# A STUDY OF THE SULPHUR MATERIAL BALANCE IN SPENT MEDIA INVOLVING THE BACTERIAL STRAIN RHODOPSEUDOMONAS GOLDAMEIRII

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# ABSTRACT

## A STUDY OF THE SULPHUR MATERIAL BALANCE IN SPENT MEDIA INVOLVING THE BACTERIAL STRAIN RHODOPSEUDOMONAS GOLDAMEIRII

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This project was undertaken to determine the end-products of the thiosulphate conversion, and its sulphur material balance, taking place in the nutrient medium used in culturing Rhodopseudomonas goldameirii. The final product(s) of the conversion are sociologically important, it was necessary to know whether or not they constituted an environmental danger.

Both instrumental techniques, polarography, x-ray fluorescence and atomic absorption, and classical wet chemical techniques, titrimetry and gravimetry, were employed in carrying out the investigation. For studies on the macro level of this nature, wet chemical techniques are superior to the more sensitive instrumental techniques.

The final product of the thiosulphate conversion as determined after the baceteria cease to grow is sulphate. The efficiency of this conversion is 99.72 ± 0.17%. The possible intermediate products of the conversion were not studied during the course of this investigation. The mechanism by which this reaction/reaction sequence takes place is yet to be investigated.

## ACKNOWLEDGEMENTS

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# 1. INTRODUCTION

The approaching depletion of many of our natural sources of energy has become a matter of considerable concern to researchers in all scientific fields of investigation, as well as to those working in the area of the economics of such sources. Modifications of the techniques of the usage of decreasing energy sources, as well as the development of new sources, have evolved into major areas of research for workers in all scientific and engineering fields. Much of this research centers around the development of economical biomass and protein sources.

Throughout such developmental work there is concern not only for the actual methodologies involved, but also for the environmental consequences devolving from the processes originated, and from the by-products of such processes. Exploratory research must concern itself with both of these factors.

Microbiologists (1), for example, endeavour to isolate and explore various bacteria capable of providing sources of energy and protein able to satisfy the requirements of society and of environmental concern.

Rhodopseudomonas goldameirri, ATTC No. 31751, is one of such bacterial strains currently under investigation in the Department of Biological Sciences at Concordia University.

R. goldameirri is an anaerobic, purple bacterium that is photosynthetic and sulphur utilizing. The bacteria owe their purple colour to the presence of carotenoid pigments ($\lambda$ = 450 to 550 nm) which mask those colours that are due to the bacteriochlorophylls ($\lambda$ = 850 to 1000 nm) (2).

R. goldameirri can be grown in a nutrient medium (3) containing thiosulphate, bicarbonate, potassium phosphate and ammonium chloride as the major essential constituents along with a number of micro-nutrients.

This bacterial strain is photosynthetic and therefore derives its energy from light through its pigment system. The thiosulphate in the medium serves as the source of reducing power, while the bicarbonate ion is the carbon source which enable the bacteria to build cell material from the constituents of the medium via the generalized reaction;

$$\underset{\text{(electron donor)}}{\text{inorganic substrate}} + CO_2 \xrightarrow{h\nu} \text{organic cell material}$$

The bicarbonate ion has a second function, in that it acts in a buffering capacity to regulate the pH of the medium.

The medium also contains potassium phosphate, which is essential in the production of both RNA and DNA which constitute about 30% of the cellular dry weight. Nitrogen assimilation is made possible by the presence of the medium of ammonium chloride.

The nutrient medium, by itself, does not provide a special problem relative to environmental hazard. There is the problem, of course, of determining the degree of hazard which might arise out of the final products in the spent medium originating through chemical and bacterial action. Such resultant products, and their possible environmental effects, must be determined.

The scope of the research project involved here was the determination of thiosulphate oxidation mechanism(s), the sulphur material and electron balances involved and the nature of the product(s) generated.

# 2. THEORETICAL CONSIDERATIONS FOR THE TECHNIQUES OF ANALYTICAL CHEMISTRY APPLIED

## 2.1 Differential Pulse Polarography

Differential pulse polarography is a technique of electrochemical analysis in which a square-wave voltage pulse is superimposed on the DC ramp voltage being applied to a mercury drop. The voltage pulse is applied at a fixed period after the birth of the drop from the tip of the capillary. The voltage pulses, as applied to successive drops, all have a constant, preselected amplitude of, typically, between ± 5 and ± 100 mV, and are superimposed on the relatively slow linear DC voltage sweep as depicted in Figure 2.1. The voltage pulse occurs near the end of the drop life, the normal life of the mercury drop having been aborted by an crystal-timed, electronically-activated device.

In the differential pulse technique, the current flowing at the dropping mercury electrode (DME) is sampled twice during the life of the drop. The first current sample is taken, for about 20 msecs, immediately before the application of the voltage pulse, as shown in Figure 2.2. The voltage pulse is then applied over a period of from 40 to 60 msecs. The application of the pulse produces a change in the current factor, and this may be greater or less depending on the position of the DC voltage ramp. The change in the current arises out of two factors. The first is the increased current required to maintain the electrical double-layer

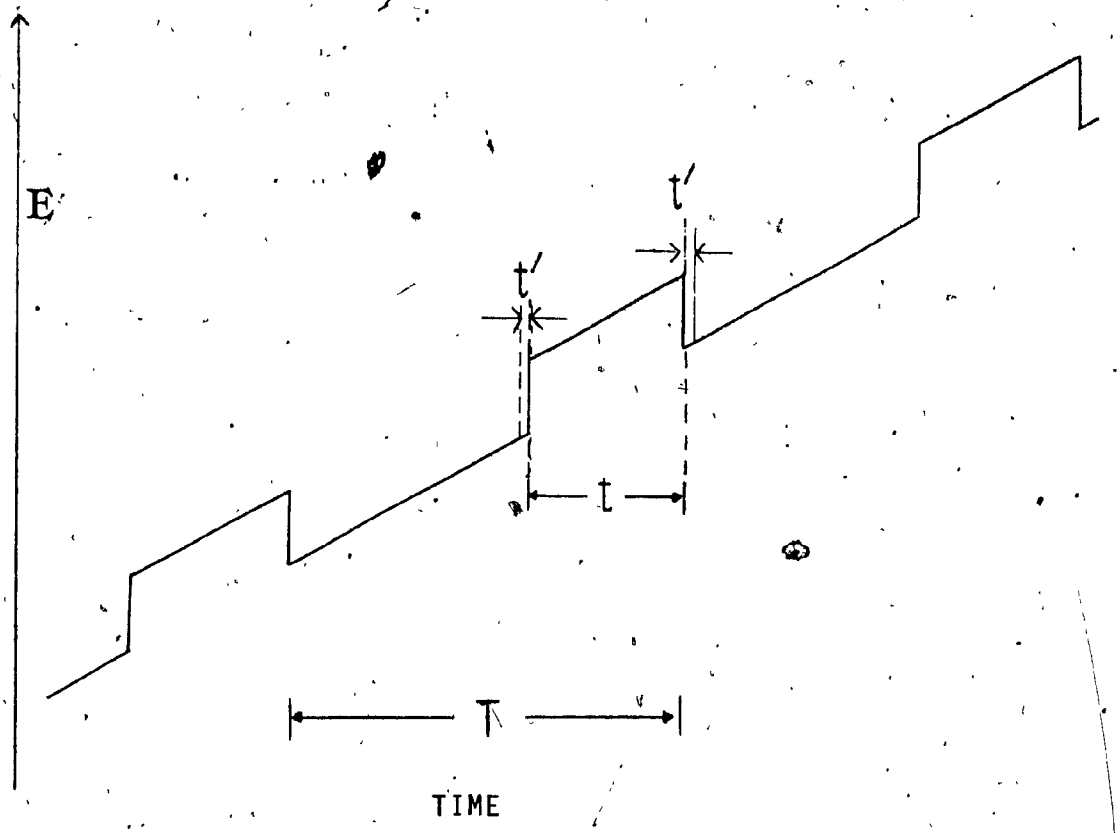


FIGURE 2.1 Application of Square-Wave Pulses to Slowly-Varying DC Potential Ramp

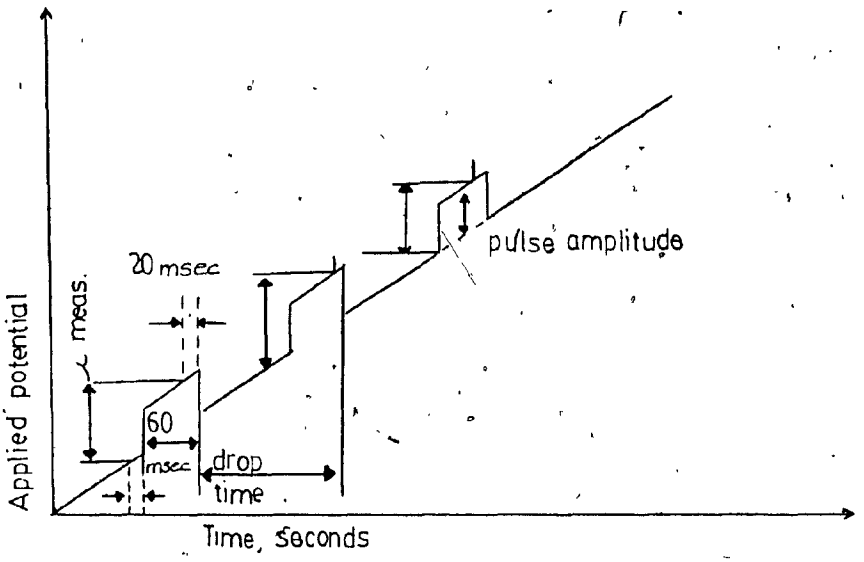


FIGURE 2.2 Signal Waveform and Current Measurements in Differential Pulse Polarography

charge at the new applied potential. This capacity current, as it is called, normally decays very rapidly at a rate governed by the magnitude of the capacitance and series resistance of the system. The second and simultaneous, additional current change is that due to the faradic current, and this will be increased if the new potential is such that the equilibrium between the oxidized and reduced forms of the electroactive species is shifted. Where the faradic current increases, its rate of decay is very slow compared to that for the capacity current increase. There is a second current sampling, for a 20 msec period, just before the drop is knocked off.

During the growth of the mercury drop, the charging current decreases as the faradic current increases. Immediately before the application of a pulse, the current is sampled. The voltage pulse is then applied and, if the DC ramp is in the critical zone, an increase in the current is noted. The capacity current component of this increase decays rapidly compared to the rate of decay of the faradic component. Over the last few milliseconds of the voltage pulse, the current is mainly faradic in nature, and it is here that the second current sample is taken. The difference between the two sampled currents is the measured current in differential pulse polarography, and this difference is plotted against the slowly-increasing DC ramp. Note that this technique minimizes the influence of the capacity current factor, thus improving considerably the limit of detection over that available from the classical DC polaro-

graphic technique.

At potentials where no faradic current flows, the two currents measured will be almost identical and almost exclusively capacity current in nature. At potentials corresponding to the plateau of the DC polarographic wave, the currents for the two samples will again be almost identical, but will be almost exclusively faradic in nature. At all potentials between the start and finish of the rising portion of the DC polarographic wave, differences will exist between the two current measurements, and the difference will be a maximum at that potential which corresponds almost exactly with the half-wave potential for the electroactive species involved (4,5).

## 2.2 X-Ray Fluorescence

X-ray radiation occupies that portion of the electromagnetic spectrum lying between 0.01Å and 100Å. Their range of approximate quantum energy is from $2 \times 10^{-6}$ to $2 \times 10^{-10}$ erg, corresponding to $10^6$ to 100eV. Important x-ray analytical methods are based on:-

a) absorption
b) emission
c) diffraction
d) fluorescence

All of the foregoing methodologies are used in both

the qualitative and quantitative senses to determine the elements and elemental contents of complex mixtures, the internal atomic, molecular and crystalline spacings of materials.

In the x-ray fluorescence methods, primary x-rays are used to excite the sample under investigation. The primary x-rays must be more energetic than the minimum absorption energy for the analyte(s) in the sample. The emitted x-rays from the sample, or secondary x-rays as they are called, will be of lower energy, and of a relatively simple pattern characteristic for each analyte element being excited.

X-rays are emitted by atoms which are bombarded by energetic electrons generated in the x-ray tube. This emission of x-rays results from two separate effects. These are:-

a) the deceleration of high-speed electrons as they pass through the material of the x-ray tube target.

b) the ionization of the individual atoms of the target material of absorption of electron energies.

The first effect provides the continuous spectrum common to all primary x-ray emmissions, while the second effect provides the x-ray spectrum characteristic of the elemental nature of the target element.

2.2.1 X-ray spectral lines

X-ray spectral lines are characteristic for specific

elements whether these be present as a primary beam tube target or as a component(s) in the sample under investigation. They are produced where incident electrons or photons knock orbital electrons out of the atoms of the primary or secondary target material(s). If an ejected electron is from one of the inner orbitals of the atoms (Figure 2.3), an electron from an outer shell may drop to fill the inner orbital vacancy created. The decrease in potential energy for this outer orbital electron as it takes up an inner orbital shell position results in the emission of a photon having exactly the energy of the decrease. The wavelength, $\lambda$ , for such photons is related to $\Delta E$, the potential energy decrease by:-

$$\lambda = \frac{hc}{\Delta E} \qquad (1)$$

where:-

$c$ = velocity of electromagnetic radiation in a vacuum (cm/s)

$h$ = Planck's constant (erg.s)

$\Delta E$ = energy decrease for electron (erg)

$\lambda$ = wavelength (cm)

Because the energy of the orbital electron is quantized, the x-ray photons will show certain definite wavelengths characteristic of the element involved.

2.2.2 Production of x-rays

Since all x-ray tube sources of x-rays depend on electron bombardement for excitation, the x-ray continuum is

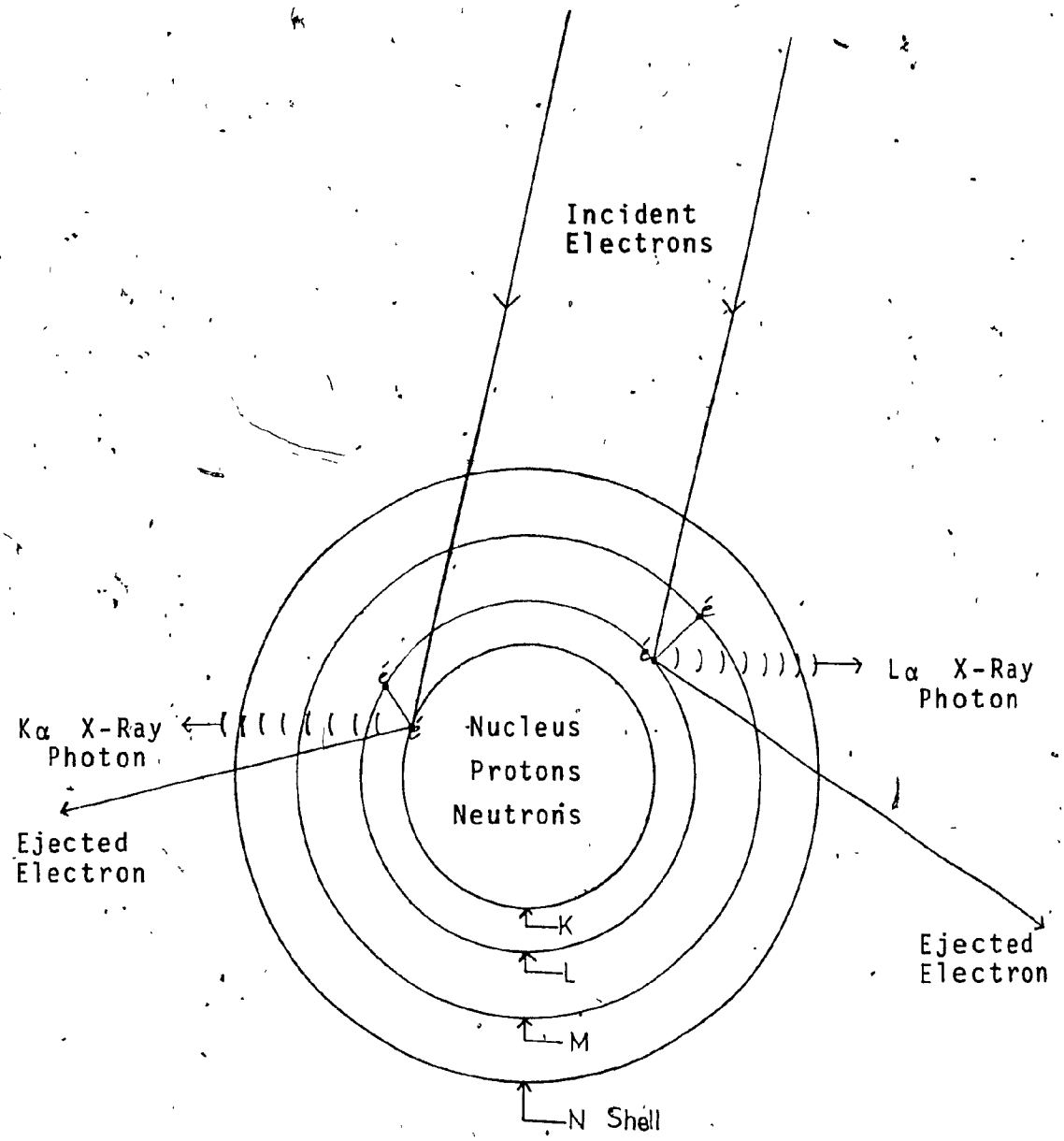


Figure 2.3 Origin of X-Ray Spectra, Primary Radiation

important. The continuum is due to the rapid deceleration of the bombarding electrons as they pass through the atoms of the target material. The energy lost in this slowing-down action is emitted as the continuum of x-ray radiation. There is a sharp minimum wavelength, $\lambda min$, for this continuum, corresponding to the energy of the accelerating voltage, and we have:-

$$\lambda min = \frac{hc}{Vev} = \frac{12.4}{V} \qquad (2)$$

where:-

$\lambda min$ = minimum wavelength ($\mathring{A}$)

h = Planck's constant (erg.s)

c = velocity emr in vacuum (cm/s)

ev = electron volt (erg)

V = accelerating voltage (kV)

The characteristic spectrum results from the impact removal of orbital electrons by electronic or photonic energies. The extent of the absorption of these energies depends only on the number of atoms of the element of interest in the path of the electron stream or x-ray stream from the primary source, and is independent of the physical or chemical state of the element.

The absorption of x-rays by the sample material follows Beer's law written in the form:-

$$I = I_0 \exp(-upx) \qquad (3)$$

where:-

$I$ = transmitted intensity of x-rays

$I_o$ = incident x-ray intensity

$u$ = mass absorption coefficient ($cm^2/g$)

$p$ = density of absorbing substance ($g/cm^3$)

$x$ = distance traversed in medium penetrated (cm)

The mass absorption coefficient, $u$, is a function of the wavelength and of the atomic number of the absorbing element, and it can be taken as the measure of the probability of the absorption of an incoming x-ray photon.

The conditions for diffraction of an x-ray beam by a crystal are subject to Bragg's law (6), and the general situation is shown in Figure 2.4. Reinforcement of reflected rays emerging from the two crystalline planes will occur only if the difference in path lengths of the two rays is equal to an integral number of wavelengths. The condition for reinforcement is therefore:-

$$n\lambda = 2d\sin\theta \qquad (4)$$

where:-

$n$ = order of reflection

$\lambda$ = wavelength of radiation (Å)

$d$ = crystal plane spacing (Å)

$\theta$ = angle of diffraction (deg)

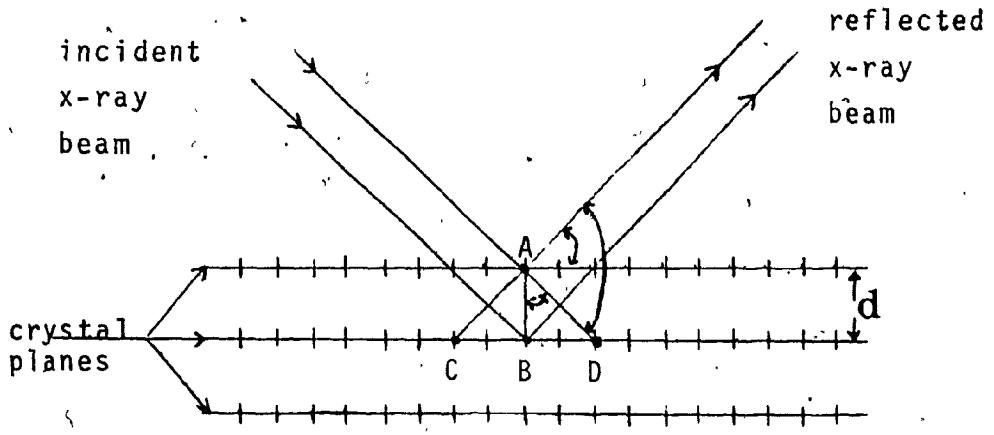


Figure 2.4 Diffraction of X-Rays from Analyzing Crystal Planes

### 2.2.3 Detection of x-rays

In order to detect the intensity and quantum energy of x-rays it is necessary to convert the x-ray energy to another energy form which lends itself to easy measurement. The two major devices used for the detection and measurement of x-rays are:-

a) the proportional flow counter
b) the scintillation counter

Both counter or detector forms depend on the ability of x-rays to ionize matter, and they differ only in the subsequent fate of the electrons produced by the ionization process.

#### 2.2.3.1 Proportional flow counters/detectors

A proportional flow counter consists of a tube (outer electrode or cathode) filled with an inert gas such as argon, xenon or krypton and a central collecting wire (anode). A difference in potential is applied between the cathode and the anode. Figure 2.5 indicates the general design and principle. When an ionizing radiation such as x-ray radiation enters through the external tube window, collisions with the slow-flow filling gas produces an ion pair, with the electron produced migrating to the central collecting wire and the positive ion migrating to the external tube cathode. The migrating electron is accelerated to the central wire under the difference in potential applied, and causes by

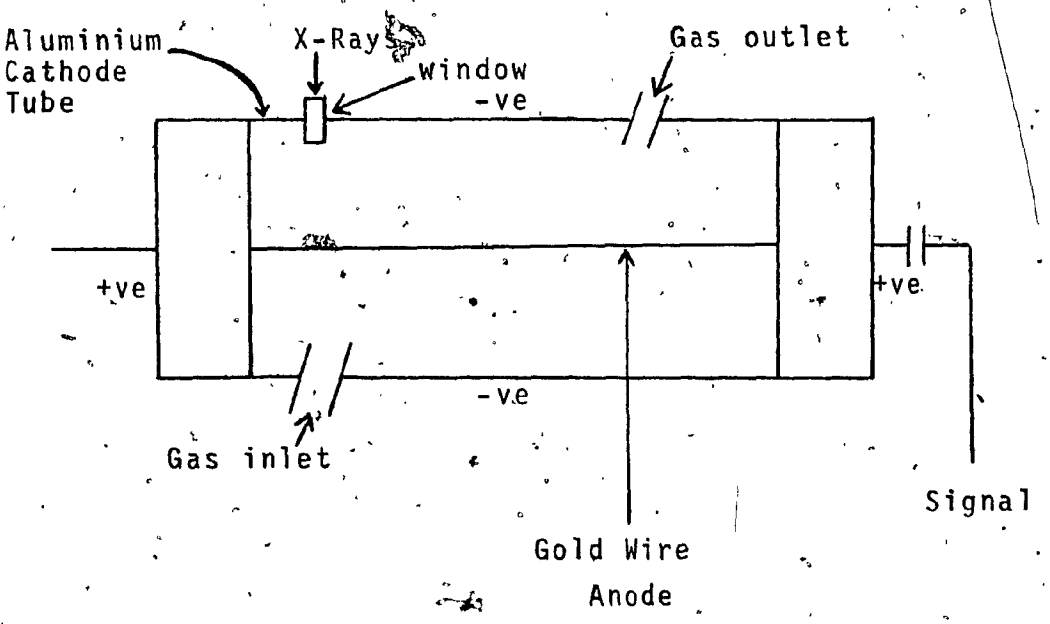


Figure 2.5 Diagram of a Proportional Flow Detector/Counter

collision the ionization of numerous other filler gas molecules. The result of this is each entering x-ray photon results in a multiplication or avalanche of electrons travelling to the central anode. By this internal multiplication process, a single ionizing radiation may result in an output pulse of 1 to 10 volts.

2.2.3.2 Scintillation counters/detectors

The usual scintillation crystal for x-ray analysis consists of a large sodium iodide crystal activated by a small content of the element thallium. The absorption of an x-ray photon by the crystal is followed by the emission of photons of visible light, the number of photons of visible light issues per photon of x-ray radiation being approximately on an energy-ratio basis. The light photons are detected by a photomultiplier tube (Figure 2.6). The light pulses generated in the scintillation crystal strike the light sensitive surface of the photomultiplier, causing the ejection of electrons. The primary ejection of electrons, by passage through a series of accelerating grids, provides for a high electron emission multiplication factor. By the time the final collector anode has been reached, the multiplication factor has attained a value of $10^6$ or greater. As with the proportional flow counter, the magnitude of the output current signal represents the intensity of the x-ray radiation; the analyzed individual pulse amplitudes in potential will relate to the energy of each type of x-ray

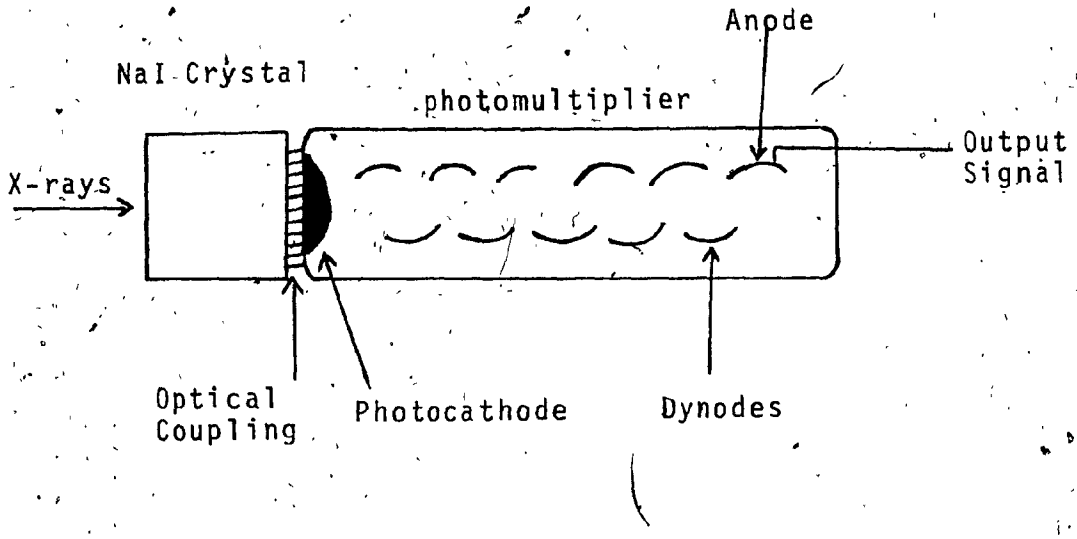


Figure 2.6 Diagram of a Scintillation Detector/Counter

photon (x-ray radiation) entering the counter.

## 2.3 Flame Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry is an analytical technique capable of determining many elemental substances in the parts per million or less ranges. There are, in general, two atomic absorption methods, flame and flameless.

In the flame approach the sample, usually in the form of a homogeneous liquid, is aspirated into a flame. Thermal and chemical reactions occur in the flame which cause the analyte material to appear as free atoms. These free atoms can be observed to absorb electromagnetic radiation of specific wavelengths characteristic of the analyte element involved. The degree of absorption can be directly related to the concentration of the analyte in the aspirated solution. Figure 2.7 indicates the schematic arrangement for a flame atomic absorption spectrophotometer.

When an atom formed by dissociation as indicated above, at can be assumed that, under the flame conditions involved, it will be in the ground state; that is, at the lowest potential energy state. Absorption by such a ground state atom of the photon energy for electromagnetic radiation of the proper wavelength raises the atom, by electronic orbital shifts, to a higher energy state. The photon energy is provided by electromagnetic radiation of wavelength capable of providing the exact quantum energy for the orbital shift(s)

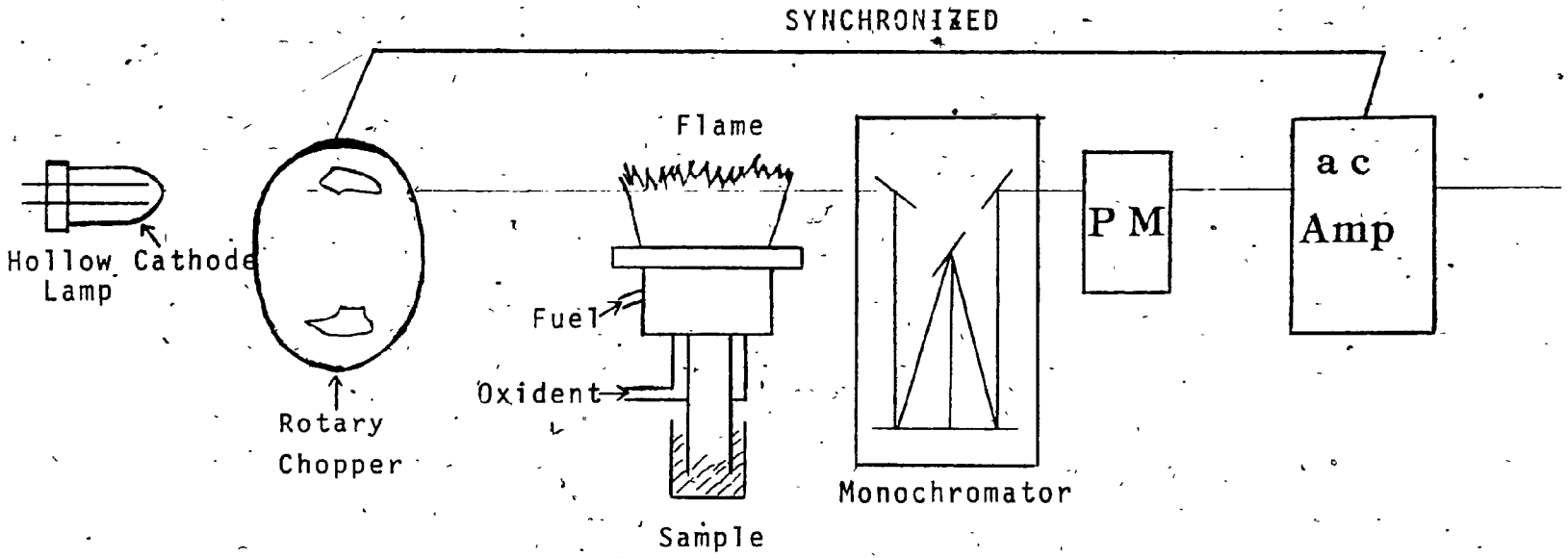


Figure 2.7 Diagram of a Flame Atomic Absorption Spectrophotometer from:-
G.W. Ewing, "Instrumental Methods of Chemical Analysis", 3rd edition, McGraw-Hill, (1969).

involved. The loss of radiation intensity from this absorption process can be determined as absorption, and the degree of absorption or absorbance will be directly related to the concentration of the active atomic species, or analyte, in the flame, which itself will be directly proportional to the analyte concentration in the aspirated solution (7,8).

# 3. EXPERIMENTAL PROCEDURES

## 3.1 Instrumental Analytical Techniques and Their Applications

### 3.1.1 Polarography

Differential pulse polarography was carried out at the DME, using an Ag/AgCl (sat. KCl) reference electrode and a platinum auxiliary electrode. A Metrohm E626 Polarecord and a Metrohm E505 Polarography Stand were applied. The prepared sample solutions were all tested for sulphite, sulphide and thiosulphate ions, the quantitative estimation being carried out by the standard additions or spiking technique (9).

The general purpose of this approach was to determine the amount of thiosulphate ion present in new media and in media spent as the result of bacterial action. The presence of sulphite and/or sulphide ions in the spent media would also be tested, these ions then arising out of bacterial and/or chemical action. If sulphite and/or sulphide ions were found, their quantities could then be determined by the spiking technique. This approach permitted the determination of all three ions in the same solution.

#### 3.1.1.1 Sulphide ion detection and determination

The supporting electrolyte solution was prepared by adding 1 ml of 2M sodium hydroxide solution to 19 ml of

deionized water. This solution was deaerated for 5 minutes by the passage of nitrogen gas. A known volume of the analyte (either prepared media, prepared media aged without bacteria present or exhausted media resulting from bacterial action) was then added and mixed in with a quick burst of nitrogen gas. A polarographic scan was conducted in the differential pulse mode over the potential range of - 0.3V to - 1.25V vs Ag/AgCl (sat. KCl). Multiple spiking with a standard known concentration solution of sulphide ion was then carried out, a polarogram being obtained after each spike. Linear regression of the blank-corrected obtained polarographic peaks was carried out to determine the concentration of sulphide ion, if present, in each of the analyte solutions.

