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Laboratory Procedures: Analysis of Sodium-based Dual-alkali Process Streams

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Laboratory Procedures: Analysis of Sodium-based Dual-alkali Process Streams

by

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ABSTRACT

A flue gas desulfurization (FGD) system utilizing the Combustion Equipment Associates/Arthur D. Little sodium-based dual alkali (D/A) process has been installed on Louisville Gas and Electric's Cane Run Unit No. 6. The U.S. Environmental Protection Agency has contracted with Bechtel National, Inc. to develop and implement a test program to characterize this FGD process. As part of this effort, Bechtel has established a laboratory at the site for routine chemical analyses of the pertinent process streams. The methods used for these chemical analyses comprise this laboratory procedures manual. The various procedures were extracted from three principle sources:

"Chemical Analysis Procedures for Dual Alkali Process Stream Samples", Arthur D. Little, Inc., Report No. 75833, April 22, 1976.

"Laboratory Procedures Manual", Shawnee Test Facility, Paducah, Kentucky, prepared by Bechtel National, Inc., March 1976.

Standard Methods for the Examination of Water and Wastewater, 14th Edition, (1975).

Procedures were verified by actual analyses carried out at the site in accordance with the quality assurance section of the manual. In some cases, modifications were made to adapt the standard procedures to the specific process conditions and to best utilize the resources available at the site.

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FOREWORD

This manual has been prepared by the Air Quality Group of Bechtel National, Inc. It is a source of analytical procedures for the analyses to be carried out during operation of the Combustion Equipment Associates/A.D. Little, Dual Alkali (D/A) FGD Demonstration System at the Cane Run Station of Louisville Gas and Electric Company. The bases of the methods presented in this manual have been extracted from three principal sources:

"Chemical Analysis Procedures for Dual Alkali Process Stream Samples," Arthur D. Little, Inc. Report No. 75833, 4/22/76

"Laboratory Procedures Manual", Shawnee Test Facility, Paducah, Kentucky, Prepared by Bechtel National Inc., March 1976.

Standard Methods for the Examination of Water and Wastewater, American Health Assoc., 14th Edition, (1975).

Some of the methods presented have been extensively modified from their references sources. These modifications have been made to simplify the procedures and to adapt the methods to the specific chemical process and the laboratory equipment available at the Bechtel Dual Alkali field laboratory. These modifications are currently being and will continue to be verified according to procedures presented in the quality assurance section prior to routine use in the laboratory.

It is planned to employ a Dionex Model 12 Automatic Ion Chromatograph for many routine chemical analyses. The material requisition for the I.C. is

presented in Appendix A. Back-up methods to the ion chromatograph and other primary methods are included. Table 1 is a list of the primary and backup analytical methods to be used in the D/A laboratory.

Short form procedures for many of the analytical methods presented are given in Appendix B. These short form procedures are intended as handy references in the laboratory and are not intended to replace analytical methods.

A comprehensive quality assurance (QA) program will be instituted in the D/A laboratory to ensure that the precision and accuracy of the data generated meet required limits of acceptability. Section 4 of this manual contains details of this program. Quality Assurance forms are presented in Appendix C. The D/A QA program is based on a QA program developed by LFE Environmental Analysis Laboratories, Richmond, California.

This manual is not intended to be a comprehensive laboratory manual and hence does not include routine laboratory procedures or techniques. For questions concerning routine procedures refer to "Standard Methods for the Examination of Water and Wastewater". For questions concerning laboratory safety, refer to the "Guide for Safety in the Chemistry Laboratory" published by the Manufacturing Chemists Association. Manufacturers' operating manuals will be the major source of information concerning individual instruments.

The manual is a working document and as such modifications to the procedures will be developed in the field. All modifications will be tested, documented and published. The methods presented here are those currently being used in the field laboratory as of January 1980.

