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METHODS FOR THE DETERMINATION OF INORGANIC CONSTITUENTS IN TRENCH LEACHATES FROM SHALLOW LAND RADIOACTIVE WASTE DISPOSAL SITES

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NOTICE

METHODS FOR THE DETERMINATION OF INORGANIC CONSTITUENTS IN TRENCH LEACHATES FROM SHALLOW LAND RADIOACTIVE WASTE DISPOSAL SITES

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March, 1980

INFORMAL REPORT

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INTRODUCTION

The methods described are derived from established procedures frequently involving modifications due to the unique case at hand. The value of this manual is that all the recommended techniques have been tested on samples of chemically complex radioactive waste waters and therefore are applicable to a varied range of aqueous samples having different matrices.

Although specifically written as a guide for the inorganic analyses of low-level radioactive waste waters, the methods described are also applicable to waste waters derived from land fills, waste disposal plants and sewers.

It is the intention of the author that the procedures described will be usable by any competent analyst. In several methods, reagents or equipment are cited by proprietary name. This is not intended as an endorsement and equivalent products may be substituted.

This manual contains methods for the determination of inorganic constituents in waters obtained from shallow land radioactive waste disposal sites.

Preparation and Storage of Samples

Samples received in our laboratory are stored prior to filtration at 4°C in anoxic glass collection bottles. The samples are analyzed for dissolved ammonia immediately after anoxic filtration. Analysis of other nutrients such as phosphate, nitrate, nitrite and sulfate are completed within 48 hours. The samples are stored at 4°C in tightly capped polypropylene bottles or, more recently, in sterile nitrogen purged glass serum bottles.

AMMONIA (By Probe)

1. Application

This method is applicable to dissolved ammonia in a homogeneous liquid solution.

2. Summary of Method

The ammonia electrode uses a hydrophobic gas-permeable membrane which permits dissolved ammonia to diffuse through until the partial pressure of ammonia is the same on both sides. The partial pressure of ammonia will then be proportional to the concentration as determined by Henry's Law.

$$K_h = \frac{[NH_3]}{P_{NH_3}} \sim = 56 \text{ moles/liter-atom } (25^{\circ}C)$$

Standards and samples should contain about the same concentration level of dissolved species at a given temperature. The method of standard additions is preferred over direct reading methods.

3. Interferences

Volatile amines interfere with measurements. Mercury, silver, copper, gold, nickel, cobalt, cadmium, and zinc form complexes with ammonia. Most of these metal interferences can be removed by hydroxide precipitation or complex formation. Mercury interference can be eliminated by the addition of iodide.

Water vapor can move across the membrane and change the concentration of the filling solution thus causing an electrode drift. Water vapor transport is not a problem when electrode and sample temperatures are the same and the osmotic strength of the solution is below 1 molar. The following procedure is used most often in our laboratory.

(1) dilute samples with high osmotic strength, high ammonia concentration

(2) add 10 molar NaOH to samples of low osmotic strength

(3) add 4.25 g solid $NaNO_3$ to each 100 mL of filling solution to samples of high osmotic strength (above 1 molar) and low ammonium levels (below 10^{-5} molar).

Surfactants wet the membrane and the liquid solution can then penetrate. The probe must then be placed in a closed system where the electrode can respond to ammonia in the gas phase.

4. Apparatus

A 407A specific ion meter with an Orion ammonia electrode model 95-10.

5. Reagents

DISTILLED OR DEIONIZED WATER

Preparation: Pass distilled or deionized water through an ion-exchange column containing a strongly acidic cation exchange resin, such as Dowex 50W-X8.

10 M NaOH
Sodium Hydroxide	40 g
Distilled Water	100 mL

Preparation: To prepare 10 M NaOH, add 40 g reagent-grade NaOH to 80 mL distilled water in a 100-mL volumetric flask, dissolve, and dilute to volume with distilled water, or dilute 80 mL of commercially available 50% NaOH to 100 mL with distilled water.

STANDARDS
STOCK STANDARD, 100 mg N/L
Ammonium Chloride (NH_4Cl)	0.382 g
Distilled Water	1000 mL

Preparation: Dissolve 0.382 g of ammonium chloride in distilled water and dilute to 1 liter.

STANDARD SOLUTION

0.1 M ammonium chloride standard, Orion Cat. No. 95-10-06,
or 1000 mg N/L as nitrogen standard, Orion Cat. No. 95-10-07.

Preparation: To prepare a 0.1 M ammonium chloride standard from laboratory supplies, add 0.535 g reagent-grade NH_4Cl to 50 mL distilled water in a 100-mL volumetric flask, stir to dissolve, and dilute to volume with distilled water. To prepare a 1000 mg/L as N standard from laboratory supplies, add 0.382 g reagent-grade NH_4Cl to 50 mL distilled water in a 100-mL volumetric flask. Stir to dissolve and dilute to volume with distilled water.

INTERNAL FILLING SOLUTION

Orion Cat. No. 95-10-02.

6. Procedure

Obtain a rough concentration range by direct measurement. Then adjust the concentration of sample and standards for the method of standard additions. To measure ammonia in samples containing surfactants adjust the sample pH to 12 with 10 M NaOH. Alizarin yellow b is a good indicator for this. Immediately transfer the solution to a 125-mL Erlenmeyer flask fitted with a rubber stopper with a hole large enough to hold the electrode.

Direct measurement using 407A specific ion meter-ppm

(1) Prepare 100 and 10 mg N/L standards by serial dilution of the 1000 mg N/L standard.

(2) Place electrode in the 10 mg N/L standard. Add 1 mL 10 M NaOH to each 100 mL of standard. Turn the function switch to X^-. Adjust the meter needle to "1" (center scale) on the red logarithmic scale with the calibration control. Use magnetic stirring throughout the procedure.

(3) Rinse electrode and place in the 100 m/L standard. Add 1 mL 10 M NaOH to each 100 mL of standard. Stir thoroughly. Turn the temperature compensator knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.

(4) Rinse electrode and place in sample. Add 1 mL 10 M NaOH to each 100 mL of sample. Stir thoroughly. Multiply the meter reading on the red logarithmic scale by 10 to determine sample concentration in mg/L of nitrogen.

Standard addition using 407A specific ion meter

(1) Prepare a standard solution about a hundred times as concentrated as the sample concentration by diluting the 0.1 M or 1000 mg N/L standard.

(2) Add 1 mL 10 M NaOH to each 100 mL sample. Place the electrode in the solution. When checking a direct measurement, leave the electrode in 100 mL of the same sample used for direct measurement. Use magnetic stirring throughout the known addition procedure.

(3) Turn the function switch to X⁻. Turn the slope indicator and dial to the percent slope of the electrode as determined in the daily electrode check. Turn the temperature compensator knob until the white arrow points to the solution temperature. Adjust the calibration control knob to set the needle to "∞" on the green increment scale.

(4) Pipet 1 mL standard solution into 100 mL sample. Stir thoroughly. Record the reading, Q, from the green increment scale.

7. Calculations

(1) To determine the total sample concentration, use the following equation:

$$C_0 = (Q/100)C_s$$

where:

C_0 = total sample concentration
Q = reading from green increment scale
C_s = concentration of added standard

(2) To check a direct measurement, compare results of the two methods. If they agree within ±4%, the measurements are probably good. If the known standard addition result is much larger than the direct measurement, the sample may contain complexing agents, and measurements should be confirmed by another method of analysis.

8. References

1. Orion Research Instruction Manual for the Ammonia Electrode 95-10
   Orion Research Incorporated Form IM95-10/679, 1976. Available from
   Orion Research, 380 Putnam Avenue, Cambridge, Massachusetts 02139.

AMMONIA (Colorimetric)

1. Application

This automated procedure for the determination of ammonia is applicable in the range 0-10 mg/L of ammonia in filtered liquid samples. Approximately sixty samples per hour can be analyzed.

2. Summary of Method

The Berthelot reaction involves the formation of a green compound believed to be related to induphenol when a solution of an ammonium salt is added to sodium phenoxide followed by the addition of sodium hypochlorite. A solution of potassium sodium tartrate is added to the sample stream to eliminate the precipitation of the heavy metals.

3. Interferences

Air must be scrubbed through acid to remove ammonia before introduction into the system.

In some instances a high salt concentration may interfere. The previously described probe procedure is then the method of choice.

In samples of high ammonia concentration, dilution of sample eliminates refractive index interferences.

In other complex matrices the method of standard additions may be used by spiking successive sample cups containing the same volume with increasing amounts of a concentrated standard.

4. Apparatus

Technicon auto analyzer equipped with manifold #116-D186-01.

5. Reagents

ALKALINE PHENOL (Technicon No. T01-0115)

Sodium Hydroxide (NaOH)	200	g
Liquified Phenol, 88% (C_6H_5OH)	276	mL
Distilled Water, q.s.	1000	mL
Brij-35 Wetting Agent	0.5	mL
(Technicon No. T21-0010-01)		

Preparation: Dissolve 200 g of sodium hydroxide to approximately 600 mL of distilled water contained in a vessel surrounded by circulating cold water. Slowly add while cooling 276 mL liquified phenol (88%) stirring continuously. Dilute to 1 liter with distilled water and store in a brown bottle. Add 0.5 mL of Brij-35 per liter.

SODIUM HYPOCHLORITE (Technicon No. T01-0114)
Household bleach having 5.25% available chlorine may be used.

POTASSIUM SODIUM TARTRATE

Potassium Sodium Tartrate	150 g
$(KNaC_4H_4O_6 \cdot 4H_2O)$	
Distilled Water	1000 mL
Brij-35	0.5 mL

Preparation: Dissolve 150 g of potassium sodium tartrate in 850 mL distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 per liter.

STANDARDS
STOCK STANDARD, 100 mg N/L

Ammonium Chloride (NH_4Cl)	0.382 g
Distilled water	1000 mL

Preparation: Dissolve 0.382 g of ammonium chloride in distilled water and dilute to 1 liter.

6. Procedure

Samples and wash water should be adjusted to a pH of 6.5 - 7.0 using 0.1 N HCl or 0.1 N NaOH. Arrange ammonia standards in decreasing concentrations of ammonia and alternate each sample and standard with a wash cup of ultrapure pH adjusted water. Ultrapure water may be obtained by additional treatment of laboratory grade water by a Millipore "Milli-Q" or similar system.

7. Calculations

Prepare appropriate curve and determine concentration value of samples directly. This then is compared to values obtained using the ammonia probe.

8. References

1. D.D. Van Slyke and A.J. Hiller, J. Bio. Chem., Vol. 2, 1933, p. 499.

2. J. Fiore and J.E. O'Brien, "Ammonia Determination by Automatic Analysis", Wastes Engineering 33, 352 (1962). Available in public technical libraries.