3.1.1.2 Sulphite ion detection and determination

To each of the solutions from the sulphide assay was now added 2 ml of 2M acetic acid solution. A differential pulse polarogram was recorded over the potential range from - 0.45V to - 1.15V vs Ag/AgCl (sat. KCl). Multiple spikes of a standard sulphite ion solution were added, and polarograms obtained after each spike. Linear regression of the corrected obtained peaks was carried out to determine the concentration of sulphite ion, if present, in each of the analyte solutions.

3.1.1.3 Thiosulphate ion detection and determination

The resulting solutions, at the conclusion of the sulphite analyses, were analyzed directly for thiosulphate ion concentration by recording differential pulse polarograms in the range from - 0.1V to - 0.3V vs Ag/AgCl (sat. KCl). Multiple spikes of a standard thiosulphate ion solution were added, and a polarogram obtained after each addition. Linear regression of the background-corrected polarographic peaks obtained for each solution was carried out to determine the concentration of thiosulphate in each of the analyte solutions.

3.1.2 X-ray fluorescence

X-ray fluorescence analyses for total sulphur in the various forms of solution media were carried out on a Picker Nuclear X-Ray Fluorescence Spectrometer. The sulphur K line was used for the determination, the chromium target x-ray tube was used and counting was carried out with a proportional flow counter.

Calibration standards were prepared, based on sulphur weight-fraction, and were contained in liquid sample holders or cells covered with Mylar* film. The standards were used to determine the extent of the linear relationship between counting intensity and weight-fraction of sulphur. Once the linear relationship zone was determined, the media samples of various origins were analyzed for sulphur under the same

conditions of sample preparation and under the same x-ray parameters.

### 3.1.3 Flame atomic absorption spectrophotometry

The concentration for the heavy metals present as constituents and/or contaminants in the culture media were determined by flame atomic absorption spectrophotometry. The analytes looked for included copper, lead, cadmium, iron, zinc, nickel, antimony, manganese, chromium, tin, bismuth, vanadium, cobalt and molybdenum.

A set of standard solutions was prepared for each of the heavy metal analytes involved, and deionized, glass-distilled water was used throughout. These standards were used to calibrate the Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer for each element, and to determine the linearity range of absorbance versus concentration in each case. Once the calibration curve was obtained, the necessary linear equation was calculated, and samples of the various media forms were aspirated into the flame (10). The linear equation was then applied in the calculation of the media content of each heavy metal on the list.

## 3.2 Wet Chemical Analysis Techniques and Their Applications

### 3.2.1 Preparation of culture media

The relative concentration of the various constituents of the culture media are shown in Table 3.1. Two methods for

TABLE 3.1

MEDIA CONSTITUENTS AND THEIR APPROXIMATE CONCENTRATIONS *

| Chemical Name | Chemical Formula | Concentration (g/L) | |
|---|---|---|---|
| Sodium thiosulphate pentahydrate | $Na_2S_2O_3.5H_2O$ | 16.0000 | (1) |
| Sodium bicarbonate | $NaHCO_3$ | 10.00 | (2) |
| Potassium phosphate | $K_2HPO_4$ | 2.0000 | (1) |
| Sodium chloride | NaCl | 10.00 | (2) |
| Magnesium sulphate heptahydrate | $MgSO_4.7H_2O$ | 0.5000 | (1) |
| Ammonium chloride | $NH_4Cl$ | 1.00 | (2) |
| Sodium molybdate dihydrate | $Na_2MoO_4.2H_2O$ | 0.0001 | (3) |
| Calcium chloride | $CaCl_2$ | 0.0020 | (3) |
| Manganese chloride | $MnCl_2$ | 0.00012 | (3) |
| Ferrous sulphate heptahydrate | $FeSO_4.7H_2O$ | 0.0050 | (3) |

* The exact concentrations of prepared, initial, control and spent media samples can be found in Appendix A.

(1) Weighed accurately on an analytical balance

(2) Weighed accurately on a top-loading balance

(3) Added to the media in the form of a 1.00 ml volume of a concentrate capable of giving the required final media concentration indicated

the preparation of the culture media were employed at different times during the course of the study. These methods will henceforth be described as Method No. 1 and Method No. 2, and the methodologies themselves are indicated below. All of the water used in culture media preparation was deionized, glass-distilled water, and has been designated as $H_2O_D$ (3).

3.2.1.1 Preparation method no. 1

In this methodology the sodium thiosulphate, sodium bicarbonate and potassium phosphate components were dissolved in 400 ml of $H_2O_D$. This solution constituted Solution A.

The sodium chloride and magnesium sulphate components were dissolved in 200 ml of $H_2O_D$, this constituting Solution B.

Finally, Solution C was prepared by adding the ammonium chloride and the trace metal salts to 200 ml of $H_2O_D$.

Solution C was added to Solution B with thorough mixing, and the resultant solution was then added to Solution A with thorough mixing. The final volume was adjusted to slightly below 1000 ml, the solution was passed through a ceramic bacterial filter and was then diluted to 1000.00 $\pm$ 0.15 ml in a volumetric flask. For experimental media the solution was inoculated from a stock culture of *R. goldameirri* and was then deaerated by passing nitrogen gas for a

5 minute period. The same preparation procedure, without bacterial inoculation, was followed for the initial and control media. The control and experimental media were incubated at 28 ± 1°C, under incandescent lighting at 40 watt.

3.2.1.2 Preparation method no. 2

The sodium thiosulphate, sodium bicarbonate and potassium phosphate components were dissolved in about 400 ml of $H_2O_D$, the solution was mixed thoroughly, diluted to 500.00 ± 0.08 ml in a volumetric flask and the contents transferred to a 1 liter Erlenmeyer flask. The same procedure was followed for the additions of sodium chloride, ammonium chloride and magnesium sulphate. Both 500 ml solutions were autoclaved separately for fifteen minutes, under conditions involving 270°F and 17 psig. The cooled solutions were mixed together thoroughly, the trace metal components being then added as concentrates through a syringe-type bacterial filter. The inoculation and deaeration procedures conformed to those outlined in Section 3.2.1.1.

3.2.2 Thiosulphate determination

The thiosulphate content of the bacterial culture media, whether initial, control or experimental, was determined titrimetrically using the iodimetric method of analysis.

An appropriate volume of the media sample was pipetted into an Erlemeyer flask, and the solution pH was adjusted to 4.0 by means of additions of glacial acetic acid. The resulting solution was titrated with a standard iodine solution, using starch solution as the endpoint indicator. Appendix B provides the general methodology and its application (11).

3.2.3 Sulphate determination

An appropriate media sample volume was transferred by pipette to a beaker, and $H_2O_D$ was added to provide a final volume of 100 ml. The solution was acidified by adding 6.0 ml of 1:1 hydrochloric acid by pipette. The solution was brought to boiling, and 30 ml of 10% w/v barium chloride solution was added slowly and with constant stirring. The solution was then heated to just under the boiling point for a two-hour period. It was then allowed to stand overnight.

After the settling period, the solution was warmed to 60 - 70°C, and this warmed solution was filtered through a previously-conditioned and weighed Gooch crucible. The filter was washed repeatedly with hot $H_2O_D$, until a silver nitrate solution test showed freedom of a filtrate portion from chlorides. The cruicibles were air-dried and weighed to obtain a constant combined weight for barium sulphate and volatiles, the latter present mainly as elemental sulphur. The crucible was then ignited to constant temperature at

950°C (11,12).

### 3.2.4 Hydrochloric acid blank and sulphur dioxide determination

Since, on acidulation of a thiosulphate solution, the thiosulphate is destroyed, yielding elemental sulphur and sulphur dioxide in accordance with:-

$$S_2O_3^{2-} + 2HCl \rightleftharpoons 2Cl^- + SO_2 + S^\circ + H_2O$$

these constituents of the experimental media must be accounted for before a material balance for sulphur can be made.

#### 3.2.4.1 Hydrochloric acid blank

A volume of the sample media equal to that used for the sulphate determination was pipetted into a beaker, and the final volume was adjusted to 100 ml with $H_2O_D$. 6.0 ml of 1:1 hydrochloric acid was added by pipette. The resulting solution was heated to just under boiling for two hours, and then allowed to stand overnight. This solution was subsequently heated to 60 - 70°C, filtered through a previously-conditioned and weighed Gooch crucible, and washed with hot $H_2O_D$ until a portion of the filtrate showed freedom from chlorides upon silver nitrate solution testing. The crucible was air-dried and weighed at constant weight, and this was followed by ignition to constant weight at 950°C to determine the weight of nonvolatile residues contributing to the volatile weight previously recorded (11).

3.4.2.2 Sulphur dioxide determination

In order to determine quantitatively the sulphur dioxide evolved, the generated sulphur dioxide was oxidized to sulphate, the resultant sulphate precipitated as barium sulphate and the determination completed gravimetrically.

A sample volume of the media equal to that used in the sulphate determination was pipetted into a cell which provided a closed system. Figure 3.1 shows the general lay-out for this system.

Exactly 6.00 ml of a 1:1 hydrochloric acid solution was added by means of a separatory funnel. Oxygen gas was passed through the solution and over the surface at a low rate of flow, this addition acting as both a reagent in the subsequent reaction and as a purging agent. The mixed gases were then passed to an absorption bulb containing $H_2O_D$, and 2 ml of 6M ferrous nitrate solution to catalyze the conversion of sulphur dioxide to sulphuric acid. The oxygen was passed through the sample solution for a two-hour period.

The absorbing solution was then quantitatively transferred to a beaker, heated to just under boiling and 30 ml of 10% w/v barium chloride solution was added slowly and with constant stirring. The resulting solution was heated for two hours, at just under the boiling point, and then allowed to stand overnight at room temperature. This solution was subsequently heated to 60 - 70°C, filtered through a

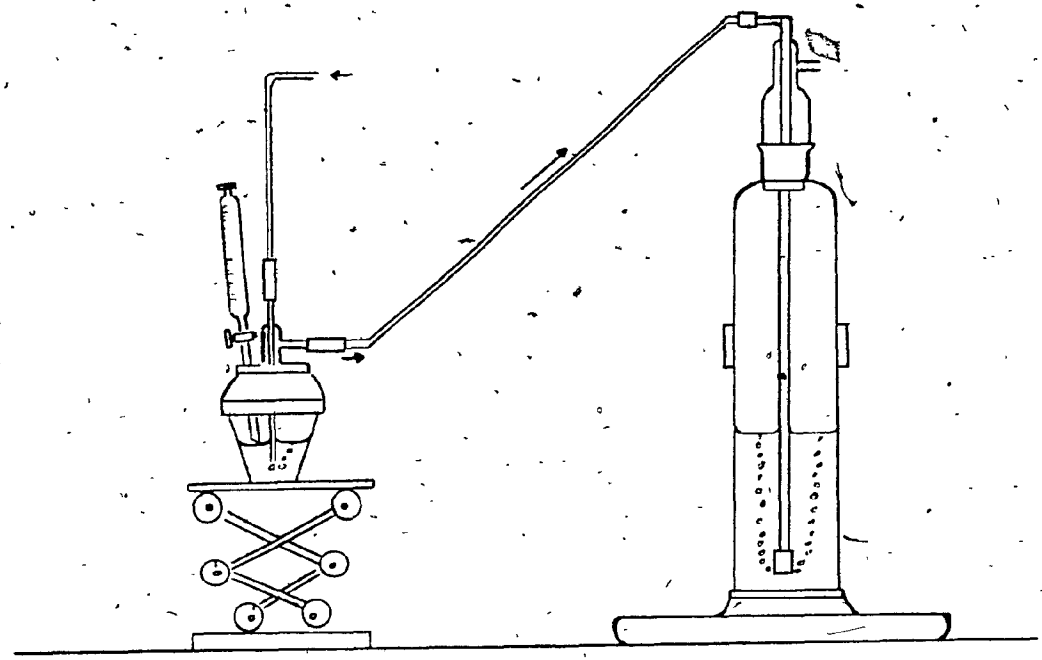

FIGURE 3.1 Diagram of Closed System for $SO_2$ Evolution, Conversion and Measurement.

previously-conditioned and weighed Gooch crucible and washed with hot $H_2O_D$ until a filtrate portion showed freedom from chlorides upon testing with silver nitrate solution. The crucible was then heated to constant weight at 950°C (13).

3.2.5 Determination of the bacterial weight per liter of media

The bacteria suspended in various samples of exhausted or spent media were centrifuged for 10 minutes in a centrifuge rotating at 10,000 rpm. The pellet thus obtained was freeze dried in a lyophilizer (Varian Model 801) and weighed as grams of bacteria per liter of media.

3.2.6 Determination of the total sulphur in bacteria

Sulphur and/or sulphur-containing compounds might be incorporated in the bacteria during the incubation period and, consequently, must be determined in order to obtain a valid material balance.

Bacterial samples weighing 0.5 g were dissolved in 20 ml of concentrated nitric acid. After dissolution was complete, 0.5 g of sodium carbonate was added and the resultant solution was evaporated at low heat until the volume was reduced to 10 ml. After cooling, 10 ml of concentrated hydrochloric acid was added, and the solution was evaporated to dryness. An additional 10 ml of concentrated hydrochloric acid was added to dissolve the caked salts. This mixture was then reduced to a syrupy consistency by heating.

The solution was subsequently allowed to cool to room temperature. An addition of 10 ml of concentrated hydrochloric acid, 25 ml of $H_2O_D$ and 5 g of zinc dust was made. The solution was warmed gently until the evolution of hydrogen ceased. The warm solution was filtered through a Whatman No. 42 filter paper. The original vessel and the filter paper were washed with 75 ml of a 1:99 hydrochloric acid solution. The filter paper was discarded, and the filtrate warmed to 60 - 70°C, 20 ml of 10% w/v barium chloride solution was then added slowly and with constant stirring. This solution was then heated to just under the boiling point for two hours, and then allowed to stand overnight at room temperature. The solution was subsequently filtered through a Whatman No. 42 filter paper, and the filtrate was discarded. The barium sulphate filter was washed with two 10 ml portions of a cold 1:500 hydrochloric acid solution, and this was followed by repeated washings with hot $H_2O_D$ until portions of the filtrate showed freedom from chloride when tested with silver nitrate solution. The filter was reserved. The washings were collected, and 2 ml of a 10% w/v barium chloride solution was added. The solution was evaporated to dryness without baking. The residue was treated with 2 ml of a 1:1 hydrochloric acid solution and 25 ml of warm $H_2O_D$, and was subsequently digested at 70°C for two hours. The warm solution was filtered on the original filter paper, and the total precipitate was washed with $H_2O_D$ until chloride-free. The filter paper and contents were

charred in a previously-weighed platinum crucible, and this was followed by ignition to constant weight at 950°C. The crucible and contents were taken, and one drop of 1:1 sulphuric acid and 1 ml of concentrated hydrofluoric acid were added. The crucible contents were then evaporated to dryness. The crucible was then ignited to constant weight at 950°C. A reagent blank was carried through the entire procedure (14).

# 4. RESULTS AND DISCUSSION

## 4.1 Results from the Application of Instrumental Techniques

### 4.1.1 Polarography

As indicated in the previous Sections, differential pulse polarography was applied to attempt the detection and determination of sulphite, sulphide and thiosulphate ions in various forms of the culture media.

Sulphide was suspected to be present in the spent media, since an odour reminiscent of sulphide was occasionally detected in this media.

Sulphite was a possible bacterial degredation product, either final or intermediate, of the thiosulphate ion oxidative process.

No peaks of significant magnitude were located at the half-wave potentials characteristic of sulphite and sulphide were noted for any of the media samples analyzed. On this basis, sulphite and sulphide ions were considered to be absent in all of the tested media, so that these ions did not originate as the results of either bacterial or chemical action.

A half-wave potential of about - 0.11V vs Ag/AgCl (sat. KCl) was determined for the thiosulphate ion. A summary of the data and the results obtained from several differential

pulse polarographic examinations for thiosulphate ion are shown in Table 4.1.

The results shown for this technique of determination of thiosulphate ion concentration indicate a significant and consistent error. The obtained results always indicate, for the initial and control culture media samples, more thiosulphate than was actually used to prepare the media. In addition, the results obtained polarographically do not agree with those obtained by the titrimetric method of analysis.

The most likely reason for the failure of the differential pulse polarographic technique to provide accurate and reliable data was the inordinately high concentration of thiosulphate ion in the samples under test. Differential pulse polarography is a relatively sensitive technique, and the concentration of thiosulphate ion under analysis in the samples involved exceeded significantly the upper detection limits for the linearly responsive zone. The logical manner in which to overcome this situation would be to dilute the original sample of the media to the point where the thiosulphate concentration would have been within the range of linearity of response. In order to carry out this requirement, the degree of dilution would have been such that the error associated with the high multiplication factor involved would have seriously affected the reliability of the analytical results.

TABLE 4.1

DIFFERENTIAL PULSE POLAROGRAPHIC RESULTS FOR THIOSULPHATE ION

| | Peak current (uA) | | | Spike concen. (ppm) | | Concen. $S_2O_3$ (g/L) | |
|---|---|---|---|---|---|---|---|
| Sample | original | spike 1 | spike 2 | spike 1 | spike 2 | polarographic | wet analysis |
| A1 | 10.00 | 12.00 | 13.50 | 78.12 | 144.92 | 11.10 | 6.92 |
| B1 | 10.25 | 12.50 | 13.50 | 76.04 | 141.43 | 10.27 | 7.05 |
| C1 | 5.50 | 7.50 | 9.50 | 79.05 | 146.52 | 5.71 | 1.68 |
| C2 | 5.00 | 7.50 | 9.50 | 79.05 | 146.52 | 4.38 | 1.68 |
| C3 | 4.25 | 6.50 | 8.50 | 78.89 | 146.25 | 4.03 | 3.67 |

4.1.2 X-ray fluorescence

An attempt was made, as indicated in Section 3.1.2, to determine the total sulphur concentration for the bacterial culture media by the x-ray fluorescence spectrometric technique.

The calibration standard prepared ranged from 0 to 4.5 grams of sulphur per kilogram of solution. The parameters used on the x-ray fluorescence spectrometer for calibration and all subsequent analyses are shown in Table 4.2. The calibration data are shown in graphic and linear equation form in Figure 4.1 and Table 4.3.

It was assumed that the bacteria incorporated a negligible amount of sulphur and sulphur-containing substances. The total sulphur contained in the media should therefore closely approximate the total amounts of thiosulphate and sulphate, as sulphur, added initially in making up the media.

A portion of each media sample was filtered and analyzed by the x-ray fluorescence technique. The results for each sample tested are shown in Table 4.4. Samples of unfiltered media were also analyzed, and the results for these are shown in Table 4.5.

Inspection of the total data indicates that the experimental results were consistently and significantly lower than the expected results, as based on the makeup of the media. Initially, the low values for sulphur in the filtered

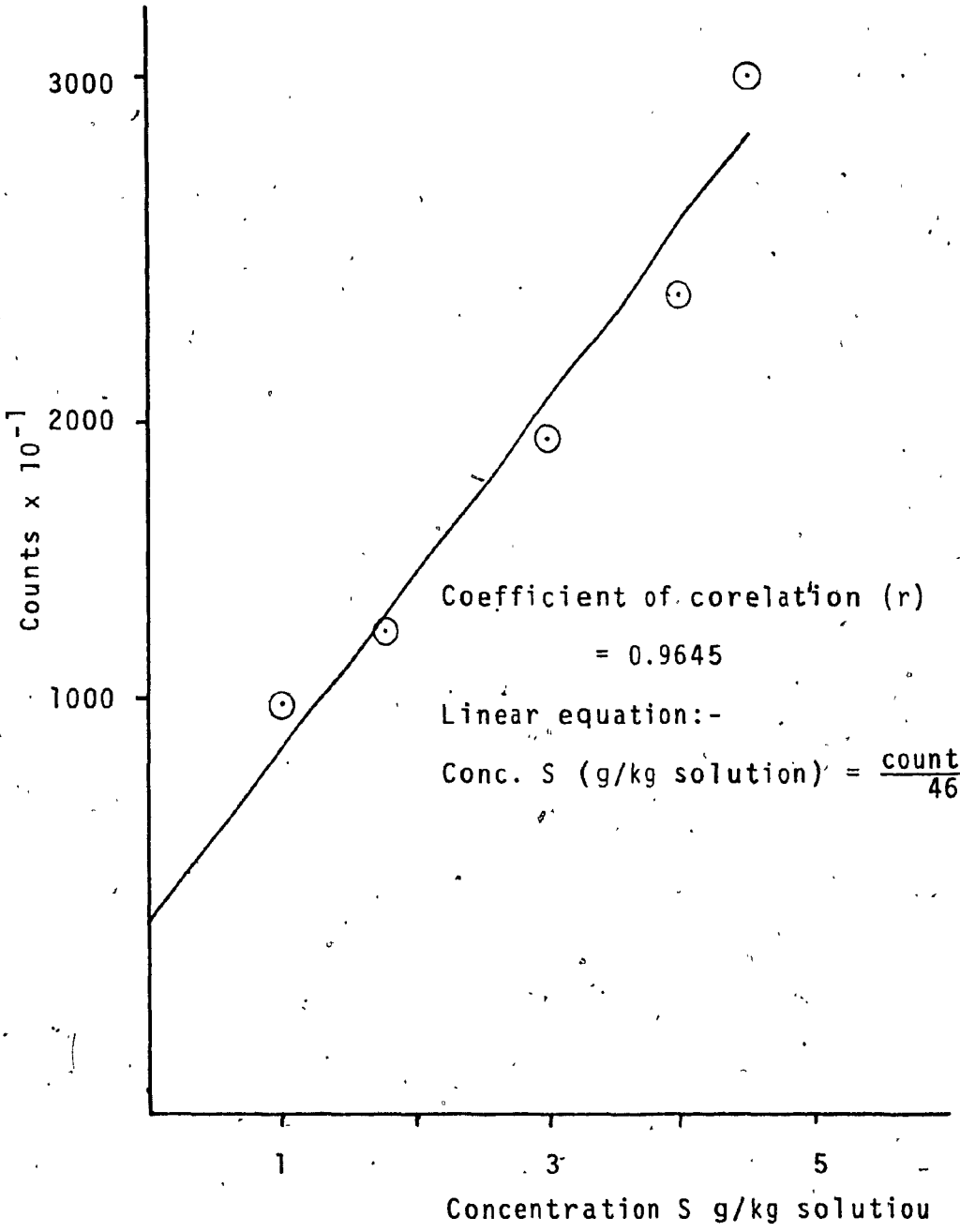


FIGURE 4.1 Calibration Curve - X-Ray Fluorescence Determination of Sulphur

TABLE 4.2

INSTRUMENTAL PARAMETERS FOR X-RAY FLUORESCENCE

| | |
|---|---|
| Target | Chromium |
| Counter | Proportional flow |
| Excitation Conditions | 48 kV 30 mA |
| Diffraction Angle | 75.75° |
| Counting Time | 30 seconds |
| Range | 1 K |
| Time Constant | 1 |
| High Voltage Setting | 2.40 kV (dial). 1.35 kV (meter) |
| Scale Expansion | 1 |
| Zero Supression | 0.0 |
| Gain | 10 |

TABLE 4.3

CALIBRATION DATA FOR XRF DETERMINATION OF TOTAL SULPHUR.

| Concentration (g $S^{o}$/kg soln) | Intensity counts x $10^{-1}$ | Ave. intensity counts x $10^{-1}$ |
|---|---|---|
| 0.0000 | 512, 509, 521*, 513, 508 | 510 ($510^{5}$) |
| 0.9983 | 1266, 1266, 1247, 1244, 1226 | 1250 ($1249^{8}$) |
| 1.7813 | 1400, 1369, 1363, 1377, 1329 | 1368 ($1367^{6}$) |
| 3.0183 | 1829, 1816, 1831, 1810, 1742* | 1822 ($1821^{5}$) |
| 4.0017 | 2172, 2156, 2146, 2133, 2133 | 2146 ($2146^{0}$) |
| 4.4818 | 2977, 2981, 3000, 2917, 2893 | 2954 ($2953^{6}$) |

* Data rejected with rejection based on std. dev. x 1.5

Linear regression analysis yielded:-

coefficient of corelation (r) = 0.9645

$$\text{Conc. } S^{o} \text{ (g/kg soln)} \quad \frac{\text{counts} \times 10^{-1} - 579}{461}$$

TABLE 4.4

X-RAY RESULTS FOR FILTERED SAMPLES

| Sample | Concentration (g/L) | Expected Concentration (g/L) |
|---|---|---|
| A1 | 4.2575 | 4.4071 |
| A2 | 3.7967 | 4.3843 |
| A3 | 3.8697 | 4.3837 |
| A4 | 4.3029 | 4.4465 |
| A5 | 3.9559 | 4.3927 |
| A6 | 3.2192 | 4.3871 |
| A7 | 3.7147 | 4.3863 |
| A8 | 3.6725 | 4.3848 |
| A9 | 4.3309 | 4.3893 |
| A10 | 3.5129 | 4.3832 |
| A11 | 3.8322 | 4.3834 |
| B1 | 3.8820 | 4.3839 |
| B2 | 3.4056 | 4.3842 |
| C1 | 3.3115 | 4.3848 |
| C2 | 3.0369 | 4.3836 |
| B3 | 3.1412 | 4.3846 |
| B4 | 2.7115 | 4.3853 |
| C3 | 3.0446 | 4.3856 |
| C4 | 3.0800 | 4.3833 |
| B5 | 3.1375 | 4.3858 |
| B6 | 3.0456 | 4.3827 |
| C5 | 2.6310 | 4.3906 |
| C6 | 2.7247 | 4.3825 |
| B7 | 2.9428 | 4.3792 |
| B8 | 3.0371 | 4.3832 |
| C7 | 2.6756 | 4.3813 |
| C8 | 2.6321 | 4.3838 |
| B9 | 3.0018 | 4.3839 |
| B10 | 2.9583 | 4.3873 |
| C9 | 2.5530 | 4.3836 |
| C10 | 2.3660 | 4.3892 |

TABLE 4.5

X-RAY RESULTS FOR UNFILTERED SAMPLES

| Sample | Concentration (g/L) | Expected Concentration (g/L) |
|---|---|---|
| A1 | 4.2714 | 4.4071 |
| A2 | 4.2395 | 4.3843 |
| A3 | 4.1841 | 4.3837 |
| A4 | 4.2833 | 4.4465 |
| A5 | 4.0082 | 4.3927 |
| A6 | 4.0429 | 4.3871 |
| A7 | 4.0647 | 4.3863 |
| A8 | 4.0732 | 4.3848 |
| A9 | 3.9885 | 4.3893 |
| A10 | 3.9942 | 4.3832 |
| A11 | 4.1465 | 4.3834 |
| B1 | 3.3295 | 4.3839 |
| B2 | 2.8257 | 4.3842 |
| C1 | 2.3939 | 4.3848 |
| C2 | 2.6052 | 4.3836 |
| B3 | 2.6022 | 4.3846 |
| B4 | 2.2057 | 4.3853 |
| C3 | 2.3367 | 4.3856 |
| C4 | 2.5831 | 4.3833 |
| B5 | 2.4040 | 4.3858 |
| B6 | 2.5437 | 4.3827 |
| C5 | 2.1795 | 4.3906 |
| C6 | 2.2894 | 4.3825 |
| B7 | 2.3502 | 4.3792 |
| B8 | 2.3863 | 4.3832 |
| C7 | 2.1363 | 4.3813 |
| C8 | 2.2754 | 4.3838 |
| B9 | 2.3150 | 4.3839 |
| B10 | 2.3327 | 4.3873 |
| C9 | 2.1553 | 4.3836 |
| C10 | 1.0074 | 4.3892 |

samples were thought to have originated as the result of sulphur or sulphur-containing compound loss as precipitate material during the filtration process. The unfiltered samples, however, gave equally erroneous results, and these were assume to be due to the turbid nature of the spent media, the finely-divided, suspended particulate matter causing some diffraction of the x-ray beam with correspondingly lower sulphur results.

It should be noted that the ease of determining elemental substances by x-ray fluorescence decreases with decreasing atomic number of the analyte, becoming important with the lighter elements. This is due to (15):-

a) Reduction in excitation efficiency.

b) An increase in absorption for the fluorescent or emitted radiation throughout the optical path of the spectrometer from specimen to detector.

c) A decrease in the signal-to-noise ratio and thus a decrease in sensitivity.

d) Less reflectivity for the crystals used to examine relatively long x-rays (16).

### 4.1.3 Flame atomic absorption spectrophotometry

Microbes respond to heavy metals in different ways, and these depend on both the type of microorganism involved and the concentration of the heavy metal in the environment. All microbes require certain heavy metals in their nutrition cycles, and these include cobalt, copper, magnesium and zinc

(17,18), and some require in addition such metals as molybdenum, vanadium and nickel (19,20,21,22,23). All of these metals are involved mainly in enzyme functions, and they required only in very low concentrations in the nutrient media (24).

Sufficiently elevated concentrations of any of the metals result in toxic situations for the microorganisms involved. This toxicity may manifest itself in various ways, such as:-

a) Altered cell morphology (25,26,27)
b) Altered cell metabolism (28,29,30)
c) Bacteriostasis (30)
d) Lethality (30)

The constituents of the culture media were analyzed individually by the flame atomic absorption technique. The following metals were involved in these analyses:- cadmium, lead, iron, copper, zinc, nickel, antimony, manganese, chromium, bismuth, tin, vanadium, cobalt and molybdenum. A sample of the deionized, plain-distilled water used by the Biological Sciences group in media preparation was also analyzed for these metals. All samples were prepared for atomic absorption analysis using deionized, glass-distilled water from a separate source. This latter water was also used for zeroing the atomic absorption unit.

The calibration curves for each of the analytes are shown in Figures 4.2 to 4.15. Linear regression analysis was applied to yield the best straight line for the data obtained and, in each case, the equation for the straight line is shown on the calibration curve. The results obtained for the metal contents of the various media constituents are shown in Table 4.16, and these results are expressed in ppm. The total data obtained can be found in Appendix C.

The results of the various analyses indicated a high tin content in the deionized, plain-distilled water used by the Biological Sciences group. This elevated tin content has now been attributed to the tin block condenser used in the still from which this water was prepared.

The cadmium, zinc, tin and cobalt found in the media constituents were probably contaminating materials in the solid salts involved. The calcium, manganese and iron salts used were, for example, all technical grade products and as such capable of containing a significant heavy metal contaminants content.

The antimony results obtained are of a doubtful nature, this being due largely to the age and lack of reliable output of the antimony hollow cathode lamp used. The results were not repeated, using other analytical techniques, since it was felt that the influence of antimony in the range indicated was not critical (31).