Table 1

ANALYTICAL METHODS

DETERMINATION	METHOD	
	Primary	Backup
Liquor Analyses		
Calcium	EDTA Titration	Ion Chromatograph
Magnesium	EDTA Titration	Ion Chromatograph
Sodium	Flame Photometer	Specific Ion Electrode
Sulfate	Calculated	Turbidimetry
Total Sulfur	Ion Chromatograph	Turbidimetry
Chloride	Ion Chromatograph	$Hg(NO_3)_2$ Titration
Fluoride	Ion Chromatograph	Specific Ion Electrode
Nitrate	Ion Chromatograph	Chromotropic Acid
Thiosulfate	Ion Chromatograph	I_2/Thio Titration
Alkalinity	HCl Titration	
Hydroxide	HCl Titration	
Total Oxidizable Sulfur	I_2/Thio Titration	Ion Chromatograph
Dissolved Solids	Gravimetry or Calculation	
Trace Metals	Atomic Absorption	
Solid Analyses		
% HCl Insol	Gravimetry	
Suspended Solids	Gravimetry	
Alkalinity	HCl/NaOH Titration	
Carbonate	CO_2 Evolution	
Hydroxide	HCl Titration	
Sulfite (TOS)	I_2/Thio Titration	
Particle Size Distribution	Sieves/Sub-sieve analysis	
Calcium	EDTA Titration	Ion Chromatograph
Magnesium	EDTA Titration	Ion Chromatograph
Sodium	Flame Photometer	Specific Ion Electrode
Total Sulfur	LECO Sulfur Determinator	Turbidimetric
Nitrate	Ion Chromatograph	Chromotropic Acid
Chloride	Ion Chromatograph	$Hg(NO_3)_2$ Titration
Trace Metals	Atomic Absorption	

ACKNOWLEDGMENTS

The authors are indebted to the EPA Project Officer, Mr. Norman Kaplan, for his technical direction and encouragement during this project.

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R. H. Borgwardt and W. B. Kuykendal of the EPA for their review of the initial draft; S. P. Spellenberg of Arthur D. Little, Inc., for providing consultation on the newly developed procedures included in the manual; C. L. DaMassa of Bechtel for technical editing and D. Y. Kawahara and M. A. Smith, also of Bechtel, for their untiring efforts and cheerful dispositions in typing this manuscript.

Section 1

SAMPLE HANDLING

1.1 INTRODUCTION

This section outlines requirements for the collection, verification, documentation, initial preparation, storage and reporting of samples at the D/A facility. The requirements presented here are planned to minimize problems associated with sampling and unnecessary work analyzing non-representative samples. Figure 1.1 is a flow chart showing the sequence of steps from sample collection to reporting.

1.2 SAMPLE COLLECTION

Obtaining a representative sample of the D/A process streams can present special problems. The system streams contain chemical species, which react rapidly to affect pH changes and oxidation of sulfite to sulfate. Furthermore, some streams contain solids which can settle out and result in erroneous suspended solids values. The following procedure presents steps to minimize errors in sampling and to initially screen samples to minimize unnecessary work.

1. All samples must be taken (if possible) from sample taps located on a vertical run of pipe at the discharge side of a pump. Such sample points allow sampling of a well-mixed, non-stratified stream.
2. Samples must be collected in clean, labeled wide-mouth sample jars. The label must contain the name of the stream being sampled and the sample point number. The same bottles must always be used for each sample point.
3. The sample line must be purged prior to taking the sample; the sample bottle must be rinsed with sample at least three times and filled to the top to minimize entrainment of air.

4. At this point the sample pH must be determined using a calibrated portable pH meter. Record the pH value. This is the first step in sample verification. If the sample pH is outside of control limits then resample and determine pH again.

5. Quickly take samples to the laboratory for documentation, verification and analyses.

1.3 SAMPLE DOCUMENTATION

Upon returning to the laboratory all samples must be logged in the sample logbook. A daily analytical data sheet and labels for sample storage must be prepared.

