.80	0.10	0.41	2.80	1.14	5.56	4.13	ND
NSX-RP	ref value (1)	67.54	15.27	4.07	0.082	0.57	2.10	1.15	3.93	3.35	0.16
	exp value (2)	N/A	14.82	4.17	0.112	0.62	2.53	1.61	5.58	3.90	ND
NBS-70a	ref value (1)	67.10	17.90	0.075	-	0.01	0.11	-	11.80	2.55	-
	exp value (2)	N/A	17.81	0.079	ND	ND	0.32	0.52	13.42	3.39	ND

(1) F. J. Flanagan, 1973 and 1976.

(2) A. Turek, personal communication, 1978.

(3) Total Fe expressed as Fe_2O_3

* single solution dissolution

TABLE 93

Summary of Results - Flame Method - Atomic Absorption

Sample		%SiO_2	%Al_2O_3	%Fe_2O_3[3]	%MnO	%TiO_2	%CaO[4]	%MgO	%K_2O[4]	%NaO[4]	%P_2O_5
BCR-1	ref value (1)	54.50	13.61	13.40	0.18	2.20	6.92	3.46	1.70	3.27	0.36
	exp value (2)	N/A	13.81	12.73	0.21	4.62	7.43	4.19	1.81	3.38	N/A
GA	ref value (1)	69.90	14.50	2.83	0.09	0.38	2.45	0.95	4.03	3.55	0.12
	exp value (2)	68.78*	14.88	2.80	0.10	0.78	2.99	1.05	4.01	3.50	N/A
NSX-RP	ref value (1)	67.54	15.27	4.07	0.082	0.57	2.10	1.15	3.93	3.35	0.16
	exp value (2)	N/A	14.82	3.89	0.086	1.30	2.65	1.31	3.99	3.51	N/A
NBS-70a	ref value (1)	67.10	17.90	0.075	-	0.01	0.11	-	11.80	2.55	-
	exp value (2)	N/A	17.82	0.091	0.001	ND	0.15	0.43	11.83	2.97	N/A

(1) F. J. Flanagan, 1973 and 1976.

(2) A. Turek, personal communication, 1978.

(3) Total Fe expressed as Fe_2O_3.

(4) Analysis by flame emission.

* Single solution dissolution.

TABLE 94

Comparison of Sensitivities and Detection Limits

Element	Max. Sensitivity (ug/ml)		Detection Limit (ug/ml)	
	Flame (1)	Plasma	Flame (1)	Plasma
Si	0.0029	0.0265	0.3346	0.0624
Al	0.0063	0.0185	0.2039	0.0864
Fe	0.0719	0.0192	0.0127	0.0775
Mn	0.1492	0.0719	0.0083	0.0127
Ti	0.0016	0.0495	0.6673	0.0197
Ca	1.5219*	0.9359	0.0011*	0.0019
Mg	0.3188	0.8475	0.0052	0.0035
K	1.4009*	0.0189	0.0012*	0.1968
Na	1.5009*	0.4984	0.0018*	0.0101
P	N/A	0.0059	N/A	0.2351

(1) analysis by atomic absorption unless marked by * where analysis was by flame emission.

TABLE 95
Method Comparison

element	Flame much better	Flame somewhat better	No difference	Plasma somewhat better	Plasma much better
Si				X	
Al		X			
Fe				X	
Mn	X				
Ti					X
Ca			X		
Mg	X				
K	X				
Na	X				
P					X

TABLE 96

Summary of Analytical Results

Oxide	SAMPLE (% OXIDE)											
	GA (1)			BCR-1 (1)			NBS-70a (1)			NSX-RP (2)		
	record.	plasma emiss	atomic absorp	record.	plasma emiss	atomic absorp	record.	plasma emiss	atomic absorp	record.	plasma emiss	atomic absorp
S_iO_2	69.90	70.012	68.78	54.50	N/A	N/A	67.10	N/A	N/A	67.54	N/A	N/A
Al_2O_3	14.50	14.26	14.88	13.61	13.81	13.18	17.90	17.81	17.82	15.27	14.82	14.82
Fe_2O_3	2.83	2.80	2.80	13.40	14.09	12.73	0.075	0.079	0.091	4.07	4.17	3.89
MnO	0.090	0.104	0.095	0.180	0.275	0.207	-	ND	0.001	0.082	0.112	0.086
TiO_2	0.38	0.41	0.78	2.20	2.10	4.62	0.01	ND	ND	0.57	0.62	1.30
CaO	2.45	2.80	2.99	6.92	6.98	7.43	0.11	0.32	0.15	2.10	2.53	2.65
MgO	0.95	1.14	1.05	3.46	5.39	4.19	-	0.052	0.043	1.15	1.61	1.31
K_2O*	4.03	5.56	4.01	1.70	3.66	1.81	11.80	13.42	11.83	3.93	5.58	3.99
Na_2O*	3.55	4.13	3.50	3.27	3.66	3.38	2.55	3.39	2.97	3.35	3.90	3.51
P_2O_5	0.12	**	N/A	0.36	0.40	N/A	-	**	N/A	0.16	**	N/A