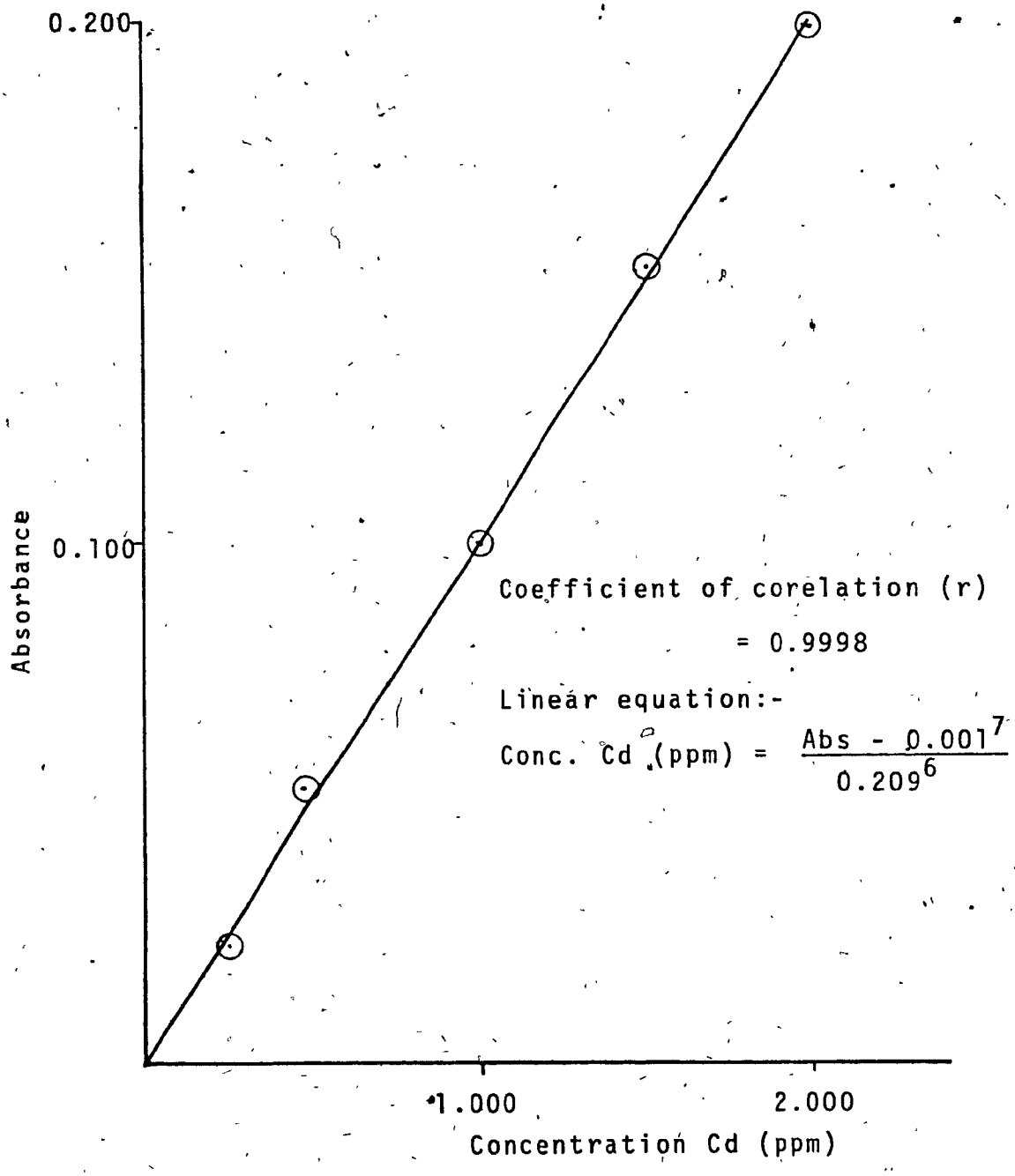


FIGURE 4.2 Calibration Curve for Cd - Flame Atomic Absorption

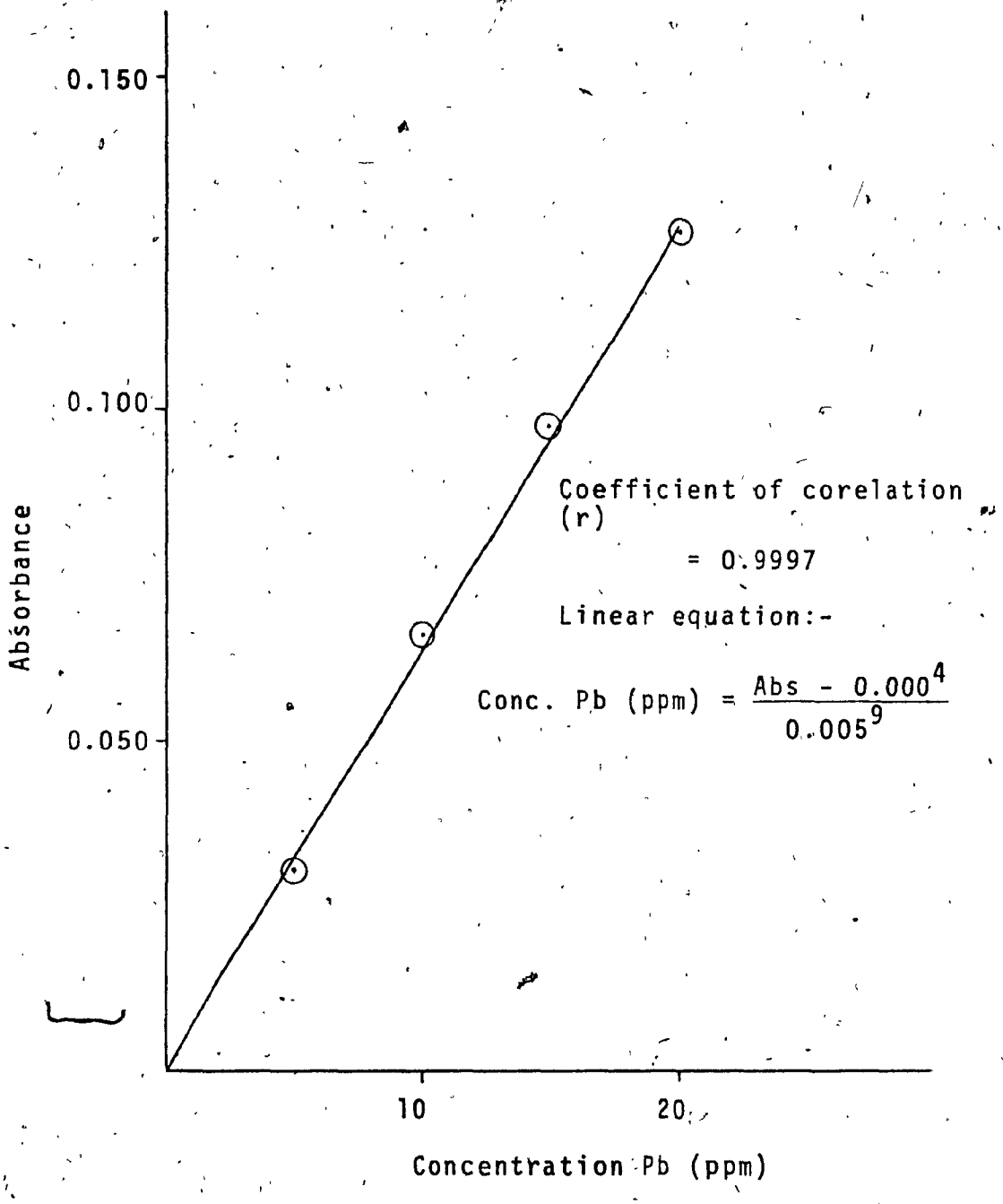


FIGURE 4.3 Calibration Curve for Pb - Flame Atomic Absorption

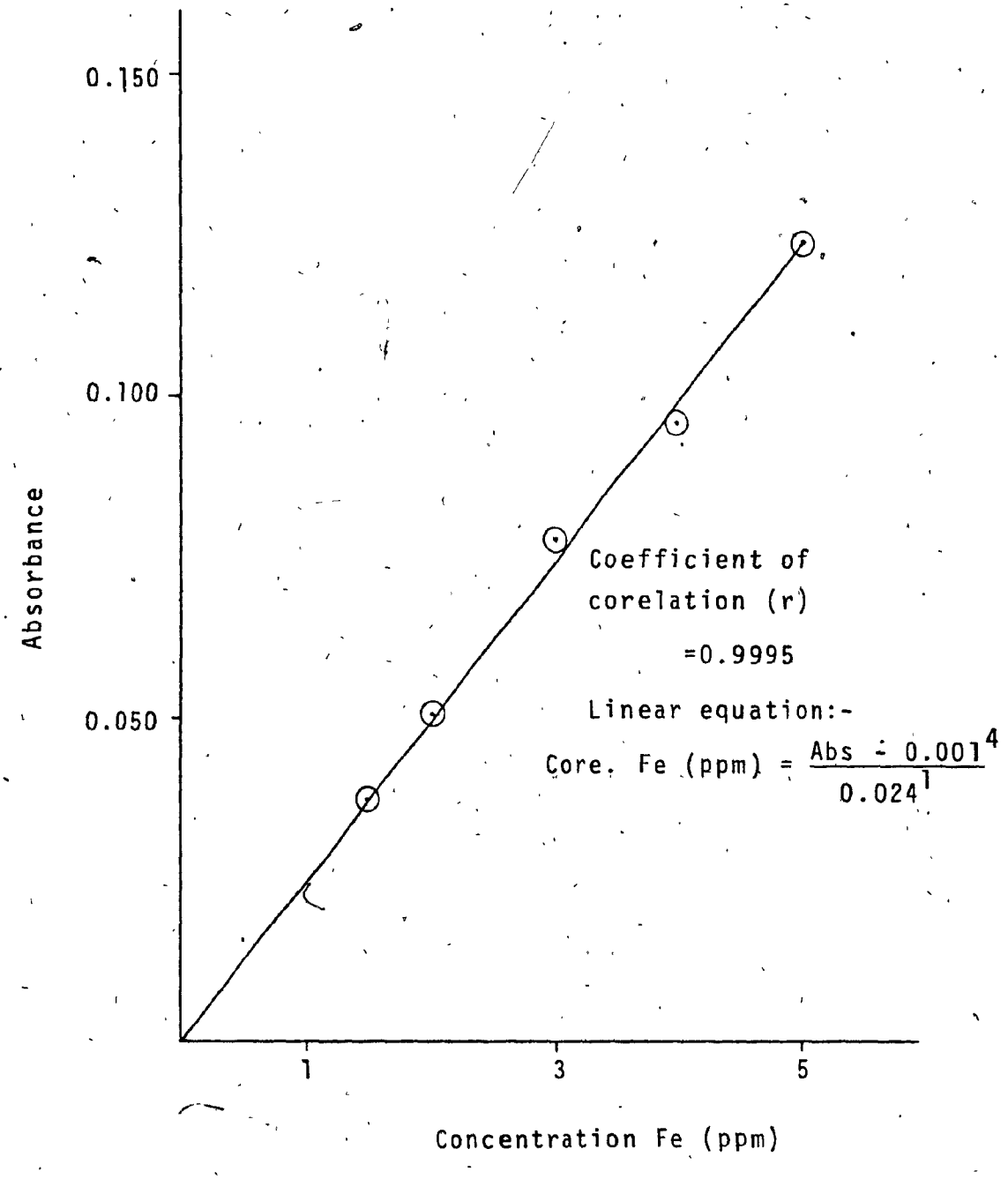


FIGURE 4.4 Calibration Curve for Fe - Flame Atomic Absorption

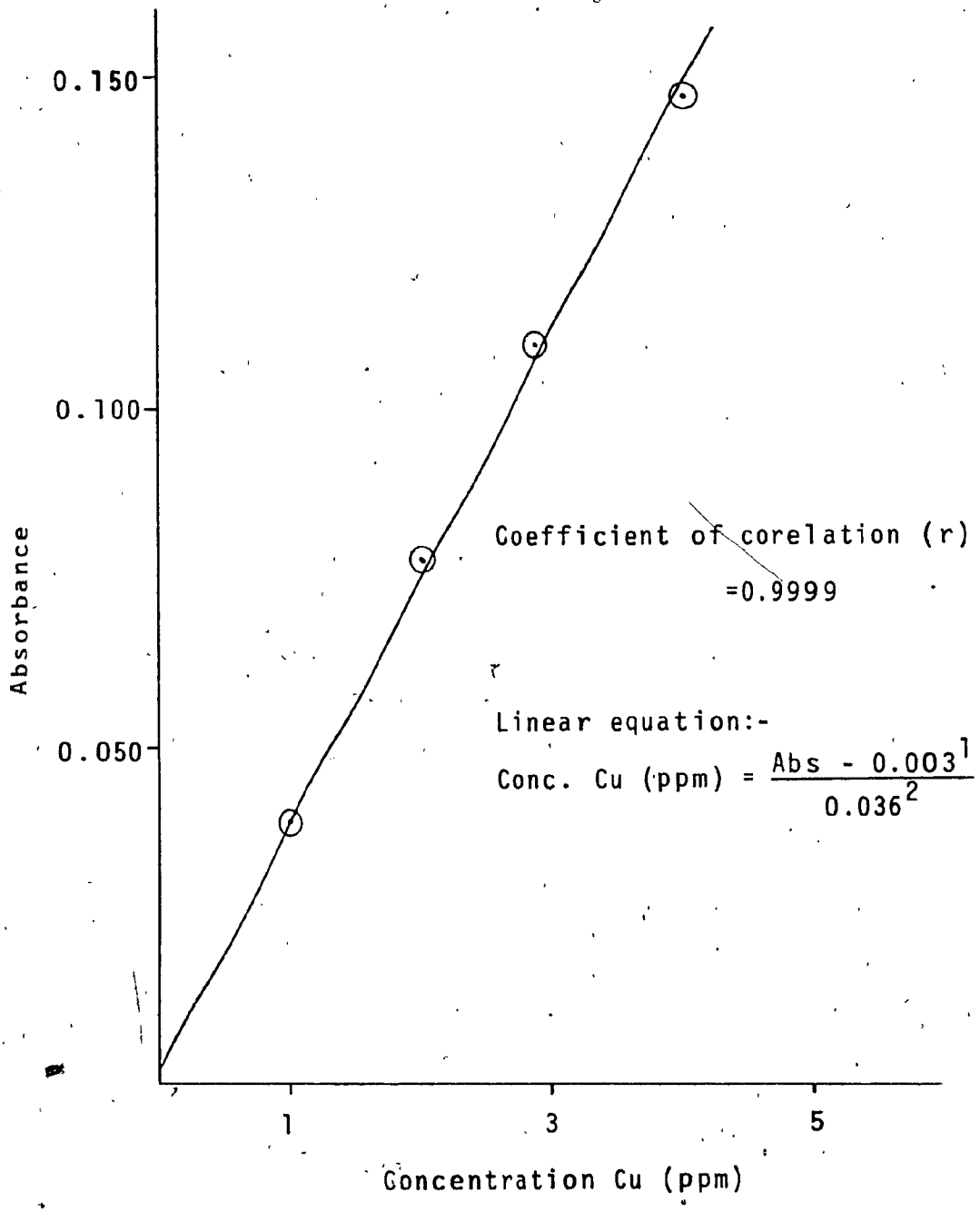


FIGURE 4.5 Calibration Curve for Cu - Flame Atomic Absorption

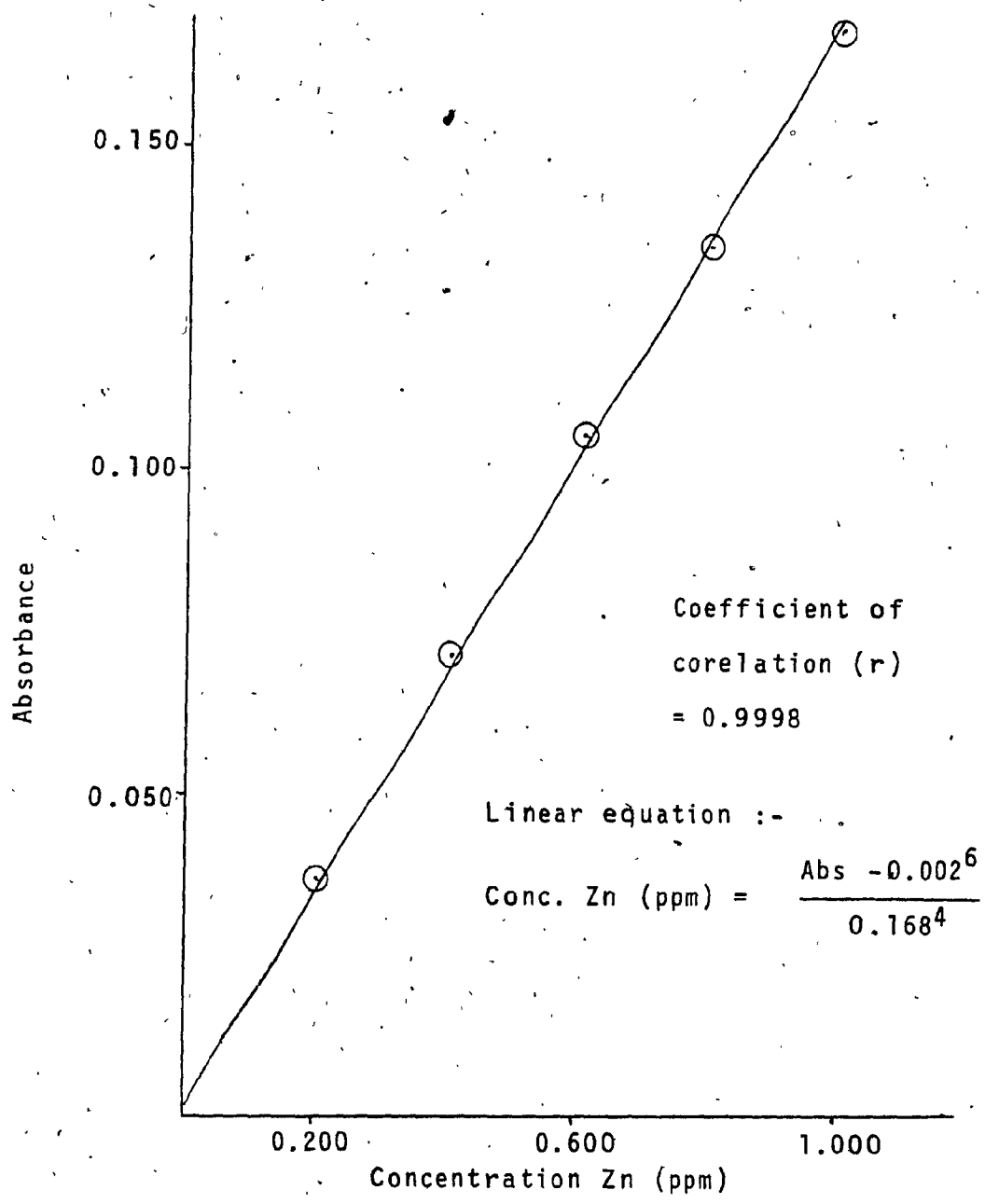


Figure 4.6 Calibration Curve Zn - Flame Atomic Absorption

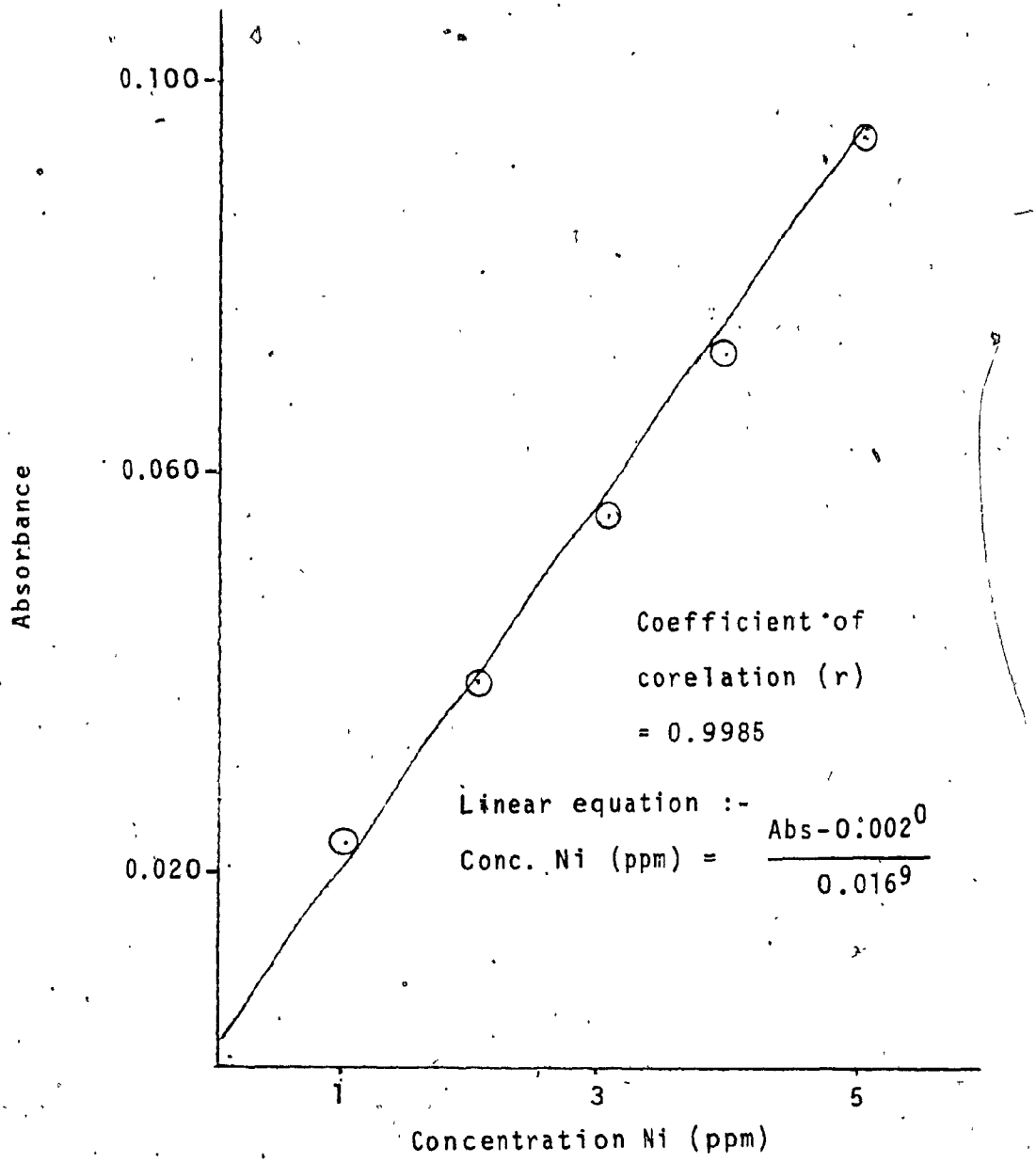


Figure 4.7 Calibration Curve for Ni - Flame Atomic Absorption

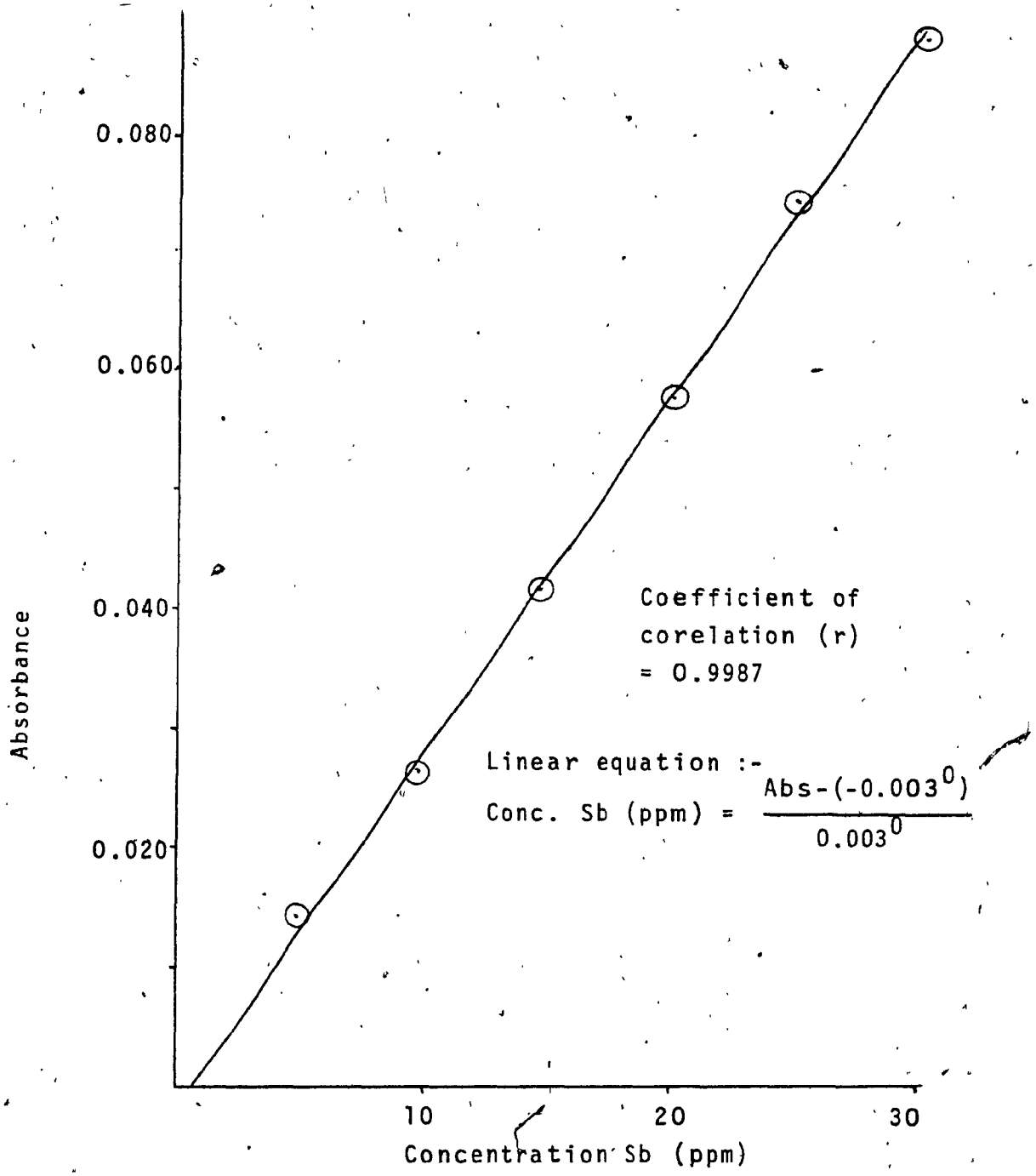


Figure 4.8 Calibration Curve for Sb - Flame Atomic Absorption

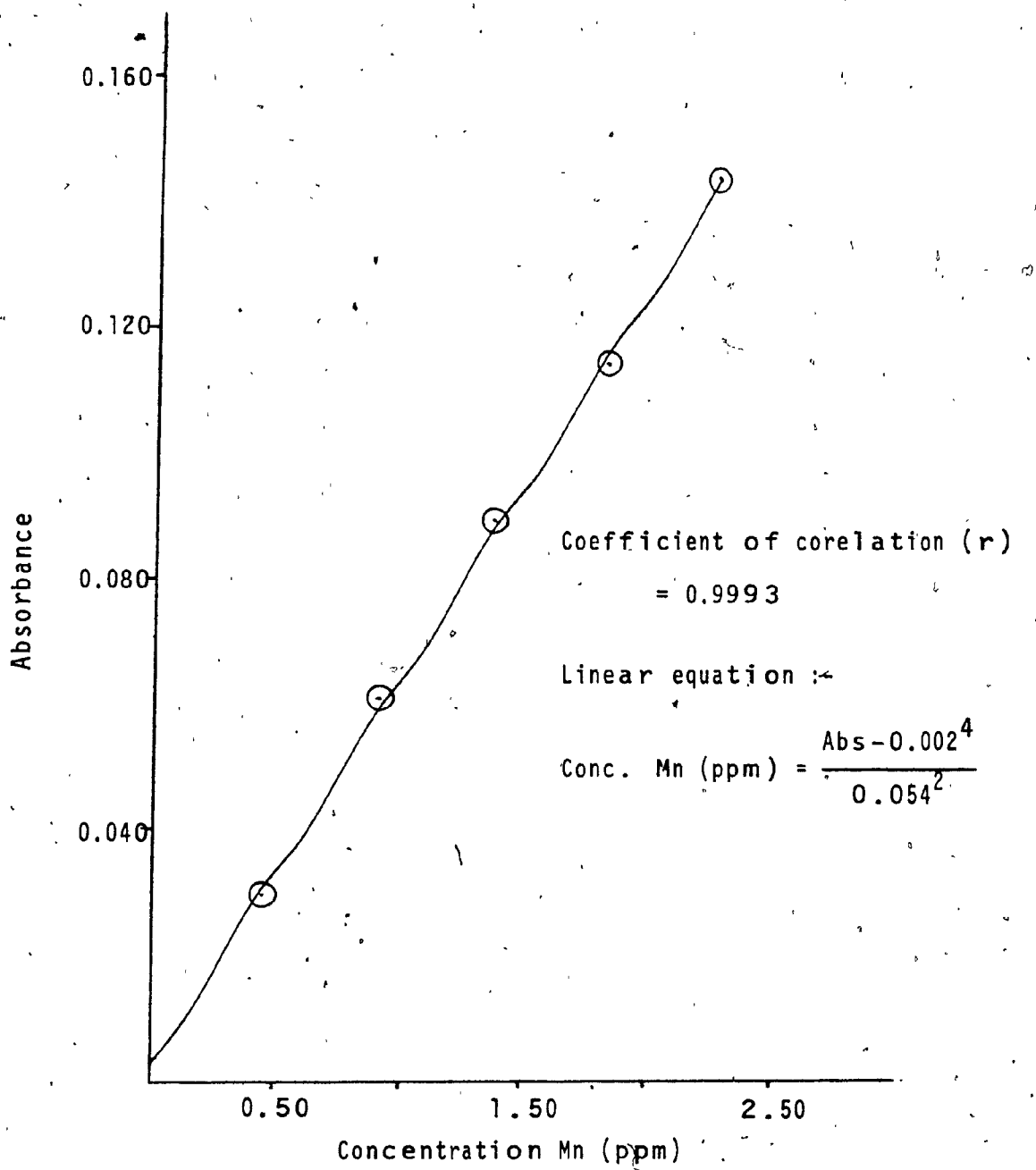


Figure 4.9 Calibration Curve for Mn - Flame Atomic Absorption

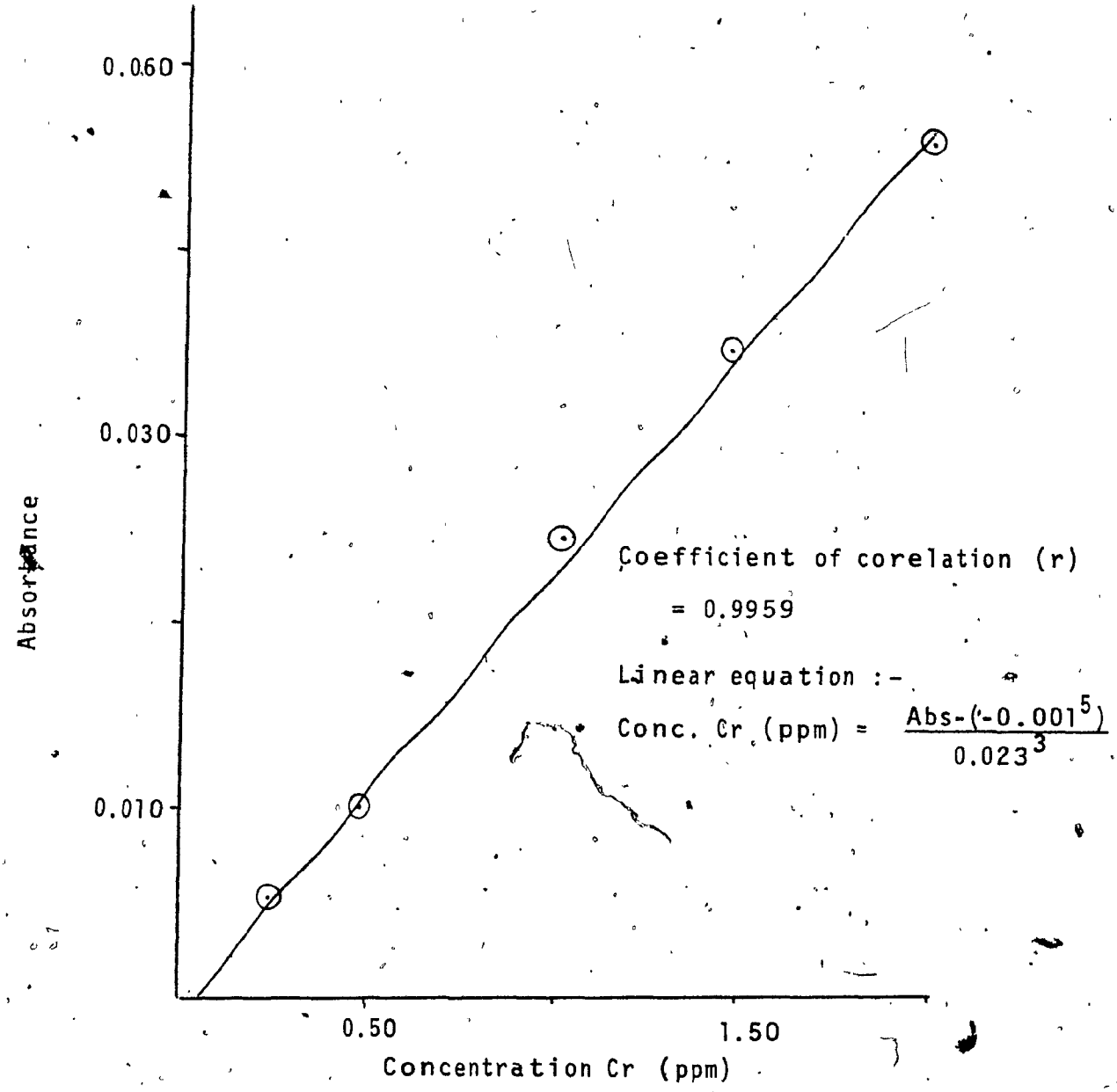


Figure 4.10 Calibration Curve for Cr - Flame Atomic Absorption

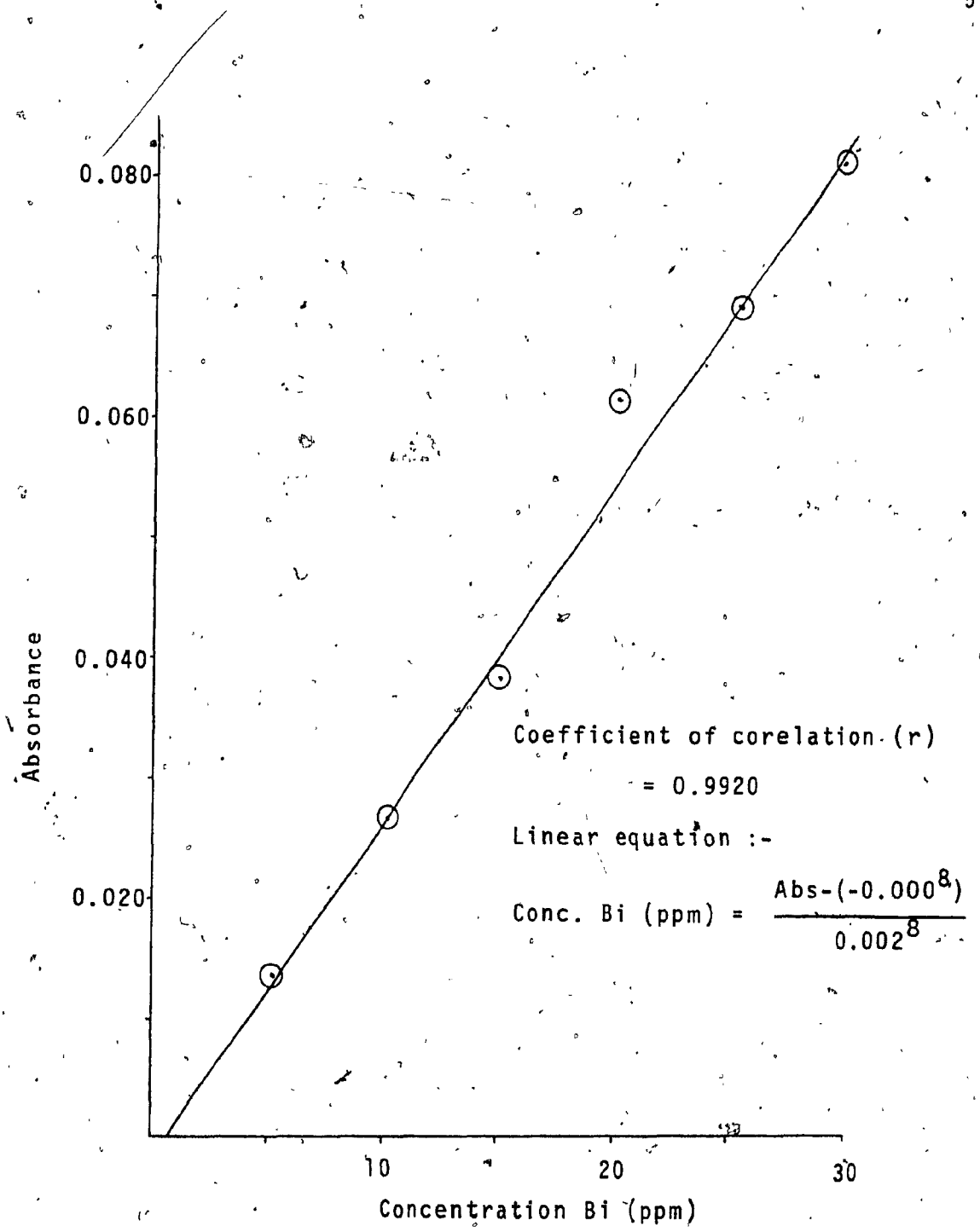


Figure 4.11 Calibration Curve for Bi - Flame Atomic Absorption

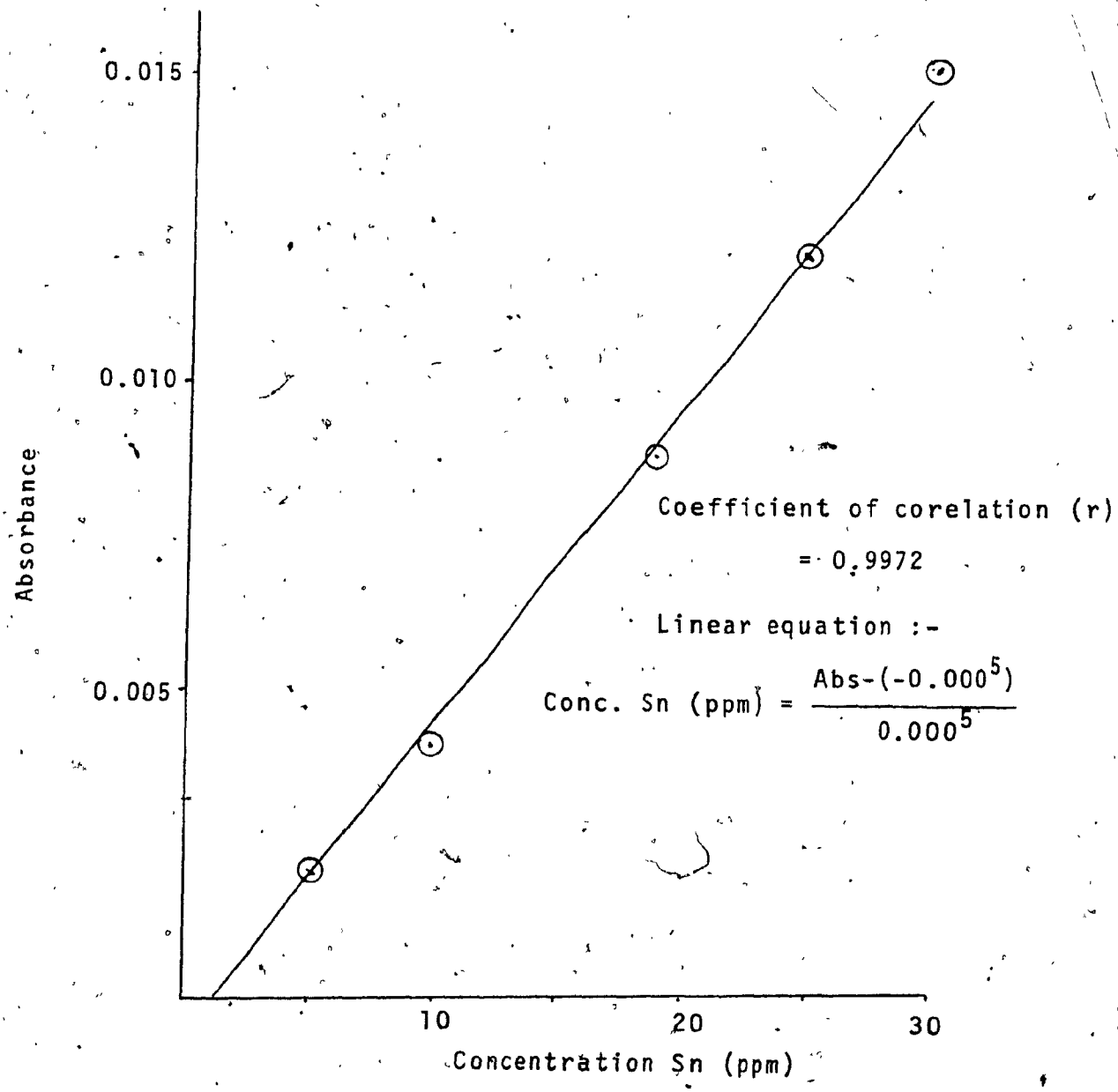


Figure 4.12 Calibration Curve for Sn - Flame Atomic Absorption

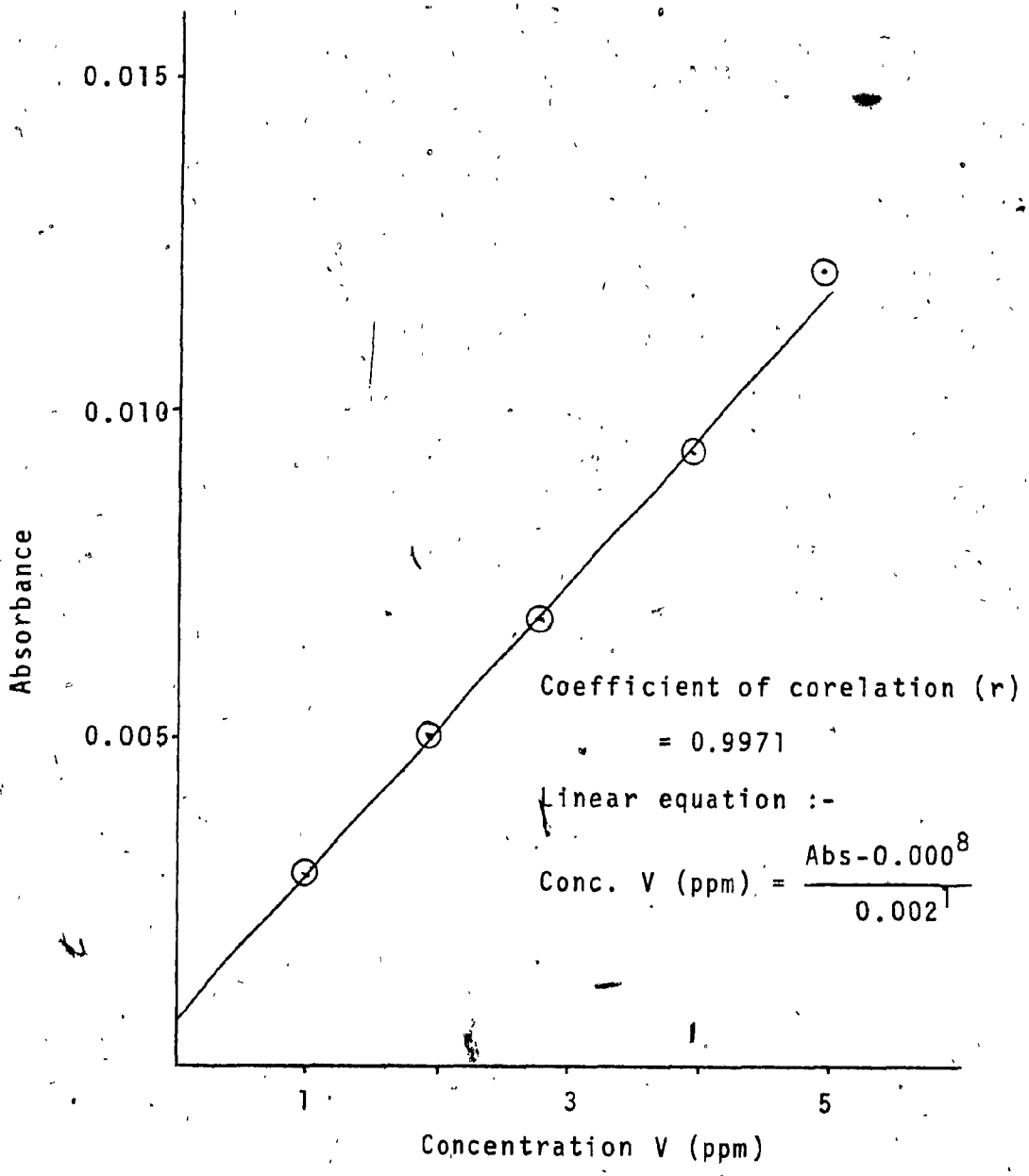


Figure 4.13 Calibration Curve for V by Flame Atomic Absorption

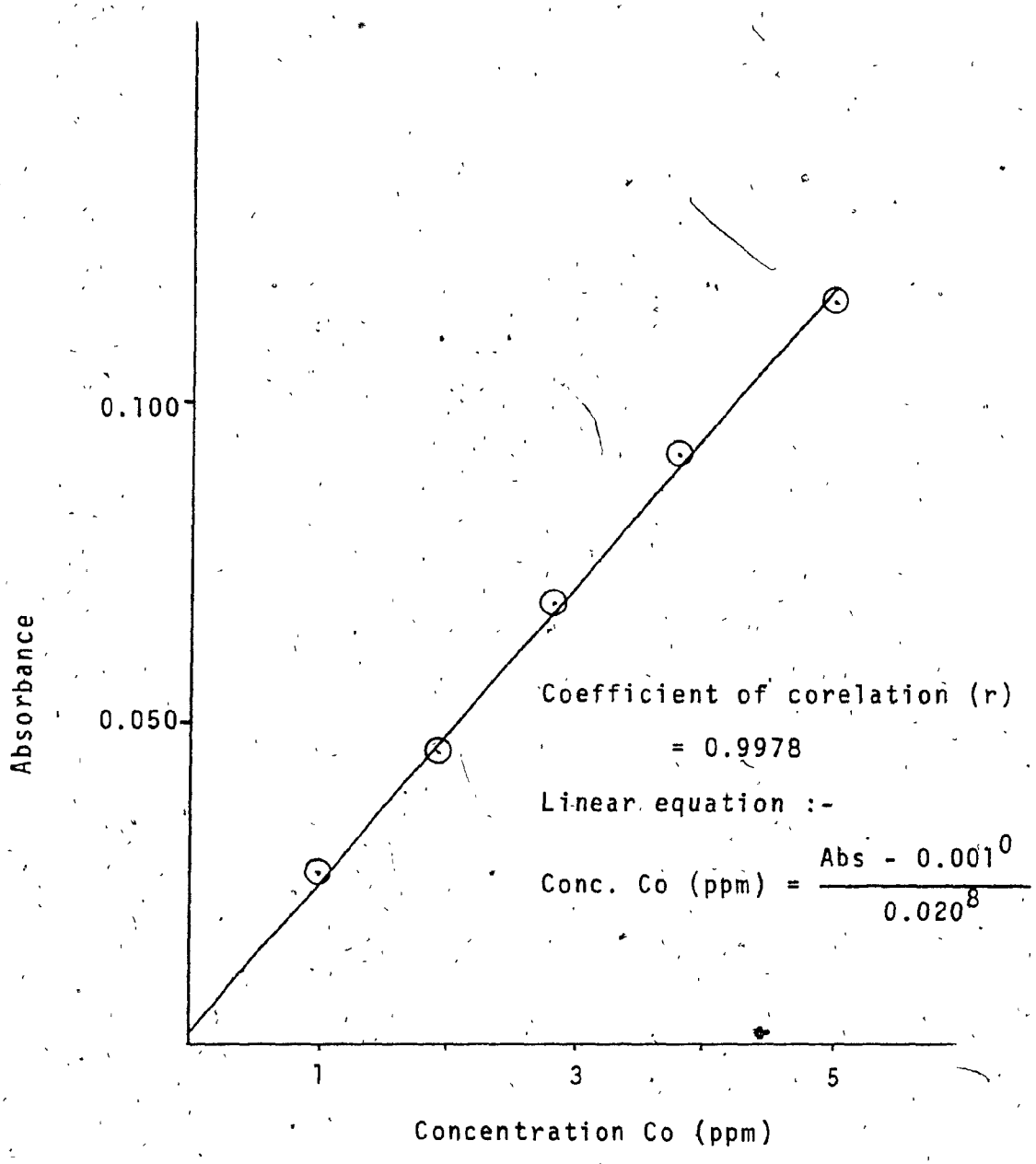


Figure 4.14 Calibration Curve for Co - Flame Atomic Absorption

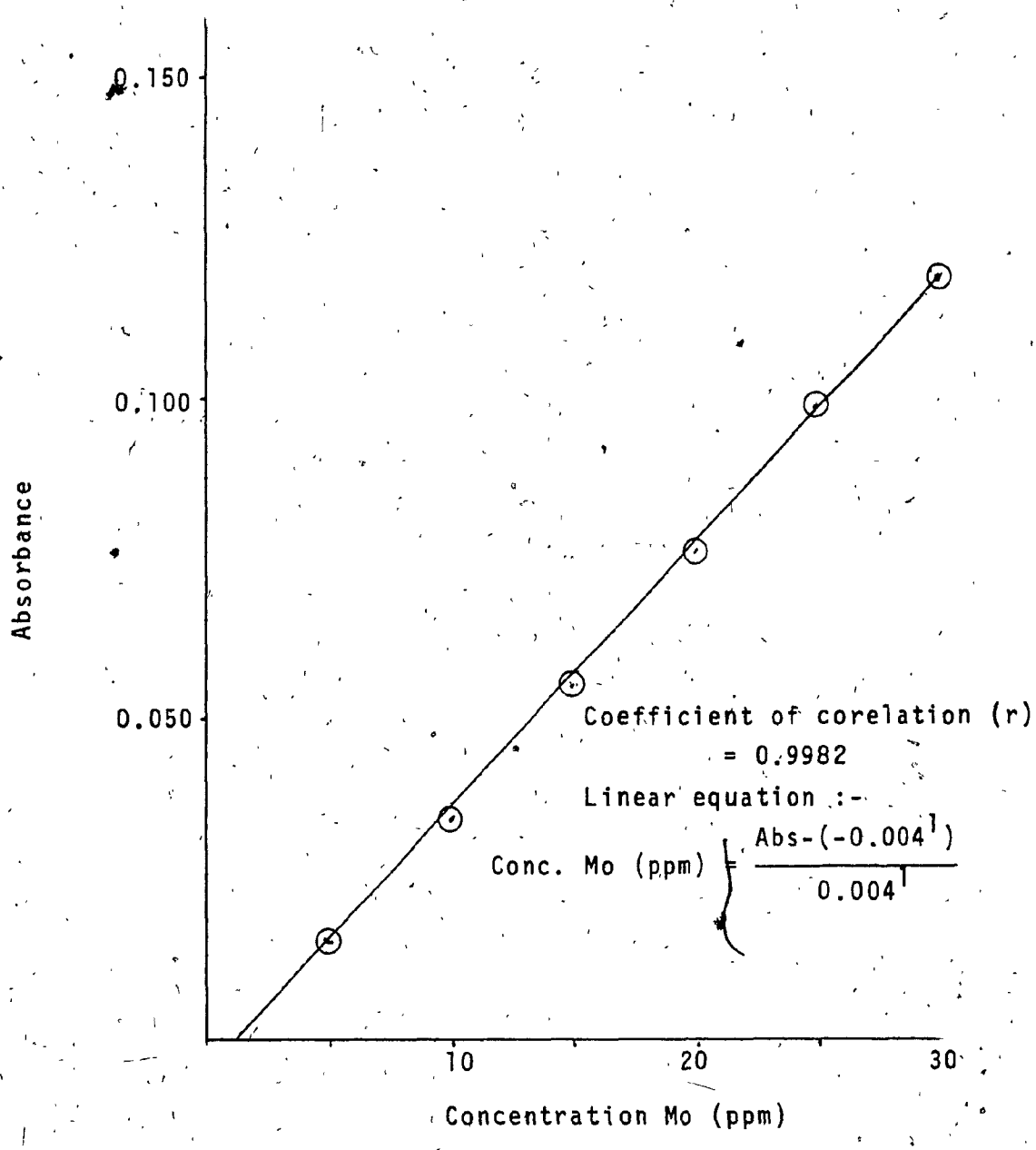


Figure 4.15 Calibration Curve for Mo - Flame Atomic Absorption

TABLE 4.6

SUMMARY OF FLAME ATOMIC ABSORPTION RESULTS

Concentration (ppm)

| Sample | Cd | Pb | Fe | Cu | Zn | Ni | Sb | Mn | Cr | Bi | Sn | V | Co | Mo |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B.S. ($H_2O$) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 13.0 | ND | ND | ND |
| $Na_2S_2O_3 \cdot 5H_2O$ | 0.02 | ND | ND | ND | 0.10 | ND | 1.67 | ND | ND | ND | ND | ND | 0.34 | ND |
| $NaHCO_3$ | ND | ND | ND | ND | ND | ND | 2.00 | ND | ND | ND | ND | ND | ND | ND |
| $K_2HPO_4$ | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 0.53 | ND |
| NaCl | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| $MgSO_4 \cdot 7H_2O$ | ND | ND | ND | ND | ND | ND | 1.67 | ND | ND | ND | ND | ND | ND | ND |
| $NH_4Cl$ | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| $Na_2MoO_4 \cdot 2H_2O$ | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | NT |
| $CaCl_2$ | ND | ND | ND | ND | ND | ND | 2.67 | ND | ND | ND | 33.0 | ND | ND | ND |
| $MnCl_2$ | ND | ND | ND | ND | ND | ND | 2.67 | ND | NT | ND | 25.0 | ND | ND | ND |
| $FeSO_4 \cdot 7H_2O$ | ND | ND | NT | ND | ND | ND | 2.67 | ND | ND | ND | 25.0 | ND | ND | ND |

ND = not detected - See appendix C for detection limits

NT = not tested

## 4.2 Results from the Application of Wet Methods of Chemical Analysis

Most instrumental methods of analysis, such as x-ray fluorescence spectrometry, atomic absorption spectrophotometry, emission spectroscopy, etc. are aimed at the determination of elemental species. Methods, such as several of the electrochemical techniques, are capable of molecular as well as elemental detection and determination. Many of the classical wet chemical analysis techniques are still the preferred methods for the detection and determination of molecular species.

Gravimetric and titrimetric methods of analysis were applied in determination of thiosulphate, sulphate, elemental sulphur and sulphur dioxide in the various media and associated materials involved.

A summary of the results obtained are given in the tables indicated below. The totality of data and supporting information can be found in Appendix B.

a) Thiosulphate determinations - Tables 4.7 - 4.15

b) Sulphate determinations - Tables 4.16 - 4.24

c) HCl-blank sulphur determinations - Tables 4.25 - 4.33

d) Sulphur dioxide determinations - Tables 4.34 - 4.35

In general, the analytical data indicate that Rhodopseudomonas goldameirii utilize thiosulphate in the culture

media as the source of reducing power, converting the thiosulphate to sulphate by an overall oxidation of sulphur according to:-

$$S^{2+} - 4e \longrightarrow S^{6+}$$

This oxidative process may occur as a single step, such as:-

$$S_2O_3^{=} + 10\ OH^- - 8e \longrightarrow 2SO_4^{=} + 5\ H_2O$$

or it may occur in a series of step-wise processes, with some of the possibilities being:-

(1)
$$2S_2O_3^{=} - 2e \longrightarrow S_4O_6^{=}$$

$$S_4O_6^{=} + 20\ OH^- - 14e \longrightarrow 4SO_4^{=} + 10\ H_2O$$

(2)
$$2S_2O_3^{=} - 2e \longrightarrow S_4O_6^{=}$$

$$2S_4O_6^{=} \longrightarrow S_5O_6^{=} + S_3O_6^{=}$$

$$S_3O_6^{=} + 12\ OH^- - 8e \longrightarrow 3SO_4^{=} + 6\ H_2O$$

The exact sequence of reactional steps was not determined in this project, but suggestions in this connection are included in Section 5, "Suggestions for Future Work".

The chemical material balance works in conjunction with the bacterial material balance. In the course of carrying out the wet chemical analysis work, in particular, the sample of media must be made acid with hydrochloric acid (11, 12). In the presence of this acid content, thiosulphate

TABLE 4.7

DETERMINATION OF THIOSULPHATE SERIES I

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A1 | 6.92 ± 0.00 | 7.59 ± 0.00 | 0.67 ± 0.00 | 0.04 | Appendix B |
| A2 | 7.32 ± 0.00 | 7.55 ± 0.00 | 0.23 ± 0.00 | 0.04 | Appendix B |
| B1 | 7.05 ± 0.00 | 7.55 ± 0.00 | 0.50 ± 0.00 | 0.04 | Appendix B |
| B2 | 6.79 ± 0.00 | 7.55 ± 0.00 | 0.76 ± 0.00 | 0.04 | Appendix B |
| C1 | 1.68 ± 0.00 | 7.55 ± 0.00 | 5.87 ± 0.00 | 0.03 | Appendix B |