Figures 1.2 and 1.3 are examples of a sample log book page and Daily Analytical Data Sheet. Figure 1.4 is an example of the information required on the sample storage tag.

1.4 SAMPLE VERIFICATION

The purpose of sample verification is to determine if the sample is valid prior to separating the solids from the liquor. Sample pH, conductivity and specific gravity (or density) are used to quickly determine sample validity. The pH is taken at the sampling port, conductivity and specific gravity are determined after the sample has been logged. If any of these analyses give values outside of the set control limits, then it is necessary to take another sample and/or check with operations to determine if they are operating at off-normal conditions. If the plant is operating at off-normal conditions, the onsite manager will decide whether to continue with analysis of the sample.

1.5 SAMPLE PREPARATION

Sample preparation consists of separating solids from liquor and drying the solids. Liquor analysis is initiated immediately following separation and liquor samples are stored in labeled plastic bottles. Portions of dried solids samples are dissolved, analyzed, and placed in labeled resealable plastic bags.

1.6 SAMPLE REPORTING

All routine analytical results must be entered in the Daily Analytical Data Sheet (see Figure 1.3). Percent ionic imbalance must be calculated for both liquor and solid sample analyses. In liquors which are analyzed for the individual sulfur species present, the Total Sulfur concentration (TS) must be calculated based on the individual sulfur species and compared to measured TS values. Any unusual circumstances concerning the sample must be noted at the bottom of the data sheet. When the sample has been analyzed, a record of analyses completed must be entered in the log book.