* flame method was emission

** detected but not quantitatively measured

(1) recorded values for GA, BCR-1 and NBS-70a are from F. J. Flanagan, 1973 and 1976.

(2) recorded values for NSX-RP are from A. Turek, personal communication, 1978.

APPENDIX I

APPENDIX I

Spectral Interferences by Method

(1) Argon Plasma Emission

element	major interferent	minor interferent	wavelength (nm)
Si	nil	nil	251.612
Al	nil	nil	396.155
Fe	nil	nil	371.994
Mn	Fe	nil	403.076
Ti	nil	nil	334.903
Ca	Al, Na, K	nil	393.367
Mg	Mn	Fe	279.553
K	Mg	Fe	766.490
Na	K	nil	588.995
P	nil	nil	214.980

(2) Atomic Absorption

element	major interferent	minor interferent	wavelength (nm)
Si	nil	nil	251.612
Al	nil	nil	309.271
Fe	nil	nil	248.330
Mn	Fe, Mg	nil	279.480
Ti	nil	nil	363.300
Ca	Al, Na, K	Fe	422.700
Mg	Fe	Na, Al	285.213

(3) Atomic (Flame) Emission

element	major interferent	minor interferent	wavelength (nm)
Ca	Al, Na, K	nil	422.750
K	nil	Na	766.490
Na	K	nil	588.995

APPENDIX II.

APPENDIX II
Instrument Operating Procedures - by Method

(1) Argon Plasma Emission

ON - cooling water and fan on, monochromator , photo-multiplier and chopper on
- argon on, power supply on
- extend cathode 1/8" beyond ceramic sleeve
- set plasma current to 7.0A
- ignite plasma
- retract cathode approximately 1/4"
- pump on and aspirate distilled water - allow arc to stabilize
- set wavelength and optimize parameters

OFF- pump off, turn off arc
- argon off, power supply off
- cooling water and turn off, monochronometer, photomultiplier and chopper off

(2) Atomic Absorption and Flame Emission

- for atomic absorption:

ON - fan on, monochromator , lamp, indicating module on
- wait 10-15 minutes for warm up
- set controls to 'T', select 'normal', set with gain approximately 80%T
- maximize reading using 'λ set'
- light flame
- adjust gain to 100%T, zero with backing control
- select 'Abs', 'Auto-set', use 'adj. Auto-set' to read 0.0000 of Abs
- adjust burner position and flame stoichiometry

(2) Atomic Absorption and Flame Emission (Cont'd.)

OFF- acetylene off, air off, lamp, monochromator,
indicating module

- for N_2O Support Gas - use N_2O burner and gas

ON - as for air, turn on N_2O
  - increase acetylene flame to 9
  - rotate support switch to N_2O

OFF- increase acetylene to luminous flame
  - switch to air

- for flame emission - as for atomic absorption but ignore lamps and turn on chopper
  - all readings in 'T' mode at 'high gain'

APPENDIX III

APPENDIX III

CONVERSION FACTORS

$$\mathrm{Al} \underset{0.5291}{\overset{1.8899}{\rightleftarrows}} \mathrm{Al_2O_3}$$

$$\mathrm{Fe} \underset{0.6994}{\overset{1.4297}{\rightleftarrows}} \mathrm{Fe_2O_3}$$

$$\mathrm{K} \underset{0.8302}{\overset{1.2046}{\rightleftarrows}} \mathrm{K_2O}$$

$$\mathrm{Mg} \underset{0.6032}{\overset{1.6579}{\rightleftarrows}} \mathrm{MgO}$$

$$\mathrm{Mn} \underset{0.7744}{\overset{1.2913}{\rightleftarrows}} \mathrm{MnO}$$

$$\mathrm{Na} \underset{0.7919}{\overset{1.3480}{\rightleftarrows}} \mathrm{Na_2O}$$

$$\mathrm{P} \underset{0.4365}{\overset{2.2912}{\rightleftarrows}} \mathrm{P_2O_5}$$

$$\mathrm{Ti} \underset{0.5995}{\overset{1.6681}{\rightleftarrows}} \mathrm{TiO_2}$$

$$\mathrm{Si} \underset{0.4675}{\overset{2.1392}{\rightleftarrows}} \mathrm{SiO_2}$$

$$\mathrm{Ca} \underset{0.7147}{\overset{1.3992}{\rightleftarrows}} \mathrm{CaO}$$