AMMONIA IN WATER AND WASTEWATER
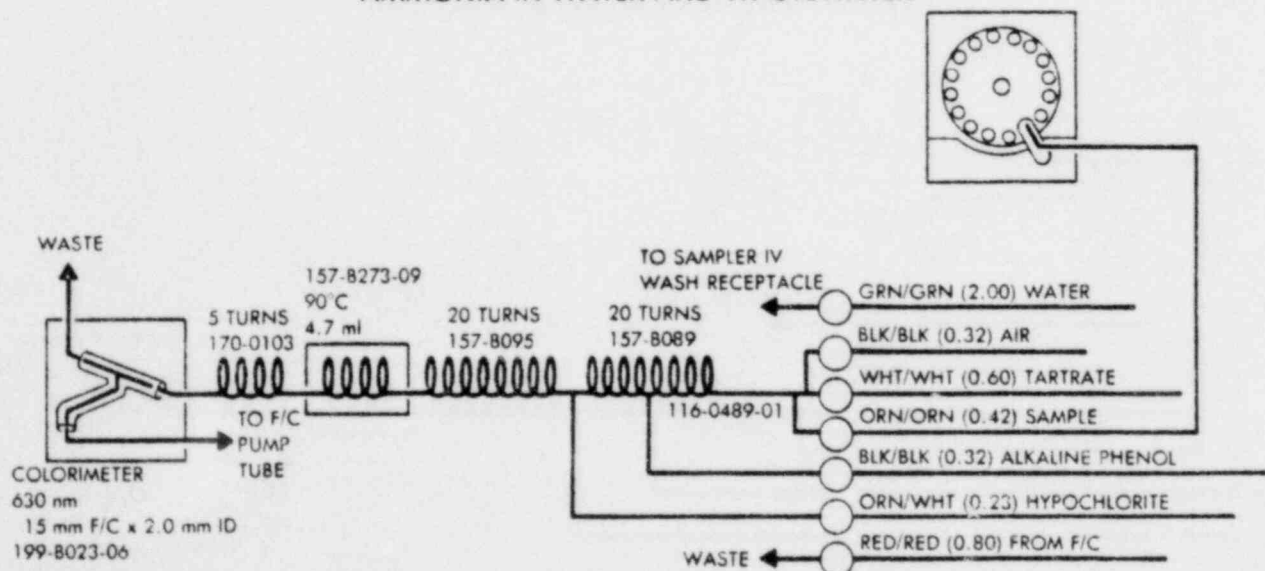
1. Application

This automated method is applicable to filtered waters in the ranges of 0.2-10 mg/L and 2-100 mg/L. Approximately forty samples per hour can be analyzed.

2. Summary of Method

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of non-ionic but soluble mercuric chloride. In the presence of ferric ion the liberated thiocyanate forms a highly colored ferric thiocyanate complex, the color intensity being proportional to the original chloride concentration.

3. Interferences

Filtration just prior to analysis is desirable. In our laboratory the samples are injected into the sample cups utilizing a Millipore millex sterile 0.45 um filter.

4. Apparatus

Technicon Auto Analyzer Manifold No. 116-0051-01

5. Reagents

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MERCURIC THIOCYANATE (STOCK)
    Mercuric Thiocyanate (Hg (SCN)₂)          4.17 g
    Methanol, (CH₃OH)                    1000    mL
```

Preparation: Transfer 500 mL of methanol into a 1-liter volumetric flask containing 4.17 g of mercuric thiocyanate and dissolve. Dilute to volume with methanol, mix and filter through filter paper.

```
FERRIC NITRATE, 20.2% (Stock) (Technicon No. T01-0028)
    Ferric Nitrate (Fe (NO₃)₃·9H₂O)        202   g
    Nitric Acid, Concentrated (HNO₃)       31.5 mL
    Distilled Water                       1000   mL
```

Preparation: Place the ferric nitrate in a 1 liter volumetric flask, and add approximately 500 mL of distilled water. Shake until all the ferric nitrate is dissolved. Carefully add the concentrated nitric acid to the flask, and mix, bring to volume with distilled water. Filter through an analytical grade of filter paper and store in a sealed amber reagent bottle.