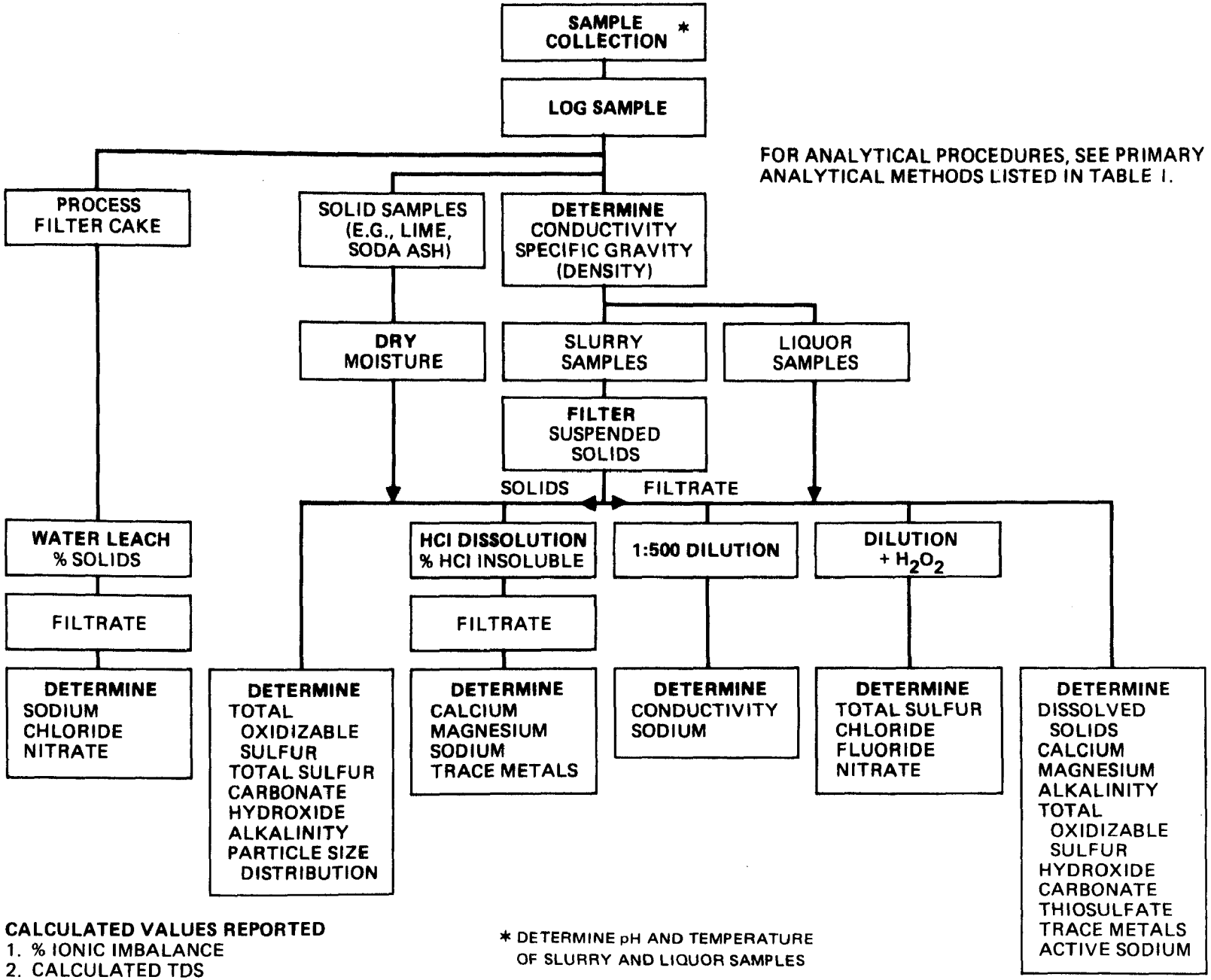


Figure 1.1 ANALYTICAL FLOW CHART

DATE	TIME	SAMPLE PT #	ANALYSES	COMPLETE/REMARKS	ANALYST

Figure 1.2

SAMPLE LOG BOOK PAGE

D/A LABORATORY

DAILY ANALYTICAL DATA SHEET

Date						
Time						
Sample Pt#						
pH						
Conductivity						
S.G. (Density)						
LIQUOR ANALYSIS						
Ca^{++}						
Mg^{++}						
Na^{+}						
F^{-}						
Cl^{-}						
$SO_3^{=}$						
$NO_3^{=}$						
$SO_4^{=}$/TS						
TDS						
Alkalinity						
OH^{-}						
$CO_3^{=}$						
TOS						
% Ionic Imbalances						
TDS (Calculated)						
Other						
SOLIDS ANALYSIS						
Ca^{++}						
Mg^{++}						
Na^{+}						
F^{-}						
Cl^{-}						
$SO_3^{=}$						
$NO_3^{=}$						
$SO_4^{=}$/TS						
Suspended Solids						
Alkalinity						
OH^{-}						
$CO_3^{=}$						
TOS						
% HCl Insol. (PIS)						
Moisture						
% Ionic Imbalance						
Other						
REMARKS						

FIGURE 1.3

CHEMIST_____

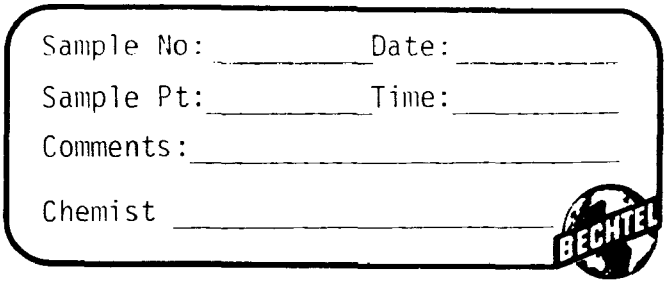


FIGURE 1.4

SAMPLE STORAGE TAG

Section 2

ION CHROMATOGRAPHY

2.1 INTRODUCTION

This section covers the use of Ion Chromatography (I.C.) for routine analytical determination of ions in dual alkali process streams. The I.C. is highly specific, rapid, requires small sample volumes, and has the ability to analyze a wide range of concentrations of several ions in a single run.