-example Aluminum

Al to Al_2O_3

$$\text{conversion factor} = \frac{\text{molecular wt.}Al_2O_3}{(\text{atomic wt Al}) \times 2} = \frac{2 \times 27 + 3 \times 16}{2 \times 27} =$$

$$\frac{102}{54} = 1.8899$$

-general form of equation for metal to oxide

$$CF = \frac{\text{molecular wt.}}{\text{atomic wt x n}}$$

-general form of equation for oxide to metal

$$CF = \frac{\text{atomic wt. x n}}{\text{molecular wt.}}$$

-where n is frequency of metal in oxide forumla

APPENDIX IV

APPENDIX IV

COMPUTATIONAL PROGRAMS FOR WANG CORP. MODEL 2200 MINICOMPUTER

1) Program for 't' - test for rejection of values

```
10 SELECT PRINT 005
20 DIM A (60), D1 (60), E1(30), H(60), B8(60)
30 INPUT "OXIDE, SAMPLE, METHOD", O$.S$,M$
40 PRINT HEX (03)
50 INPUT "NUMBER OF DETERMINATIONS=",N1
60 PRINT HEX(03)
70 PRINT "REPLICATE VALUES="
80 W6=N1
90 FOR B=1 TO W6
100 INPUT A(B)
110 NEXT B
120 J=0
130 INPUT "ROW TO BE CORRECTED=",J
140 IF J= 0 THEN 170
150 GOSUB '1 (J,A(J))
160 GOTO 130
170 S1-0
180 FOR B=1 TO W6
190 IF A(B) = 9999 THEN 210
200 S1 = S1 + A(B)
210 NEXT B
220 M1 = S1/N1
230 D9=0
240 FOR B=1 TO W6
250 IF A(E) = 9999 THEN 300
260 D1(B) = A(B)-M1
270 D9 = D9 + (D1(B)½2)
280 IF D1(B)1 = 0 THEN 300
290 D1(B) = D1(B)*(-1)
300 NEXT B
310 IF D9!10 THEN 330
320 D9 = .0000000001
330 V1 = D9/N1
340 S2 = SQR(V1)
350 FOR B = 1 TO W6
360 IF A(B) = 9999 THEN 390
370 D3 = (2*S2)-D1(B)
380 IF D3!=0 THEN 440
390 NEXT B
400 N2 = N1-1
410 W5 = N2-0.85
420 T3 - 1.96 - 0.00554568(W5) + 2.405933/W5 + 0.671777/W5½
2) - 0.3831214/(W5½3)
430 GOTO 670
```

```
440 D7 = A(B)
450 C7 = 0
460 FOR H = 1 TO W6
470 IF A(H) = D7 THEN 490
480 GOTO 500
490 C7 = C7 + 1
500 NEXT H
510 T1 = A(B) - M1
520 IF T11 = 0 THEN 540
530 T1 = T1*(-1)
540 T2 = (T1*SQR(C7))/S2
550 N2 = N1 - 1
560 W5 - N2 - 0.85
570 T3 - 1.96 - 0.00554568/SQR(W5) + 2.4059333/W5 +
0.671777/(W5½ 2) - 0.3831214/(W5½3)
580 IF T31T2 THEN 670
590 FOR K=1 TO W6
600 IF A(K)=D7 THEN 620
610 GOTO 640
620 B8(K) = A(K)
630 A(K) = 999
640 NEXT K
650 N1 = N1 - C7
660 GOTO 170
670 SELECT PRINT 211(120)
680 PRINT "T-TEST FOR REJECTION OF VALUES"
690 PRINT "******************************
700 PRINT "*************************************
%******************"
710 PRINT USING 720,0$,S$,M$
720 % ALL FOLLOWING VALUES FOR ##### FOR ##### BY #########
 ARE SIGNIFICANT
730 FOR B = 1 0 W6
740 IF A(B) = 9999 THEN 770
750 PRINT USING 760,A(B)
760 %                  ##.####
770 NEXT B
780 PRINT "   **********************************
*******************"
790 PRINT "REJECTED VALUES ARE-"
800 FOR B = 1 TO W6
810 IF B8(B) = 0 THEN 840
820 PRINT USING 760,B8(B)
830 X6 = X6 + 1
840 NEXT B
850 IF X6! 10 THEN 870
860 PRINT "NO VALUES REJECTED"
870 PRINT "   **********************************
 ******************"
880 C1 = S2/M1* 100
890 M4 = S2/SQR(N2 + 1)
```

```
900 S3 = T3 + S4
910 PRINT USING 920, M1, S3, N2, S4
920 % MEAN = ##.### +/- #.#### (ug/ml) WITH D.F. = STD
 ERROR =  .###
930 PRINT
940 PRINT USING 950,S2,C1,T3
950 %  STD. DEVIATION = #.###  REL. TD. DEVIATION = ##.####
 t-Tab = #.###
960 GOTO 1020
970 DEFFN '1  (J,H(J))
980 PRINT "INCORRECT VALUE=", H(J)
990 INPUT "CORRECT VALUE = H(J)
1000 A(J) = H(J)
1010 RETURN
1020 STOP
1030 END
```