```
CHLORIDE COLOR REAGENT (Technicon No. T01-0352)
    Mercuric Thiocyanate (Stock)           150   mL
    Ferric Nitrate 20.2% (Stock)           150   mL
        (Technicon No. T01-0028)
    Distilled Water                       1000   mL
    Brij-35, 30% Solution                  1.0  mL
        (Technicon No. T21-0110)
```

Preparation: Place 150 mL of mercuric thiocyanate into a 1-liter volumetric flask. Add 150 mL of 20.2% ferric nitrate, and mix. Dilute to volume with distilled water. Add 1 mL of Brij-35 per liter.

DILUENT WATER, 10 mL/L   -35 (.2-10 mg/L Range)
    Distilled Water   1000   mL
    Brij-35, 30% solution   10   mL

Preparation: Add 10 mL of Brij-35, 30% solution, to 1 liter of distilled water and mix thoroughly.

DILUENT WATER, 1 mL/L Brij-35 (2-100 mg/L Range)
    Distilled water   1000   mL
    Brij-35, 30% solution   1   mL

Preparation: Add 1 mL of Brij-35, 30% solution, to 1 liter of distille water and mix thoroughly.

STANDARDS
STOCK SODIUM CHLORIDE STANDARD SOLUTIONS
    Stock A, 1000 mg/L Cl (for 2-100 mg/L Range)
    Stock B, 100 mg/L Cl (for 0.2-10 mg/L Range)

STOCK SOLUTION A, 1000 mg/L Cl
    Sodium Chloride (NaCl)   1.648   g
    Distilled Water   1000   mL

Preparation: Dissolve 1.648 g of sodium chloride in about 600 mL of distilled water. Dilute to 1 liter with distilled water and mix thoroughly.

STOCK SOLUTION B, 100 mg/L Cl
    Sodium Choride   0.165   g
    Distilled Water   1000   mL

Preparation: Dissolve 0.165 g of sodium chloride in about 600 mL of distilled water. Dilute to 1 liter with distilled water and mix thoroughly.

6. Procedure

A series of standards corresponding to the anticipated concentration range of the samples are analyzed. Technicon advises that the range of analysis for this manifold is 0.2-100 mg/L. However, because this chemistry does not conform to Beer's law and produces several predictable slope changes, it is found to be more practical to analyze in concentration ranges of 0.2-10 mg/L and 2-100 mg/L. These concentration ranges approximately correspond to the linear portions of the curve. At all times the sample is "bracketed" by standards, i.e., a standard with a concentration above and below that of the sample is analyzed on the same sampler tray. Water blanks of the diluent water are also run routinely.

Ideally the standards would be prepared having the same chemical matrix as the samples. However, due to the complexity of the samples received, duplicating the chemical composition is difficult. We have found a hundred-fold dilution and analyses at the lower concentration range to be quite satisfactory.

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7. Calculations

Compute concentration of samples by comparing with standard curve.

8. References

1. J.E. O'Brien, "Automatic Analysis of Chlorides in Sewage", *Wastes Engineering* 33, 670-672 (December 1962).[a]

2. D.M. Zall, D. Fisher, and M.D. Garner, *Anal. Chem.* 28 (1956).[a]

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[a]Available in public technical libraries.

CHLORIDE IN WATER AND WASTEWATER

TO SAMPLER IV
WASH RECEPTACLE

GRN/GRN (2.00) WATER

BLK/BLK (0.32) AIR

WASTE — WHT/WHT (0.60)

MICRO PROBE

SAMPLER IV

WASTE

14 TURNS
116-0152-02

5 TURNS
170-0103

BLK/BLK (0.32) AIR

ORN/GN (.1) SAMPLE

GRY/GRY (1.0) DILUENT WATER

GRY/GRY (1.00) COLOR REAGENT

GRY/GRY (1.00) FROM F/C

A10

116-0489-01

021-G001-01

TO F/C
PUMP TUBE

COLORIMETER
480 nm
15 mm F/C
162-8040

WASTE

0.034" POLYETHYLENE

COIL
170-0103

GRY/GRY (1.0)   DILUENT H$_2$O

OPTIONAL DILUENT SYSTEM
FOR CONCENTRATED SAMPLES

NOTE: FIGURES IN PARENTHESES SIGNIFY
FLOW RATES IN ML/MIN.

FLUORIDE

1. Application

This method is applicable to fluoride in a homogenous liquid solution which does not contain highly polar solvents.

2. Summary of Method

Fluoride is determined with a specific ion electrode consisting of a single-crystal lanthanum fluoride membrane and an internal reference. The crystal is an ionic conductor in which only fluoride ions are mobile. The potential developed across the membrane in the Orion 94-09 probe is proportional to the fluoride ions in solution and is measured against an external reference with the Orion 407A specific ion meter.

3. Interferences

Fluoride forms complexes with aluminum, silicon, iron (+3) and other polyvalent cations. The extent of complexation depends on the concentration of the above cations, the total fluoride concentration, the pH of the solution and the total ionic strength of the solution.

Addition of TISAB to fluoride standards and samples buffers the pH between 5.0 and 5.5 to avoid hydroxide interferences or the formation of hydrogen complexes of fluoride. It is advisable to check the pH of the buffered samples prior to analysis.

4. Apparatus

A 407A specific ion meter with an Orion fluoride electrode.

5. Reagents

TOTAL IONIC STRENGTH ADJUSTOR (TISAB III Orion Cat. No. 94-09-11)
    Sodium Fluoride (NaF)   0.221 g
    Distilled Water   100   mL

Preparation: Dissolve 0.221 g of sodium fluoride in distilled water and dilute to 100 mL.

6. Procedure

Obtain a rough concentration range by direct measurement. Then, adjust the concentration of sample and standards for the method of standard additions. Direct measurement using 407A specific ion meter is as follows:

(1) Prepare a 10 mg/L fluoride as F^- standard by serial dilution of the 100 mg/L standard. Place 50 mL of 10 mg/L standard and 50 mL of 100 mg/L standard into separate 250-mL beakers. Add 50 mL TISAB II or IV, or 5 mL TISAB III, to each 50 mL standard. Use the nominal values of the standards in calibrating

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the electrodes; e.g., if a 100 mg/L standard is diluted with TISAB, the reading obtained is still designated "100 mg/L".

(2) Place electrodes in the 10 mg/L standard. Turn Function Switch to X⁻. Stir thoroughly. Adjust the meter needle to "1" (center scale) on the red logarithmic scale with the Calibration Control.

(3) Rinse electrodes, blot dry, and place in the 100 mg/L standard. Stir thoroughly. Turn the Temperature Compensator knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.

(4) Transfer 50 to 100 mL of sample to a 150-mL plastic beaker. Add 50 mL TISAB II or IV, or 5 mL TISAB III, to each 50 mL sample.

(5) Rinse electrodes, blot dry, and place in sample. Stir thoroughly. Multiply the meter reading on the red logarithmic scale by 10 to determine the sample concentration in mg/L.

(6) Recalibrate every 1 or 2 hours. If the ambient temperature has not changed, repeat step 2. If the temperature has changed, repeat steps 2 and 3.

Known Addition

Known addition is convenient for measuring occasional samples because no calibration is needed. Since an accurate measurement requires that the concentration double as a result of the addition, sample concentration must be known within a factor of three. Total concentration of fluoride can be measured in the absence of complexing agents down to 2×10^{-5} M fluoride or in the presence of a large excess (50 to 100 times) of complexing agent if there is a high level of fluoride (over 10^{-2} M) in solution. Known addition is a convenient check on the results of direct measurement.

Using the 407A Specific Ion Meter

(1) When measuring an occasional sample, add 50 mL TISAB II or IV to 50 mL sample, or add 5 mL TISAB III to 50 mL sample. Place the electrodes in the solution. When checking a direct measurement, leave the electrodes in 100 mL of the same sample used for direct measurement. Use magnetic stirring throughout the known addition procedure.

(2) Prepare a standard solution about a hundred times as concentrated as the sample concentration by diluting the 0.1 M or 100 mg/L standard. Add 50 mL TISAB II or IV, or 5 mL TISAB III, to each 50 mL standard. Use the nominal value of the standard in calculating results; e.g., if a 100 mg/L standard is diluted with TISAB, the standard is still designated "100 mg/L".

(3) Set the Function Switch to X⁻. Turn the Slope Indicator dial to the percent slope of the electrode as determined in the daily electrode check. Turn the Temperature Compensator knob until the white arrow points to the solution temperature. Adjust the Calibration Control knob to set the needle to "∞" on the green increment scale.

(4) Pipet 1 mL standard solution into 100 mL sample. Stir thoroughly. Record the reading, Q, from the green increment scale.

7. Calculations

To determine the total sample concentration, use the following equation:

$$C_o = (Q/100)C_s$$

where:

C_o = total sample concentration
Q = reading from green increment scale
C_s = concentration of added standard before addition of TISAB

To check a direct measurement, compare results of the two methods. If they agree within $\pm 4\%$, the measurements are probably good. If the known addition result is much larger than the direct measurement, the sample probably contains complexing agents.

For example, suppose that the meter reading, Q, after the addition of 100 mg/L standard, was 3.5. Sample concentration then is:

$$
\begin{aligned}
C_o &= (Q/100)C_s \\
&= (3.5/100) \times 100 \\
&= 3.5 \text{ mg/L}
\end{aligned}
$$

If a result of previous direct measurement had been in the range 3.4 to 3.6 mg/L, the result is probably good.

8. References

1. Orion, "Fluoride Electrode", U.S. Patent No. 3, 431, 182, March 4, 1969. Information available from Orion, 380 Putnam Avenue, Cambridge, Massachusetts 02139.

NITRATE AND NITRITE

1. Application

This method may be used to determine nitrite alone or the sum of nitrite plus nitrate nitrogen in the 0-2 mg/L range.

2. Summary of Method

The nitrate is reduced to nitrite by a copper-cadmium column. The nitrite ion is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-(1-napthyl)-ethylenediamine dihydrochloride to form a red colored compound.

3. Interferences

Large concentrations of metal ions particularly divalent copper and mercury will form a colored complex having absorption bands in the 520 nm region. This may be compensated for only by spiking the standard with the determined concentration of these ions. Hence, standards must be prepared for each individual sample matrix.

Highly turbid samples are pre-treated off-line with zinc sulfate and then filtered using an in-line filter cartridge, such as millipore millex filters, just prior to analysis.

In most trench water smaples it is necessary to add EDTA to eliminate the interference from iron.

Samples that contain large amounts of organic are extracted with chloroform to facilitate good hydrolysis through the column.

All samples must be pH adjusted to 6-8 prior to analysis as acid will destroy the cadmium column.

4. Apparatus