Figure 2.1 shows the flow schemes for Ion Chromatography. I.C. combines the separation capabilities of ion exchange resins with conductimetric detection. Conductimetric detection has relatively universal and linear response to solutions of ions and is therefore a good technique to monitor ion exchange separations. A suppressor column in series with the analytical column eliminates eluent background conductance and allows the use of conductivity detection. A Dionex Model 12 automatic Ion Chromatograph has been purchased for use in the D/A laboratory.

The remainder of this section presents a brief description of the Dionex Model 12 I.C. and the general run conditions for routine anionic and cationic analyses. For further information and operating instructions refer to the manufacturer's operating and maintenance manual.

2.2 MODEL 12 DESCRIPTION

2.2.1 General

The Dionex Model 12 Ion Chromatograph uses an ion exchange separator column to separate mixtures of ions, followed by an ion exchange suppressor column to remove the background eluting ions from the separator effluent while converting the sample ions to a common form. After sample species separation and eluent suppression, the effluent stream passes through a conductivity cell, which is connected to a meter and recorder for continuous monitoring of the conductivity of the sample ions. The Model 12 consists of a programmable controller unit, a conductimetric detector and meter, an eluent pump, a regenerant pump (which is used to restore the suppressor column capacity) and reservoirs for liquid storage. A system of valves directs liquid flow through the instrument.

Figure 2.2 shows the flow schemes for an anionic and for a cationic analysis systems. Only one system can be operated at one time with the Model 12. Changing from one system to the other requires changing the columns, eluents, and regenerant.

2.2.2 Dionex Model 12 Automatic Ion Chromatograph Specifications

Analytical System

- Four eluent reservoirs (including one for DI H_2O which is also used during regeneration), each a 4-liter, collapsible polyethylene bottle with quick disconnect fittings. 20-liter polyethylene bottles are used for eluent and DI H_2O storage for the Dual Alkali instrument.
- Constant volume pump, flow rates adjustable 40-460 ml/hr., 0.3% accuracy above 100 psi

- Programmable Controller allows automatic or manual selection of operating parameters. Total of 16 available controller programs with 15 steps each.

- Sample capacity of 99

Sample Injection

- Sample injection valve with 0.1 ml sample loop

Column System

- Accepts one separator and one suppressor column up to 500 mm in length and 12 mm OD. A pre-column is used in the Dual Alkali system to prolong separator column life.

Conductimetric Detector

- Offset: calibrated 0-1000 μmho/cm
  Output: 0-1 v full scale

Two modes of operation:

Manual

- Range: linear, 0.1, 0.3, 1.0, 3.0, 10, 30, 100, 300, 1000, μmho/cm full scale, logarithmic: 1-10,000 μmho/cm full scale

- Calibrate: used to check full scale deflection of the reorder

- Zero: sets zero baseline position

Automatic

- Range: linear, 0.1, 0.3, 1.0, 3.0, 10, 30, 100, 300, 1000, μmho/cm full scale, logarithmic: 1-10,000 μmho/cm full scale

Regeneration System

- Regenerant pump, water reservoir, regenerant reservoir. Manual or automatic control.

Dimensions and Weight

- 30"H x 24"W x 22"D, 140 lbs

Regeneration System

- Regenerant pump, water reservoir, regenerant reservoir. Manual or automatic control.

Dimensions and Weight

- 30"H x 24"W x 22"D, 140 lbs

Utilities

- 115 VAC 60 Hz/20 amperes
- 80-120 psi air supplied from a compressed air storage bottle

Accessories

- Sample Changer: stores and sequentially loads for analysis up to 99 discrete samples
- Recorder: Dual pen recorder provides a permanent chromatograph trace of each analysis. One pen provides a trace with 10x the sensitivity of the other pen.

Appendix A contains the material requisition for the Model 12 I.C. purchased for the D/A laboratory.