SAMPLE PROGRAM RUN

```
                t-TEST FOR REJECTION OF VALUES
***************************************************************
ALL FOLLOWING VALUES FOR MnO  FOR GA   BY PLASMA  ARE SIGNIFICANT
                    0.0980
                    0.1020
                    0.1030
                    0.1070
                    0.1030
                    0.1120
                    0.0980
                    0.1120
                    0.1030
                    0.1070
                    0.0980
                    0.1070
***************************************************************

     REJECTED VALUES ARE-
                NO VALUES REJECTED
***************************************************************
MEAN = 0.104 +/- 0.0030 (ug/ml)WITH D.F. = 11  STD. ERROR =0.0013

STD. DEVIATION = 0.0047 , REL. STD. DEVIATION = 4.5508

T-TAB. = 2.2014
```

2) Slope and Detection Limit Program

```
10 SELECT  PRINT 005
20 DIM A(25), C(25), F(25), H(25), G(25)
30 N2 = 1
40 PRINT HEX(03)
50 INPUT  "SLOPE S3=0  DETECTION LIMIT S3=1
           PROGRAM TYPE=", S3
60 PRINT HEX(03)
70 INPUT  "PLASMA L1=1  FLAME L1=0
           EXCITATION SOURCE=", L1
80 PRINT HEX(03)
90 INPUT  "ELEMENT,
           ATOMIC OR PLASMA,
           ABSORPTION OR EMISSION",E$,O$,T$
100 PRINT HEX(03)
110 INPUT  "WAVELENGTH USED=
            GAIN USED=
            SLIT WIDTH USED=", A1,B1,C1
120 PRINT HEX(03)
130 IF  L1=0 THEN 150
140 INPUT  "PLASMA CURRENT USED=", D1
150 IF L1=1 THEN 240
160 INPUT  "LAMP CURRENT USED=", E1
170 PRINT HEX(03)
180 INPUT  "STOICHIOMETRY - OXIDIZING M1=1 REDUCING M1=0
            FLAME STOICHIOMETRY USED=", M1
190 PRINT HEX(03)
200 INPUT  "SUPPORT AIR N1=1  NITROUS OXIDE N1=0
            SUPPORT GAS USED=", N1
210 PRINT HEX(03)
220 INPUT  "MODE TRANSMISSION N2=1  ABSORPTION N2=0
            MODE USED =", N2
230 PRINT HEX(03)
240 INPUT  "NUMBER OF VARIABLES=", K
250 PRINT HEX(03)
260 IF  S3=0 THEN 280
270 INPUT  "SLOPE=", S9
280 PRINT  "STANDARD CONCENTRATIONS"
290 N4=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(N4,A(J))
370 GOTO 340
380 PRINT  "ACTUAL READING"
390 N4=2
400 FOR B=1 TO K
```

```
410 INPUT C(B)
420 IF S3=0 THEN 440
430 S4=S4 + C(B)
440 NEXT B
450 J=0
460 INPUT  "ROW TO BE CORRECTED=",J
470 IF J=0 THEN 500
480 GOSUB ' 1 (N4,C(J))
490 GOTO 460
500 IF S3=0 THEN 590
510 W6=S4/K
520 FOR B=1 TO K
530 D4= D4 + ((C(B)-W6)½2)
540 NEXT B
550 V6=D4/K
560 S7=SQR(V6)
570 D5=2*S7
580 D8=D5/S9
590 SELECT PRINT 211
600 IF S3=1 THEN 810
610 Y=K/2
620 FOR B=1 TO Y
630 F(B) = (C(B) + C(B+Y))/2
640 G(B) = A(B)
650 NEXT B
660 Z = Y+8
670 FOR B = 1 TO Z
680 L = L+ G(B)
690 M = M+ F(B)
700 NEXT B
710 N=L/Z
720 P=M/Z
730 FOR B=1 TO Z
740 Q= Q+ ((G(B)-N)* (F(B)-P)
750 R= R+  ((G(B)-N)½2)
760 U= U+ ((F(B)-P)½2)
770 NEXT B
780 S=Q/R
790 T= P-(S*N)
800 V= Q/SQR(R*U)
810 IF S3= 0 THEN 850
820 PRINT USING 830,E$,O$,T$
830 %   DETECTION LIMIT FOR ########## BY ###### ##########