| C2 | 1.68 ± 0.00 | 7.55 ± 0.00 | 5.77 ± 0.00 | 0.03 | Appendix B |

TABLE 4.8

DETERMINATION OF THIOSULPHATE SERIES II

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A3 | 7.09 ± 0.00 | 7.55 ± 0.00 | 0.46 ± 0.00 | 0.04 | Appendix B |
| A4 | 7.27 ± 0.00 | 7.66 ± 0.00 | 0.39 ± 0.00 | 0.04 | Appendix B |
| B3 | 6.85 ± 0.00 | 7.55 ± 0.00 | 0.70 ± 0.00 | 0.04 | Appendix B |
| B4 | 6.72 ± 0.00 | 7.55 ± 0.00 | 0.83 ± 0.00 | 0.04 | Appendix B |
| C3 | 3.67 ± 0.00 | 7.55 ± 0.00 | 3.88 ± 0.00 | 0.04 | Appendix B |
| C4 | 2.89 ± 0.00 | 7.55 ± 0.00 | 4.66 ± 0.00 | 0.03 | Appendix B |

TABLE 4.9

DETERMINATION OF THIOSULPHATE SERIES III

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A5 | 7.05 ± 0.00 | 7.57 ± 0.00 | 0.51 ± 0.00 | 0.04 | Appendix B |
| A6 | 6.92 ± 0.00 | 7.56 ± 0.00 | 0.64 ± 0.00 | 0.04 | Appendix B |
| B5 | 7.02 ± 0.00 | 7.55 ± 0.00 | 0.53 ± 0.00 | 0.04 | Appendix B |
| B6 | 6.92 ± 0.00 | 7.55 ± 0.00 | 0.63 ± 0.00 | 0.04 | Appendix B |
| C5 | 3.29 ± 0.00 | 7.56 ± 0.00 | 4.27 ± 0.00 | 0.03 | Appendix B |
| C6 | 3.96 ± 0.00 | 7.55 ± 0.00 | 3.58 ± 0.00 | 0.04 | Appendix B |

TABLE 4.10

DETERMINATION OF THIOSULPHATE SERIES IV

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A7 | 7.38 ± 0.00 | 7.55 ± 0.00 | 0.17 ± 0.00 | 0.04 | Appendix B |
| A8 | 6.92 ± 0.00 | 7.55 ± 0.00 | 0.63 ± 0.00 | 0.04 | Appendix B |
| B7 | 7.39 ± 0.00 | 7.54 ± 0.00 | 0.15 ± 0.00 | 0.04 | Appendix B |
| B8 | 7.46 ± 0.00 | 7.55 ± 0.00 | 0.09 ± 0.00 | 0.04 | Appendix B |
| C7 | 3.76 ± 0.00 | 7.55 ± 0.00 | 3.79 ± 0.00 | 0.04 | Appendix B |
| C8 | 3.62 ± 0.00 | 7.55 ± 0.00 | 3.93 ± 0.00 | 0.04 | Appendix B |

TABLE 4.11

DETERMINATION OF THIOSULPHATE SERIES V

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A9 | 7.02 ± 0.00 | 7.56 ± 0.00 | 0.54 ± 0.00 | 0.04 | Appendix B |
| A10 | 7.19 ± 0.00 | 7.55 ± 0.00 | 0.36 ± 0.00 | 0.04 | Appendix B |
| B9 | 7.17 ± 0.01 | 7.55 ± 0.00 | 0.38 ± 0.01 | 0.04 | Appendix B |
| B10 | 7.05 ± 0.01 | 7.56 ± 0.00 | 0.51 ± 0.01 | 0.04 | Appendix B |
| C9 | 2.82 ± 0.00 | 7.55 ± 0.00 | 4.73 ± 0.00 | 0.03 | Appendix B |
| C10 | 2.02 ± 0.00 | 7.56 ± 0.00 | 5.54 ± 0.00 | 0.02 | Appendix B |

TABLE 4.12

DETERMINATION OF THIOSULPHATE SERIES VI

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A11 | 7.50 ± 0.01 | 7.55 ± 0.00 | 0.05 ± 0.01 | 0.04 | Appendix B |
| C11 | 2.22 ± 0.00 | 7.55 ± 0.00 | 5.33 ± 0.00 | 0.03 | Appendix B |
| C12 | 2.89 ± 0.00 | 7.55 ± 0.00 | 4.66 ± 0.00 | 0.03 | Appendix B |
| C13 | 2.55 ± 0.00 | 7.55 ± 0.00 | 5.00 ± 0.00 | 0.03 | Appendix B |
| C14 | 2.52 ± 0.00 | 7.55 ± 0.00 | 5.03 ± 0.00 | 0.03 | Appendix B |

TABLE 4.13

DETERMINATION OF THIOSULPHATE SERIES VII

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A13 | 7.44 ± 0.00 | 7.55 ± 0.00 | 0.11 ± 0.00 | 0.04 | Appendix B |
| A14 | 7.39 ± 0.00 | 7.55 ± 0.00 | 0.16 ± 0.00 | 0.04 | Appendix B |
| B11 | 7.52 ± 0.00 | 7.55 ± 0.00 | 0.03 ± 0.00 | 0.04 | Appendix B |
| B12 | 7.53 ± 0.00 | 7.55 ± 0.00 | 0.02 ± 0.00 | 0.04 | Appendix B |
| C15 | 2.33 ± 0.00 | 7.55 ± 0.00 | 5.21 ± 0.00 | 0.03 | Appendix B |
| C16 | 3.36 ± 0.00 | 7.55 ± 0.00 | 4.19 ± 0.00 | 0.03 | Appendix B |

TABLE 4.14

DETERMINATION OF THIOSULPHATE SERIES VIII

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A14 | 7.46 ± 0.00 | 7.55 ± 0.00 | 0.09 ± 0.00 | 0.04 | Appendix B |
| A15 | 7.46 ± 0.00 | 7.55 ± 0.00 | 0.09 ± 0.00 | 0.04 | Appendix B |
| B13 | 7.43 ± 0.00 | 7.55 ± 0.00 | 0.12 ± 0.00 | 0.04 | Appendix B |
| B14 | 7.54 ± 0.00 | 7.55 ± 0.00 | 0.01 ± 0.00 | 0.04 | Appendix B |
| C17 | 2.48 ± 0.00 | 7.55 ± 0.00 | 5.07 ± 0.00 | 0.02 | Appendix B |
| C18 | 1.77 ± 0.00 | 7.55 ± 0.00 | 5.78 ± 0.00 | 0.02 | Appendix B |

TABLE 4.15

DETERMINATION OF THIOSULPHATE SERIES IX

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A16 | 7.47 ± 0.00 | 7.55 ± 0.00 | 0.08 ± 0.00 | 0.04 | Appendix B |
| A17 | 7.47 ± 0.00 | 7.55 ± 0.00 | 0.08 ± 0.00 | 0.04 | Appendix B |
| B15 | 7.39 ± 0.00 | 7.55 ± 0.00 | 0.16 ± 0.00 | 0.04 | Appendix B |
| B16 | 7.42 ± 0.00 | 7.55 ± 0.00 | 0.12 ± 0.00 | 0.04 | Appendix B |
| C19 | 2.96 ± 0.00 | 7.55 ± 0.00 | 4.58 ± 0.00 | 0.03 | Appendix B |
| C20 | 2.92 ± 0.00 | 7.55 ± 0.00 | 4.63 ± 0.00 | 0.03 | Appendix B |
| C21 | 2.93 ± 0.00 | 7.55 ± 0.00 | 4.62 ± 0.00 | 0.03 | Appendix B |
| C22 | 2.79 ± 0.00 | 7.55 ± 0.00 | 4.76 ± 0.00 | 0.02 | Appendix B |

TABLE 4.15 Continued

| Sample | Concentration of thiosulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| C23 | 7.47 ± 0.00 | 7.55 ± 0.00 | 4.50 ± 0.00 | 0.03 | Appendix B |
| C24 | 7.47 ± 0.00 | 7.55 ± 0.00 | 5.94 ± 0.00 | 0.02 | Appendix B |
| C25 | 7.39 ± 0.00 | 7.55 ± 0.00 | 6.26 ± 0.00 | 0.02 | Appendix B |
| C26 | 7.42 ± 0.00 | 7.55 ± 0.00 | 4.58 ± 0.00 | 0.03 | Appendix B |
| C27 | 3.22 ± 0.00 | 7.55 ± 0.00 | 4.33 ± 0.00 | 0.03 | Appendix B |
| C28 | 2.38 ± 0.00 | 7.55 ± 0.00 | 5.16 ± 0.00 | 0.02 | Appendix B |
| C29 | 1.07 ± 0.00 | 7.55 ± 0.00 | 6.47 ± 0.00 | 0.02 | Appendix B |
| C30 | 1.55 ± 0.00 | 7.55 ± 0.00 | 6.00 ± 0.00 | 0.02 | Appendix B |

TABLE 4.16

DETERMINATION OF SULPHATE SERIES I

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A1 | 0.24 ± 0.01 | 0.20 ± 0.00 | 0.04 ± 0.01 | 0.01 | Appendix B |
| A2 | 0.28 ± 0.02 | 0.20 ± 0.00 | 0.09 ± 0.02 | 0.01 | Appendix B |
| B1 | 0.394 ± 0.0000 | 0.197 ± 0.000 | 0.197 ± 0.000 | 0.002 | Appendix B |
| B2 | 0.383 ± 0.001 | 0.197 ± 0.000 | 0.186 ± 0.001 | 0.002 | Appendix B |
| C1 | 9.63 ± 0.00 | 0.20 ± 0.00 | 9.43 ± 0.00 | 0.01 | Appendix B |
| C2 | 9.90 ± 0.000 | 0.20 ± 0.00 | 9.70 ± 0.00 | 0.01 | Appendix B |