2.3 ANALYTICAL METHODS

2.3.1 Cation Anaylses (Na^+, Mg^{++}, Ca^{++})

Discussion

Samples of scrubbing liquor (or solids after dissolution) are diluted with deionized water and injected into the Model 12 I.C. The eluent used is 0.001M m-phenylenediamine dihydrochloride. Identification and quantitation are performed by comparison of retention times and peak heights respectively with those of standard solutions. Figure 2.3 shows a typical chromatogram and instrumental conditions for this analysis.

Apparatus

a. Model 12 I.C. with auto sampler and dual pen recorder

b. 6x250 mm Alkaline Earth Separator column

c. 9x250 mm Alkaline Earth Suppressor column

d. 3x150 mm Cation pre-column

Reagents

a. m-Phenylenediamine Dihydrochloride (0.001M) Eluent.
Dissolve 0.724 grams m-phenylenediamine dihydrochloride with 8 ml of 1N HNO_3 in 4 liters deionized water. Prepare fresh eluent weekly. Note: the addition of HNO_3 to the eluent has been found to give better resolution of the magnesium peak.

b. Cation Pre-Column Cleaning Eluent (3N HCl).
Dilute 775 ml concentrated hydrochloric acid in 4 liters deionized water. This eluent is used to remove substances from the resin bed which adversely affect its capacity. One 15 minutes flush followed by 1 5-10 hour deionized water rinse constitutes one cleaning cycle.

c. Regeneration Solution (0.5N NaOH).
Dissolve 80 grams of NaOH in 4.0 liters deionized water.

d. Calcium Standard Solution (1000 mg/liter).
Dissolve 2.500 grams of dried $CaCO_3$ by dropwise addition of concentrated HCl then dilute to one liter with deionized water.

e. Magnesium Standard Solution (1000 mg/liter).
Dissolve 10.136 grams undried $MgSO_4 \cdot 7H_2O$ in one liter of deionized water. Determine exact concentration by EDTA titration.

f. Potassium Standard Solution (1000 mg/liter).
Dissolve 1.907 grams dried KCl in one liter deionized water.

g. Sodium Standard Solution (1000 mg/liter).
Dissolve 2.542 grams dried NaCl in one liter deionized water.

h. Mixed Cation Standard Solution.
(5 mg/l Ca^{++}, 5 mg/l Mg^{++}, 5 mg/l Na^{+}).

Add in a 1 liter volumetric flask and dilute to one liter with deionized water the following quantities of 1000 mg/l standard solutions.

Calcium solution	:	5 mls
Magnesium solution	:	5 mls
Sodium solution	:	5 mls

Procedure

a. Place 5-10 mls of the diluted scrubbing liquor or dissolved solids solution into the auto sampler test tubes. Record sample numbers and order of position in the sampler rack.

b. Before the first sample and after every 10 samples, place a test tube of cation standard solution, a duplicate sample and a sample spiked with a known amount of standards. Record rack positions.

c. Set-up the Model 12 I.C. for alkaline earth cation analysis. Insure that the proper columns are installed, the proper eluents and regenerant are in the instrument, and that the analytical system has been flushed well with deionized water.

d. Check eluent flow rate, inspect system for leaks, and zero conductivity meter.

e. After a steady baseline has been obtained, initiate automatic operation by programming the controller memory and pushing the start/step button. Refer to the Dionex "Operating and Maintenance Manual" for programming instructions.

f. After ten samples have been analyzed (or at least once per day) regenerate the suppressor column and flush the system with deionized water.

g. Identify and quantitate the sample ions by comparing the chromatograms of the samples with those of the standards (retention times and peak heights).

Reference

Analysis of Ions in Flue Gas Scrubber Solutions, Application Notes #12, Dionex Corporation, September 1, 1978.