A Technicon Auto Analyzer with manifold No. 116-D049-01. The manifold has a three way valve in line to permit the column to be by-passed for nitrite analysis.

Preparation of column:

A purple/purple Auto Analyzer I pump tube is used for the reductor column. Before filling the column prepare the cadmium.

Cadmium powder is obtained from E. M. Laboratories, Elmsford, NY 10523, (40-60 mesh). It is then ground and carefully sieved. The fraction which passes through a 20 mesh sieve but is retained on a 40 mesh sieve is used. All ferrous metal is removed by a magnet.

The powder is then degreased with acetone and air dried. The cadmium is then placed in a small beaker and covered with water. Add conc. HNO_3 dropwise until nitrogen dioxide is evolved. This addition pits the surface of the powder. Next rinse thoroughly (10 times) with distilled water then treat the cleaned cadmium repeatedly with 50 mL portions of 2% w/v copper sulfate until the blue color does not fade. Rinse thoroughly with 1% NH_4Cl to remove all collodial cadmium.

The cadmium is then packed in the column using a large disposable syringe fitted with a tygon sleeve. This permits back-flushing. Condition the column with 50 mL of a mid-range standard prior to analysis.

5. Reagents

GRANULATED CADMIUM (E. M. Laboratories)
STANDARDS
STOCK STANDARD A, 100 mg N/L

Potassium Nitrate (KNO_3) (Technicon No. T13-5074)	0.722	g
Distilled Water	1000	mL
Chloroform ($CHCl_3$)	1	mL

Preparation: Dissolve 0.722 g of potassium nitrate in distilled water and dilute to 1 liter. Store in a dark bottle. Add 1 mL of chloroform as a preservative.

STANDARDS
NITRITE NITROGEN STANDARD, 100 mg N/L

Sodium Nitrite ($NaNO_2$)	0.493	g
Distilled Water	1000	mL

Preparation: Dissolve 0.493 g of sodium nitrite in distilled water and dilute to 1 liter. Store in a dark bottle. Add 1 mL of chloroform.

COLOR REAGENT

Sulfanilamide ($C_6H_8N_2O_2S$)	20	g
Concentrated Phosphoric Acid (H_3PO_4)	200	mL
N-1-Naphthylethylenediamine Dihydrochloride ($C_{12}H_{14}N_2 \cdot 2HCl$)	1	g
Distilled Water	2000	mL
Brij-35 (Technicon No. T21-0110)	1.0	mL

Preparation: To approximately 1500 mL of distilled water add 200 mL of concentrated phosphoric acid and 20 g of sulfanilamide. Dissolve completely. Heat, if necessary. Add 1 g of N-1-naphthylethylenediamine dihydrochloride and dissolve. Dilute to 2 liters. Add 1.0 mL of Brij-35. Store in a brown bottle, preferably flushed with nitrogen and keep in refrigerator.

AMMONIUM CHLORIDE - EDTA SOLUTION

Ammonium Chloride	10	g
Disodium ethylendiamine tetracetate	1.7	g
Distilled Water	1000	mL

Preparation: Dissolve 10 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 mL of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide, add 0.5 mL Brij-35, dilute to 1 liter, use for analysis when Fe is present.

ZINC SULFATE SOLUTION

Zinc Sulfate $ZnSO_4 \cdot 7H_2O$	100	g
Distilled Water	1000	ml

Preparation: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

SODIUM HYDROXIDE SOLUTION, 6N

Sodium Hydroxide NaOH	240	g
Distilled Water	1000	mL

Preparation: Dissolve 240 g NaOH in approximately six hundred mL distilled water, cool and dilute to 1 liter.

DILUTE HYDROCHLORIC ACID, 6N

Conc. Hydrochloric Acid	50	mL
Distilled Water	100	mL

Preparation: Dilute 50 mL of conc. HCl to 100 mL with distilled water.

COPPER SULFATE SOLUTION, 2%

Copper Sulfate $CuSO_4 \cdot 5H_2O$	20	g

Preparation: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 mL of distilled water and dilute to 1 liter.

6. Procedure

Ideally samples are analyzed immediately after filtering or refrigerated at 4°C.

Sample Pre-Treatment

Turbidity removal

Add the zinc sulfate solution, 1 mL for each mL of sample and mix thoroughly. Add sufficient sodium hydroxide solution to obtain a pH of 10.5, let sample stand and filter through a glass fiber filter.

Organic extraction

Extract the organics from the aqueous solution using two 10 mL portions of chloroform for each 20 mL sample portion.

pH adjustment

Using HCl or NaOH, the pH is adusted off-line to between 6 and 8.

A series of standards corresponding to the 0.01 - 2.0 mg N/L concentration range are analyzed. The samples are loaded with a mid-range standard every five samples and an ultrapure water blank after each group of ten.

7. Calculations

Compute concentration of samples by comparing with standard curve.

8. References

1. L.J. Kamphake, S.A. Hannah, and J.M. Cohen, Automated Analyses for Nitrate by Hydrazine Reduction, Water Research 1, 206 (1967).[a]

2. J. Fiore and J.E. O'Brien, "Automation in Sanitary Chemistry - parts 1 and 2, Determination of Nitrates and Nitrites", Wastes Engineering 33, 128 and 238 (1962).[a]

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[a]Available in public technical libraries.

NITRATE AND NITRITE IN WATER AND WASTEWATER
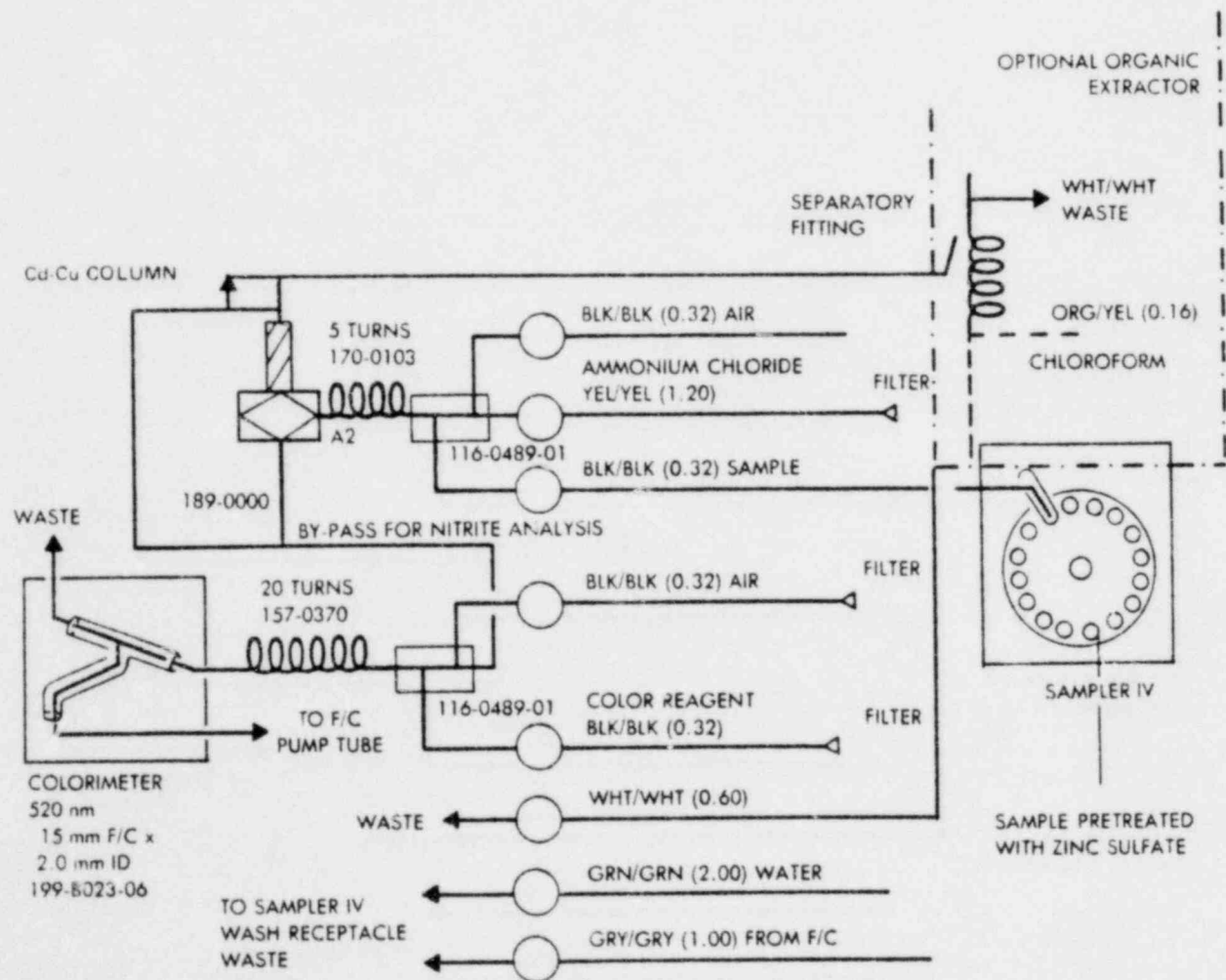
NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES IN
ML/MIN.
*0.034 POLYETHYLENE

1. Application

This method is applicable to dissolved ortho-phosphate in the range 0.2-10 mg/L in water.

2. Summary of Method

The determination of ortho-phosphate depends on the formation of a molybdo-phosphoric acid which is reduced to a molybdenum blue complex by reaction with ascorbic acid.

3. Interferences

An excess of dissolved silica interferes, but the magnitude of this inter-ference can be estimated by analyzing for dissolved SiO_2 and PO_4 simultane-ously. Interference from nitrite or sulfide ions can be minimized by adding an excess of saturated potassium permanganate solution.

Interference from sample color, turbidity, etc., is determined by running sample color blanks; that is, repeating the analysis using 0.1 N H_2SO_4 rather than the ammonium molybdate reagent.

Iron above 50 mg/L can cause an erroneously positive value.

4. Apparatus

Technicon auto analyzer equipped with manifold No. 116-D136-01.

5. Reagents

ASCROBIC ACID REAGENT

Ascorbic Acid, U.S.P. ($C_6H_8O_6$)	17.6 g
Acetone (CH_3COCH_3)	50 mL
Distilled Water	1000 mL
Levor IV (technicon No. T21-0332)	0.5 mL

Preparation: Dissolve 17.6 g of U.S.P. quality ascorbic acid in approxi-mately 600 mL of distilled water containing 50 mL of acetone. Mix and dilute to 1 liter with distilled water. Add 0.5 mL of Levor IV per liter of reagent.

AMMONIUM MOLYBDATE REAGENT

Ammonium Molybdate $(NH_4)_6 Mo_7 O_{24} \cdot 4H_2O$	10 g
Sulfuric Acid 2.2N	1000 mL

Preparation: Dissolve 10 g of ammonium molybdate in 1 liter of 2.2N sul-furic acid (62 mL of concentrated sulfuric acid, sp.gr. 1.84). Filter and store in an amber bottle. Discard if discolored.

STANDARD
STOCK STANDARD, 100 mg/L PO4
        Anhydrous Potassium Dihydrogen
            Phosphate (KH2PO4)   0.143 g
        Concentrated Sulfuric Acid   1   mL
        Distilled Water   1000   mL

Preparation: Dissolve the anhydrous potassium dihydrogen phosphate in approximately 600 mL of distilled water. Add 1 mL of sulfuric acid and dilute to 1 liter with distilled water.

6. Procedure

All glassware should be well rinsed and care exercised in the use of detergents which frequently contain phosphates. If a manifold employing Brij-35 was used prior to phosphate analysis it is recommended that the flow cell of the colorimeter be flushed with a solution of 5 mL of Levor IV/liter of water.

7. Calculations

The concentration of samples is read by comparing with a standard curve. Subtract any sample color value determined.

8. References

1. ASTM "water", 1978 Annual Book of ASTM Standards, part 31, R.P. Lukens, Ed. (American Society for Testing and Materials, Pa. 1978). Available from the ASTM, 1916 Race Street, Philadelphia, Pennsylvania 19103.

ORTHO PHOSPHATE IN WATER AND WASTEWATER

SAMPLER IV

WASTE

TO SAMPLER IV
WASH RECEPTACLE

GRN/GRN (2.00) WATER
BLK/BLK (0.32) AIR
ORN/WHT (0.23) AMMONIUM MOLYBDATE
ORN/ORN (0.42) SAMPLE
ORN/WHT (0.23) ASCORBIC ACID
WHT/WHT (0.60) FROM F/C

37°C
157-8273-03
5 TURNS
170-0103
5 TURNS
170-0103
00000   0000   A10   0000
116-0489-01
WASTE

COLORIMETER
660 nm
15 mm F/C x 2.0 mm ID
199-8023-06

* NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES
IN ML/MIN.

-19-
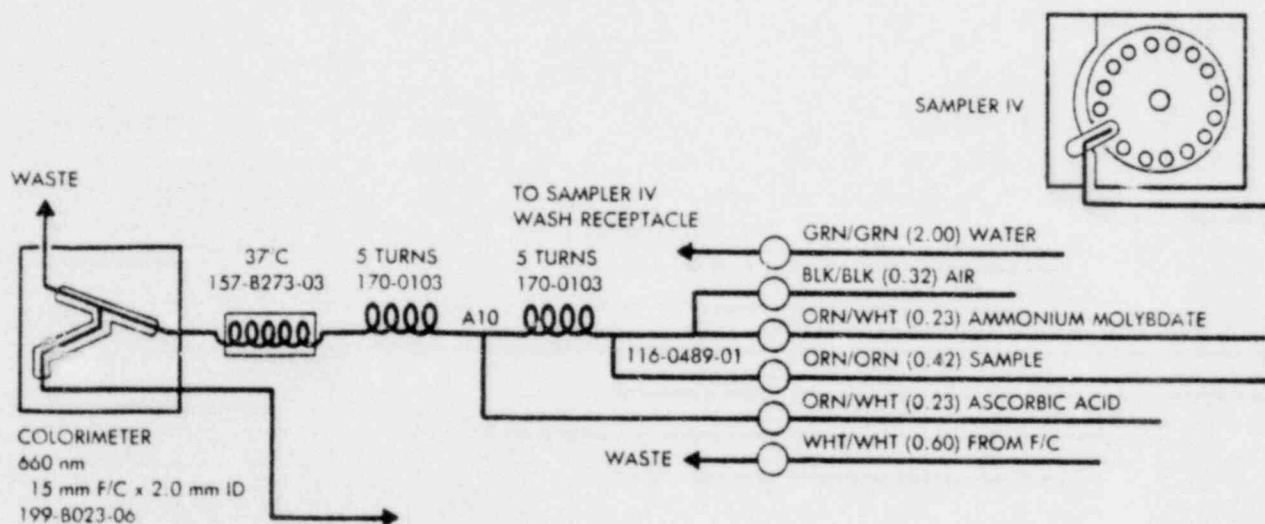
SILICATE

1. Application

This method is applicable to the determination of monomeric reactive silica in the 0.2-10 mg/L range.

2. Summary of Method

Ammonium molybdate reacts with dissolved silica in acid medium to form a silcomolybdate complex. This is reduced to molybdenum blue by ascorbic acid.

3. Interferences

Phosphate also reacts with ammonium molybdate to form molybdophosphoric acid. This complex is destroyed with oxalic acid. Tannin, large amounts of iron color, turbidity and sulfide interfere. Sulfide may be removed by boiling the acidified sample prior to analysis. Turbidity and color are corrected for by running sample color blanks; that is, repeating the analysis using 0.1 N H_2SO_4 rather than the ammonium molybdate reagent. Tannin interference is controlled by the addition of oxalic acid. The method of standard additions is suggested for dealing with iron interferences.

4. Apparatus

Technicon auto analyzer equipped with manifold #116-0056-01.

5. Reagents

AMMONIUM MOLYBDATE REAGENT (Technicon No. T01-5050)
Ammonium Molybdate
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ 10   g
Sulfuric Acid, 0.1 N   1000   mL

Preparation: Dissolve 10 g of ammonium molybdate in 1 liter of 0.1 N sulfuric acid (2.8 ml concentrated sulfuric acid, sp. gr. - 1.84/L). Filter and store in an amber plastic container.

OXALIC ACID
Oxalic Acid $(H_2C_2O_4)$
(Technicon No. T11-5051)   50   g
Distilled Water   1000   mL

Preparation: Dissolve 50 g of oxalic acid in 900 mL of distilled water and dilute to 1 liter.

ASCORBIC ACID REAGENT
Ascorbic Acid, U.S.P. $(C_6H_8O_6)$
(Technicon No. T11-5070)   17.6   g
Acetone (CH_3COCH_3)
(Technicon No. T21-5071)   50   mL
Distilled Water, q.s.   1000   mL
Levor IV (Technicon No. T21-0332)   0.5   mL

Preparation: Dissolve 17.6 g of U.S.P. quality ascorbic acid in 500 mL of distilled water containing 50 mL of acetone. Mix and dilute to 1 liter with distilled water. Add 0.5 mL of Levor IV per liter of reagent.

STANDARDS
STOCK STANDARD, 100 mg/L SiO_2
    Sodium Metasilicate Nonahydrate
      ($Na_2SiO_3 \cdot 9H_2O$)
      (Technicon No. T13-5080)   0.473 g
    Distilled Water   1000   mL

Preparation: Dissolve 0.473 g of sodium metasilicate nonahydrate in 1 liter of recently boiled and cooled distilled water. Store this stock solution in a tightly stoppered plastic bottle.

6. Procedure

The use of glassware should be avoided. A dilution of sample is usually necessary. This is accomplished in line by adding an injection of polished water after the sampler and decreasing the size of the sampler tubing. An orange-green sampler tube and gray water tube have been most satisfactory. Standards are then made to be 10 times more concentrated.