840 GOTO 870
850 PRINT USING 860,E$,O$,T$
860 %           ########## BY ###### ##########
870 PRINT
880 PRINT  "    *******************************************
890 PRINT  "     WORKING CONDITIONS"
```

```
900 PRINT USING 910,A1,B1
910 %  WAVELENGTH ###.# nm, GAIN ##
920 IF L1=0 THEN 950
930 PRINT USING 940,C1,D1
940 %  SLIT WIDTH ### MICRONS, PLASMA CURRENT USED= #.# Amps
950 IF.L1=1 THEN 1060
960 PRINT USING 970,C1,E1
970 %  SLIT WIDTH ### MICRONS, LAMP CURRENT USED= ## mA
980 IF N1=0 THEN 1000
990 PRINT  "   SUPPORT GAS USED WITH AIR"
1000 IF N1=1 THEN 1020
1010 P" NT "  SUPPORT GAS USED WAS NITROUS OXIDE"
1020 IF M1=0 THEN 1040
1030 PRINT  "  FLAME STOICHIOMETRY WAS OXIDIZING"
1040 IF M1=1 THEN 1060
1050 PRINT  "  FLAME STOICHIOMETRY WAS REDUCING"
1060 IF N2=0 THEN 1080
1070 PRINT  "  TRANSMISSION MODE"
1080 IF N2-1 THEN 1100
1090 PRINT  "  ABSORPTION MODE"
1100 PRINT  "  *****************************************
***"
1110 IF S3=1 THEN 1400
1120 PRINT  "  CONC. OF         ACTUAL              AVERAGE
1130 PRINT  "  STANDARD         READING             READ
1140 IF N2=0 THEN 1160
1150 PRINT  "  ug/ml               %T                  %T
"
1160 IF N2=1 THEN 1180
1170 PRINT  "  ug/ml               %Abs                %Abs
1180 PRINT  "  *****************************************"
1190 FOR B=1 TO Y
1200 PRINT USING 1210,A(B),C(B),F(B)
1210 %      ###.##             ##.#                ##.##
1220 NEXT B
1230 Y=Y + 1
1240 FOR B=Y TO K
1250 PRINT USING 1210, A(B),C(B)
1260 NEXT B
1270 PRINT  "  *****************************************
***"
1280 S2=S/100
1290 PRINT USING 1300,S
1300 %       THE SLOPE IS ###.####
1310 PRINT
1320 PRINT USING 1330,T
1330 %       THE INTERCEPT IS #.####
1340 PRINT
1350 PRINT USING 1360, ✓
1360 %       THE CORRELATION COEFFICIENT IS #.####
```

```
1370 PRINT
1380 PRINT USING 1390,S2
1390 %       THE SENSITIVITY IS ##.#### ug/ml
1400 IF S3=0 THEN 1610
1410 PRINT  "      CONC. OF             ACTUAL"
1420 PRINT  "      STANDARD             READING"
1430 IF N2=0 THEN 1450
1440 PRINT  "       ug/ml                %T"
1450 IF N2=1 THEN 1470
1460 PRINT  "       ug/ml                %Abs"
1470 PRINT  "     **************************************
***"
1480 FOR B=1 TO K
1490 PRINT USING 1500,A(B),C(B)
1500 %              ##.##            ##.#
1510 NEXT B
1520 PRINT  "     **************************************
***"
1530 PRINT USING 1540,W6
1540 %            THE MEAN IS #.##
1550 PRINT USING 1560,S7
1560 %            THE STD. DEV. IS #.###
1570 PRINT USING 1580,S9
1580 %            THE SLOPE IS ###.###
1590 PRINT USING 1600,D8
1600 %            THE DETECTION LIMIT IS ##.#### ug/ml
1610 GOTO 1700
1620 DEFFN ' 1 (N4,H(5))
1630 PRINT  " INCORRECT VALUE=",H(J)
1640 INPUT  "  CORRECT VALUE=", H(J)
1650 IF N4=2 THEN 1680
1660 A(J) = H(J)
1670 GOTO 1690
1680 C(J) = H(J)
1690 RETURN
1700 STOP
1710 END
```