TABLE 4.17

DETERMINATION OF SULPHATE SERIES II

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A3 | 0.422 ± 0.005 | 0.196 ± 0.000 | 0.225 ± 0.005 | 0.004 | Appendix B |
| A4 | 0.422 ± 0.005 | 0.199 ± 0.000 | 0.223 ± 0.005 | 0.004 | Appendix B |
| B3 | 0.716 ± 0.000 | 0.196 ± 0.000 | 0.529 ± 0.000 | 0.002 | Appendix B |
| B4 | 0.698 ± 0.015 | 0.199 ± 0.000 | 0.499 ± 0.015 | 0.002 | Appendix B |
| C3 | 7.407 ± 0.001 | 0.197 ± 0.000 | 7.210 ± 0.001 | 0.009 | Appendix B |
| C4 | 8.358 ± 0.002 | 0.198 ± 0.000 | 8.160 ± 0.002 | 0.010 | Appendix B |

TABLE 4.18

DETERMINATION OF SULPHATE SERIES III

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A5 | 0.351 ± 0.003 | 0.196 ± 0.000 | 0.155 ± 0.003 | 0.002 | Appendix B |
| A6 | 0.406 ± 0.002 | 0.198 ± 0.000 | 0.208 ± 0.002 | 0.002 | Appendix B |
| B5 | 0.362 ± 0.003 | 0.196 ± 0.000 | 0.166 ± 0.003 | 0.002 | Appendix B |
| B6 | 0.369 ± 0.001 | 0.197 ± 0.000 | 0.172 ± 0.001 | 0.002 | Appendix B |
| C5 | 6.340 ± 0.004 | 0.199 ± 0.000 | 6.141 ± 0.004 | 0.008 | Appendix B |
| C6 | 6.123 ± 0.002 | 0.196 ± 0.000 | 5.927 ± 0.002 | 0.008 | Appendix B |

TABLE 4.19

DETERMINATION OF SULPHATE SERIES IV

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A7 | 0.355 ± 0.004 | 0.197 ± 0.000 | 0.158 ± 0.004 | 0.002 | Appendix B |
| A8 | 0.294 ± 0.002 | 0.196 ± 0.000 | 0.098 ± 0.002 | 0.002 | Appendix B |
| B7 | 0.350 ± 0.000 | 0.196 ± 0.000 | 0.154 ± 0.000 | 0.002 | Appendix B |
| B8 | 0.376 ± 0.001 | 0.197 ± 0.000 | 0.179 ± 0.000 | 0.002 | Appendix B |
| C7 | 6.160 ± 0.121 | 0.197 ± 0.000 | 5.963 ± 0.121 | 0.008 | Appendix B |
| C8 | 6.256 ± 0.004 | 0.198 ± 0.000 | 6.058 ± 0.004 | 0.008 | Appendix B |

TABLE 4.20

DETERMINATION OF SULPHATE SERIES V

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A9 | 0.409 ± 0.005 | 0.197 ± 0.000 | 0.212 ± 0.005 | 0.002 | Appendix B |
| A10 | 0.372 ± 0.002 | 0.200 ± 0.000 | 0.172 ± 0.002 | 0.002 | Appendix B |
| B9 | 0.411 ± 0.004 | 0.197 ± 0.000 | 0.214 ± 0.004 | 0.002 | Appendix B |
| B10 | 0.500 ± 0.003 | 0.197 ± 0.000 | 0.303 ± 0.003 | 0.002 | Appendix B |
| C9 | 7.824 ± 0.001 | 0.197 ± 0.000 | 7.627 ± 0.001 | 0.009 | Appendix B |
| C10 | 8.586 ± 0.002 | 0.198 ± 0.000 | 8.388 ± 0.002 | 0.009 | Appendix B |

TABLE 4.21

DETERMINATION OF SULPHATE SERIES VI

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A11 | 0.740 ± 0.000 | 0.196 ± 0.000 | 0.544 ± 0.000 | 0.002 | Appendix B |
| C11 | 9.34 ± 0.01 | 0.20 ± 0.00 | 9.14 ± 0.01 | 0.01 | Appendix B |
| C12 | 8.112 ± 0.006 | 0.197 ± 0.000 | 7.915 ± 0.006 | 0.009 | Appendix B |
| C13 | 7.434 ± 0.025 | 0.201 ± 0.000 | 7.233 ± 0.025 | 0.009 | Appendix B |
| C14 | 7.750 ± 0.002 | 0.197 ± 0.000 | 7.553 ± 0.002 | 0.009 | Appendix B |

TABLE 4.22

DETERMINATION OF SULPHATE SERIES VII

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A12 | 0.925 ± 0.006 | 0.197 ± 0.000 | 0.728 ± 0.006 | 0.002 | Appendix B |
| A13 | 1.094 ± 0.010 | 0.197 ± 0.000 | 0.897 ± 0.010 | 0.002 | Appendix B |
| B11 | 0.567 ± 0.001 | 0.197 ± 0.000 | 0.370 ± 0.001 | 0.002 | Appendix B |
| B12 | 0.565 ± 0.001 | 0.197 ± 0.000 | 0.368 ± 0.001 | 0.002 | Appendix B |
| C15 | 9.16 ± 0.00 | 0.20 ± 0.00 | 8.96 ± 0.00 | 0.02 | Appendix B |
| C16 | 9.16 ± 0.00 | 0.20 ± 0.00 | 8.96 ± 0.00 | 0.02 | Appendix B |

TABLE 4.23

DETERMINATION OF SULPHATE · SERIES VIII

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A14 | 0.831 ± 0.009 | 0.197 ± 0.000 | 0.634 ± 0.009 | 0.004 | Appendix B |
| A15 | 0.830 ± 0.003 | 0.197 ± 0.000 | 0.633 ± 0.003 | 0.004 | Appendix B |
| B13 | 0.407 ± 0.002 | 0.197 ± 0.000 | 0.210 ± 0.002 | 0.004 | Appendix B |
| B14 | 0.408 ± 0.001 | 0.197 ± 0.000 | 0.211 ± 0.001 | 0.004 | Appendix B |
| C17 | 8.92 ± 0.00 | 0.20 ± 0.00 | 8.72 ± 0.00 | 0.01 | Appendix B |
| C18 | 10.26 ± 0.01 | 0.20 ± 0.00 | 10.06 ± 0.01 | 0.02 | Appendix B |

TABLE 4.24

DETERMINATION OF SULPHATE SERIES IX

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| A16 | 0.276 ± 0.007 | 0.197 ± 0.000 | 0.079 ± 0.007 | 0.012 | Appendix B |
| A17 | 0.282 ± 0.009 | 0.197 ± 0.000 | 0.085 ± 0.009 | 0.012 | Appendix B |
| B15 | 0.464 ± 0.007 | 0.197 ± 0.000 | 0.267 ± 0.007 | 0.004 | Appendix B |
| B16 | 0.409 ± 0.002 | 0.197 ± 0.000 | 0.212 ± 0.002 | 0.004 | Appendix B |
| C19 | 8.02 ± 0.01 | 0.20 ± 0.00 | 7.82 ± 0.01 | 0.01 | Appendix B |
| C20 | 8.11 ± 0.00 | 0.20 ± 0.00 | 7.91 ± 0.00 | 0.01 | Appendix B |
| C21 | 8.11 ± 0.01 | 0.20 ± 0.00 | 7.91 ± 0.00 | 0.01 | Appendix B |
| C22 | 8.33 ± 0.00 | 0.20 ± 0.00 | 8.13 ± 0.00 | 0.01 | Appendix B |

TABLE 4.24 continued

| Sample | Concentration of sulphate and ave. dev. (g/L) | | | Max. poss. error | Reference |
|---|---|---|---|---|---|
| | Found | Added | Difference | | |
| C23 | 7.95 ± 0.01 | 0.20 ± 0.00 | 7.75 ± 0.01 | 0.01 | Appendix B |
| C24 | 10.33 ± 0.00 | 0.20 ± 0.00 | 10.13 ± 0.00 | 0.02 | Appendix B |
| C25 | 10.95 ± 0.00 | 0.20 ± 0.00 | 10.75 ± 0.00 | 0.02 | Appendix B |
| C26 | 8.02 ± 0.00 | 0.20 ± 0.00 | 7.82 ± 0.00 | 0.01 | Appendix B |
| C27 | 7.61 ± 0.01 | 0.20 ± 0.00 | 7.41 ± 0.01 | 0.01 | Appendix B |
| C28 | 9.03 ± 0.01 | 0.20 ± 0.00 | 8.83 ± 0.01 | 0.01 | Appendix B |
| C29 | 11.26 ± 0.00 | 0.20 ± 0.00 | 11.06 ± 0.00 | 0.02 | Appendix B |
| C30 | 10.49 ± 0.00 | 0.20 ± 0.00 | 10.29 ± 0.00 | 0.02 | Appendix B |

TABLE 4.25

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES I

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A1 | 1.81 ± 0.02 | 0.02 | Appendix B |
| A2 | 1.69 ± 0.02 | 0.02 | Appendix B |
| B1 | 1.931 ± 0.003 | 0.005 | Appendix B |
| B2 | 1.849 ± 0.001 | 0.005 | Appendix B |
| C1 | 0.858 ± 0.002 | 0.005 | Appendix B |
| C2 | 0.949 ± 0.001 | 0.005 | Appendix B |

TABLE 4.26

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES II

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A3 | 1.59 ± 0.01 | 0.01 | Appendix B |
| A4 | 1.96 ± 0.01 | 0.01 | Appendix B |
| B3 | 0.949 ± 0.013 | 0.005 | Appendix B |
| B4 | 0.918 ± 0.040 | 0.005 | Appendix B |
| C3 | 1.465 ± 0.011 | 0.005 | Appendix B |
| C4 | 1.246 ± 0.005 | 0.010 | Appendix B |

TABLE 4.27

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES III

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A5 | 1.864 ± 0.008 | 0.005 | Appendix B |
| A6 | 1.341 ± 0.001 | 0.005 | Appendix B |
| B5 | 1.767 ± 0.009 | 0.005 | Appendix B |
| B6 | 1.693 ± 0.007 | 0.005 | Appendix B |
| C5 | 1.111 ± 0.001 | 0.005 | Appendix B |
| C6 | 1.126 ± 0.000 | 0.005 | Appendix B |

TABLE 4.28

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES IV

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A7 | 1.866 ± 0.006 | 0.005 | Appendix B |
| A8 | 1.894 ± 0.006 | 0.005 | Appendix B |
| B7 | 1.829 ± 0.011 | 0.005 | Appendix B |
| B8 | 1.830 ± 0.004 | 0.005 | Appendix B |
| C7 | 1.830 ± 0.029 | 0.005 | Appendix B |
| C8 | 1.222 ± 0.078 | 0.005 | Appendix B |

TABLE 4.29

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES V

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A9 | 1.812 ± 0.004 | 0.005 | Appendix B |
| A10 | 1.764 ± 0.005 | 0.005 | Appendix B |
| B9 | 1.872 ± 0.010 | 0.005 | Appendix B |
| B10 | 1.859 ± 0.007 | 0.005 | Appendix B |
| C9 | 1.341 ± 0.061 | 0.005 | Appendix B |
| C10 | 1.435 ± 0.053 | 0.005 | Appendix B |

TABLE 4.30

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES VI

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A11 | 1.534 ± 0.004 | 0.005 | Appendix B |
| C11 | 1.129 ± 0.101 | 0.005 | Appendix B |
| C12 | 1.150 ± 0.072 | 0.005 | Appendix B |
| C13 | 1.318 ± 0.070 | 0.005 | Appendix B |
| C14 | 1.238 ± 0.034 | 0.005 | Appendix B |

TABLE 4.31

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES VII

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A12 | 1.251 ± 0.272 | 0.003 | Appendix B |
| A13 | 0.190 ± 0.092 | 0.002 | Appendix B |
| B11 | NO DATA | | |
| B12 | NO DATA | | |
| C15 | NO DATA | | |
| C16 | NO DATA | | |

TABLE 4.32

DETERMINATION OF HCl-BLANK FOR SULPHUR SERIES VIII

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A14 | 2.16 ± 0.01 | 0.01 | Appendix B |
| A15 | 2.14 ± 0.02 | 0.01 | Appendix B |
| B13 | 2.04 ± 0.00 | 0.02 | Appendix B |
| B14 | 2.08 ± 0.01 | 0.02 | Appendix B |
| C17 | 0.07 ± 0.02 | 0.01 | Appendix B |
| C18 | 0.51 ± 0.00 | 0.01 | Appendix B |

TABLE 4.33

DETERMINATION OF HCl-BLANK FOR SULPHUR - SERIES IX

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. pass. error | Reference |
|---|---|---|---|
| A16 | 2.16 ± 0.00 | 0.01 | Appendix B |
| A17 | 2.18 ± 0.01 | 0.01 | Appendix B |
| B15 | 2.11 ± 0.01 | 0.01 | Appendix B |
| B16 | 2.12 ± 0.00 | 0.01 | Appendix B |
| C19 | 0.83 ± 0.01 | 0.01 | Appendix B |
| C20 | 0.82 ± 0.01 | 0.01 | Appendix B |
| C21 | 0.83 ± 0.01 | 0.01 | Appendix B |
| C22 | 0.79 ± 0.01 | 0.01 | Appendix B |

TABLE 4.33

DETERMINATION OF HCl-BLANK FOR SULPHUR · SERIES IX

| Sample | Concentration of sulphur and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| C23 | 0.86 ± 0.02 | 0.01 | Appendix B |
| C24 | 0.43 ± 0.00 | 0.01 | Appendix B |
| C25 | 0.37 ± 0.01 | 0.01 | Appendix B |
| C26 | 0.83 ± 0.01 | 0.01 | Appendix B |
| C27 | 0.92 ± 0.01 | 0.01 | Appendix B |
| C28 | 0.68 ± 0.02 | 0.01 | Appendix B |
| C29 | 0.29 ± 0.01 | 0.01 | Appendix B |
| C30 | 0.44 ± 0.01 | 0.01 | Appendix B |

## TABLE 4.34

DETERMINATION OF SULPHUR DIOXIDE SERIES VIII

| Sample | Concentration of sulphur dioxide and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A14 | NO DATA | | |
| A15 | NO DATA | | |
| B13 | 0.739 ± 0.002 | 0.003 | Appendix B |
| B14 | 0.666 ± 0.002 | 0.003 | Appendix B |
| C17 | 0.745 ± 0.002 | 0.003 | Appendix B |
| C18 | 0.725 ± 0.002 | 0.003 | Appendix B |

TABLE 4.35

DETERMINATION OF SULPHUR DIOXIDE SERIES IX

| Sample | Concentration of sulphur dioxide and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| A16 | 4.340 ± 0.004 | 0.009 | Appendix B |
| A17 | 4.352 ± 0.008 | 0.009 | Appendix B |
| B15 | 4.220 ± 0.003 | 0.008 | Appendix B |
| B16 | 4.252 ± 0.004 | 0.008 | Appendix B |
| C19 | 1.678 ± 0.002 | 0.005 | Appendix B |
| C20 | 1.667 ± 0.003 | 0.005 | Appendix B |
| C21 | 1.670 ± 0.004 | 0.005 | Appendix B |
| C22 | 1.589 ± 0.002 | 0.005 | Appendix B |

TABLE 4.35

DETERMINATION OF SULPHUR DIOXIDE SERIES IX

| Sample | Concentration of sulphur dioxide and ave. dev. (g/L) | Max. poss. error | Reference |
|---|---|---|---|
| C23 | 1.748 ± 0.003 | 0.005 | Appendix B |
| C24 | 0.914 ± 0.002 | 0.004 | Appendix B |
| C25 | 0.735 ± 0.003 | 0.003 | Appendix B |
| C26 | 1.685 ± 0.002 | 0.005 | Appendix B |
| C27 | 1.836 ± 0.005 | 0.005 | Appendix B |
| C28 | 1.357 ± 0.006 | 0.004 | Appendix B |
| C29 | 0.596 ± 0.002 | 0.003 | Appendix B |
| C30 | 0.887 ± 0.004 | 0.004 | Appendix B |

disproportionates to sulphur and sulphur dioxide according to the reaction:-

$$S_2O_3^{=} + 2HCl \longrightarrow SO_2 + S^0 + 2Cl^- + H_2O$$

so that, for all of the sulphur and sulphur dioxide involved, these compounds must be accounted for in order to determine the overall material balance.

Part of the Series IX sample analyses system, from Appendix B, will be used here as an example of the bacterial and chemical material balances. Tables 4.36 and 4.37 respectively indicate the bacterial material balance and the chemical material balance. Appendix B provides further data and details. It will be noted that the information obtained agrees with the expectations from the suggested reactional steps.

TABLE 4.36

BACTERIAL MATERIAL BALANCE

| Sample | Due to conversion (g/L) | | | |
|---|---|---|---|---|
| | $S_2O_3^{2-}$ lost | (as $SO_4^{2-}$) | $SO_4^{2-}$ gained | (as $S_2O_3^{2-}$) |
| C19 | 4.44 | (7.61) | 7.58 | (4.43) |
| C20 | 4.49 | (7.69) | 7.67 | (4.47) |
| C21 | 4.48 | (7.68) | 7.67 | (4.47) |
| C22 | 4.62 | (7.91) | 8.11 | (4.73) |
| C23 | 4.36 | (7.46) | 7.51 | (4.38) |
| C24 | 5.80 | (9.93) | 9.89 | (5.77) |
| C25 | 6.12 | (10.48) | 10.51 | (6.13) |
| C26 | 4.44 | (7.61) | 7.58 | (4.42) |

| Sample | Due to conversion (g/L) | | | |
|---|---|---|---|---|
| | $S_2O_3^{2-}$ lost | (as $SO_4^{2-}$) | $SO_4^{2-}$ gained | (as $S_2O_3^{2-}$) |
| C27 | 4.18 | (7.17) | 7.17 | (4.18) |
| C28 | 5.02 | (8.61) | 8.59 | (5.01) |
| C29 | 6.33 | (10.85) | 10.82 | (6.31) |
| C30 | 5.86 | (10.04) | 10.04 | (5.86) |

TABLE 4.37

CHEMICAL MATERIAL BALANCE

| Sample | g/ found $S_2O_3^{2-}$ | $SO_2$ | $S^o$ | Ratio Found |
|---|---|---|---|---|
| C19 | 2.96 | 1.678 | 0.83 | 0.5001 |
| C20 | 2.92 | 1.667 | 0.82 | 0.4895 |
| C21 | 2.93 | 1.670 | 0.83 | 0.4972 |
| C22 | 2.79 | 1.589 | 0.79 | 0.4958 |
| C23 | 3.05 | 1.748 | 0.86 | 0.4897 |
| C24 | 1.61 | 0.914 | 0.43 | 0.4728 |
| C25 | 1.29 | 0.736 | 0.37 | 0.5057 |
| C26 | 2.96 | 1.685 | 0.83 | 0.4915 |
| C27 | 3.22 | 1.836 | 0.92 | 0.4990 |
| C28 | 2.38 | 1.357 | 0.68 | 0.4981 |
| C29 | 1.07 | 0.596 | 0.29 | 0.4929 |
| C30 | 1.55 | 0.887 | 0.44 | 0.4961 |

## 5.1 Conclusions

(a) The differential pulse polarographic techniques and methods used in this study were too sensitive for the nature of the media. The upper detection limit for this technique was well in excess of concentrations found in the media. Dilution of the test solution would lead to errors so large that the results would not be valid.

(b) X-ray fluoresence techniques also failed to lead to any valuable information on the total slphur concentration in the culture solution. The untreated samples were turbid, leading to diffraction of the analytical beam, filtered samples suffered from losses of particulate sulphur containing compounds.

(c) The heavy metal concentrations in the media due to contamination in the reagents used in the preparation of the culture solution were below a critical or lethal level as determined by flame atomic absorption.

(d) The general reaction occurring in the inocculated media is the conversion of thiosulphate to sulphate. The oxidation of sulphur occurs according to

$$S^{2+} - 4e \qquad S^{6+} \qquad (1)$$

The bacteria achieve an efficiency of 99.72 ± 0.17% for the conversion of thiosulphate to sulphate. This oxidation may occur as a single step reaction

$$S_2O_3^{=} + 10\ OH^- - 8e \qquad 2SO_4^{=} + 5H_2O \qquad (2)$$

or it may proceed as a series of reactions leading to sulphate as the end product, such as

$$2S_2O_3^{=} - 2e \longrightarrow S_4O_6^{=}$$

$$S_4O_6^{=} + 20\ OH^- - 14e \longrightarrow 4SO_4^{=} + 10\ H_2O \qquad (3)$$

or

$$2S_2O_3^{=} - 2e \longrightarrow S_4O_6^{=}$$

$$4S_4O_6^{=} \longrightarrow S_5O_6^{=} + S_3O_6^{=}$$

$$S_3O_6^{=} + 12\ OH^- - 8e \longrightarrow 3SO_4^{=} + 6H_2O \qquad (4)$$

The net reaction may proceed by all of the above examples simultaneously or in some sequence of the above scheme, whereby one reaction will proceed to a given equilibrium and another reaction will take over yielding the same end product with different intermediates. The above mentioned reactions are in no way conclusive and are only stated as possibilities.

## 5.2 SUGGESTIONS FOR FURTHER WORK

Based on the conclusion previously described, the following suggestions are submitted as a possible guideline for further studies related to this project.

-1-The incubation period should be terminated immediately following the cessation of bacterial growth. This would aid in the determination of the thiosulphate oxidation end-product(s) in the short time:

-2-A series of experiments should be set up whereby the incubation period of the culture would be interrupted sequentially. This should take place over both the long and short term. In this manner, any intermediate product(s) of the thiosulphate oxidation during different phases of bacterial growth could be monitored and subsequently determined:

-3-The culture media should be prepared by substituting reduced sulphur-containing compounds other than thiosulphate to determine the efficiency of the bacteria to utilize these compounds. Elemental sulphur and sulphur dioxide could both be used as a source of reduced sulphur in such an experiment. The intermediate and end-product(s) of these oxidations could also be resolved via suggestions # 1 and # 2:

-4-Further studies should be made on media prepared containing elemental sulphur in particular, since it has been observed that the bacterial induce the elemental sulphur to undergo a change whereby the sulphur no longer floats on the surface of the aqueous media, but settles at the bottom of the vessel. A study of the change of the physical property(s) of elemental sulphur due to the bacteria should be pursued further:

-5-A complete biochemical survey should be conducted to determine and further study the enzymes present in Rhodopseudomonas Goldameirii.

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# APPENDIX A

## MEDIA - PREPARATION, INITIAL, CONTROL AND EXPERIMENTAL

TABLE A1

Made: June 2/80

Harvested: June 18/80

| SAMPLE # REAGENT | INITIAL A1 g/L | INITIAL A2 g/L |
|---|---|---|
| $Na_2S_2O_3.5H_2O$ | 16.0873 | 16.0043 |
| as $S_2O_3^{2-}$ | 7.5901 | 7.5510 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0000 | 1.9998 |
| as $PO_4$ | 1.0905 | 1.0904 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5047 | 0.5018 |
| as $SO_4^{2-}$ | 0.1967 | 0.1956 |
| as Mg | 0.0498 | 0.0495 |
| $NH_4Cl$ | 1.0009 | 1.0000 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1984 | 0.1973 |

TABLE A2

Made: June 2/80

Harvested: June 18/80

| SAMPLE # | CONTROL B1 | CONTROL B2 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0036 | 16.0048 |
| as $S_2O_3$ | 7.5506 | 7.5512 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9992 | 2.0093 |
| as $PO_4^{3-}$ | 1.0900 | 1.0956 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5000 | 0.5000 |
| as $SO_4^{2-}$ | 0.1949 | 0.1949 |
| as Mg | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.0000 | 1.0000 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1966 | 0.1966 |

TABLE A3

Made: June 2/80

Harvested: June 18/80

| SAMPLE # REAGENT | EXPERIMENTAL C1 g/L | EXPERIMENTAL C2 g/L |
|---|---|---|
| $Na_2S_2O_3.5H_2O$ | 16.0076 | 16.0021 |
| as $S_2O_3^{2-}$ | 7.5525 | 7.5499 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0000 | 2.0021 |
| as $PO_4^{3-}$ | 1.0905 | 1.0916 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5015 | 0.5011 |
| as $SO_4^{2-}$ | 0.1954 | 0.1953 |
| as Mg | 0.0495 | 0.0494 |
| $NH_4Cl$ | 1.0000 | 1.0000 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1962 | 0.1970 |

TABLE A4

Made: June 12/80

Harvested: July 2/80

| SAMPLE # | INITIAL A3 | INITIAL A4 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0033 | 16.2331 |
| as $S_2O_3^{2-}$ | 7.5505 | 7.6589 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0000 | 2.0057 |
| as $PO_4^{3-}$ | 1.0905 | 1.0936 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4995 | 0.5056 |
| as $SO_4^{2-}$ | 0.1947 | 0.0970 |
| as $Mg^{2+}$ | 0.0493 | 0.0499 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1964 | 0.1987 |

TABLE A5

Made: June 12/80

Harvested: July 2/80

| SAMPLE # | CONTROL B3 | CONTROL B4 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0064 | 16.0063 |
| as $S_2O_3^{2-}$ | 7.5520 | 7.5519 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0000 | 2.0019 |
| as $PO_4^{3-}$ | 1.0905 | 1.0915 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4995 | 0.5056 |
| as $SO_4^{2-}$ | 0.1947 | 0.1970 |
| as $Mg^{2+}$ | 0.0493 | 0.0499 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1964 | 0.1987 |

TABLE A6

Made: June 12/80

Harvested: July 2/80

| SAMPLE # | EXPERIMENTAL C3 | EXPERIMENTAL C4 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0100 | 16.0000 |
| as $S_2O_3^{2-}$ | 7.5537 | 7.5489 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9995 | 2.0000 |
| as $PO_4^{3-}$ | 1.0902 | 1.0905 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5002 | 0.5032 |
| as $SO_4^{2-}$ | 0.1949 | 0.1961 |
| as $Mg^{2+}$ | 0.0493 | 0.0496 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.7H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1966 | 0.1978 |

TABLE A7

Made: June 16/80

Harvested: July 7/80

| SAMPLE # | INITIAL A5 | INITIAL A6 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0366 | 16.0140 |
| as $S_2O_3^{2-}$ | 7.5662 | 7.5555 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0030 | 2.0025 |
| as $PO_4^{3-}$ | 1.0921 | 1.0918 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4997 | 0.5028 |
| as $SO_4^{2-}$ | 0.1947 | 0.1947 |
| as $Mg^{2+}$ | 0.0493 | 0.0496 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1964 | 0.1977 |

TABLE A8

Made: June 16/80

Harvested: July 7/80

| SAMPLE # | CONTROL B5 | CONTROL B6 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0113 | 15.9985 |
| as $S_2O_3^{2-}$ | 7.5543 | 7.5482 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0031 | 2.0047 |
| as $PO_4^{3-}$ | 1.0922 | 1.0955 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4988 | 0.5017 |
| as $SO_4^{2-}$ | 0.1944 | 0.1955 |
| as $Mg^{2+}$ | 0.0492 | 0.0495 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.h017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1961 | 0.1972 |

TABLE A9

Made: June 16/80

Harvested: July 7/80

| SAMPLE # | EXPERIMENTAL C5 | EXPERIMENTAL C6 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0254 | 15.9986 |
| as $S_2O_3^{2-}$ | 7.5609 | 7.5483 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0025 | 2.0083 |
| as $PO_4^{3-}$ | 1.0918 | 1.0950 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5064 | 0.4995 |
| as $SO_4^{2-}$ | 0.1974 | 0.1947 |
| as $Mg^{2+}$ | 0.0499 | 0.0495 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1991 | 0.1964 |

TABLE A10

Made: June 26/80

Harvested: July 7/80

| SAMPLE # | INITIAL A7 | INITIAL A8 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0124 | 16.0072 |
| as $S_2O_3^{2-}$ | 7.5548 | 7.5523 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0019 | 2.0030 |
| as $PO_4^{3-}$ | 1.0915 | 1.0921 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5004 | 0.4998 |
| as $SO_4^{2-}$ | 0.1950 | 0.1949 |
| as $Mg^{2+}$ | 0.0494 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1967 | 0.1965 |

TABLE A11

Made: June 26/80

Harvested: July 7/80

| SAMPLE # | CONTROL B7 | CONTROL B8 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 15.9863 | 16.0003 |
| as $S_2O_3^{2-}$ | 7.5425 | 7.5491 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0000 | 2.0057 |
| as $PO_4^{3-}$ | 1.0905 | 1.0936 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4999 | 0.5016 |
| as $SO_4^{2-}$ | 0.1948 | 0.1955 |
| as $Mg^{2+}$ | 0.0493 | 0.0495 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.7H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1965 | 0.1972 |

TABLE A12

Made: June 26/80

Harvested: July 7/80

| SAMPLE # | EXPERIMENTAL C7 | EXPERIMENTAL C8 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0045 | 16.0020 |
| as $S_2O_3^{2-}$ | 7.5511 | 7.5499 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0071 | 1.9997 |
| as $PO_4^{3-}$ | 1.0944 | 1.0903 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5002 | 0.5026 |
| as $SO_4^{2-}$ | 0.1949 | 0.1959 |
| as $Mg^{2+}$ | 0.0493 | 0.0496 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1966 | 0.1976 |

TABLE A13

Made: July 7/80

Harvested: July 31/80

| SAMPLE # | INITIAL A9 | INITIAL A10 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0233 | 15.9973 |
| as $S_2O_3^{2-}$ | 7.5599 | 7.5477 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0003 | 2.0009 |
| as $PO_4^{3-}$ | 1.0921 | 1.0910 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5005 | 0.5075 |
| as $SO_4^{2-}$ | 0.1951 | 0.1978 |
| as $Mg^{2+}$ | 0.0494 | 0.0501 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1968 | 0.1995 |

TABLE A14

Made: July 7/80

| SAMPLE # | CONTROL B9 | CONTROL B10 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0032 | 16.0156 |
| as $S_2O_3^{2-}$ | 7.5504 | 7.5563 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0017 | 2.0028 |
| as $PO_4^{3-}$ | 1.0906 | 1.0920 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5008 | 0.5010 |
| as $SO_4^{2-}$ | 0.1952 | 0.1953 |
| as $Mg^{2+}$ | 0.0494 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1969 | 0.1970 |

TABLE A15

Made: July 7/80

Harvested: July 31/80

| SAMPLE # | EXPERIMENTAL C9 | EXPERIMENTAL C10 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0025 | 16.0213 |
| as $S_2O_3^{2-}$ | 7.5501 | 7.5590 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9988 | 2.0096 |
| as $PO_4^{3-}$ | 1.0898 | 1.0957 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 00.5004 | 0.5039 |
| as $SO_4^{2-}$ | 0.1950 | 0.1964 |
| as $Mg^{2+}$ | 0.0494 | 0.0497 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1967 | 0.1981 |

TABLE A16

Made: July 31/80

Harvested : Sept. 5/80

| SAMPLE # | INITIAL A11 |
|---|---|
| REAGENT | g/L |
| $Na_2S_3O_3.5H_2O$ | 16.0023 |
| as $S_2O_3^{2-}$ | 7.5500 |
| $NaHCO_3$ | 10.00 |
| $K_2HPO_4$ | 2.0004 |
| as $PO_4^{3-}$ | 1.0907 |
| NaCl | 10.00 |
| $MgSO_4.7H_2O$ | 0.4991 |
| as $SO_4^{2-}$ | 0.1945 |
| as $Mg^{2+}$ | 0.0492 |
| $NH_4Cl$ | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 |
| $CaCl_2$ | 0.0020 |
| $MnCl_2$ | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 |
| total $SO_4^{2-}$ | 0.1962 |

TABLE A17

Made: July 31/80

Harvested: Sept. 5/80

| SAMPLE # | EXPERIMENTAL C11 | EXPERIMENTAL C12 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0023 | 16.0013 |
| as $S_2O_3^{2-}$ | 7.5500 | 7.5495 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0004 | 2.0020 |
| as $PO_4^{3-}$ | 1.0907 | 1.0916 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5012 | 0.5001 |
| as $SO_4^{2-}$ | 0.1953 | 0.1949 |
| as $Mg^{2+}$ | 0.0494 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1970 | 0.1966 |

TABLE A.18

Made: July 31/80

Harvested: Sept. 5/80

| SAMPLE # | EXPERIMENTAL C13 | EXPERIMENTAL C14 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0034 | 16.0110 |
| as $S_2O_3^{2-}$ | 7.5505 | 7.5541 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0016 | 2.0002 |
| as $PO_4^{3-}$ | 1.0914 | 1.0906 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5109 | 0.5005 |
| as $SO_4^{2-}$ | 0.1991 | 0.1951 |
| as $Mg^{2+}$ | 0.0504 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.2008 | 0.1968 |