The method of standard additions may be used by spiking successive sample cups containing the same volume with increasing amounts of a concentrated standard. However, we have found the off-line preparation of samples for standard addition to be more accurate.

7. Calculations

The concentration of samples is initially determined by comparing with a standard curve. Subtract any sample color value contribution determined.

The concentration of sample as determined by standard addition is calculated by extrapolation thru the origin and that value multipled by any dilution factors.

8. References

1. APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Waste Water, 13th edition, 303-306 (1971). Available in public technical libraries.

SILICATES IN WATER AND WASTEWATER

WASTE

TO SAMPLER IV
WASH RECEPTACLE

22 TURNS
157-0320

20 TURNS
157-8089

GRN/GRN (2.00) WATER

BLK/BLK (0.32) AIR

GRY/GRY (1.00) WATER

157-8095
20 TURNS

116-0489-01

ORN/ORN (0.42) MOLYBDATE

ORN/GRN (.10) SAMPLE

TO F/C
PUMP TUBE

BLK/BLK (0.32) OXALIC ACID

COLORIMETER
660 nm
15 mm F/C x 2.0 mm ID
199-B023-06

ORN/ORN (0.42) ASCORBIC ACID

WASTE

GRY/GRY (1.00) FROM F/C

*STD SPIKE (AUTOMATED STD. ADD.)

ORN/GRN
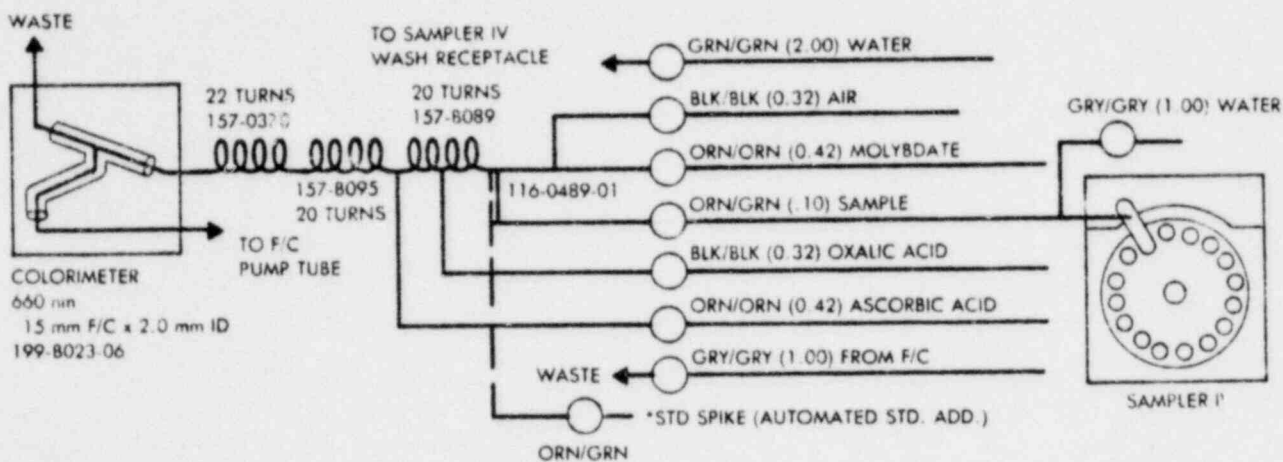
SAMPLER I'

*For automated std addition, the sample is run using

(1) H_2O

(2) a std soln equal to the initial concentration of the sample

(3) a std soln equal to 2 × the initial conc. of the sample

NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES IN
ML/MIN.

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1. Application

This automated method is applicable to filtered waters in the range of 10 to 300 mg SO_4/L. Approximately fifteen samples per hour can be analyzed.

2. Summary of Method

Sulfate is reacted with barium chloride at a pH of 2.5-3.0 to form barium sulfate. Excess barium then reacts with methylthymol blue to form a blue-colored chelate at a pH of 12.5-13.0. Initially the reagents are prepared to be equimolar in barium chloride and methylthymol blue, thus the amount of uncomplexed grey methylthymol blue, measured at 460 nm, is equal to the sulfate present.

3. Interferences

Cations such as calcium, aluminum and iron interfere by complexing the methylthymol blue. These ions are removed by passage through an ion-exchange column of Dowex-50W-X8. In most instances, a length of resin-filled .018-ID-tubing may be put in line. For samples of unusual ionic concentration pretreatment utilizing a standard ion exchange column is recommended.

As $BaSO_4$ is appreciably more soluble in acids than water, precipitations of $BaSO_4$ should be made from solutions that are only slightly acidic. It is therefore advisable to adjust the pH of samples prior to analysis. In samples displaying unusual buffering action, an off-line pH check of the sample/reagent combination is necessary to assure a pH of 2.5-3.0. An in line addition of a citrate buffer is suggested in those instances where voluminous quantities of samples display a wide variation in pH. The buffer addition is accomplished by means of an injection fitting prior to the mixing coil on the commercially available manifold.

4. Apparatus

Technicon auto analyzer equipped with MTB manifold No. 116-D096-01 and 460 nm filters. Additional p/p pump tubing or .018-I.D.-glass tubing and injection fitting No. 116-0489-01.

5. Reagents

STANDARD STOCK SOLUTION

Preparation: Dissolve 1.47 g of sodium sulfate in water, dilute to 1 liter.

BARIUM CHLORIDE SOLUTION
      Barium Chloride Dihydrate
         ($BaCl_2 \cdot 2H_2O$)   1.526   g
      Reagent Grade Water   1000   mL

Preparation: Dissolve 1.526 g of barium chloride dihydrate in approximately 600 mL of water. Dilute to 1000 mL. Store in a brown polyethylene bottle.

METHYLTHYMOL BLUE REAGENT
Methylthymol Blue	0.1182	g
Barium Chloride Solution	25	mL
Hydrochloric Acid (1.0 N HCl)	4	mL
Reagent Grade Water	71	mL
Ethanol	500	mL

Preparation: Dissolve 0.1182 g of methylthymol blue in 25 mL of barium chloride solution. Add 4 mL of 1.0 N HCl. Add 71 mL of water and dilute to 500 mL with ethanol. Check pH of solution to be 2.6. Store in an amber glass bottle and prepare fresh daily.

BUFFER pH 10.5 $\pm$ 0.5
NH_4Cl	6.75	g
NH_4OH Concentrated (28M)	57	mL
Reagent Water	1000	mL

Preparation: Dissolve 6.75 g of NH_4Cl in 500 mL of water. Add 57 of concentrated NH_4OH and dilute to 1 liter with water. Store in a brown polyethylene bottle.

BUFFERED EDTA
Tetrasodium EDTA	40	g
Buffer pH 10.5	1000	mL

Preparation: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer and q.s. to 1 liter with buffer.

SODIUM HYDROXIDE 0.18 N
Sodium Hydroxide	7.2	g
Reagent Water	1000	mL

Preparation: Dissolve 7.2 g of sodium hydroxide in 800 mL distilled water. Allow to cool and dilute to volume with water.

Ion Exchange Column

The in-line column consists of "purple/purple AAI" pump tubing (2.0-mm-I.D.) or a length of glass tubing 3.6-mm-I.D. no larger than 2.0-mm-I.D. (available from Gamma, Mt. Vernon, N.Y. 10550). The Bio-Rex 70 resin is freed from fines by backflushing. A large quantity may be processed by backflushing a 17-mm by 315-mm column or burette. The ends of the purple/purple tube are plugged with glass wool, care should be taken that air is not trapped within the column and that excess glass wool does not cause back pressure.

6. Procedure

A series of standards corresponding to the anticipated concentration range of the samples are analyzed. Technicon advises that the range of analysis for this manifold is 10-300 mg/L. However, because this chemistry does not conform

-24-

to Beer's law and produces several predictable slope changes; it is found to be more practical to analyze in concentration ranges of 1-50, 20-150, 100-300. These ranges roughly correspond to the linear portions of the absorbance/concentration curve. The observed changes in slope are commonly attributed to precipitation phenomenon. At all times the sample is "bracketed" by standards, i.e., a standard with a concentration above and below that of the sample analyzed on the same sampler tray. Water blanks of the diluent water are also run routinely

Ideally, the standards would be prepared in the same chemical matrix as the samples. However, due to the complexity of the samples received, duplicating the chemical composition is impossible. It is desirable to dilute the sample and analyze at a lower concentration range whenever possible. Then the matrix of the sample closely approximates that of the water used in the preparation of the standards.

Dilution alone is not sufficient to remove suspected interferences. This is particularly true if the sample contains appreciable colloidal material or substances which pass thru a filter but interfere with the hydraulics of the manifold and flow cell. The method of additions is then recommended; determinations are verified by adding a known amount of standard to aliquots of the sample and all aliquots diluted to the same final volume. Additions of standard are made to be approximately the same concentrations as that anticipated for the diluted sample solutions.

In samples that are intensely turbid or in some manner contribute to the gray color of the uncomplexed methylthymol blue, the color value of the samples must be determined. All reagents and standards are prepared as described except no MTB is added to the MTB reagent. The pH of the solutions individually and combined is adjusted to be consistent with the methodology. The absorbance reading subsequently obtained approximates the absorbance value contributed to the system by the individual sample.

8. References

1. M.E. Gales, W.H. Kaylor, Jr., and J.E. Longbottom, "Determination of Sulfate by Automatic Colorimetric Analysis", Analyst, 93, 97 (1968). Available in public technical libraries.

SULFATE IN WATER AND WASTEWATER

TO SAMPLER IV
WASH RECEPTACLE

GRN/GRN (2.00) WATER

OPTIONAL BUFFER ADDITION

BLK/BLK (0.32) AIR

ION EXCHANGE COLUMN

170-0103-01

A2   0000
5 TURNS   116-0489-01

GRN/GRN (2.00) WATER

ORN/GRN (0.10) SAMPLE

GRY/GRY (1.00) WASTE

0.110 STANDARD
SLEEVING

30/HR.
6:1

WASTE

157-8095   157-0370

20 TURNS   22 TURNS   116-0489-01

BLK/BLK (0.32) AIR

SAMPLER IV

COLORIMETER
460 nm
15 mm F/C x 2.0 mm ID
199-B023-06

TO F/C
PUMP
TUBE

WASTE

RED/RED (0.70) METHYLTHYMOL BLUE**

ORN/GRN (0.42) SODIUM HYDROXIDE

GRN/GRN (2.00) FROM F/C**

NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES IN
ML/MIN.

*0.034 POLYETHYLENE
**SILICONE RUBBER

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METALS

(Atomic Absorption, Flame Emission Methods)

General discussion as applicable in our studies:

1. Application

These methods are applicable to cation analysis on homogeneous liquid samples.

2. Summary of Method

Atomic absorption spectrometry and flame emission are closely related analytical techniques for the quantitative determination at the part per million range or less. In both methods, a homogeneous liquid sample is aspirated into a chemical flame, where thermal and chemical reactions cause the sample to break into free atoms. These free atoms can then be observed to emit or absorb light of a specific wavelength, characteristic of the element being determined.

Flame photometry measures the amount of light emitted, whereas in atomic absorption a light beam is directed through the flame into a monochromator and onto a detector. The atoms in the flame absorb the light and re-emit it equally in all directions, hence the monochromator measures only a percentage of the original light source, those photons not scattered in the flame.

A major difference between flame emission and atomic absorption is the comparative analytical sensitivities for elements whose excited states lie about and below 3500 A. If the principle spectral line of an element is below 3500 A, then flame emission is the method of choice; above 3500 A atomic absorption provides more sensitivity.

Copper is particularly useful in that its principle absorption is 3247 A, hence it is only slightly more sensitive by absorption than by emission. This dual sensitivity makes copper standards applicable in both modes, thus providing a convenient cross-reference.

3. Interferences