3) Program for 'F' and 't'-Test Comparisons

```
10 SELECT PRINT 005
20 PRINT HEX(03)
30 INPUT "    SAMPLE STD. =
              ELEMENT=",S$,E$
40 INPUT "IF ERROR - INPUT '1'",Z9
50 IF Z9 = 1 THEN 30
60 PRINT HEX(03)
70 INPUT "  ATOMIC ABSORPTION - MEAN =
                                STD. DEV.=
                                N=,A1,B1,N1
80 INPUT "  IF ERROR - INPUT '1'",Z9
90 IF Z9-1 THEN 70
100 PRINT HEX(03)
110 INPUT  " PLASMA EMISSION -  MEAN =
                                STD. DEV. =
                                N=",A2,B2,N2
120 INPUT  " IF ERROR - INPUT '1'".Z9
130 IF Z9=1 THEN 110
140 F1=(B1½2)/(B2½2)
150 N8=N1-1
160 N9=N2-1
170 IF F111 THEN 240
180 F1-1/F1
190 PRINT HEX(03)
200 IF    (B1½2)1(B2½2) THEN 240
210 PRINT USING 220,N9,N8
220 %     DEGREES OF FREEDOM ARE - G= ### and L=###
230 GOTO 270
240 PRINT HEX(03)
250 PRINT USING 260,N8,N9
260 %    DEGREES OF FREEDOM ARE- G= ### and L=###
270 INPUT  "THE F-tab CORRESPONDING TO THE ABOVE DEGREES
                    OF FREEDOM=",F2
280 IF F1!=F2 THEN 310
290 F3=1
300 GOTO 320
310 F3=2
320 IF F3=2 THEN 350
330 N$="   "
340 GOTO 360
350 N$="NOT"
360 SELECT PRINT 211
370 PRINT USING 380,S$,E$
380 %     STATISTICS FOR SAMPLE ###### FOR ##########
390 PRINT
400 PRINT  "      ****************************************
****************"
410 PRINT
```

```
420 PRINT USING 430,F1,F2,N1,N2
430 %         F-Calc= ##.####       F-tab= ##.####    N-Abs= ##   N
-Plas= ##
440 PRINT
450 PRINT USING 450,N$
460 %               VARIANCE VALUES= ### SIGNIFICANTLY DIFFERENT
470 PRINT"                        (AT THE 5% SIGNIFICANCE LEVEL)"
480 PRINT
490 PRINT    "  ********************************************
***************"
500 SELECT PRINT 005
510 A9=A1-A2
520 IF A910 THEN 540
530 A9=A9*(-1)
540 B9=SQR(B1½2 + B2½2)
550 T1=A9/B9
560 K2=(B1½2 + B2½2)½2
570 K3=(B1½4/(N1-1)) + (B2½4/(N2-1))
580 K1=K2/K3
590 W= K1 - 0.85
600 T2= 1.96 - 0.00554568/SQR(W) + 2.4059333/W + 0.671777/(W½2)
-0.383121/(W½3)
610 IF T1!=T2 THEN 640
620 T3=1
630 GOTO 650
640 T3=2
650 IF T3=2 THEN 680
660 T$="    "
670 GOTO 690
680 T$="NOT"
690 SELECT PRINT 211(120)
700 PRINT USING 710,T1,T2,K1
710 %      T-Calc= ##.####       T-Tab= ##.####     K= ###
720 PRINT
730 PRINT USING 740,T$
740 %               MEAN VALUES= ### SIGNIFICANTLY DIFFERENT
750 PRINT  "                  (AT THE 5% SIGNIFICANCE LEVEL)"
760 STOP
770 END
```

```
                SAMPLE PROGRAM RUN

            STATISTICS FOR SAMPLE JA FOR Si
****************************************************************

F-calc=  1.2915          F-tab= 2.8200    n-abs= 12  n-plas= 12

     VARIANCE VALUES= NOT SIGNIFICANTLY DIFFERENT
             (AT THE 5% SIGNIFICANCE LEVEL)
****************************************************************
t-calc=  1.4042          t-tab=  2.0759         k=  21

       MEAN VALUES= NOT SIGNIFICANTLY DIFFERENT
             (AT THE 5% SIGNIFICANCE LEVEL)
```