TABLE A19

Made: Sept. 5/80

Harvested: Sept. 16/80

| SAMPLE # | INITIAL A12 | INITIAL A13 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0009 | 16.0009 |
| as $S_2O_3^{2-}$ | 7.5494 | 7.5494 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.0004 | 1.0004 |
| as $PO_4^{3-}$ | 0.5455 | 0.5455 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5012 | 0.5012 |
| as $SO_4^{2-}$ | 0.1953 | 0.1953 |
| as $Mg^{2+}$ | 0.0494 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1970 | 0.1970 |

TABLE A20

Made: Sept 5/80

Harvested: Sept 16/80

| SAMPLE # | CONTROL B11 | CONTROL B12 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0000 | 16.0000 |
| as $S_2O_3^{2-}$ | 7.5489 | 7.5489 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_3$ | 1.0003 | 1.0003 |
| as $PO_4^{3-}$ | 0.5454 | 0.5454 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5009 | 0.5009 |
| as $SO_4^{2-}$ | 0.1952 | 0.1952 |
| as $Mg^{2+}$ | 0.0494 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1969 | 0.1969 |

TABLE A21

Made: Sept. 5/80

Harvested: Sept. 16/80

| SAMPLE # | EXPERIMENTAL C15 | EXPERIMENTAL C16 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0000 | 16.0000 |
| as $S_2O_3^{2-}$ | 7.5489 | 7.5489 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.0003 | 1.0003 |
| as $PO_4^{3-}$ | 0.5454 | 0.5454 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5009 | 0.5009 |
| as $SO_4^{2-}$ | 0.1952 | 0.1952 |
| as $Mg^{2+}$ | 0.0494 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1969 | 0.1969 |

TABLE A22

Made: Sept. 22/80

Harvested: Oct. 3/80

| SAMPLE # | INITIAL A14 | INITIAL A15 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0022 | 16.0022 |
| as $S_2O_3^{2-}$ | 7.5500 | 7.5500 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0018 | 2.0018 |
| as $PO_4^{3-}$ | 1.0915 | 1.0915 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5016 | 0.5016 |
| as $SO_4^{2-}$ | 0.1955 | 0.1955 |
| as $Mg^{2+}$ | 0.0495 | 0.0495 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1972 | 0.1972 |

TABLE A23

Made: Sept. 22/80

Harvested: Oct. 3/80

| SAMPLE # | CONTROL B13 | CONTROL B14 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0035 | 16.0035 |
| as $S_2O_3^{2-}$ | 7.5506 | 7.5506 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0004 | 2.0004 |
| as $PO_4^{3-}$ | 1.0907 | 1.0907 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5006 | 0.5006 |
| as $SO_4^{2-}$ | 0.1951 | 0.1951 |
| as $Mg^{2+}$ | 0.0494 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $So_4^{2-}$ | 0.1968 | 0.1968 |

TABLE A24

Made: Sept. 22/80

Harvested: Oct. 3/80

| SAMPLE # | EXPERIMENTAL C17 | EXPERIMENTAL C18 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0035 | 16.0035 |
| as $S_2O_3^{2-}$ | 7.5506 | 7.5506 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0004 | 2.0004 |
| as $PO_4^{3-}$ | 1.0904 | 1.0904 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5006 | 0.5006 |
| as $SO_4^{2-}$ | 0.1951 | 0.1951 |
| as $Mg^{2+}$ | 0.0494 | 0.0494 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1968 | 0.1968 |

TABLE A25

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | INITIAL A16 | INITIAL A17 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0006 | 16.0006 |
| as $S_2O_3^{2-}$ | 7.5492 | 7.5492 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0003 | 2.0003 |
| as $PO_4^{3-}$ | 1.0906 | 1.0906 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5002 | 0.5002 |
| as $SO_4^{2-}$ | 0.1949 | 0.1949 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1966 | 0.1966 |

TABLE A26

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | CONTROL B15 | CONTROL B16 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0006 | 16.0006 |
| as $S_2O_3^{2-}$ | 7.5492 | 7.5492 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0003 | 2.0003 |
| as $PO_4^{3-}$ | 1.0906 | 1.0906 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5002 | 0.5002 |
| as $SO_4^{2-}$ | 0.1949 | 0.1949 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $So_4^{2-}$ | 0.1966 | 0.1966 |

TABLE A27

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | EXPERIMENTAL C19 | EXPERIMENTAL C20 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0008 | 16.0008 |
| as $S_2O_3^{2-}$ | 7.5493 | 7.5493 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0007 | 2.0007 |
| as $PO_4^{3-}$ | 1.0908 | 1.0908 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5002 | 0.5002 |
| as $SO_4^{2-}$ | 0.1949 | 0.1949 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1966 | 0.1966 |

TABLE A28

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | EXPERIMENTAL C21 | EXPERIMENTAL C22 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0008 | 16.0008 |
| as $S_2O_3^{2-}$ | 7.5493 | 7.5493 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 2.0007 | 2.0007 |
| as $PO_4^{3-}$ | 1.0908 | 1.0908 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5002 | 0.5002 |
| as $SO_4^{2-}$ | 0.1949 | 0.1949 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1966 | 0.1966 |

TABLE A29

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | EXPERIMENTAL C23 | EXPERIMENTAL C24 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0014 | 16.0014 |
| as $S_2O_3^{2-}$ | 7.5496 | 7.5496 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9999 | 1.9999 |
| as $PO_4^{3-}$ | 1.0904 | 1.0904 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4998 | 0.4998 |
| as $SO_4^{2-}$ | 0.1948 | 0.1948 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1965 | 0.1965 |

TABLE A30

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | EXPERIMENTAL C25 | EXPERIMENTAL C26 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0014 | 16.0014 |
| as $S_2O_3^{2-}$ | 7.5496 | 7.5496 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9999 | 1.9999 |
| as $PO_4^{3-}$ | 1.0904 | 1.0904 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.4998 | 0.4998 |
| as $SO_4^{2-}$ | 0.1948 | 0.1948 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1965 | 0.1965 |

TABLE A31

Made: Nov 7/80

Harvested: Dec. 5/80

| SAMPLE # | EXPERIMENTAL C27 | EXPERIMENTAL C28 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0004 | 16.0004 |
| as $S_2O_3^{2-}$ | 7.5491 | 7.5491 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9999 | 1.9999 |
| as $PO_4^{3-}$ | 1.0904 | 1.0904 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5003 | 0.5003 |
| as $SO_4^{2-}$ | 0.1950 | 0.1950 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1967 | 0.1967 |

TABLE A32

Made: Nov. 7/80

Harvested: Dec. 5/80

| SAMPLE # | EXPERIMENTAL C29 | EXPERIMENTAL C30 |
|---|---|---|
| REAGENT | g/L | g/L |
| $Na_2S_2O_3.5H_2O$ | 16.0004 | 16.0004 |
| as $S_2O_3^{2-}$ | 7.5491 | 7.5491 |
| $NaHCO_3$ | 10.00 | 10.00 |
| $K_2HPO_4$ | 1.9999 | 1.9999 |
| as $PO_4^{3-}$ | 1.0904 | 1.0904 |
| NaCl | 10.00 | 10.00 |
| $MgSO_4.7H_2O$ | 0.5003 | 0.5003 |
| as $SO_4^{2-}$ | 0.1950 | 0.1950 |
| as $Mg^{2+}$ | 0.0493 | 0.0493 |
| $NH_4Cl$ | 1.00 | 1.00 |
| $Na_2MoO_4.2H_2O$ | 0.0001 | 0.0001 |
| $CaCl_2$ | 0.0020 | 0.0020 |
| $MnCl_2$ | 0.00012 | 0.00012 |
| $FeSO_4.7H_2O$ | 0.0050 | 0.0050 |
| as $SO_4^{2-}$ | 0.0017 | 0.0017 |
| total $SO_4^{2-}$ | 0.1967 | 0.1967 |

# APPENDIX B

## WET CHEMICAL ANALYSES

Preparation and standardization of $I_3^-$ solution.

Preparation of $I_3^-$ ($0.07^5$ M or 4.15 N)

Weigh about 12.7g of iodine and 40.0g of potassium iodide. Dissolve in 400 ml of water and dilute to approximately 1 liter.

Standardization of $I_3^-$

Dry about 1g of $As_2O_3$ at 110°C for one hour. Weigh out 0.20 ± 0.01g portions of $As_2O_3$. Dissolve in 10 ml of 1M NaOH, dilute to 75 ml with water. Add 2 drops of 1% phenolphthalein. Add 1:1 HCl dropwise until the pink colour disappears, add about 1 ml in excess.

Carefully add $NaHCO_3$ in small portions until effervescences ceases. Add about 3g in excess.

Add 2 ml of starch indicator and titrate with $I_3^-$ solution until the first blue that persists

Reaction:

$$As_2O_3 + 3H_2O \longrightarrow 2H_3AsO_3$$

$$H_3AsO_3 + I_2 + 5H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 4H_3O^+$$

Preparation of starch indicator: 3% Starch in Formamide.

Make a paste of 3g of soluble starch in 30 ml of formamide. Add the paste to 70 ml of boiling formamide. Boil for 2 minutes with stirring. Cool to room temperature before using.

SERIES I:

Each sample was prepared according to Method #1, section 3.2.1.1 page 27. The final solution volume after sterilization was 1000.00 ± 0.15 ml. The HCl-Blank was done as part of the sulphate determination. No sulphur dioxide determination was performed. Each sample was analyzed in duplicate.

EXPERIMENTAL RESULTS OF THIOSULPHATE ION DETERMINATION

A 25.00 ± 0.02 ml aliquot was titrated with a 0.0749 ± 0.0001 M $I_3^-$ solution.

TABLE B1

THIOSULPHATE DETERMINATION SERIES I

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A1 - 1 | 10.30 | $6.92^0 \pm 0.00^0$ | 1:258 |
| - 2 | 10.30 | | |
| A2 - 1 | 10.90 | $7.32^3 \pm 0.00^0$ | 1:272 |
| - 2 | 10.90 | | |
| B1 - 1 | 10.50 | $7.05^4 \pm 0.00^0$ | 1:263 |
| - 2 | 10.50 | | |
| B2 - 1 | 10.10 | $6.79^0 \pm 0.00^0$ | 1:252 |
| - 2 | 10.10 | | |
| C1 - 1 | 2.50 | $1.68^0 \pm 0.00^0$ | 1:62 |
| - 2 | 2.50 | | |
| C2 - 1 | 2.50 | $1.68^0 \pm 0.00^0$ | 1:62 |
| - 2 | 2.50 | | |

TABLE B2

HCl-BLANK DETERMINATION SERIES I

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $S^0$ g/vol (± 0.0002 g)* | Average $S^0$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A1 - 1 | $10.00 \pm 0.01^1$ | 0.0183 | $1.81^1 \pm 0.02^0$ | 1:90 |
| - 2 | $10.00 \pm 0.01^1$ | 0.0179 | | |
| A2 - 1 | $10.00 \pm 0.01^1$ | 0.0171 | $1.68^5 \pm 0.02^5$ | 1:84 |
| - 2 | $10.00 \pm 0.01^1$ | 0.0166 | | |
| B1 - 1 | $50.00 \pm 0.02^7$ | 0.0967 | $1.931^0 \pm 0.003^0$ | 1:484 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0964 | | |
| B2 - 1 | $50.00 \pm 0.02^7$ | 0.0925 | $1.849^0 \pm 0.001^0$ | 1:462 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0924 | | |
| C1 - 1 | $50.00 \pm 0.02^7$ | 0.0428 | $0.858^0 \pm 0.004^6$ | 1:214 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0430 | | |
| C2 - 1 | $50.00 \pm 0.02^7$ | 0.0474 | $0.949^0 \pm 0.001^0$ | 1:237 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0475 | | |

* balance uncertainty

TABLE B3

SULPHATE DETERMINATION SERIES I

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A1 - 1 | $10.00 \pm 0.01^1$ | 0.0061 | $0.23^6 \pm 0.01^4$ | 1:30 |
| - 2 | $10.00 \pm 0.01^1$ | 0.0054 | | |
| A2 - 1 | $10.00 \pm 0.01^1$ | 0.0063 | $0.28^2 \pm 0.02^3$ | 1:36 |
| - 2 | $10.00 \pm 0.01^1$ | 0.0074 | | |
| B1 - 1 | $50.00 \pm 0.02^7$ | 0.0478 | $0.393^5 \pm 0.000^0$ | 1:239 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0478 | | |
| B2 - 1 | $50.00 \pm 0.02^7$ | 0.0464 | $0.382^8 \pm 0.000^8$ | 1:232 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0466 | | |
| C1 - 1 | $50.00 \pm 0.02^7$ | 1.1693 | $9.62^7 \pm 0.00^1$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 1.1697 | | |
| C2 - 1 | $50.00 \pm 0.02^7$ | 1.2024 | $9.89^7 \pm 0.00^1$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 1.2021 | | |

* balance uncertainty

SERIES II:

Each sample was prepared according to Method #1, section 3.2.1.1, page 27. The final solution volume was adjusted to 1000.00 ± 0.15 ml after sterilization. The HCl-Blank determination was done as part of the sulphate determination. Sulphur dioxide oxidation products were not determined. Each sample was analyzed in duplicate.

EXPERIMENTAL RESULTS FOR THIOSULPHATE ION DETERMINATION:

A 25.00 ± 0.02 ml aliquot was titrated with a 0.0749 ± 0.0001 M $I_3^-$ solution.

TABLE B4

THIOSULPHATE DETERMINATION SERIES II

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A3 - 1 | 10.55 | $7.08^8 \pm 0.00^0$ | 1:264 |
| - 2 | 10.55 | | |
| A4 - 1 | 10.82 | $7.26^9 \pm 0.00^0$ | 1:270 |
| - 2 | 10.82 | | |
| B3 - 1 | 10.20 | $6.85^3 \pm 0.00^0$ | 1:255 |
| - 2 | 10.20 | | |
| B4 - 1 | 10.00 | $6.71^8 \pm 0.00^0$ | 1:250 |
| - 2 | 10.00 | | |
| C3 - 1 | 5.46 | $3.66^8 \pm 0.00^0$ | 1:137 |
| - 2 | 5.46 | | |
| C4 - 1 | 4.30 | $2.88^9 \pm 0.00^0$ | 1:108 |
| - 2 | 4.30 | | |

TABLE B5

## HCl-BLANK DETERMINATION SERIES II

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $S^0$ g/vol (± 0.0002 g)* | Average $S^0$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A3 - 1 | $25.00 \pm 0.02^4$ | 0.0400 | $1.58^8 \pm 0.01^2$ | 1:200 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0394 | | |
| A4 - 1 | $25.00 \pm 0.02^4$ | 0.0492 | $1.95^8 \pm 0.01^0$ | 1:242 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0487 | | |
| B3 - 1 | $50.00 \pm 0.02^7$ | 0.0468 | $0.949^0 \pm 0.013^0$ | 1:237 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0481 | | |
| B4 - 1 | $50.00 \pm 0.02^7$ | 0.0479 | $0.918^0 \pm 0.060^0$ | 1:230 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0439 | | |
| C3 - 1 | $50.00 \pm 0.02^7$ | 0.0738 | $1.465^0 \pm 0.011^0$ | 1:368 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0727 | | |
| C4 - 1 | $50.00 \pm 0.02^7$ | 0.0624 | $1.246^0 \pm 0.002^0$ | 1:311 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0622 | | |

* balance uncertainty

TABLE B6

SULPHATE DETERMINATION SERIES II

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A3 - 1 | $25.00 \pm 0.02^4$ | 0.0259 | $0.421^5 \pm 0.005^0$ | 1:130 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0253 | | |
| A4 - 1 | $25.00 \pm 0.02^4$ | 0.0253 | $0.421^5 \pm 0.005^0$ | 1:130 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0259 | | |
| B3 - 1 | $50.00 \pm 0.02^7$ | 0.0870 | $0.715^8 \pm 0.000^4$ | 1:420 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0869 | | |
| B4 - 1 | $50.00 \pm 0.02^7$ | 0.0830 | $0.698^1 \pm 0.014^7$ | 1:420 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0866 | | |
| C3 - 1 | $50.00 \pm 0.02^7$ | 0.8997 | $7.407^0 \pm 0.001^0$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.8998 | | |
| C4 - 1 | $50.00 \pm 0.02^7$ | 1.0150 | $8.357^6 \pm 0.002^1$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 1.0155 | | |

* balance uncertainty

SERIES III:

Each sample was prepared according to Method #2, page 28, section 3.2.1.2. The solution volume was 2 x 500.00 ± 0.08 ml, or 1000.00 ± 0.16 ml, prior to autoclaving. The solution volume was not adjusted after this process and any changes in volume were assumed to be negligible with respect to the total. The HCl-Blank was done as part of the sulphate determination. Sulphur dioxide oxidation products were not determined. Each sample was analyzed in duplicate.

TABLE B7

THIOSULPHATE DETERMINATION SERIES III

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A5 - 1 | 10.50 | $7.05^4 \pm 0.00^0$ | 1:263 |
| - 2 | 10.50 | | |
| A6 - 1 | 10.30 | $6.92^0 \pm 0.00^0$ | 1:258 |
| - 2 | 10.30 | | |
| B5 - 1 | 10.45 | $7.02^1 \pm 0.00^0$ | 1:261 |
| - 2 | 10.45 | | |
| B6 - 1 | 10.30 | $6.92^0 \pm 0.00^0$ | 1:258 |
| - 2 | 10.30 | | |
| C5 - 1 | 4.90 | $3.29^2 \pm 0.00^0$ | 1:123 |
| - 2 | 4.90 | | |
| C6 - 1 | 5.90 | $3.69^4 \pm 0.00^0$ | 1:148 |
| - 2 | 5.90 | | |

TABLE B8

HCl-BLANK DETERMINATION SERIES III

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of S° g/vol (± 0.0002 g)* | Average S° ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A5 - 1 | $50.00 \pm 0.02^{7}$ | 0.0928 | $1.864^{0} \pm 0.008^{0}$ | 1:466 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0936 | | |
| A6 - 1 | $50.00 \pm 0.02^{7}$ | 0.0670 | $1.341^{0} \pm 0.001^{0}$ | 1:335 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0671 | | |
| B5 - 1 | $50.00 \pm 0.02^{7}$ | 0.0879 | $1.767^{0} \pm 0.009^{0}$ | 1:442 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0888 | | |
| B6 - 1 | $50.00 \pm 0.02^{7}$ | 0.0858 | $1.693^{0} \pm 0.007^{0}$ | 1:423 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0843 | | |
| C5 - 1 | $50.00 \pm 0.02^{7}$ | 0.0556 | $1.111^{0} \pm 0.001^{0}$ | 1:278 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0555 | | |
| C6 - 1 | $50.00 \pm 0.02^{7}$ | 0.0563 | $1.126^{0} \pm 0.000^{0}$ | 1:282 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0563 | | |

*. balance uncertainty

TABLE B9

SULPHATE DETERMINATION SERIES III

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A5 - 1 | $50.00 \pm 0.02^7$ | 0.0429 | $0.350^7 \pm 0.003^3$ | 1:212 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0422 | | |
| A6 - 1 | $50.00 \pm 0.02^7$ | 0.0496 | $0.406^3 \pm 0.002^0$ | 1:247 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0491 | | |
| B5 - 1 | $50.00 \pm 0.02^7$ | 0.0443 | $0.361^8 \pm 0.002^9$ | 1:220 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0436 | | |
| B6 - 1 | $50.00 \pm 0.02^7$ | 0.0446 | $0.369^2 \pm 0.001^2$ | 1:224 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0450 | | |
| C5 - 1 | $50.00 \pm 0.02^7$ | 0.7697 | $6.339^9 \pm 0.003^7$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.7706 | | |
| C6 - 1 | $50.00 \pm 0.02^7$ | 0.7435 | $6.122^6 \pm 0.002^0$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.7440 | | |

* balance uncertainty

SERIES IV:

Each sample was prepared according to Method #2, section 3.2.1.2, page 28. The solution volume was 2 x 500.00 ± 0.08 ml or 1000.00 ± 0.16 ml prior to autoclaving. The solution volume was not adjusted after this process, and any change in volume was assumed to be negligible with respect to the total.

Each sample was analyzed in duplicate. The HCl-Blank was done as part of the sulphate determination. The sulphur dioxide oxidation products were not determined.

TABLE B10

THIOSULPHATE DETERMINATION SERIES IV

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A7 - 1 | 10.97 | $7.38^4 \pm 0.00^6$ | 1:275 |
| - 2 | 11.01 | | |
| A8 - 1 | 10.30 | $6.92^0 \pm 0.00^0$ | 1:258 |
| - 2 | 10.30 | | |
| B7 - 1 | 11.00 | $7.39^6 \pm 0.00^0$ | 1:275 |
| - 2 | 11.00 | | |
| B8 - 1 | 11.10 | $7.45^7 \pm 0.00^0$ | 1:278 |
| - 2 | 11.10 | | |
| C7 - 1 | 5.60 | $3.76^2 \pm 0.00^0$ | 1:140 |
| - 2 | 5.60 | | |
| C8 - 1 | 5.39 | $3.62^1 \pm 0.00^0$ | 1:135 |
| - 2 | 5.39 | | |

TABLE B11

HCl-BLANK DETERMINATION SERIES IV

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of S° g/vol (± 0.0002 g)* | Average S° ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A7 - 1 | 50.00 ± $0.02^7$ | 0.0936 | $1.866^0 \pm 0.006^0$ | 1:467 |
| - 2 | 50.00 ± $0.02^7$ | 0.0930 | | |
| A8 - 1 | 50.00 ± $0.02^7$ | 0.0944 | $1.894^0 \pm 0.006^0$ | 1:474 |
| - 2 | 50.00 ± $0.02^7$ | 0.0950 | | |
| B7 - 1 | 50.00 ± $0.02^7$ | 0.0909 | $1.829^0 \pm 0.011^0$ | 1:458 |
| - 2 | 50.00 ± $0.02^7$ | 0.0920 | | |
| B8 - 1 | 50.00 ± $0.02^7$ | 0.0913 | $1.830^0 \pm 0.004^0$ | 1:458 |
| - 2 | 50.00 ± $0.02^7$ | 0.0917 | | |
| C7 - 1 | 50.00 ± $0.02^7$ | 0.0782 | $1.593^0 \pm 0.029^0$ | 1:391 |
| - 2 | 50.00 ± $0.02^7$ | 0.0811 | | |
| C8 - 1 | 50.00 ± $0.02^7$ | 0.0650 | $1.222^0 \pm 0.078^0$ | 1:286 |
| - 2 | 50.00 ± $0.02^7$ | 0.0573 | | |

* balance uncertainty

TABLE B12

SULPHATE DETERMINATION SERIES IV

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A7 - 1 | $50.00 \pm 0.02^7$ | 0.0426 | $0.354^8 \pm 0.004^1$ | 1:215 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0436 | | |
| A8 - 1 | $50.00 \pm 0.02^7$ | 0.0360 | $0.293^9 \pm 0.002^5$ | 1:179 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0354 | | |
| B7 - 1 | $50.00 \pm 0.02^7$ | 0.0425 | $0.349^9 \pm 0.000^0$ | 1:212 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0425 | | |
| B8 - 1 | $50.00 \pm 0.02^7$ | 0.0456 | $0.376^2 \pm 0.000^8$ | 1:229 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0458 | | |
| C7 - 1 | $50.00 \pm 0.02^7$ | 0.7336 | $6.160^4 \pm 0.121^4$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.7631 | | |
| C8 - 1 | $50.00 \pm 0.02^7$ | 0.7594 | $6.255^9 \pm 0.004^5$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.7605 | | |

* balance uncertainty

SERIES V:

Each sample was prepared according to Method #2, section 3.2.1.2, page 28. The solution volume was 500.00 ± 0.08 ml x 2, or 1000.00 ± 0.16 ml prior to autoclaving. The solution volume was not adjusted after this process, and any change in volume was assumed to be negligible with respect to the total:

Each sample was analyzed in duplicate. The HCl-Blank was done as part of the sulphate determination. The sulphur dioxide oxidation products were not determined.

TABLE B13

THIOSULPHATE DETERMINATION SERIES V

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^{=}$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A9 - 1 | 10.72 | $7.02^{2} \pm 0.00^{0}$ | 1:268 |
| - 2 | 10.72 | | |
| A10 - 1 | 10.70 | $7.18^{9} \pm 0.00^{0}$ | 1:268 |
| - 2 | 10.70 | | |
| B9 - 1 | 10.65 | $7.16^{9} \pm 0.01^{3}$ | 1:266 |
| - 2 | 10.69 | | |
| B10 - 1 | 10.48 | $7.04^{8} \pm 0.00^{6}$ | 1:263 |
| - 2 | 10.50 | | |
| C9 - 1 | 4.20 | $2.82^{1} \pm 0.00^{0}$ | 1:105 |
| - 2 | 4.20 | | |
| C10 - 1 | 4.50 | $2.02^{3} \pm 0.00^{0}$ | 1:113 |
| - 2 | 4.50 | | |

TABLE B14

HCl-BLANK DETERMINATION SERIES V

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of S° g/vol (± 0.0002 g)* | Average S° ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A9 - 1 | 50.00 ± $0.02^7$ | 0.0908 | $1.812^0 \pm 0.004^0$ | 1:453 |
| - 2 | 50.00 ± $0.02^7$ | 0.0904 | | |
| A10 - 1 | 50.00 ± $0.02^7$ | 0.0877 | $1.764^0 \pm 0.005^0$ | 1:442 |
| - 2 | 50.00 ± $0.02^7$ | 0.0887 | | |
| B9 - 1 | 50.00 ± $0.02^7$ | 0.0931 | $1.872^0 \pm 0.010^0$ | 1:468 |
| - 2 | 50.00 ± $0.02^7$ | 0.0941 | | |
| B10 - 1 | 50.00 ± $0.02^7$ | 0.0933 | $1.859^0 \pm 0.007^0$ | 1:465 |
| - 2 | 50.00 ± $0.02^7$ | 0.0926 | | |
| C9 - 1 | 50.00 ± $0.02^7$ | 0.0701 | $1.341^0 \pm 0.061^0$ | 1:320 |
| - 2 | 50.00 ± $0.02^7$ | 0.0640 | | |
| C10 - 1 | 50.00 ± $0.02^7$ | 0.0691 | $1.435^0 \pm 0.053^0$ | 1:345 |
| - 2 | 50.00 ± $0.02^7$ | 0.0744 | | |

* balance uncertainty

TABLE B15

SULPHATE DETERMINATION - SERIES V

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A9 - 1 | $50.00 \pm 0.02^7$ | 0.0503 | $0.409^2 \pm 0.005^0$ | 1:250 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0491 | | |
| A10 - 1 | $50.00 \pm 0.02^7$ | 0.0454 | $0.372^1 \pm 0.001^7$ | 1:226 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0450 | | |
| B9 - 1 | $50.00 \pm 0.02^7$ | 0.0493 | $0.410^8 \pm 0.004^5$ | 1:250 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0505 | | |
| B10 - 1 | $50.00 \pm 0.02^7$ | 0.0604 | $0.500^1 \pm 0.003^0$ | 1:304 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0611 | | |
| C9 - 1 | $50.00 \pm 0.02^7$ | 0.9506 | $7.824^1 \pm 0.001^2$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.9503 | | |
| C10 - 1 | $50.00 \pm 0.02^7$ | 1.0432 | $8.585^8 \pm 0.002^2$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 1.0427 | | |

* balance uncertainty

SERIES VI:

Each sample was prepared according to Method #2, section 3.2.1.2, page 28. The solution volume was 2 x 500.00 ± 0.08 ml, or 1000.00 ± 0.16 ml prior to autoclaving. The solution volume was not adjusted after this process, and any change in volume was assumed to be negligible with respect to the total.

Each sample was analyzed in duplicate. The HCl-Blank was done as part of the sulphate determination. The sulphur dioxide oxidation products were not determined.

TABLE B16

THIOSULPHATE DETERMINATION SERIES VI

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A11 - 1 | 11.14 | $7.49^8 \pm 0.00^6$ | 1:279 |
| - 2 | 11.18 | | |
| C11 - 1 | 3.30 | $2.21^7 \pm 0.00^0$ | 1:83 |
| - 2 | 3.30 | | |
| C12 - 1 | 4.30 | $2.88^9 \pm 0.00^0$ | 1:108 |
| - 2 | 4.30 | | |
| C13 - 1 | 3.80 | $2.55^3 \pm 0.00^0$ | 1:95 |
| - 2 | 3.80 | | |
| C14 - 1 | 3.75 | $2.51^9 \pm 0.00^0$ | 1:94 |
| - 2 | 3.75 | | |

TABLE B17

HCl-BLANK DETERMINATION SERIES VI

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of S° g/vol (± 0.0002 g)* | Average S° ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A11 - 1 | $50.00 \pm 0.02^{7}$ | 0.0769 | $1.534^{0} \pm 0.004^{0}$ | 1:383 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0765 | | |
| C11 - 1 | $50.00 \pm 0.02^{7}$ | 0.0615 | $1.129^{9} \pm 0.101^{0}$ | 1:257 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0514 | | |
| C12 - 1 | $50.00 \pm 0.02^{7}$ | 0.0539 | $1.150^{0} \pm 0.072^{0}$ | 1:270 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0611 | | |
| C13 - 1 | $50.00 \pm 0.02^{7}$ | 0.0694 | $1.318^{0} \pm 0.070^{0}$ | 1:312 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0624 | | |
| C14 - 1 | $50.00 \pm 0.02^{7}$ | 0.0602 | $1.238^{0} \pm 0.034^{0}$ | 1:301 |
| - 2 | $50.00 \pm 0.02^{7}$ | 0.0636 | | |

* balance uncertainty

TABLE B18

SULPHATE DETERMINATION SERIES VI

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A11 - 1 | $50.00 \pm 0.02^7$ | 0.0899 | $0.740^1 \pm 0.000^0$ | 1:450 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0899 | | |
| C11 - 1 | $50.00 \pm 0.02^7$ | 1.1358 | $9.33^7 \pm 0.01^2$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 1.1327 | | |
| C12 - 1 | $50.00 \pm 0.02^7$ | 0.9847 | $8.112^3 \pm 0.006^1$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.9862 | | |
| C13 - 1 | $50.00 \pm 0.02^7$ | 0.9061 | $7.434^3 \pm 0.024^7$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.9001 | | |
| C14 - 1 | $50.00 \pm 0.02^7$ | 0.9411 | $7.749^6 \pm 0.002^5$ | 1:1820 |
| - 2 | $50.00 \pm 0.02^7$ | 0.9417 | | |

* balance uncertainty

SERIES VII:

Each sample was prepared according to Method #2, section 3.2.1.2, page 28. The solution volume was 2 x 500.00 ± 0.08 ml, or 1000.00 ± 0.16 ml prior to autoclaving. The solution volume was not adjusted after this process, and any change in volume was assumed to be negligible with respect to the total.

Each sample was analyzed in duplicate. The HCl-Blank was done as part of the sulphate determination for samples A 12 and A 13. The sulphur dioxide oxidation products were not determined.