Chemical interferences occur when a chemical compound is formed between the element of interest and some other material present in the sample. If the compound formed is refractory and resists atomization, the free atom concentration in the flame is lowered. Most multivalent cations and multivalent anions such as sulfate, silicate, phosphate, etc., exhibit chemical interferences. A releasing agent such as lanthanum is added as standard practice for the analysis of any Group II element and sometimes for the transition metals. Generally, chemical interferences are not significant with Group I elements, but ionization of the species depopulates both the state and excited state causing reduction in both the emission and scatter signals. To suppress this ionization effect, a surplus of a readily ionized element is added to both samples and standards.

By using the higher temperature nitrous oxide flame as the oxidant, some elements which form refractory oxides can be atomized more readily. However, the increased temperature can cause excessive ionization, necessitating the use of an ionization suppressant if the element of interest has a low ionization potential.

4. Apparatus

Perkin-Elmer atomic absorption spectrophotometer equipped with vent containing an absolute filter (Figure C.1).

A Platinum-rhodium nebulizer is recommended. Earlier analysis utilizing a corrosion resistant (Kel-F) nebulizer indicated that preferential adhesion occurred on the nebulizer surface.

5. Reagents

Standards: All standards are obtained as prepared concentrates or from a precisely weighed primary standard dissolved in an appropriate acid or base. The acid or base employed for dissolution should contain only monovalent cations and anions. In most cases the standard stock containing 1000 mg/L is adjusted with acid to a pH between 1 and 2.

Glass containers are not considered operable for the storage of standards primarily because glass surfaces are very efficient ion exchangers and will exchange polyvalent cations in the solutions for monovalent cations present in the glass. In addition, elements subject to hydrolysis will plate out. Wide capped bottles made of linear polyethylene are the containers of choice.

Standards below 1 mg/L must be prepared fresh daily. All standards should be kept in the bottle in which samples of the same concentration of the same element have been stored.

Occasionally a polyethylene bottle is blow molded in air that was too hot and some oxidation occurred at the inner surface resulting in the formation of hydroxyl or acetate groups on the surface of the plastic. These act as ion exchangers and cause an initial loss of material from a standard. Thus re-use of the same bottles for the same concentration of species conditions the container.

6. Procedure

Ideally the standards would be prepared in the same chemical and physical matrix as the samples, then any interferences that may occur in the sample will be compensated for in the standards. One commonly used method of insuring similarity of matrix is the method of Standard Additions. In this procedure known amounts of standard are added to aliquots of the sample and all samples diluted to the same final volume. The signals from the samples are plotted vs concentration of standard added, (at least three points must be linear) and the line is extrapolated beyond the origin. The concentration of the diluted sample is read at the intersection with the axis.

Secondary standardization is another technique, useful for a larger number of similar samples. One sample is analyzed by the method of standard additions
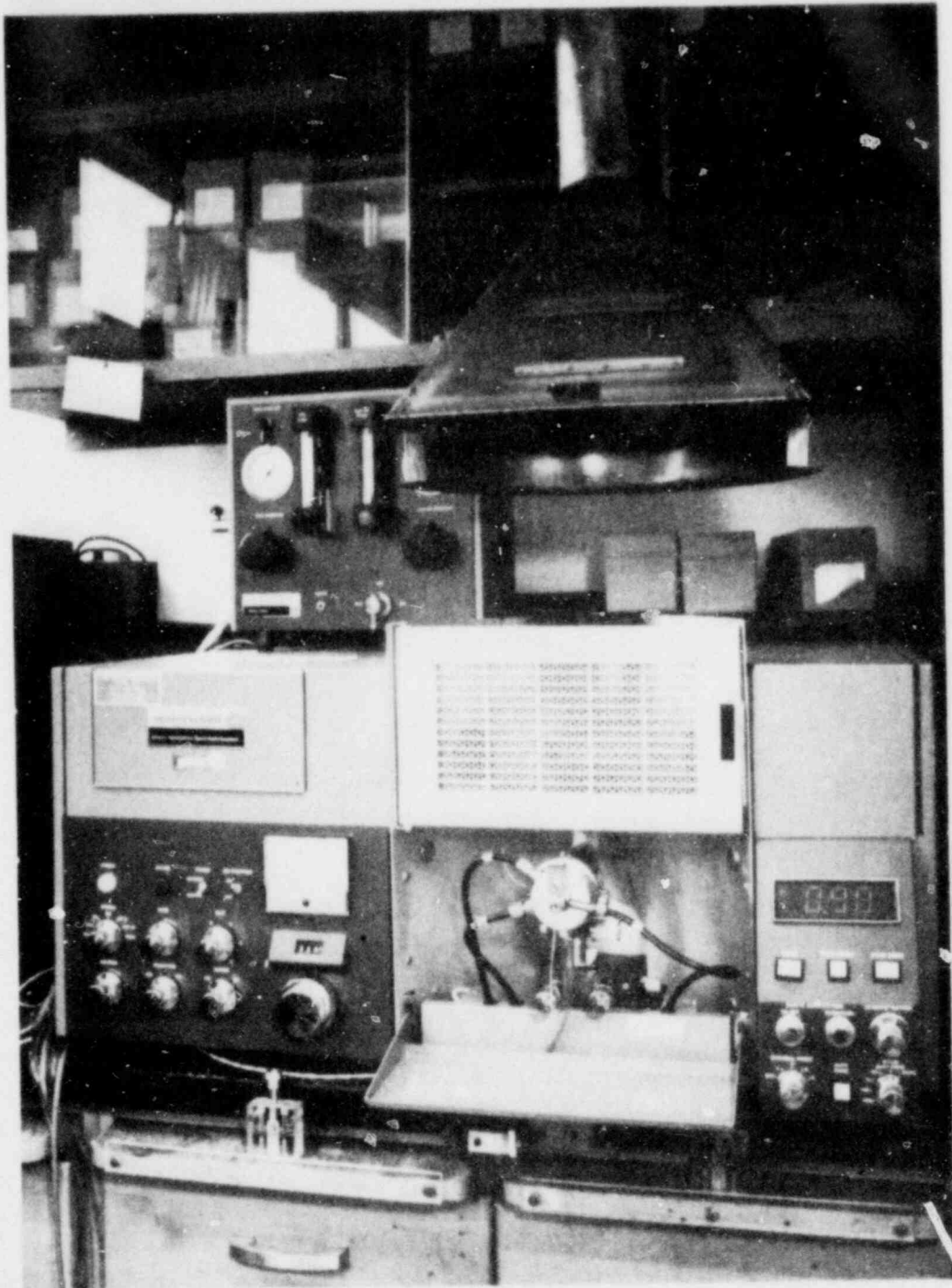
Figure 1. Atomic absorbtion apparatus vented to hood and absolute filter.

and then those solutions are used as standards for the remainder of the analysis, thus the standards are closely matched in physical and chemical properties.

7. Calculations

Waste water samples which frequently contain high solids, high acid concentrations, organic solvents or matrices which may cause light scatter or molecular absorption will require the use of background correction. This is determined by obtaining a reading at a nearby non-absorbing wavelength, or by installing a deuterum arc background corrector.

Sensitivity is defined as that concentration of an element that will produce a 1% absorption.

Detection limit is that concentration of standard that will produce a signal that is twice the mean variation in the baseline measurement.

8. References

1. H.L. Kahn, "Principles and Practice of Atomic Absorption - Trace Inorganics in Water", Advances in Chemistry Series Number 73, American Chemical Society, 1968. Available from the American Chemical Society, Washington, D.C.

2. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973.[a]

3. M.J. Fisman, "The Use of Atomic Absorption for Analysis of Natural Waters," Atomic Absorption Newsletter, Vol. 5, No. 5, September-October, 1966.[a]

4. R.A. Isaac and J.D. Kerber, "Atomic Absorption and Flame Photometry: Techniques and Uses in Soil, Plant and Water Analysis", Instrumental Methods for Analysis of Soils and Plant Tissue, SSSA, Wisconsin 1971. Available from SSSA, 677 South Segoe Road, Madison, Wisconsin 53711.

5. E.E. Pickett and S.R. Kovityohann, "Emission Flame Photometry - A New Look at an Old Method", Analytical Chemistry 41, No. 14, 28-42 (December 1969).[b]

7. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectrophotometry to Water Analysis, Determinatin of Sodium, Potassium and Calcium", Anal. Chem. 22, 667 (1950).[b]

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[a]Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.
[b]Available from public technical libraries.

CALCIUM

1. Application

Under standard conditions, the working range for calcium is linear up to 7 mg/L in aqueous solution.

2. Summary of Method

Atomic absorption, utilizing a hollow cathode lamp at 422.7 nm-visible in an acetylene/nitrous oxide flame.

The most sensitive emission wavelength is 422.7 nm. However, there is a definite emission interference in the nitrous oxide/acetylene flame at calcium concentrations greater than 4.0 mg/L.

3. Interferences

The air-acetylene flame is more stable at high calcium concentrations, but has more chemical interferences and lower sensitivity. The addition of $LaCl_3$ is suggested to suppress these interferences.

Generally the dilution of the sample to a concentration of approximately two mg/L and the use of nitrous oxide/acetylene is the method of choice. The addition of an alkali salt is necessary to suppress ionization.

Welders acetylene which contains acetone depresses the calcium absorption. We have found Matheson lab grade acetylene satisfactory as a fuel.

Most organic matrices cause a molecular absorption in the flame. This may be eliminated by using a strongly oxidizing flame at optimum adjustment.

4. Apparatus

High quality two stage regulators.

5. Reagents

CALCIUM STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5114 or dissolve 2.4973 g calcium carbonite, $CaCO_3$, with dropwise addition in a minimum volume of HCl and dilute to 1 liter with water.

POTASSIUM SOLUTION   1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in water and dilute to 1 liter.

6. Procedure

Since the absorption of Ca is dependent on the fuel to air ratio and height of the light beam the following adjustments should be made:

(1) High quality two stage regulators should be used on the gas line.

(2) Purified acetylene should be used.

(3) The flame should be ignited and water aspirated at least 15 min before analysis.

(4) Maximum hollow cathode current should be used to overcome the flame emission of calcium in nitrous oxide/acetylene flame.

(5) The flame is further optimized while aspirating a 4 mg/L standard until maximum sensitivity is reached (about 40% absorption). In making this adjustment the potassium blank solution is frequently re-zeroed so the absorption readings represent the difference between the blank and 4 mg/L calcium. Water is aspirated between standard and blank adjustments to clear the nebulizer and maintain thermal equilibrium of the burner head.

(6) Rotation of the burner head is not recommended since calcium is very emissive at high concentrations.

(7) The nebulizer uptake is adjusted to a reduced level. This is accomplished by aspirating a solution and turning the knurled end cap of the nebulizer counter clockwise until air bubbles back into the solution. Then the end cap is turned clockwise and the locking ring turned until it rests against the nebulizer end cap. Readings of standards and samples are taken by utilizing the longest instrument intergration available and averaging at least three reported values.

Although the working range for calcium is linear up to 7 mg/L it is desirable to dilute all samples to a final concentration between 1-2 mg/L.

The method of additions utilizing incremental 1 mg/L increases is desirable. (The method of additions is described in Metals, Section 6.)

In this analysis it is important to match the pH of samples and standards. An initial 1 to 100 dilution of sample utilizing the potassium solution is recommended, but in some instances this is insufficient to adjust the pH to that of the standard matrix. It is then necessary to alter the pH of the standards using 0.1 N HCl or 0.1 N NaoH.

7. Calculations

Blank correction is always necessary. Standard additions is the method of choice.

The sensitivity for calcium is 0.08 mg/L for absorption. The lower limit of detection is 0.02 mg/L units.

Concentration may be read directly or calculated from a plot of absorbance vs standard concentrations.

8. <u>References</u>

1. Perkin-Elmer, <u>Analytical Methods for Atomic Absorption Spectrophotometry</u>
   Perkin-Elmer, Connecticut 1973. Available from Perkin-Elmer, Main
   Avenue, Norwalk, Connecticut 06856.

2. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectro-
   photometry to Water Analysis, Determination of Sodium, Potassium and
   Calcium", <u>Anal. Chem.</u> 22, 667 (1950). Available in public technical
   libraries.

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CESIUM

1. Application

This method is applicable to homogeno solutions up to 15 mg/L.

2. Summary of Method

Atomic absorption utilizing an arc discharge lamp at 852.2 nm-visible, a slit setting of 4.0 nm and an air-acetylene flame.

The most sensitive emission wavelength is 852.2 nm using an air/acetylene flame.

3. Interferences

Cesium has a lower ionization potential than any other metal so alkali salts must be added. Solutions containing 1500 mg/L sodium ion are preferable. Potassium salts, while effective ionizers, tend to produce high blank values.

4. Apparatus

A second order red filter is necessary.

A continium lamp or background correction using the 848.0 nm line is utilized for emission analysis.

5. Reagents

CESIUM STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5115 or dissolve 1.267 g of cesium chloride, CsCl, in 1 liter of purified water.

SODIUM SOLUTION   1500 mg/L