4) Program for Reproducibility Statistics

```
10 SELECT PRINT 005
20 DIM A(20),A1(20),M9(2),S8(4),S9(2),N7(2),T9(2),M9(2),B
9(20),B8(20),H920)
30 INPUT  "    OXIDE
                # OF REPLICATES- FOR ABS., FOR PLASMA",
                O$,N1,N6
40 N7(1)=N1
50 N7(2)=N6
60 FOR C9=1 TO 2
70 IF C9= 1 THEN 110
80 W6= N6
90 N1= N6
100 GOTO 120
110 W6= N1
120 IF C9= 1 THEN 160
130 PRINT HEX(03)
140 PRINT  "    PLASMA VALUES"
150 GOTO 170
160 PRINT  "    ABS. VALUES"
170 FOR B=1 TO W6
180 INPUT A(B)
190 NEXT B
200 B5= 0
210 INPUT  "    ROW TO BE CORRECTED=",B5
220 IF B5= 0 THEN 250
230 GOSUB '1 (B5,A(B5))
240 GOTO 210
250 S1=0
260 FOR B=1 TO W6
270 IF A(B)  = 0000 THEN 290
280 S1= S1  + A(B)
290 NEXT B
300 M1= S1/N1
310 M9(C9)= M1.
320 D9=0
330 FOR B=1 TO W6
340 IF A(B)= 9999 THEN 390
350 D1(B)= A(B)-M1
360 D9= D9 + (D1(B)½2)
370 IF D1(B)1=0 THEN 390
380 D1(B)= D1(B)*(-1)
390 NEXT B
400 IF D9!10 THEN 420
410 D9= .0000000001
420 V1= D9/N1
430 S2= SQR(V1)
440 S9(C9)= S2
450 FOR Z9=1 TO W6
```

```
460 IF A(Z9)= 9999 THEN 490
470 D3= (2*S2)-D1(Z9)
480 IF D3!=0 THEN 540
490 NEXT Z9
500 Ns= N1-1
510 W5= N2- 0.85
520 T3- 1.96 - 0.00554568/SQR(W5) + 2.4059333/W5 +
0.671777/(W5½2) - 0.3831214/(W5½3)
530 GOTO 790
540 D7= A(Z9)
550 C7=0
560 FOR H=1 TO W6
570 IF A(H)=D7 THEN 590
580 GOTO 600
590 C7= C7 + 1
600 NEXT H
610 T1= A(B) - M1
620 IF T11=0 THEN 640
630 T1= T1*(-1)
640 T2= (T1*SQR(C7))/S2
650 N2= N1 - 1
660 W5- N2- 0.85
670 T3= 1.96 - 0.00554568/SQR(W5) + 2.4059333/W5 +
0.671777(W5½2) - 0.3831214(W5½3)
680 IF T31T2 THEN 790
690 FOR K=1 TO W6
700 IF A(K)=D7 THEN 720
710 GOTO 770
720 IF C9= 2 THEN 750
730 B8(K)= A(K)
740 GOTO 760
750 B9(K)= A(K)
760 A(K)= 9999
770 NEXT K
780 N1= N1 - C7
790 T9(C9)= T3
800 IF C9= 2 THEN 850
810 FOR B=1 TO W6
820 A1(B)= A(B)
830 A(B)= 0
840 NEXT B
850 S8(C9)= T9(C9) * (S9(C9)/SQR(N2))
860 S8(C9+2) = (S9(C9)/M9(C9))*100
870 NEXT C9
880 IF N61N1 THEN 920
890 FOR B= (N6+1) TO N1
900 A(B)= 0
910 NEXT B
920 SELECT PRINT 211
930 PRINT USING 940,0$
```

```
940 %             REPRODUCIBILITY STATISTICS FOR #####
950 PRINT
960 PRINT  "         ****************************************
*******"
970 PRINT  "     ALL FOLLOWING VALUES ARE SIGNIFICANT FOR-"
980 PRINT  "       ATOMIC ABSORPTION  PLASMA EMISSION"
990 PRINT  "         ****************************************
*******"
1000 IF N11=N6 THEN 1030
1010 K7= N6
1020 GOTO 1040
1030 K7= N1
1040 FOR B= 1 TO K7
1050 PRINT USING 1060,A1(B),A(B)
1060 %            ##.##                ##.##
1070 NEXT B
1080 PRINT  "       ****************************************
********"
1090 PRINT  "            REJECTED VALUES ARE"
1100 FOR B=1 TO K7
1110 IF B8(B) + B9(B)= 0 THEN 1140
1120 PRINT USING 1060, B8(B),B9(B)
1130 X6= X6+1
1140 NEXT B
1150 IF X6!10 THEN 1170