TABLE B19

THIOSULPHATE DETERMINATION , SERIES VII

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A12 - 1 | 11.07 | $7.43^7 \pm 0.00^0$ | 1:277 |
| - 2 | 11.07 | | |
| A13 - 1 | 11.00 | $7.39^0 \pm 0.00^0$ | 1:275 |
| - 2 | 11.00 | | |
| B11 - 1 | 11.20 | $7.51^5 \pm 0.00^0$ | 1:280 |
| - 2 | 11.20 | | |
| B12 - 1 | 11.21 | $7.53^1 \pm 0.00^0$ | 1:280 |
| - 2 | 11.21 | | |
| C15 - 1 | 3.48 | $2.33^4 \pm 0.00^0$ | 1:87 |
| - 2 | 3.48 | | |
| C16 - 1 | 5.00 | $3.35^9 \pm 0.00^0$ | 1:125 |
| - 2 | 5.00 | | |

TABLE B20

HCl-BLANK DETERMINATION SERIES VII

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of S° g/vol (± 0.0002 g)* | Average S° ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A12 - 1 | $100.00 \pm 0.05^{6}$ | 0.1523 | $1.250^{5} \pm 0.272^{5}$ | 1:495 |
| - 2 | $100.00 \pm 0.05^{6}$ | 0.0978 | | |
| A13 - 1 | $100.00 \pm 0.05^{6}$ | 0.0098 | $0.190^{0} \pm 0.092^{0}$ | 1:49 |
| - 2 | $100.00 \pm 0.05^{6}$ | 0.0282 | | |
| B11 - 1 | ← NO DATA → | | | |
| - 2 | | | | |
| B12 - 1 | ← NO DATA → | | | |
| - 2 | | | | |
| C15 - 1 | ← NO DATA → | | | |
| - 2 | | | | |
| C16 - 1 | ← NO DATA → | | | |
| - 2 | | | | |

* balance uncertainty

TABLE B21

SULPHATE DETERMINATION SERIES VII

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A12 - 1 | $100.00 \pm 0.05^6$ | 0.2263 | $0.925^3 \pm 0.006^2$ | 1:1130 |
| - 2 | $100.00 \pm 0.05^6$ | 0.2233 | | |
| A13 - 1 | $100.00 \pm 0.05^6$ | 0.2685 | $1.904^5 \pm 0.010^5$ | 1:1325 |
| - 2 | $100.00 \pm 0.05^6$ | 0.2634 | | |
| B11 - 1 | $50.00 \pm 0.02^7$ | 0.0690 | $0.566^8 \pm 0.001^3$ | 1:345 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0687 | | |
| B12 - 1 | $50.00 \pm 0.02^7$ | 0.0685 | $0.564^7 \pm 0.000^8$ | 1:345 |
| - 2 | $50.00 \pm 0.02^7$ | 0.0687 | | |
| C15 - 1 | $25.00 \pm 0.02^4$ | 0.5566 | $9.16^0 \pm 0.00^3$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.5562 | | |
| C16 - 1 | $25.00 \pm 0.02^4$ | 0.5560 | $9.15^6 \pm 0.00^2$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.5563 | | |

*balance uncertainty

TABLE B22

SAMPLE N$^{o}$: A 12

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | 0.11[2] | 0.19[1] |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | 0.728[3] | 0.425[1] |
| AVAILABLE | ----- | ----- |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ | + | $S^o$ |
|---|---|---|---|---|
| moles | 0.0663 | 0.0663 | | 0.0663 |
| g expected | 7.43[7] | ------ | | 2.126[6] |
| g found | 7.43[7] | ------ | 1.250[5] ± | 0.272[5] |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = ------

% error ------

TABLE B23

SAMPLE N$^{O}$: A 13

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.15^{8}$ | $0.27^{0}$ |
| AVAILABLE | ------ | ------ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.897^{5}$ | $0.523^{8}$ |
| AVAILABLE | ------ | ------ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow SO_2$ | | + | $S^{O}$ |
|---|---|---|---|---|
| moles | 0.0659 | 0.0659 | | 0.0659 |
| g expected | $7.39^{0}$ | ---- | | 2.1130 |
| g found | $7.39^{0}$ | ---- | $0.190^{0} \pm 0.092^{0}$ | |

ratio $S^{O}/SO_2$ expected = 0.5005

ratio $S^{O}/SO_2$ found = ------

% error ------

SERIES VIII:

Each sample was prepared according to Method #2, section 3.2.1.2, page 28. The solution volume was 2 x 500.00 ± 0.08 ml, or 1000.00 ± 0.16 ml prior to autoclaving. The solution volume was not adjusted after this process, and any change in volume was assumed to be negligible with respect to the total.

Each sample was analyzed in duplicate. The HCl-Blank and sulphur dioxide oxidation products were determined according to the methods previously described in sections 3.2.4.1 and 3.2.4.2 respectively.

TABLE B24

THIOSULPHATE DETERMINATION SERIES VIII

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A14 - 1 | 11.10 | $7.45^7 \pm 0.00^0$ | 1:278 |
| - 2 | 11.10 | | |
| A15 - 1 | 11.10 | $7.45^7 \pm 0.00^0$ | 1:278 |
| - 2 | 11.10 | | |
| B13 - 1 | 17.40 | $7.42^9 \pm 0.00^0$ | 1:435 |
| - 2 | 17.40 | | |
| B14 - 1 | 17.65 | $7.53^6 \pm 0.00^0$ | 1:440 |
| - 2 | 17.65 | | |
| C17 - 1 | 5.80 | $2.47^6 \pm 0.00^0$ | 1:145 |
| - 2 | 5.80 | | |
| C18 - 1 | 4.15 | $1.77^2 \pm 0.00^0$ | 1:104 |
| - 2 | 4.15 | | |

TABLE B25

HCl-BLANK DETERMINATION SERIES VIII

| Sample & Replicate | Volume of Sample (ml ± error) | Wt. of $S^o$ g/vol (± 0.0002 g)* | Average $S^o$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A14 - 1 | $25.00 \pm 0.02^4$ | 0.0537 | $2.15^8 \pm 0.01^0$ | 1:270 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0542 | | |
| A15 - 1 | $25.00 \pm 0.02^4$ | 0.0531 | $2.14^2 \pm 0.01^8$ | 1:265 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0540 | | |
| B13 - 1 | $25.00 \pm 0.02^4$ | 0.0469 | $1.88^0 \pm 0.00^4$ | 1:235 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0471 | | |
| B14 - 1 | $25.00 \pm 0.02^4$ | 0.0468 | $1.86^0 \pm 0.01^2$ | 1:233 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0462 | | |
| C17 - 1 | $25.00 \pm 0.02^4$ | 0.0108 | $0.43^6 \pm 0.00^4$ | 1:54 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0110 | | |
| C18 - 1 | $25.00 \pm 0.02^4$ | 0.0078 | $0.31^0 \pm 0.00^2$ | 1:40 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0077 | | |

* balance uncertainty

TABLE B26

SULPHATE DETERMINATION SERIES VIII

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A14 - 1 | $25.00 \pm 0.02^4$ | 0.0510 | $0.830^7 \pm 0.009^1$ | 1:252 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0499 | | |
| A15 - 1 | $25.00 \pm 0.02^4$ | 0.0502 | $0.829^8 \pm 0.003^3$ | 1:253 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0506 | | |
| B13 - 1 | $25.00 \pm 0.02^4$ | 0.0248 | $0.406^7 \pm 0.001^7$ | 1:123 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0246 | | |
| B14 - 1 | $25.00 \pm 0.02^4$ | 0.0247 | $0.407^5 \pm 0.000^8$ | 1:124 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0248 | | |
| C17 - 1 | $25.00 \pm 0.02^4$ | 0.5128 | $8.44^2 \pm 0.00^0$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.5128 | | |
| C18 - 1 | $25.00 \pm 0.02^4$ | 0.5746 | $9.45^6 \pm 0.00^4$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.5741 | | |

* balance uncertainty

TABLE B27

SULPHUR DIOXIDE DETERMINATION SERIES VIII

| Sample & Replicate | Wt. of $BaSO_4$ (± 0.0002)* | Ave. $SO_2$ evolved ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| B13 - 1 | 0.0675 | $0.739^2 \pm 0.001^6$ | 1:336 |
| - 2 | 0.0672 | | |
| B14 - 1 | 0.0605 | $0.666^2 \pm 0.002^0$ | 1:305 |
| - 2 | 0.0609 | | |
| C17 - 1 | 0.0677 | $0.744^7 \pm 0.001^6$ | 1:340 |
| - 2 | 0.0680 | | |
| C18 - 1 | 0.0659 | $0.725^0 \pm 0.001^7$ | 1:330 |
| - 2 | 0.0662 | | |

* balance uncertainty

TABLE B28

SAMPLE N$^{O}$: A 14

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.09^2$ | $0.15^7$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.633^5$ | $0.369^7$ |
| AVAILABLE | ----- | ----- |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ | + | $S^o$ |
|---|---|---|---|---|
| moles | 0.0665 | 0.0665 | | 0.0665 |
| g expected | $7.45^7$ | ------ | | 2.1324 |
| g found | $7.45^7$ | ------ | $2.15^8 \pm 0.01^o$ | |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = ------

% error ------

TABLE B29

SAMPLE N$^{0}$: A 15

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.09^2$ | $0.15^7$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.632^5$ | $0.369^2$ |
| AVAILABLE | ?----- | ----- |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ | + | $S^o$ |
|---|---|---|---|---|
| moles | 0.0665 | 0.0665 | | 0.0665 |
| g expected | $7.45^7$ | ------ | | 2.1324 |
| g found | $7.45^7$ | ------ | $2.14^2 \pm 0.01^8$ | |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = ------

% error ------

TABLE B30

SAMPLE N$^{0}$: B 13

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.12^{1}$ | $0.20^{7}$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.209^{9}$ | $0.122^{5}$ |
| AVAILABLE | ----- | ----- |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0663 | 0.0663 | 0.0663 |
| g expected | $7.42^{9}$ | $4.247^{4}$ | $2.12^{4}$ |
| g found | $7.42^{9}$ | $4.237^{9} \pm 0.004^{3}$ | $2.04^{0} \pm 0.00^{4}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4814

error = 3.8%

TABLE B31

SAMPLE N$^{O}$: B 14

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.01^4$ | $0.02^4$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $0.210^7$ | $0.123^0$ |
| AVAILABLE | ----- | ----- |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow SO_2$ | + | $S^o$ |
|---|---|---|---|
| moles | 0.0672 | 0.0672 | 0.0672 |
| g expected | $7.53^6$ | $4.305^0$ | $2.15^4$ |
| g found | $7.53^6$ | $4.267^5 \pm 0.014^3$ | $2.08^0 \pm 0.00^8$ |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = 0.4874

error = 2.6%

TABLE B32

SAMPLE N$^{0}$: C17

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $5.07^{4}$ | $8.69^{3}$ |
| AVAILABLE | $4.98^{1}$ | $8.53^{4}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $8.71^{9}$ | $5.08^{8}$ |
| AVAILABLE | $8.51^{2}$ | $4.96^{8}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0221 | 0.0221 | 0.0221 |
| g expected | $2.47^{6}$ | $1.415^{8}$ | $0.70^{8}$ |
| g found | $2.47^{6}$ | $1.414^{8} \pm 0.000^{7}$ | $0.69^{6} \pm 0.01^{6}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4919

error = 1.7%

TABLE B33

SAMPLE N$^{0}$: C 18

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/L | as $SO_4^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $5.77^{7}$ | $9.89^{8}$ |
| AVAILABLE | $5.68^{5}$ | $9.74^{0}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/L | as $S_2O_3^{2-}$ g/L |
|---|---|---|
| ORIGINAL | $10.05^{9}$ | $5.87^{1}$ |
| AVAILABLE | $9.85^{3}$ | $5.75^{0}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ | + | $S^{0}$ |
|---|---|---|---|---|
| moles | 0.0158 | 0.0158 | | 0.0158 |
| g expected | $1.77^{2}$ | $1.012^{2}$ | | $0.50^{6}$ |
| g found | $1.77^{2}$ | $1.011^{1} \pm 0.004^{4}$ | | $0.50 \pm 0.00^{0}$ |

ratio $S^{0}/SO_2$ expected = 0.5005

ratio $S^{0}/SO_2$ found = 0.5024

error 0.37%

SERIES IX:

Each sample was prepared according to Method #2, section 3.2.1.2, page 28. The solution volume was 2 x 500.00 ± 0.08 ml, or 1000.00 ± 0.16 ml prior to autoclaving. The solution volume was not adjusted after this process, and any change in volume was assumed to be negligible with respect to the total.

Each sample was analyzed in duplicate. The HCl-Blank and sulphur dioxide oxidation products were determined according to the methods previously described in sections 3.2.4.1 and 3.2.4.2 respectively.

TABLE B34

THIOSULPHATE DETERMINATION : SERIES IX

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3$ = ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| A16 - 1 | 17.38 | $7.46^{7} \pm 0.00^{0}$ | 1:435 |
| - 2 | 17.38 | | |
| A17 - 1 | 17.38 | $7.46^{7} \pm 0.00^{0}$ | 1:435 |
| - 2 | 17.38 | | |
| B15 - 1 | 17.20 | $7.39^{0} \pm 0.00^{0}$ | 1:430 |
| - 2 | 17.20 | | |
| B16 - 1 | 17.28 | $7.42^{4} \pm 0.00^{0}$ | 1:432 |
| - 2 | 17.28 | | |
| B19 - 1 | 6.90 | $2.96^{4} \pm 0.00^{0}$ | 1:173 |
| - 2 | 6.90 | | |
| B20 - 1 | 6.80 | $2.92^{1} \pm 0.00^{0}$ | 1:170 |
| - 2 | 6.80 | | |

TABLE B34 continued

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| B21 - 1 | 6.81 | $2.92^6 \pm 0.00^0$ | 1:170 |
| - 2 | 6.81 | | |
| B22 - 1 | 6.50 | $2.79^2 \pm 0.00^0$ | 1:163 |
| - 2 | 6.50 | | |
| B23 - 1 | 7.10 | $3.05^0 \pm 0.00^0$ | 1:178 |
| - 2 | 7.10 | | |
| B24 - 1 | 3.75 | $1.61^1 \pm 0.00^0$ | 1:94 |
| - 2 | 3.75 | | |
| C25 - 1 | 3.00 | $1.28^9 \pm 0.00^0$ | 1:75 |
| - 2 | 3.00 | | |
| C26 - 1 | 6.90 | $2.96^4 \pm 0.00^0$ | 1:173 |
| - 2 | 6.90 | | |
| C27 - 1 | 7.50 | $3.22^2 \pm 0.00^0$ | 1:188 |
| - 2 | 7.50 | | |

TABLE B34 continued

| Sample & Replicate | Titrant (ml ± 0.04 ml) | Average $S_2O_3^{=}$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|
| C28 - 1 | 5.55 | $2.38^4 \pm 0.00^0$ | 1:139 |
| - 2 | 5.55 | | |
| C29 - 1 | 2.50 | $1.07^4 \pm 0.00^0$ | 1:63 |
| - 2 | 2.50 | | |
| C30 - 1 | 3.60 | $1.54^6 \pm 0.00^0$ | 1:90 |
| - 2 | 3.60 | | |

TABLE B35

HCl-BLANK DETERMINATION SERIES IX

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $S^0$ g/vol (± 0.0002 g)* | Average $S^0$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A16 - 1 | 25.00 ± $0.02^4$ | 0.0541 | $2.16^0$ ± $0.00^4$ | 1:270 |
| - 2 | 25.00 ± $0.02^4$ | 0.0539 | | |
| A17 - 1 | 25.00 ± $0.02^4$ | 0.0549 | $2.18^2$ ± $0.01^4$ | 1:270 |
| - 2 | 25.00 ± $0.02^4$ | 0.0542 | | |
| B15 - 1 | 25.00 ± $0.02^4$ | 0.0527 | $2.11^4$ ± $0.00^6$ | 1:265 |
| - 2 | 25.00 ± $0.02^4$ | 0.0530 | | |
| B16 - 1 | 25.00 ± $0.02^4$ | 0.0530 | $2.11^6$ ± $0.00^4$ | 1:265 |
| - 2 | 25.00 ± $0.02^4$ | 0.0528 | | |
| C19 - 1 | 25.00 ± $0.02^4$ | 0.0206 | $0.83^4$ ± $0.01^0$ | 1:105 |
| - 2 | 25.00 ± $0.02^4$ | 0.0211 | | |
| C20 - 1 | 25.00 ± $0.02^4$ | 0.0201 | $0.81^6$ ± $0.01^2$ | 1:100 |
| - 2 | 25.00 ± $0.02^4$ | 0.0207 | | |

TABLE B35 continued

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $S^0$ g/vol (± 0.0002 g)* | Average ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| C21 - 1 | $25.00 \pm 0.02^4$ | 0.0205 | $0.83^0 \pm 0.01^0$ | 1:105 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0210 | | |
| C22 - 1 | $25.00 \pm 0.02^4$ | 0.0194 | $0.78^8 \pm 0.01^2$ | 1:100 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0200 | | |
| C23 - 1 | $25.00 \pm 0.02^4$ | 0.0211 | $0.85^6 \pm 0.01^6$ | 1:105 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0217 | | |
| C24 - 1 | $25.00 \pm 0.02^4$ | 0.0109 | $0.43^2 \pm 0.00^4$ | 1:50 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0107 | | |
| C25 - 1 | $25.00 \pm 0.02^4$ | 0.0096 | $0.37^2 \pm 0.01^2$ | 1:48 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0090 | | |
| C26 - 1 | $25.00 \pm 0.02^4$ | 0.0204 | $0.82^8 \pm 0.01^2$ | 1:102 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0210 | | |
| C27 - 1 | $25.00 \pm 0.02^4$ | 0.0232 | $0.91^6 \pm 0.01^2$ | 1:113 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0226 | | |

TABLE B35 continued

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $S^o$ g/vol (± 0.0002 g)* | Average ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| C28 - 1 | $25.00 \pm 0.02^4$ | 0.0165 | $0.67^6 \pm 0.01^6$ | 1:83 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0173 | | |
| C29 - 1 | $25.00 \pm 0.02^4$ | 0.0072 | $0.29^4 \pm 0.00^6$ | 1:36 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0075 | | |
| C30 - 1 | $25.00 \pm 0.02^4$ | 0.0107 | $0.44^0 \pm 0.01^2$ | 1:52 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0113 | | |

* balance uncertainty

TABLE B36

SULPHATE DETERMINATION , SERIES IX

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average $SO_4^=$ ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A16 - 1 | $25.00 \pm 0.02^4$ | 0.0172 | $0.275^8 \pm 0.007^4$ | 1:83 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0163 | | |
| A17 - 1 | $25.00 \pm 0.02^4$ | 0.0166 | $0.282^4 \pm 0.009^9$ | 1:86 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0177 | | |
| B15 - 1 | $25.00 \pm 0.02^4$ | 0.0278 | $0.464^3 \pm 0.006^6$ | 1:140 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0286 | | |
| B16 - 1 | $25.00 \pm 0.02^4$ | 0.0247 | $0.409^2 \pm 0.002^5$ | 1:125 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0250 | | |
| C19 - 1 | $25.00 \pm 0.02^4$ | 0.4871 | $8.02^4 \pm 0.00^5$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.4877 | | |
| G20 - 1 | $25.00 \pm 0.02^4$ | 0.4927 | $8.10^7 \pm 0.00^4$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.4922 | | |

TABLE B36 continued

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (±-0.0002 g)* | Average $SO_4^=$ ± ave. dev: (g/L) | Precision |
|---|---|---|---|---|
| C21 - 1 | 25.00 ± $0.02^4$ | 0.4927 | $8.10^6 \pm 0.00^5$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.4922 | | |
| C22 - 1 | 25.00 ± $0.02^4$ | 0.5060 | $8.33^2 \pm 0.00^1$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.5062 | | |
| C23 - 1 | 25.00 ± $0.02^4$ | 0.4824 | $7.94^8 \pm 0.00^6$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.4832 | | |
| C24 - 1 | 25.00 ± $0.02^4$ | 0.6272 | $10.32^8 \pm 0.00^2$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.6275 | | |
| C25 - 1 | 25.00 ± $0.02^4$ | 0.6648 | $10.95^1 \pm 0.00^5$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.6655 | | |
| C26 - 1 | 25.00 ± $0.02^4$ | 0.4870 | $8.02^0 \pm 0.00^2$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.4872 | | |
| C27 - 1 | 25.00 ± $0.02^4$ | 0.4617 | $7.60^8 \pm 0.00^6$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.4625 | | |

TABLE B36 continued

| Sample & Replicate | Volume of sample (ml ± error) | Wt. $BaSO_4$ g/vol (± 0.0002 g)* | Average ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| C28 - 1 | 25.00 ± $0.02^4$ | 0.5480 | $9.02^8$ ± $0.00^5$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.5487 | | |
| C29 - 1 | 25.00 ± $0.02^4$ | 0.6836 | $11.25^8$ ± $0.00^3$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.6840 | | |
| C30 - 1 | 25.00 ± $0.02^4$ | 0.6371 | $10.48^5$ ± $0.00^3$ | 1:1042 |
| - 2 | 25.00 ± $0.02^4$ | 0.6367 | | |

* balance uncertainty

TABLE B37

SULPHUR DIOXIDE DETERMINATION SERIES IX

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $BaSO_4$ (± 0.0002 g)* | Ave. $SO_2$ evolved ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| A16 - 1 | $25.00 \pm 0.02^4$ | 0.3958 | $4.339^9 \pm 0.004^4$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.3950 | | |
| A17 - 1 | $25.00 \pm 0.02^4$ | 0.3978 | $4.352^0 \pm 0.007^7$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.3958 | | |
| B15 - 1 | $25.00 \pm 0.02^4$ | 0.3842 | $4.219^8 \pm 0.002^8$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.3847 | | |
| B16 - 1 | $25.00 \pm 0.02^4$ | 0.3870 | $4.251^5 \pm 0.003^8$ | 1:1042 |
| - 2 | $25.00 \pm 0.02^4$ | 0.3877 | | |
| C19 - 1 | $25.00 \pm 0.02^4$ | 0.1530 | $1.677^7 \pm 0.001^7$ | 1:765 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1527 | | |
| C20 - 1 | $25.00 \pm 0.02^4$ | 0.1516 | $1.666^7 \pm 0.002^7$ | 1:763 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1521 | | |

* balance uncertainty.

TABLE B37

SULPHUR DIOXIDE DETERMINATION SERIES IX

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $BaSO_4$ (± 0.0002 g)* | Ave. $SO_2$ evolved ± ave. dev. (g/L) | Precision |
|---|---|---|---|---|
| C21 - 1 | $25.00 \pm 0.02^4$ | 0.1525 | $1.669^5 \pm 0.004^4$ | 1:763 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1517 | | |
| C22 - 1 | $25.00 \pm 0.02^4$ | 0.1450 | $1.589^3 \pm 0.002^2$ | 1:725 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1446 | | |
| C23 - 1 | $25.00 \pm 0.02^4$ | 0.1590 | $1.747^9 \pm 0.002^7$ | 1:795 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1595 | | |
| C24 - 1 | $25.00 \pm 0.02^4$ | 0.0834 | $0.913^8 \pm 0.001^7$ | 1:416 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0831 | | |
| C25 - 1 | $25.00 \pm 0.02^4$ | 0.0667 | $0.735^6 \pm 0.003^3$ | 1:333 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0673 | | |
| C26 - 1 | $25.00 \pm 0.02^4$ | 0.1537 | $1.684^8 \pm 0.002^2$ | 1:767 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1533 | | |

TABLE B37 continued

SULPHUR DIOXIDE DETERMINATION SERIES IX

| Sample & Replicate | Volume of sample (ml ± error) | Wt. of $BaSO_4$ (± 0.0002 g)* | Ave. $SO_2$ evolved ± ave. dev., (g/L) | Precision |
|---|---|---|---|---|
| C27 - 1 | $25.00 \pm 0.02^4$ | 0.1668 | $1.835^7 \pm 0.004^9$ | 1:837 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1677 | | |
| C28 - 1 | $25.00 \pm 0.02^4$ | 0.1231 | $1.357^2 \pm 0.006^1$ | 1:620 |
| - 2 | $25.00 \pm 0.02^4$ | 0.1242 | | |
| C29 - 1 | $25.00 \pm 0.02^4$ | 0.0545 | $0.596^6 \pm 0.001^6$ | 1:271 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0542 | | |
| C30 - 1 | $25.00 \pm 0.02^4$ | 0.0812 | $0.886^2 \pm 0.004^4$ | 1:400 |
| - 2 | $25.00 \pm 0.02^4$ | 0.0804 | | |

* balance uncertainty

# SUMMARY

SERIES IX:

CONTROL B 15

$S_2O_3^{2-}$

$7.54^9 - 7.39^0 = 0.15^8$ g $S_2O_3^{2-}$/l lost

$SO_4^{2-}$

$0.464^3 - 0.196^6 = 0.267^7$ g $SO_4^{2-}$/l gained

$S^o$

$2.11^4$ g $S^o$/l gained due to thiosulphate destruction

$SO_2$

$4.219^8$ g $SO_2$/l gained due to thiosulphate destruction

$0.15^8$ g $S_2O_3^{2-}$/l = $0.270^7$ g $SO_4^{2-}$/l

The gain of $0.267^7 \pm 0.006^8$ g $SO_4^{2-}$/l was determined. This gain has been attributed to the conversion of $S_2O_3^{2-}$ to $SO_4^{2-}$ via:

$$S_2O_3^{2-} + 10\ OH^- - 8\ e \longrightarrow 2\ SO_4^{2-} + 5\ H_2O$$

This leaves $7.39^0 \pm 0.00^0$ g $S_2O_3^{2-}$/l available for acid destruction resulting in the production of sulphur dioxide and sulphur (elemental).

| | $S_2O_3^{2-}$ | $\longrightarrow$ | $SO_2$ | + | $S^o$ |
|---|---|---|---|---|---|
| moles | 1 | | 1 | | 1 |
| M.W. | 112.13 | | 64.063 | | 32.064 |
| g expected | $7.39^0$ | | 4.2221 | | 2.1132 |
| moles expected | 0.0659 | | 0.0659 | | 0.0659 |
| g found | $7.39^0 \pm 0.00^0$ | | $4.219^8 \pm 0.002^8$ | | $2.11^4 \pm 0.00^6$ |

ratio $S^0/SO_2$ expected = 0.5005

ratio $S^0/SO_2$ found = 0.5010

0.1 % error

CONTROL: B 16

$S_2O_3^{2-}$

$7.54^9 - 7.42^4 = 0.12^4$ g $S_2O_3^{2-}$/l lost

$SO_4^{2-}$

$0.409^2 - 0.196^6 = 0.212^6$ g $SO_4^{2-}$/l gained

$S^0$

$2.11^6$ g $S^0$/l gained due to thiosulphate destruction

$SO_2$

$4.251^5$ g $SO_2$/l gained due to thiosulphate destruction

$0.12^4$ g $S_2O_3^{2-}$/l = $0.212^5$ g $SO_4^{2-}$/l

The gain of $0.212^6 \pm 0.002^7$ g $SO_4^{2-}$/l was determined. This gain has been attributed to the conversion of thiosulphate to sulphate via the reaction

$$S_2O_3^{2-} + 10\ OH^- - 8\ e \longrightarrow 2\ SO_4^{2-} + 5\ H_2O$$

This leaves $7.42^4 \pm 0.00^0$ g $S_2O_3^{2-}$/l available for acid destruction resulting in the production of sulphur dioxide and elemental sulphur.

$$S_2O_3^{2-} \longrightarrow SO_2 + S^0$$

| | | | |
|---|---|---|---|
| moles | 1 | 1 | 1 |
| M.W. | 112.13 | 64.063 | 32.064 |
| g expected | $7.42^4$ | 4.2415 | 2.1229 |
| moles expected | 0.0662 | 0.0662 | 0.0662 |
| g found | $7.42^4 \pm 0.00^0$ | $4.251^5 \pm 0.003^8$ | $2.11^6 \pm 0.00^4$ |

ratio $S^0/SO_2$ expected = 0.5005

ratio $S^0/SO_2$ found = 0.4977

0.6 % error

The results of the control solutions were averaged, and the average value was used as the "available" concentration for bacterial action.

Therefore: $7.54^{9} - 7.40^{7} \pm 0.01^{7} = 0.14^{2} \pm 0.01^{7}$ g $S_2O_3^{2-}$/l

lost $7.40^{7} \pm 0.01^{7}$ g $S_2O_3^{2-}$/l constitutes the available thiosulphate concentration.

$0.14^{2} \pm 0.01^{7}$ g $S_2O_3^{2-}$/l is assumed to undergo conversion to $SO_4^{2-}$. This value must be removed from the total to determine the amount of sulphate produced by bacterial action.

$$\frac{0.14^{2} + 0.01^{7} \times 2 \times 96.06}{112.13} = 0.24^{3} \pm 0.0 \quad \text{g } SO_4^{2-}/\text{l}$$

EXPERIMENTAL: C 19

| $S_2O_3^{2-}$ added | found | difference | from |
|---|---|---|---|
| $7.54^{9}$ | $2.96^{4}$ | $4.58^{4}$ | original |
| $7.40^{7}$ | $2.96^{4}$ | $4.44^{3}$ | available |

therefore: $4.58^{4}$ g/l or $4.44^{3}$ g/l $S_2O_3^{2-}$ was converted from the original and available respectively.

$4.58^{4}$ g $S_2O_3^{2-}$/l = $7.86^{1}$ g $SO_4^{2-}$/l from the original, or

$4.44^{3}$ g $S_2O_3^{2-}$/l = $7.61^{2}$ g $SO_4^{2-}$/l from the available.

$8.02^{4}$ g $SO_4^{2-}$/l was found in the media. This value represents ($8.02^{4} - 0.196^{6} =$ ) $7.82^{7}$ g $SO_4^{2-}$/l over the amount added to the original, or ($8.02^{4} - 0.196^{6} - 0.024^{3} =$ ) $7.80^{3}$ g $SO_4^{2-}$/l from the available.

These values are in agreement with the expected results from the thiosulphate analysis.