Preparation: Dissolve 5.6 g of $NaNO_3$ in 1 liter of water. Store in plastic.

6. Procedure

Emission analysis was the method of choice in our laboratory. The absorption method uses a discharge lamp and considerable self-reversal occurs with this source. Occasionally metal will condense on the portion of the lamp that is in the optical beam thus causing the light to be obstructed. If this occurs, it is suggested to run the lamp for 10 minutes at a higher current (1.1 amps).

7. Calculations

Background corrections are necessary with emission.

Blank corrections for the alkali addition are necessary.

Concentrations are determined from a concentration of standards vs. absorbance plot.

For the conditions described the sensitivity is 0.3 mg/L for 1% absorption.

8. <u>References</u>

1. Perkin-Elmer, <u>Analytical Methods for Atomic Absorption Spectrophotometry</u> Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

2. E.E. Pickett and S.R. Kovityohann, "Emission Flame Photometry - A New Look at an Old Method", <u>Analytical Chemistry</u> 41, No. 14, 28-42 (December 1969). Available in public technical libraries.

1. Application

Ideally this method is used on anoxically filtered samples which were immediately acidified after filtration to a pH of 2.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at a 248.3 nm uv line with a lean air/acetylene flame.

The most sensitive emission wavelength for iron is 372.0 nm using a nitrous/oxide flame.

3. Interferences

A reduction in sensitivity occurs when samples containing nickel are acidified with nitric acid.

Multi-element lamps containing cobalt demonstrate interference with the 248.3 nm line; the 372 nm uv line is recommended.

4. Apparatus

A continium lamp, or background correction using the 247.5 nm non-absorbing Fe line, is usually necessary for low Fe concentrations in the high solids matrices.

An oxidizing flame is optimum.

Best precision and accuracy is obtained if the burner is pre-ignited and the samples aspirated in such a manner as to maintain thermal stability at the burner slot.

5. Reagents

IRON STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5120 or dissolve 1.000 g of iron wire in 50 mL of conc HNO_3 and dilute to 1 liter with purified water.

6. Procedure

Sampling, Storage, Re-dissolution, Aliquoting.

Iron in the ferrous state is relatively soluble in waters but upon exposure to air the iron is oxidized to the ferric state and may hydrolyze to form a hydrated ferric oxide. Also, "iron bacteria" are considered capable of withdrawing iron and depositing it in the form of hydrated ferric hydroxide in their secretions. Samples received in the laboratory may contain iron in true

solution, as a colloid, as a suspension, or as a complex. Thus, withdrawing a representative aliquot and assuring a homogenous solution that will not clog the nebulizer then becomes of chief concern.

Determination of Dissolved Metals

(1) Samples collected and filtered anoxically with HNO added immediately.

Dilution of samples is accomplished using an Eppendort pipette and volumetric flask. All glassware is acid washed with 1:1 HCl then rinsed with polished water.*

Concentration of Samples

Samples containing below 30 ppm Fe should be concentrated for analysis. This is accomplished by gently evaporating an HNO_3 acidified sample until a light colored quiescent residue remains. The initial volume reduction isdone using a hot plate stirrer, but the last stage evaporation is accomplished utilizing an overhead heat lamp. The walls and sides of the beaker are then washed thoroughly with 1:1 HCl and the residue re-dissolved and quantitatively transferred to a volumetric flask.

(2) Samples not collected anoxically.

(a) Those with a pH 2 or below

In samples not collected anoxically, but sufficiently acidified for the ferric hydroxide to be in solution, a simple aliquot may be withdrawn and analyzed. However, it is anticipated that the reported value, while representative of the concentration in the sample vial, will be lower than that observed in the source well or trench.

(b) Samples with a pH above 2

Samples collected non-anoxically and sent to our laboratory unacidified frequently exhibit color, turbidity and visible precipitation. For routine comparative analysis the observed precipitate is dissolved using known amounts of acid and the standards adjusted accordingly. It is necessary in these instances to repeatedly police the sides of the container and to stir the now acidified samples for several hours until the sample appears clear. Subsequent analysis of the container even after two days of acid dissolution indicates that some iron does remain imbedded in the plastic walls, thus this method of sampling produces a somewhat lowered iron value.

In those studies where it is desirable to analyze only the supernate, the sample is stirred using a teflon stir bar. An aliquot is withdrawn via a disposable syringe and then filtered just prior to analysis or dilution using a Millipore "millex" disposable filter unit.

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*Polished water in our laboratory is obtained using reagent grade water and a milli-Q system.

(3) Determinations of suspended Fe.

The 0.45 µm membrane filter is digested using HNO_3. The sample is then evaporated gently and additional HNO_3 added until the residue is clear. The residue is then dissolved in 3 mL 1:1 HCl and diluted to a known volume usually 10 mL with polished water. Appropriate dilutions are then made for analysis and the standards prepared in a similar HCl matrix.

7. Calculations

As discussed, sampling can lower the amount of Fe available for analysis. For the conditions described the sensitivity is 0.12 mg/L Fe for 1% absorption.

The method of standard additions as described in Metals, section 6c, is suggested.

Concentrations may also be determined directly.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

LITHIUM

1. Application

For the described standard conditions the working range for Li is linear up to concentration of approximately 2 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 670.8 nm visible line with an oxidizing air/acetylene flame.

The most sensitive emission wavelength is 670.8 nm with a nitrous oxide/acetylene flame.

3. Interferences

Like its sister elements in Group 1, Li is partially ionized in an air/acetylene flame. This is controlled by the addition of 1500 mg/L alkali.

4. Apparatus

A red second order interference filter is necessary to mask out the neon line emitted at the secondary 335.4 nm wavelength.

5. Reagents

LITHIUM STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5122 or dissolve 5.324 g of lithium carbonate, Li_2CO_3, in a minimum volume of 1:1 HCl and dilute to 1 liter with water.

SODIUM STOCK SOLUTION   150 g/L

Preparation: Dissolve 554.3 g of $NaNO_3$ in 1 liter of water, use 100 microliters for each 10 milliliter of sample aliquot.

6. Procedure

Because of the low Li concentrations usually found in waste waters, little dilution of the sample is necessary. The alkali spike is added in microliter amounts to adjust the total alkali concentration to 1500 mg/L.

Only high purity sodium salts should be used for the spike and a blank sodium ion solution value substracted from the absorbance or concentration reading.

Background correction is not normally necessary for the determination of lithium but blank correction for lithium contamination in reagents is an important consideration.

7. Calculations

The sensitivity for Li under the conditions described is 0.035 mg/L Li for 1% absorption. The lower limit of detection under ideal conditions is 0.001 mg/L.

Concentration values are usually read directly from the instrument display.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

MAGNESIUM

1. Application

Under standard conditions the working range for Mg is linear up to concentrations of approximately 0.5 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 285.2 nm – uv, a slit setting of 0.7 nm and an oxidizing acetylene/nitrous oxide flame.

The most sensitive emission wavelength is 285.2 nm with a nitrous oxide/acetylene flame.

3. Interferences

Silcon and aluminum depress magnesium absorption in an air/acetylene flame, but 1% lanthanum may remove this interference. Studies comparing lanthanum spiked samples in air/acetylene and non-spiked samples in the recommended N_2O/acetylene indicates that the N_2O/acetylene flame is hot enough to remove these interferences.

4. Apparatus

The analytical range may be extended by rotation of the burner head.

5. Reagent

Magnesium STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5123 or dissolve 1.854 g of Ultrex Magnesium Gluconate Dehydrate and dilute to 100 mL.

6. Procedure

The recommended dilution for trench water samples is one to five hundred. This is usually sufficient to remove any matrix effects and facilitates direct reading of sample concentrations bracketed by standards.

7. Calculations

Background correction is not normally necessary for Mg and concentration values can be determined directly from the instrument display.

The sensitivity for Mg is about 0.007 mg/L Mg for 1% absorption. The lower limit of detection is 0.005 mg/L.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

1. Application

Ideally this method is used on anoxically filtered samples which are acidified or analyzed immediately. Under standard conditions, the working range for manganese is linear up to 3 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 279.5 nm-UV, a slit width of 0.2 nm and an oxidizing air/acetylene flame.

The most sensitive emission wavelength is at 403.1 nm, but a nitrous oxide/acetylene flame is necessary.

3. Interferences

There appears to be little chemical or spectral interference in this method. The low concentration of manganese present in waste water does not permit dilution so consequent clogging of the burner head and nebulizer with accumulated salts is frequently a problem. It is therefore necessary to constantly aspirate purified water and check the zero reading.

4. Apparatus

A continuum lamp or background correction using the 282.5 nm non-absorbing line is usually necessary in these complex, high solid matrices.

An oxidizing flame is optimum.

5. Reagents

MANGANESE STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5148 or dissolve 1.000 g of Mn metal in a minimum volume of (8M) HNO_3 and dilute to 1 liter with 1% v/v HCl.

POTASSIUM SOLUTION   1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in water and dilute to 1 liter.

6. Procedure

Sampling, Storage, Redissolution, Concentrating, Extracting, and Aliquoting.