1160 PRINT  "            NO VALUES REJECTED "
1170 PRINT  "       ****************************************
********"
1180 PRINT USING 1190,M9(1),M9(2)
1190 %            ##.##       MEAN    ##.##
1200 PRINT  "                         +/-        +/-"
1210 PRINT USING 1220,S8(1),S8(2)
1220 %            #.###                #.###
1230 PRINT USING 1240,S9(1),S9(2)
1240 %            #.###   STD. DEV. #.###
1250 PRINT USING 1260,S8(3),S8(4)
1260 %            #.###REL.STD.DEV. #.###
1270 SELECT PRINT 005
1280 N1= N7(1)
1290 N2= N7(2)
1300 B1= (S9(1)½2)
1310 B2= W9(2)½2)
1320 F1= B1/B2
1330 N1= N1-1
1340 N2=N2-1
1350 IF F111 THEN 1370
1360 F1= 1/F1
1370 IF B11B2 THEN 1410
1380 PRINT USING 1390,N2,N1
1390 %      DEGREES OF FREEDOM ARE- G= ## AND L= ##
```

```
1400 GOTO 1430
1410 PRINT USING 1420,N1,N2
1420 %          DEGREES OF FREEDOM ARE G= ## AND L= ##
1430 INPUT  "  THE F-tab CORRESPONDING TO THE ABOVE DEGREES
                         OF FREEDOM=",F2
1440 IF F1!=F2 THEN 1470
1450 Q3= 1
1460 GOTO 1480
1470 F3= 2
1480 IF F3= 2 THEN 1510
1490 N$=  "   "
1500 GOTO 1520
1510 N$= "NOT"
1520 SELECT PRINT 211(120)
1530 PRINT  "      *****************************************
********"
1540 PRINT USING 1550,F1,F2,N1,N2
1550 %     F-calc= ##.####  F-tab= ##.#### N-abs= ## N-plas= ##
1560 PRINT
1570 PRINT USING 1580,N$
1580 %         VARIANCE VALUES  ### SIGNIFICANTLY DIFFERENT
1590 PRINT  "              (AT THE 5% SIGNIFICANCE LEVEL)
1600 GOTO 1660
1610 DEFFN '1  (B5,D(B5))
1620 PRINT  "   INCORRECT VALUE=",H(B5)
1630 INPUT  "    CORRECT VALUE=",H(B5)
1640 A(B5)=H(B5)
1650 RETURN
1660 STOP
1670 END
```

SAMPLE PROGRAM RUN

```
          REPRODUCIBILITY STATISTICS FOR Si02
**********************************************************
     ALL FOLLOWING VALUES ARE SIGNIFICANT FOR-
       ATOMIC ABSORPTION    PLASMA EMISSION
**********************************************************

                 36.60         20.10
                 36.60         20.10
                 36.70         19.60
                 36.70         20.90
                 36.70         20.90
                 36.60         20.90
**********************************************************
                REJECTED VALUES ARE-

                 NO VALUES REJECTED
**********************************************************
                36.65   MEAN  20.41
                 +/-           +/-
                0.057         0.587
                0.050 STD.DEV.0.511
                0.136 REL.STD.2.504
                        DEV.
**********************************************************
F-calc= 104.5555  F-tab= 5.0500  N-abs=  5   N-plas=  5

   VARIANCE VALUES=          SIGNIFICANTLY DIFFERENT
              (AT THE 5% SIGNIFICANCE LEVEL)
```

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