This leaves $2.96^4$ g $S_2O_3^{2-}$/l to undergo conversion to sulphur dioxide and elemental sulphur via the reaction

$$S_2O_3^{2-} + 2\,HCl \longrightarrow 2\,Cl^- + SO_2 + S^o + H_2O.$$

| | $S_2O_3^{2-}$ | $SO_2$ | $S^o$ |
|---|---|---|---|
| g expected | $2.94^4$ | 1.6949 | 0.8483 |
| moles | 0.0265 | 0.0265 | 0.0265 |
| g found | $2.96^4 \pm 0.00^0$ | $1.677^7 \pm 0.001^7$ | $0.83^4 \pm 0.01^0$ |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = 0.5001

0.08 % error

TABLE B 38

SAMPLE N$^{0}$: A 16

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.08^{1}$ | $0.13^{8}$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.079^{2}$ | $0.046^{2}$ |
| AVAILABLE | ----- | ----- |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0666 | 0.0666 | 0.0666 |
| g expected | $7.46^{7}$ | 4.2666 | 2.1352 |
| g found | $7.46^{7} \pm 0.00^{0}$ | $4.339^{9} \pm 0.008^{6}$ | $2.16^{0} \pm 0.01^{0}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4977

error = 0.6 %

TABLE B39

SAMPLE N$^{o}$: A 17

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.08^{1}$ | $0.13^{8}$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.085^{8}$ | $0.050^{1}$ |
| AVAILABLE | ------ | ------ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ | + | $S^o$ |
|---|---|---|---|---|
| moles | 0.0666 | 0.0666 | | 0.0666 |
| g expected | $7.46^{7}$ | 4.2666 | | 2.1355 |
| g found | $7.46^{7} \pm 0.00^{0}$ | $4.352^{0} \pm 0.007^{7}$ | | $2.18^{2} \pm 0.01^{0}$ |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = 0.4977

error = 0.6 %

TABLE B40

SAMPLE N$^{0}$: B 15

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.15^{8}$ | $0.27^{0}$ |
| AVAILABLE | ------ | ------- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.267^{7}$ | $0.156^{2}$ |
| AVAILABLE | ------ | ------ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow SO_2$ | + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0659 | 0.0659 | 0.0659 |
| g expected | $7.39^{0}$ | 4.2221 | 2.1132 |
| g found | $7.39 \pm 0.00^{0}$ | $4.219^{8} \pm 0.002^{8}$ | $2.11^{4} \pm 0.00^{6}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.5010

error = 0.1 %

TABLE B41

SAMPLE N$^{0}$: B 16

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.12^4$ | $0.21^2$ |
| AVAILABLE | ----- | ----- |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $0.212^6$ | $0.124^1$ |
| AVAILABLE | ----- | ----- |

Acad breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^o$ |
|---|---|---|---|
| moles | 0.0662 | 0.0662 | 0.0662 |
| g expected | $7.42^4$ | 4.2415 | 2.1229 |
| g found | $7.42^4 \pm$ | $4.251^5 \pm$ | 2.11 $\pm$ |
| | $0.00^0$ | $0.003^8$ | $0.00^4$ |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = 0.4977

error = 0.5 %

TABLE B42

SAMPLE N$^{O}$: C 19

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.58^4$ | $7.86^1$ |
| AVAILABLE | $4.44^3$ | $7.61^2$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $7.82^7$ | $4.56^8$ |
| AVAILABLE | $7.58^4$ | $4.42^6$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^o$ |
|---|---|---|---|
| moles | 0.0265 | 0.0265 | 0.0265 |
| g expected | $2.96^4$ | 1.6949 | 0.8483 |
| g found | $2.96^4 \pm 0.00^0$ | $1.677^7 \pm 0.00^7$ | $0.83^4 \pm 0.01^0$ |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = 0.5001

error = 0.1 %

TABLE B43

SAMPLE N$^{0}$: C 20

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.62^{7}$ | $7.92^{7}$ |
| AVAILABLE | $4.48^{6}$ | $7.68^{6}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $7.91^{0}$ | $4.61^{6}$ |
| AVAILABLE | $7.66^{7}$ | $4.47^{4}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0261 | 0.0261 | 0.0261 |
| g expected | $2.92^{1}$ | 1.6917 | 0.8467 |
| g found | $2.92^{1} \pm 0.00^{0}$ | $1.666^{7} \pm 0.002^{7}$ | $0.81^{6} \pm 0.00^{8}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4895

error = 2.2 %

TABLE B44

SAMPLE N$^{0}$: C 21

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.62^{3}$ | $7.92^{0}$ |
| AVAILABLE | $4.48^{1}$ | $7.67^{7}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $7.90^{9}$ | $4.61^{6}$ |
| AVAILABLE | $7.66^{6}$ | $4.47^{4}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0261 | 0.0261 | 0.0261 |
| g expected | $2.92^{6}$ | 1.6720 | 0.8369 |
| g found | $2.92^{6} \pm 0.00^{0}$ | $1.669^{5} \pm 0.004^{4}$ | $0.83^{0} \pm 0.01^{0}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4972

error = 0.7 %

TABLE B45

SAMPLE N$^{0}$: C 22

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.75^{6}$ | $8.14^{8}$ |
| AVAILABLE | $4.61^{5}$ | $7.90^{7}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $8.13^{5}$ | $4.74^{8}$ |
| AVAILABLE | $8.11^{1}$ | $4.73^{3}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0249 | 0.0249 | 0.0249 |
| g expected | $2.79^{2}$ | 1.5951 | 0.7984 |
| g found | $2.79^{2} \pm$ | $1.589^{3} \pm$ | $0.78^{8} \pm$ |
| | $0.00^{0}$ | $0.002^{2}$ | $0.01^{2}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4958

error = 0.9 %

TABLE B46

SAMPLE N$^{0}$: C 23

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.49^{8}$ | $7.70^{6}$ |
| AVAILABLE | $4.35^{7}$ | $7.46^{5}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $7.75^{1}$ | $4.52^{3}$ |
| AVAILABLE | $7.50^{8}$ | $4.38^{2}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ | + | $S^{o}$ |
|---|---|---|---|---|
| moles | 0.0271 | 0.0272 | | 0.0272 |
| g expected | $3.05^{0}$ | 1.7425 | | 0.8722 |
| g found | $3.05^{0} \pm$ $0.00^{0}$ | $1.747^{9} \pm$ $0.002^{7}$ | | $0.85^{6} \pm$ $0.01^{6}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4897

error = 2.2 %

TABLE B47

SAMPLE N$^{0}$: C 24

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $5.93^{8}$ | $10.17^{4}$ |
| AVAILABLE | $5.79^{7}$ | $9.93^{2}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ |
|---|---|---|
| ORIGINAL | $10.13^{1}$ | $5.91^{2}$ |
| AVAILABLE | $9.88^{8}$ | $5.77^{1}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0103 | 0.0103 | 0.0103 |
| g expected | $1.61^{1}$ | 0.6598 | 0.3317 |
| g found | $1.61^{1} \pm 0.00^{0}$ | $0.913^{8} \pm 0.001^{7}$ | $0.43^{2} \pm 0.00^{8}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4728

error = 5.5 %

TABLE B48

SAMPLE N$^{0}$: C 25

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $6.26^{0}$ | $10.72^{5}$ |
| AVAILABLE | $6.11^{8}$ | $10.48^{2}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $10.75^{4}$ | $6.27^{6}$ |
| AVAILABLE | $10.51^{1}$ | $6.13^{4}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0115 | 0.0115 | 0.0115 |
| g expected | $1.28^{9}$ | 0.7367 | 0.3686 |
| g found | $1.28^{9} \pm 0.00^{0}$ | $0.735^{6} \pm 0.003^{3}$ | $0.37^{2} \pm 0.00^{8}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.5057

error = 1.0 %

TABLE B49

SAMPLE N$^{O}$: C 26

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.58^4$ | $7.85^4$ |
| AVAILABLE | $4.44^3$ | $7.61^2$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $7.82^3$ | $4.56^5$ |
| AVAILABLE | $7.58^0$ | $4.42^4$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^o$ |
|---|---|---|---|
| moles | 0.0264 | 0.0264 | 0.0264 |
| g expected | $2.96^4$ | 1.6913 | 0.8476 |
| g found | $2.96^4 \pm 0.00^0$ | $1.684^8 \pm 0.002^2$ | $0.82^8 \pm 0.01^2$ |

ratio $S^o/SO_2$ expected = 0.5005

ratio $S^o/SO_2$ found = 0.4915

error = 1.8 %

TABLE B50

SAMPLE N$^{0}$: C 27

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $4.32^{6}$ | $7.41^{2}$ |
| AVAILABLE | $4.18^{5}$ | $7.17^{0}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $7.41^{1}$ | $4.32^{5}$ |
| AVAILABLE | $7.16^{8}$ | $4.18^{3}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

$$S_2O_3^{2-} \longrightarrow SO_2 + S^0$$

| | | | |
|---|---|---|---|
| moles | 0.0287 | 0.0287 | 0.0287 |
| g expected | $3.22^{2}$ | 1.8386 | 0.9213 |
| g found | $3.22^{2} \pm$ | $1.835^{7} \pm$ | $0.91^{6} \pm$ |
| | $0.00^{0}$ | $0.004^{9}$ | $0.00^{9}$ |

ratio $S^0/SO_2$ expexted = 0.5005

ratio $S^0/SO_2$ found = 0.4990

error = 0.3 %

TABLE B 51

SAMPLE N$^{0}$: C 28

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $5.16^{4}$ | $8.84^{7}$ |
| AVAILABLE | $5.02^{3}$ | $8.60^{6}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $8.83^{1}$ | $5.15^{4}$ |
| AVAILABLE | $8.58^{8}$ | $5.01^{2}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0213 | 0.0213 | 0.0213 |
| g expected | $2.38^{4}$ | 1.3645 | 0.6817 |
| g found | $2.38^{4} \pm$ | $1.357^{2} \pm$ | $0.67^{6} \pm$ |
| | $0.00^{0}$ | $0.006^{1}$ | $0.00^{8}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4981

error = 0.5 %

TABLE B52

SAMPLE N$^{0}$: C 29

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $6.47^{4}$ | $11.09^{2}$ |
| AVAILABLE | $6.33^{3}$ | $10.85^{0}$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $11.06^{1}$ | $6.45^{5}$ |
| AVAILABLE | $10.81^{8}$ | $6.31^{3}$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^{o}$ |
|---|---|---|---|
| moles | 0.0096 | 0.0096 | 0.0096 |
| g expected | $1.07^{4}$ | 0.6150 | 0.3071 |
| g found | $1.07^{4} \pm 0.00^{0}$ | $0.596^{5} \pm 0.003^{1}$ | $0.29^{4} \pm 0.00^{8}$ |

ratio $S^{o}/SO_2$ expected = 0.5005

ratio $S^{o}/SO_2$ found = 0.4929

error = 1.5 %

TABLE B53

SAMPLE NO: C 30

$S_2O_3^{2-}$ available for conversion to $SO_4^{2-}$ from

| | as $S_2O_3^{2-}$ g/l | as $SO_4^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $6.00^2$ | $10.28^3$ |
| AVAILABLE | $5.86^1$ | $10.04^2$ |

$SO_4^{2-}$ found due to conversion from

| | as $SO_4^{2-}$ g/l | as $S_2O_3^{2-}$ g/l |
|---|---|---|
| ORIGINAL | $10.28^8$ | $6.00^4$ |
| AVAILABLE | $10.04^5$ | $5.86^2$ |

Acid breakdown of unconverted $S_2O_3^{2-}$

| | $S_2O_3^{2-} \longrightarrow$ | $SO_2$ + | $S^0$ |
|---|---|---|---|
| moles | 0.0138 | 0.0138 | 0.0138 |
| g expected | $1.54^6$ | 0.8841 | 0.4421 |
| g found | $1.54^6 \pm$ | $0.886^9 \pm$ | $0.44^0 \pm$ |
| | $0.00^0$ | $0.004^4$ | $0.01^2$ |

ratio $S^0/SO_2$ expected = 0.5005

ratio $S^0/SO_2$ found = 0.4961

error = 0.9 %

# APPENDIX C

# ATOMIC ABSORPTION ANALYSES

TABLE C1

ELEMENT: Cd

WAVELENGTH: 228.8 nm

SLIT: 4 (0.7 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 6 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 2 ppm

LOWER DETECTION LIMIT: 0.02 ppm

STANDARD STOCK SOLUTION:

1.000 g of pure cadmium metal was dissolved in a minimum of a 1:1 hydrochloric acid solution and dilute to 1000 ml yielding a 1000 ppm Cd solution.

A ten-fold dilution was carried out yielding a 100 ppm Cd solution from which all standards are made. These were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C2

PREPARATION OF STANDARDS FOR CADMIUM

| mls of Cd 100 ppm stock dilute to 100 mls | Final Cd conc. (ppm) | Absorbance |
|---|---|---|
| 1.000 | 0.000 | $0.001 \pm 0.000$ |
| 0.250 | $0.250^{3}$ | $0.027 \pm 0.000^{4}$ |
| 0.500 | $0.500^{5}$ | $0.056 \pm 0.001^{0}$ |
| 1.000 | $1.001^{0}$ | $0.106 \pm 0.001^{0}$ |
| 1.500 | $1.501^{5}$ | $0.159 \pm 0.001^{0}$ |
| 2.000 | $2.002^{0}$ | $0.208 \pm 0.000^{4}$ |

Regression Coefficient $r$ : $0.999^{8}$

Y-Intercept : $0.001^{1}$

Slope : $0.103^{6}$

TABLE C3

| SAMPLE | ABSORBANCE | CONC. Cd (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.001 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.002 ± 0.001 | ND |
| $NH_4Cl$ | 0.004 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.006 ± 0.001 | 0.049 |
| $Na_2MoO_4.2H_2O$ | 0.004 ± 0.000 | ND |
| $MnCl_2$ | 0.004 ± 0.001 | ND |
| $CaCl_2$ | 0.004 ± 0.000 | ND |
| NaCl | 0.002 ± 0.001 | ND |
| $NaHCO_3$ | 0.000 ± 0.001 | ND |
| $K_2HPO_4$ | 0.000 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.000 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C4.

ELEMENT: Pb

WAVELENGTH: 283.3 nm

SLIT: 4 (0.7 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 20 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 20 ppm

LOWER DETECTION LIMIT: 0.5 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure lead metal was dissolved in a minimum of a 1:1 nitric acid solution and diluted to volume in a 1000 ml volumetric flask, yielding a 1000 ppm Pb solution. All standards were prepared from this stock solution by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C5

PREPARATION OF STANDARDS FOR LEAD

| ml of 1000 ppm Pb stock diluted to 100 ml | Final Pb conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.001 ± 0.000 |
| 0.500 | 5.000 | 0.028 ± 0.001 |
| 1.000 | 10.000 | 0.060 ± 0.001 |
| 1.500 | 15.000 | 0.089 ± 0.001 |
| 2.0000 | 20.000 | 0.117 ± 0.001 |

Regression coefficient r : 0.9997

Y-Intercept : 0.0004

Slope : 0.0059

TABLE C6

| SAMPLE | ABSORBANCE | CONC. Pb (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.002 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.001 ± 0.001 | ND |
| $NH_4Cl$ | 0.001 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.002 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.002 ± 0.000 | ND |
| $MnCl_2$ | 0.002 ± 0.000 | ND |
| $CaCl_2$ | 0.002 ± 0.000 | ND |
| NaCl | 0.002 ± 0.000 | ND |
| $NaHCO_3$ | 0.002 ± 0.000 | ND |
| $K_2HPO_4$ | 0.002 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.002 ± 0.000 | ND |

ND = NOT DETECTED

TABLE C7

ELEMENT: Fe

WAVELENGTH: 248.3 nm

SLIT: 3 (0.2 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 30 mA

BURNER: 4 in.

FLAME: air-acetylene, oxidizing

LINEAR RANGE: 5 ppm

LOWER DETECTION LIMIT: 0.12 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure iron metal was dissolved in a minimum of a 1:1 nitric acid solution and diluted to volume in a 1000 ml volumetric flask, yielding a 1000 ppm Fe solution. A ten-fold dilution was carried out yielding a 100 ppm Fe solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C8

PREPARATION OF STANDARDS FOR IRON

| mls of 1000 ppm Fe stock diluted to 100 mls | Final Fe conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.001 ± 0.000 |
| 1.500 | 1.500 | 4.037 ± 0.001 |
| 2.000 | 2.000 | 0.050 ± 0.001 |
| 3.000 | 3.000 | 0.076 ± 0.001 |
| 4.000 | 4.000 | 0.096 ± 0.001 |
| 5.000 | 5.000 | 0.122 ± 0.001 |

Regression coefficient r: 0.9995

Y-Intercept : 0.0014

Slope : 0.0241

TABLE C9

| SAMPLE | ABSORBANCE | CONC. Fe (ppm) |
|---|---|---|
| B.S. ($H_2O$) | -0.003 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | -0.003 ± 0.001 | ND |
| $NH_4Cl$ | -0.005 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | -0.003 ± 0.000 | ND |
| $Na_2MoO_4.2H_2O$ | -0.005 ± 0.001 | ND |
| $MnCl_2$ | -0.005 ± 0.001 | ND |
| $CaCl_2$ | -0.004 ± 0.001 | ND |
| NaCl | -0.003 ± 0.000 | ND |
| $NaHCO_3$ | -0.004 ± 0.000 | ND |
| $K_2HPO_4$ | -0.003 ± 0.000 | ND |
| $FeSO_4.7H_2O$ | ---------- | NT |

ND = NOT DETECTED

NT = NOT TESTED FOR

TABLE C10

ELEMENT: Cu

WAVELENGTH: 324.7 nm

SLIT: 4 (0.7 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 15 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 5 ppm

LOWER DETECTION LIMIT: 0.09 ppm

STANDARD STOCK SOLUTION:

1.000 g of pure copper metal was dissolved in a minimum of a 1:1 nitric acid solution and diluting to 1000 ml in a volumetric flask, yielding a 1000 ppm Cu solution. A ten-fold dilution was carried out yielding a 100 ppm Cu solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C11

PREPARATION OF STANDARDS FOR Cu

| mls of 100 ppm Cu stock diluted to 100 mls | Final Cu conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.002 ± 0.001 |
| 1.000 | 1.000 | 0.039 ± 0.001 |
| 2.0000 | 2.000 | 0.077 ± 0.000 |
| 3.000 | 3.000 | 0.113 ± 0.001 |
| 4.000 | 4.000 | 0.148 ± 0.001 |
| 5.000 | 5.000 | 0.183 ± 0.001 |

Regression coefficient r: 0.9999

Y-Intercept : 0.0031

Slope : 0.0362

TABLE C12

| SAMPLE | ABSORBANCE | CONC. Cu (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.000 ± 0.000 | ND |
| $MgSO_4.7L_2O$ | 0.001 ± 0.000 | ND |
| $NH_4Cl$ | 0.001 ± 0.000 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.001 ± 0.000 | ND |
| $Na_2MoO_4.2H_2O$ | 0.000 ± 0.000 | ND |
| $MnCl_2$ | 0.000 ± 0.000 | ND |
| $CaCl_2$ | 0.000 ± 0.000 | ND |
| NaCl | 0.001 ± 0.000 | ND |
| $NaHCO_3$ | 0.001 ± 0.001 | ND |
| $K_2HPO_4$ | 0.000 ± 0.000 | ND |
| $FeSo_4.7H_2O$ | 0.000 ± 0.000 | ND |

ND = NOT DETECTED

TABLE C13

ELEMENT: Zn

WAVELENGTH: 213.9 nm

SLIT: 4 (0.7 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 10 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 1 ppm

LOWER DETECTION LIMIT: 0.018 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure zinc metal was dissolved in a minimum of a 1:1 nitric acid solution and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm Zn solution. A one-hundred-fold dilution was carried out yielding a 10 ppm Zn solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C14

PREPARATION OF STANDARDS FOR ZINC

| mls of 10 ppm stock diluted to 100 mls | Final conc. Zn (ppm) | Absorbance |
|---|---|---|
| 0.00 | 0.00 | 0.001 ± 0.000 |
| 2.00 | 0.20 | 0.037 ± 0.001 |
| 4.00 | 0.40 | 0.071 ± 0.001 |
| 6.00 | 0.60 | 0.105 ± 0.001 |
| 8.00 | 0.80 | 0.137 ± 0.001 |
| 10.00 | 1.00 | 0.170 ± 0.000 |

Regression coefficient r: 0.9998

Y-Intercept : 0.0026

Slope : 0.1684

TABLE C15

| SAMPLE | ABSORBANCE | CONC. Zn (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.003 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.003 ± 0.001 | ND |
| $NH_4Cl$ | 0.003 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.019 ± 0.001 | $0.106^5$ |
| $Na_2MoO_4.2H_2O$ | 0.002 ± 0.001 | ND |
| $MnCl_2$ | 0.002 ± 0.001 | ND |
| $CaCl_2$ | 0.003 ± 0.001 | ND |
| NaCl | 0.004 ± 0.001 | ND |
| $NaHCO_3$ | 0.004 ± 0.000 | ND |
| $K_2HPO_4$ | 0.001 ± 0.000 | ND |
| $FeSO_4.7H_2O$ | 0.002 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C16

ELEMENT: Ni

WAVELENGTH: 232.0 nm

SLIT: 3 (0.2 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 25 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 5 ppm

LOWER DETECTION LIMIT: 0.15 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure nickel metal was dissolved in a minimum of a 1:1 nitric acid solution, yielding a 1000 ppm Ni solution. A ten-fold dilution was carried out yielding a 100 ppm Ni solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimate burette to a 100 ml volumetric flask and diluting a volume with water.

TABLE C17

PREPARATION OF STANDARDS FOR NICKEL

| mls of 100 ppm Ni stock diluted to 100 mls | Final Ni conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.000 ± 0.000 |
| 1.000 | 1.000 | 0.022 ± 0.000 |
| 2.000 | 2.000 | 0.036 ± 0.001 |
| 3.000 | 3.000 | 0.052 ± 0.000 |
| 4.0000 | 4.000 | 0.069 ± 0.000 |
| 5.000 | 5.000 | 0.087 ± 0.000 |

| | |
|---|---|
| Regression coefficient | r: 0.9985 |
| Y-Intercept | : 0.0020 |
| Slope | : 0.0169 |

TABLE C18

| SAMPLE | ABSORBANCE | CONC. Ni (ppm) |
|---|---|---|
| B.S. ($H_2O$) | -0.004 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.000 ± 0.001 | ND |
| $NaHCO_3$ | -0.003 ± 0.001 | ND |
| $K_2HPO_4$ | -0.002 ± 0.001 | ND |
| NaCl | -0.003 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | -0.003 ± 0.001 | ND |
| $NH_4Cl$ | -0.003 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | -0.002 ± 0.001 | ND |
| $CaCl_2$ | -0.002 ± 0.001 | ND |
| $MnCl_2$ | -0.002 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | -0.002 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C19

ELEMENT: Sb

WAVELENGTH: 217.6 nm

SLIT: 3 (0.02 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 20 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 40 ppm

LOWER DETECTION LIMIT: 0.5 ppm

STANDARD STOCK SOLUTION:

2.743 g of potassium antimony tartarate hemihydrate ($K(SbO)C_4H_6 \cdot 1/2H_2O$) was dissolved in water and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm Sb solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C20

PREPARATION OF STANDARDS FOR ANTIMONY

| mls of 1000 ppm Sb stock diluted to 100 mls | Final Sb conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | -0.002 ± 0.001 |
| 0.500 | 5.000 | 0.015 ± 4.000 |
| 1.000 | 10.000 | 0.027 ± 0.001 |
| 1.500 | 15.000 | 0.041 ± 0.000 |
| 2.000 | 20.000 | 0.058 ± 0.000 |
| 2.5000 | 25.000 | 0.076 ± 0.000 |
| 3,000 | 30.000 | 0.088 ± 0.000 |

Regression coefficient r: 0.9987

Y-Intercept :-0.0020

Slope : 0.0030

TABLE C21

| SAMPLE | ABSORBANCE | CONC. Sb (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.000 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.003 ± 0.001 | 1.667 |
| $NaHCO_3$ | 0.004 ± 0.001 | 2.000 |
| $K_2HPO_4$ | 0.001 ± 0.001 | ND |
| NaCl | -0.001 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.003 ± 0.001 | 1.667 |
| $NH_4Cl$ | 0.000 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.001 ± 0.001 | ND |
| $CaCl_2$ | 0.006 ± 0.001 | 2.667 |
| $MnCl_2$ | 0.006 ± 0.001 | 2.667 |
| $FeSO_4.7H_2O$ | 0.006 ± 0.001 | 2.667 |

ND = NOT DETECTED

TABLE C22

ELEMENT: Mn

WAVELENGTH: 279.5 nm

SLIT: 3 (0.2 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 15 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 3 ppm

LOWER DETECTION LIMIT: 0.055 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure manganese metal was dissolved in a minimum of a 1:1 nitric acid solution and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm Mn solution. A ten-fold dilution was carried out yielding a 100 ppm Mn solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C23

PREPARATION OF STANDARDS FOR MANGANESE

| mls of 100 ppm Mn stock diluted to 100 mls | Final Mn conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.003 ± 0.000 |
| 0.500 | 0.500 | 0.027 ± 0.000 |
| 1.000 | 1.000 | 0.058 ± 0.000 |
| 1.500 | 1.500 | 0.086 ± 0.000 |
| 2.000 | 2.000 | 0.109 ± 0.000 |
| 2.500 | 2.500 | 0.138 ± 0.001 |

Regression coefficient r: 0.9993

Y-Intercept : 0.0024

Slope : 0.0542

TABLE C24

| SAMPLE | ABSORBANCE | CONC. Mn (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.000 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.000 ± 0.001 | ND |
| $NaHCO_3$ | 0.001 ± 0.001 | ND |
| $K_2HPO_4$ | 0.002 ± 0.001 | ND |
| NaCl | 0.000 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.001 ± 0.001 | ND |
| $NH_4Cl$ | 0.002 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.000 ± 0.001 | ND |
| $CaCl_2$ | 0.000 ± 0.001 | ND |
| $MnCl_2$ | ---------- | NT |
| $FeSO_4.7H_2O$ | 0.000 ± 0.001 | ND |

ND = NOT DETECTED

NT = NOT TESTED FOR

TABLE C25

ELEMENT: Cr

WAVELENGTH: 357,9 nm

SLIT: 4 (0.7 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 25 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 5 ppm

LOWER DETECTION LIMIT: 0.1 ppm

STANDARD STOCK SOLUTION:

3.735 g of potassium chromate ($K_2CrO_4$) was dissolved in water and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm Cr solution. A ten-fold dilution was carried out yielding a 100 ppm Cr solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting with water.

TABLE C26

PREPARATION OF STANDARDS FOR CHROMIUM

| mls of 100 ppm Cr stock diluted to 100 mls | Final Cr conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | -0.002 ± 0.000 |
| 0.250 | 0.250 | 0.004 ± 0.000 |
| 0.500 | 0.500 | 0.009 ± 0.000 |
| 1.000 | 1.000 | 0.024 ± 0.000 |
| 1.500 | 1.500 | 0.035 ± 0.000 |
| 2.000 | 2.000 | 0.043 ± 0.000 |

Regression coefficient r: 0.9959

Y-Intercept :-0.0015

Slope : 0.0233

TABLE C27

| SAMPLE | ABSORBANCE | CONC. Cr (ppm) |
|---|---|---|
| B.S. ($H_2O$) | -0.003 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | -0.002 ± 0.001 | ND |
| $NaHCO_3$ | 0.000 ± 0.001 | ND |
| $K_2HPO_4$ | 0.000 ± 0.001 | ND |
| NaCl | 0.001 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.001 ± 0.001 | ND |
| $NH_4Cl$ | 0.000 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.000 ± 0.001 | ND |
| $CaCl_2$ | 0.001 ± 0.001 | ND |
| $MnCl_2$ | 0.001 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.002 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C28

ELEMENT: Bi

WAVELENGTH: 223.1 nm

SLIT: 3 (0.2 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 8 mA

BURNER: 4 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 50 ppm

LOWER DETECTION LIMIT: 0.5 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure bismuth metal was dissolved in a minimum of a 1:1 nitric acid solution and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm Bi solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C29

| mls of 1000 ppm Bi stock diluted to 100 ml | Final Bi conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | -0.002 ± 0.001 |
| 0.500 | 5.000 | 0.015 ± 0.002 |
| 1.000 | 10.000 | 0.027 ± 0.002 |
| 1.500 | 15.000 | 0.036 ± 0.002 |
| 2.000 | 20.000 | 0.062 ± 0.000 |
| 2.500 | 25.000 | 0.070 ± 0.000 |
| 3.000 | 30.000 | 0.080 ± 0.000 |

Regression coefficient r: 0.9920

Y-Intercept :-0.0008

Slope : 0.0028

TABLE C30

| SAMPLE | ABSORBANCE | CONC. Bi (ppm) |
|---|---|---|
| B.S.($H_2O$) | 0.008 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.009 ± 0.001 | ND |
| $NaHCO_3$ | 0.006 ± 0.001 | ND |
| $K_3HPO_4$ | -0.003 ± 0.001 | ND |
| NaCl | 0.006 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.007 ± 0.001 | ND |
| $NH_4Cl$ | 0.005 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.007 ± 0.001 | ND |
| $CaCl_2$ | 0.005 ± 0.001 | ND |
| $MnCl_2$ | 0.005 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.006 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C31

ELEMENT: Sn

WAVELENGTH: 224.6 nm

SLIT: 3 (0.2 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 40 mA

BURNER: 2 in.

FLAME: air acetylene, oxidizing

LINEAR RANGE: 200 ppm

LOWER DETECTION LIMIT: 4.1 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure tin metal was dissolved in a 100 ml of concentrated hydrochloric acid and diluted to 1000 ml an a volumetric flask, yielding a 1000 ppm Sn solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting with water.

TABLE C32

PREPARATION OF STANDARDS FOR TIN

| mls of 1000 ppm Sn stock diluted to 100 mls | Final Sn conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.000 ± 0.000 |
| 0.500 | 5.000 | 0.002 ± 0.000 |
| 1.000 | 10.000 | 0.004 ± 0.000 |
| 2.000 | 20.000 | 0.009 ± 0.000 |
| 2.500 | 25.000 | 0.012 ± 0.000 |
| 3.000 | 30.000 | 0.015 ± 0.000 |

Regression coefficient r: 0.9972

Y-Intercept :-0.0005

Slope : 0.0005

TABLE C33

| SAMPLE | ABSORBANCE | CONC. Sn (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.006 ± 0.000 | 13.00 |
| $Na_2S_2O_3.5H_2O$ | 0.001 ± 0.000 | ND |
| $NaHCO_3$ | 0.001 ± 0.000 | ND |
| $K_2HPO_4$ | 0.001 ± 0.000 | ND |
| NaCl | 0.003 ± 0.000 | ND |
| $MgSO_4.7H_2O$ | -0.003 ± 0.000 | ND |
| $NH_4Cl$ | -0.002 ± 0.000 | ND |
| $Na_2MoO_4.2H_2O$ | -0.002 ± 0.000 | ND |
| $CaCl_2$ | 0.016 ± 0.000 | 33.00 |
| $MnCl_2$ | 0.012 ± 0.000 | 25.00 |
| $FeSO_4.7H_2O$ | -0.012 ± 0.000 | 25.00 |

ND = NOT DETECTED

TABLE C34

ELEMENT: V

318.3

WAVELENGTH: 318.4 nm

318.5

SLIT: 4 (0.7 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 40 mA

BURNER: 2 in.

FLAME: nitrous oxide-acetylene, reducing

LINEAR RANGE: 150 ppm

LOWER DETECTION LIMIT: 1.7 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure vanadium metal was dissolved in a minimum of concentrated nitric acid and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm V solution. A ten-fold dilution was carried out yielding a 100 ppm V solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C35

PREPARATION OF STANDARDS FOR VANADIUM

| mls of 100 ppm V stock diluted to 100 mls | Final V conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.001 ± 0.000 |
| 1.000 | 1.000 | 0.003 ± 0.000 |
| 2.000 | 2.000 | 0.005 ± 0.000 |
| 3.000 | 3.000 | 0.007 ± 0.000 |
| 4.000 | 4.000 | 0.009 ± 0.000 |
| 5.000 | 5.000 | 0.012 ± 0.000 |

Regression coefficient r: 0.9971

Y-Intercept : 0.0008

Slope : 0.0021

TABLE C36

| SAMPLE | ABSORBANCE | CONC. V (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.003 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.004 ± 0.001 | ND |
| $NaHCO_3$ | 0.004 ± 0.001 | ND |
| $K_2HPO_4$ | 0.003 ± 0.001 | ND |
| NaCl | 0.004 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.004 ± 0.001 | ND |
| $NH_4Cl$ | 0.004 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.005 ± 0.001 | ND |
| $CaCl_2$ | 0.005 ± 0.001 | ND |
| $MnCl_2$ | 0.003 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.005 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C37

ELEMENT: Co

WAVELENGTH: 240.7 nm

SLIT: 3 (0.2 nm)

LIGHT SOURCE: hollow cathode lamp

LAMP ENERGY: 15 mA

BURNER: 4 in.

FLAME: air acetylene

LINEAR RANGE: 5 ppm

LOWER DETECTION LIMIT: 0.15 ppm

STANDARD STOCK SOLUTION:

1.0000 g of pure cobalt metal was dissolved in a minimum of a 1:1 hydrochloric acid solution and diluted to volume in a 1000 ml volumetric flask, yielding a 1000 ppm Co solution. A ten-fold dilution was carried out yielding a 100 ppm Co solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting to volume with water.

TABLE C38

PREPARATION OF STANDARDS FOR COBALT

| mls of 100 ppm Co stock diluted to 100 mls | Final Co conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.001 ± 0.000 |
| 1.000 | 1.000 | 0.003 ± 0.000 |
| 2.000 | 2.000 | 0.005 ± 0.000 |
| 3.000 | 3.000 | 0.007 ± 0.000 |
| 4.000 | 4.000 | 0.009 ± 0.000 |
| 5.000 | 5.000 | 0.012 ± 0.000 |

| | | |
|---|---|---|
| Regression coefficient | r: | 0.9978 |
| Y-Intercept | : | 0.0010 |
| Slope | : | 0.0208 |

TABLE C39

| SAMPLE | ABSORBANCE | CONC. Co (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.003 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.004 ± 0.001 | ND |
| $NaHCO_3$ | 0.004 ± 0.001 | ND |
| $K_2HPO_4$ | 0.003 ± 0.001 | ND |
| NaCl | 0.004 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.004 ± 0.001 | ND |
| $NH_4Cl$ | 0.004 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | 0.005 ± 0.001 | ND |
| $CaCl_2$ | 0.005 ± 0.001 | ND |
| $MnCl_2$ | 0.003 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.005 ± 0.001 | ND |

ND = NOT DETECTED

TABLE C40

ELEMENT: Mo

WAVELENGTH: 313.3 nm

LIGHT SOURCE: hollow cathode lamp

SLIT: 4 (0.7 nm)

LAMP ENERGY: 30 mA

BURNER: 2 in.

FLAME: nitrous oxide-acetylene, reducing

LINEAR RANGE: 60 ppm

LOWER DETECTION LIMIT: 0.5 ppm

STANDARD STOCK SOLUTION:

1.840 g of ammonium paramolybdate ($NH_4O_{24}.4H_2O$) was dissolved in water and diluted to 1000 ml in a volumetric flask, yielding a 1000 ppm Mo solution. All standards were prepared by delivering the appropriate volume from a 5 ml Dosimat burette to a 100 ml volumetric flask and diluting with water to volume.

TABLE C41

PREPARATION OF STANDARDS FOR MOLYBDIMUM

| mls of 1000 ppm Mo stock diluted to 100 mls | Final Mo conc. (ppm) | Absorbance |
|---|---|---|
| 0.000 | 0.000 | 0.000 ± 0.000 |
| 0.500 | 5.000 | 0.016 ± 0.000 |
| 1.000 | 10.000 | 0.033 ± 0.000 |
| 1.500 | 15.000 | 0.055 ± 0.000 |
| 2.000 | 20.000 | 0.077 ± 0.000 |
| 2.500 | 25.000 | 0.099 ± 0.000 |
| 3.000 | 30.000 | 0.121 ± 0.000 |

Regression coefficient r: 0.9982

Y-Intercept : -0.0041

Slope : 0.0041

TABLE C42

| SAMPLE | ABSORBANCE | CONC. Mo (ppm) |
|---|---|---|
| B.S. ($H_2O$) | 0.001 ± 0.001 | ND |
| $Na_2S_2O_3.5H_2O$ | 0.001 ± 0.001 | ND |
| $NaHCO_3$ | 0.003 ± 0.001 | ND |
| $K_2HPO_4$ | 0.001 ± 0.001 | ND |
| NaCl. | 0.001 ± 0.001 | ND |
| $MgSO_4.7H_2O$ | 0.002 ± 0.001 | ND |
| $NH_4Cl$ | 0.002 ± 0.001 | ND |
| $Na_2MoO_4.2H_2O$ | ---------- | NT |
| $CaCl_2$ | 0.002 ± 0.001 | ND |
| $MnCl_2$ | 0.002 ± 0.001 | ND |
| $FeSO_4.7H_2O$ | 0.002 ± 0.001 | ND |

ND = NOT DETECTED

NT = NOT TESTED FOR