Manganese collected anoxically is generally present in the soluble divalent ionic form. When exposed to air it steadily oxidizes and precipitates from solution or becomes adsorbed on the walls of the container.

Determination of Dissolved Metals

Anoxic filtration and immediate acidification are most desirable. In those samples exposed to air without prior acidification, attempts at recovering the Mn from the container walls by acid digestion and ultra sonic cleaning have met with only limted success.

Concentration

EPA recommends that all samples below 25 mg/L be concentrated. This is consistent with the operational lower limit of detection experienced in our laboratory. Manganese may be concentrated by extraction at a pH 5-10 with APDC/MIBK. However, the presence of unusual organics and/or chealating agents in these trench waters occasionally results in an emulsion like interface between the aqueous and organic layers. Aspiration of this third interface layer with the Mn-MIBK layer results in definite matrix problems. Discarding the interface results in lowered Mn concentration values. Continuous back extraction yields an increased volume negating attempts at concentration.

Concentration by evaporation is then the method of preference. Gently evaporate 50 mL of an HNO_3 acidified sample on a Corning hot plate stirrer. The simultaneous use of an overhead heat lamp speeds the evaporation and hinders bumping. The residue is then dissolved in approximately two mL of 1:1 HCl and quantitatively transferred to a 10 mL-volumetric flask. The sample is now concentrated five times.

On occasion, the salt content is too high for the residue to be dissolved in 10 mL and a 25 mL volumetric is used, the sample is then concentrated two times.

Filtrating just prior to aspirating using a 0.45 μm membrane filter is frequently necessary in concentrated samples.

Alkali Spiking of Sample

It is recommended that all Mn analysis he done in a 1500 mg/L alkali salt solution to suppress ionization. However, studies done in our laboratory have indicated no difference in concentration value obtained between potassium spiked and unspiked samples. On occasion, attempts to add a potassium spike to a concentrated sample have resulted in the formation of salts ir 'cating a super saturated solution. The sample and salts must then be re-diss ived and diluted to a higher volume.

7. Calculations

As discussed, sampling can lower the amount of manganese available for analysis. For the conditions described the sensitivity is 0.055 mg/L Mn for 1% absorption.

Concentration may be read directly from the instrument display.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

2. W.B. Barnett, "Acid interferences in Atomic Absorption Spectrometry", Analytical Chemistry 44, 695-698 (April 1972). Available in public technical libraries.

POTASSIUM

1. Application

For atomic absorption operating parameters, the working range for potassium is linear up to concentrations of approximately 2 mg/L in filtered aqueous solution. Potassium is seventh in order of abundance and appears to exist in greater than trace amounts in the samples received in our laboratory. The recommended dilution is one to fifty. The optimum range 0.5 - 1.0 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 766.5 nm-visible line with a lean air/acetylene flame.

The most sensitive emission wavelength for potassium is 766.5 nm, although a much better signal to noise ratio is reported at the secondary line of 404.4 nm using an air/hydrogen flame.

3. Interferences

The red filter which absorbs radiation shorter than 650 nm should be used for this determination.

The effects of ionization may be substantially overcome by the use of diluent water containing 1500 mg Na/L.

4. Apparatus

A second order filter is necessary for this determination.

5. Reagents

POTASSIUM STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5128 or dissolve 1.907 g of potassium chloride (KCl) in 1 liter of water.

SODIUM SOLUTION   1500 mg/L

Preparation: Dissolve 5.6 g of $NaNO_3$ in 1 liter of water. Store in plastic.

All dilutions of standards are to be made to contain 1500 mg/L sodium.

6. Procedure

Dilution of samples are made one to fifty using the sodium spiked water.

A standard curve is obtained in the 0.05 to 1.0 mg/L range.

Because of the large salt concentration care should be taken to flush the nebulizer assembly, scrape the burner head and ream the nebulizer tube between each analysis. Frequent replacement of the nebulizer tube is necessary and there is a tendency for it to develop internal grooves and ridges. A platinum nebulizer is suggested as it is capable of withstanding the chemical and mechanical abuse incurred in this analysis. Periodic microscopic examination of the nebulizer is necessary to insure its integrity.

7. Calculations

A blank correction of the sodium solution is necessary.

Report and Precision

The sensitivity for the described conditions to 0.04 mg/L K for 1% absorption. The detection limit is 0.005 mg/L.

Concentration values are most frequently determined from a concentration vs absorbance plot.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

2. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectrophotometry to Water Analysis, Determination of Sodium, Potassium and Calcium", Anal. Chem. 22, 667 (1950). Available in public technical libraries.

1. Application

Under standard conditions the working range for sodium is linear up to concentrations of approximately 1 mg/L. As sodium is the sixth most abundant element and is commonly present in waste waters in appreciable quantities, dilution is usually necessary.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 589.0 nm visible line with an oxidizing flame. Because of the concentrated nature of the samples an initial thousand-fold dilution is recommended. In addition the analytical range may be extended by rotation of the burner head. To overcome the effects of ionization, 1500 mg K/L as KNO_3 is added to standards and samples.

The most sensitive emission wavelength for sodium is at 589.0 nm, the 330.2 nm line is less sensitive; (3 mg/L sodium for 1% absorption) and provides a convenient way to avoid further dilutions. An air/acetylene flame is suggested. There is usually good agreement between absorption and emission data using the described methods.

3. Interferences

Because of the large dilution necessary for analysis we have observed little interference in our laboratory. Comparisons between direct reading and standard addition values indicate there is negligible matrix effect. For the determination of low concentrations and all dilutions care should be taken that the standards and samples are not stored in glass.

4. Apparatus

A second order filter is necessary for flame emission determinations of sodium.

5. Reagents

SODIUM STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5131 or dissolve 2.5421 g of Sodium Chloride, (NaCl), in 1 liter of water.

POTASSIUM SOLUTION   1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in water and dilute to 1 liter.

6. Procedure

Dilution of samples are made 1 to 1000 using a 1500 mg/L potassium solution.

A standard curve is obtained in the .05 to 1.0 mg/L range, all standards being made from dilutions of a stock standard with 1500 mg/L potassium spiked water.

7. Calculations

Background correction does not appear necessary at the 589.0 nm wavelength and concentration values can be read directly from the machine display.

The sensitivity is about 0.015 mg/L for Na for 1% absorption.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

2. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectro-photometry to Water Analysis, Determination of Sodium, Potassium and Calcium", Anal. Chem. 22, 667 (1950). Available in public technical libraries.

1. Application

This method is applicable to homogenous solutions up to 10 mg/L although under standard operation, the working range is linear only up to concentrations of 5 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 460.7 nm visible, a slit setting of 0.4 nm and either a reducing air/acetylene or nitrous oxide/ acetylene flame.

The most sensitive emission wavelength is at 460.7 nm with a nitrous oxide/acetylene flame.

3. Interferences

Nitric acid, used to acidify samples after filtration reduces the absorption of a strontium solution. Care should be taken to have standards and samples equal in HNO_3 concentration.

Silicon, aluminum, and phosphorous depress the absorption in the air/acetylene flame. 1% lanthanum solution is suggested to control this interference. The use of a nitrous oxide/acetylene flame is another method. To control ionization, potassium is preferred as a spike because it has the highest ionization potential of the available alkali salts.

Analysts have reported varying levels of success with the aforementioned methods. Some manufacturers insist on the addition of 1% lanthanum, others prefer N_2O/acetylene flame, alkali spiked. To date in our laboratory, the use of N_2O/acetylene flame with potassium spiked standards and samples has been the method of choice. It affords a ready cross check of absorption and emission methods and has presented the least nebulizer problems.

4. Apparatus

The analytical ranges may be extended by rotation of the burner head.

5. Reagents

STRONTIUM STOCK STANDARD   1000 mg/L

Preparation: Markson Catalog #J 5132 or dissolve 2.415 g of strontium nitrate, $Sr(NO_3)_2$ in 1 liter of 1% v/v HNO_3.

POTASSIUM SOLUTION   1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in 1 liter of water.

6. Procedure

The method of standard additions is preferred. The initial concentration range is determined by direct reading of a potassium spike sample using N_2O/acetylene flame. Dilutions if necessary are made to obtain a final concentration of approximately 1 mg/L Sr. A second aliquot of the sample is then combined with standards to yield a final concentration of unknown plus 1 mg/L Sr. A third aliquot is then taken to yield a final concentration of unknown plus 2 mg/L Sr. All samples contain 1500 mg/L of potassium.

Sr may be extracted with 0.2 molar thenoyltrifluoracetone and MIBK at pH 10-12, but this has met with little success in our lab.

7. Calculations

The method of additions as described in Metals, section 6.

For the conditions described the sensitivity for a HNO_3 acidified standard is 0.12 mg/L Sr for 1% absorption. The sensitivity as observed in trench waters is usually lower.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Connecticut 06856.

2. V.J. Luciano, "Atomic Absorption", Pittsburgh Conference, 1975. Available for purchase from Fisher Scientific, Analytical Instrument Division Pittsburgh, Pennsylvania.