2.3.2 Anion Analyses (F^-, Cl^-, NO_3^-, $SO_3^=$, $SO_4^=$)

Discussion

Samples of scrubbing liquor (or solids after dissolution) are oxidized with H_2O_2 and diluted with deionized water then injected into the Model 12 I.C. The eluent used is 0.003M $NaHCO_3$/0.0024M Na_2CO_3. Identification

and quantitation of the sample ions are performed by comparison of retention times and peak heights respectively with those of standard solutions. Figure 2.4 shows a typical chromatogram and instrumental conditions for this analysis.

Apparatus

a. Model 12 I.C. with autosampler and dual pen recorder.

b. 3x500 mm Anion Separator column

c. 6x250 mm Anion Suppressor column

d. 3x150 mm Anion pre-column

Reagents

a. Sodium carbonate-bicarbonate eluent (0.003M $NaHCO_3$/0.0024M Na_2CO_3). Dissolve 1.008 grams dried $NaHCO_3$ and 1.018 grams dried Na_2CO_3 in 4 liters deionized water.

b. Anion Precolumn Cleaning Eluent (0.1M Na_2CO_3). Dissolve 42.400 grams dried Na_2CO_3 in deionized water.

c. Regeneration Solution (1N H_2SO_4). Carefully add 111 mls concentrated H_2SO_4 to 3 liters deionized water and dilute to 4 liters.

d. Fluoride Standard Solution (1000 mg/liter). Dissolve 2.210 grams dried NaF in 1 liter of deionized water.

e. Chloride Standard Solution (1000 mg/liter). Dissolve 1.648 grams dried NaCl in 1 liter deionized water.

f. Nitrate Standard Solution (1000 mg/liter). Dissolve 1.371 grams dried $NaNO_3$ in 1 liter deionized water.

g. Sulfite Standard Solution (1000 mg/liter). Dissolve 1.300 grams of dried $NaHSO_3$ in approximately 100 ml deionized water. add approximately 300 ml formaldahyde solution (37%) and dilute to 1 liter with deionized water.

h. Sulfate Standard Solution (1000 mg/liter). Dissolve 1.814 grams dried K_2SO_4 in 1 liter deionized water.

i. Mixed Anion Standard Solution
(3 mg/l F^-, 4 mg/l Cl^-, 30 mg/l NO_3^-, 50 mg/l $SO_3^=$, 50 mg/l $SO_4^=$)

Add in a 1 liter volumetric flask containing approximately 300 ml formaldahyde solution (37%) and dilute to one liter with deionized water the following quantitities of 1000 mg/l standard solutions:

Fluoride solution : 3 mls

Chloride solution : 4 mls

Nitrate solution : 30 mls

Sulfite solution : 50 mls

Sulfate solution : 50 mls

Procedure

a. Place 5-10 mls of the diluted scrubbing liquor or dissolved solids solution into the autosampler test tubes. Record sample numbers and order of position in the sampler rack.

b. Before the first sample and after every 10 samples place a test tube of anion standard, a duplicate sample and a sample spiked with a known amount of standards. Record position of each.

c. Set-up the Model 12 I.C. for anion analysis. Insure that the proper columns have been installed and allowed to equilibrate, the proper eluents and regenerant are in the instrument, and that the analytical system has been flushed well with deionized water and then eluent.

d. Check eluent flow rates, inspect system for leaks and zero conductivity meter.

e. After a steady baseline has been obtained, initiate automatic operation by programming the controller memory and pushing the START/STEP button.

f. After ten samples have been analyzed (or at least once a day) regenerate the suppressor column and flush the system with deionized water.

g. Identify and quantitate the sample ions by comparison of the chromatograms of the samples and standards (retention times and peak heights).

References

a. Analysis of Ions in Flue Gas Scrubber Solutions, Application Notes #12, Dionex Corporation, September 1978.

b. Dionex Auto Ion System 12 Analyzer Instrument Manual, Dionex Corporation, Sunnyvale, California.

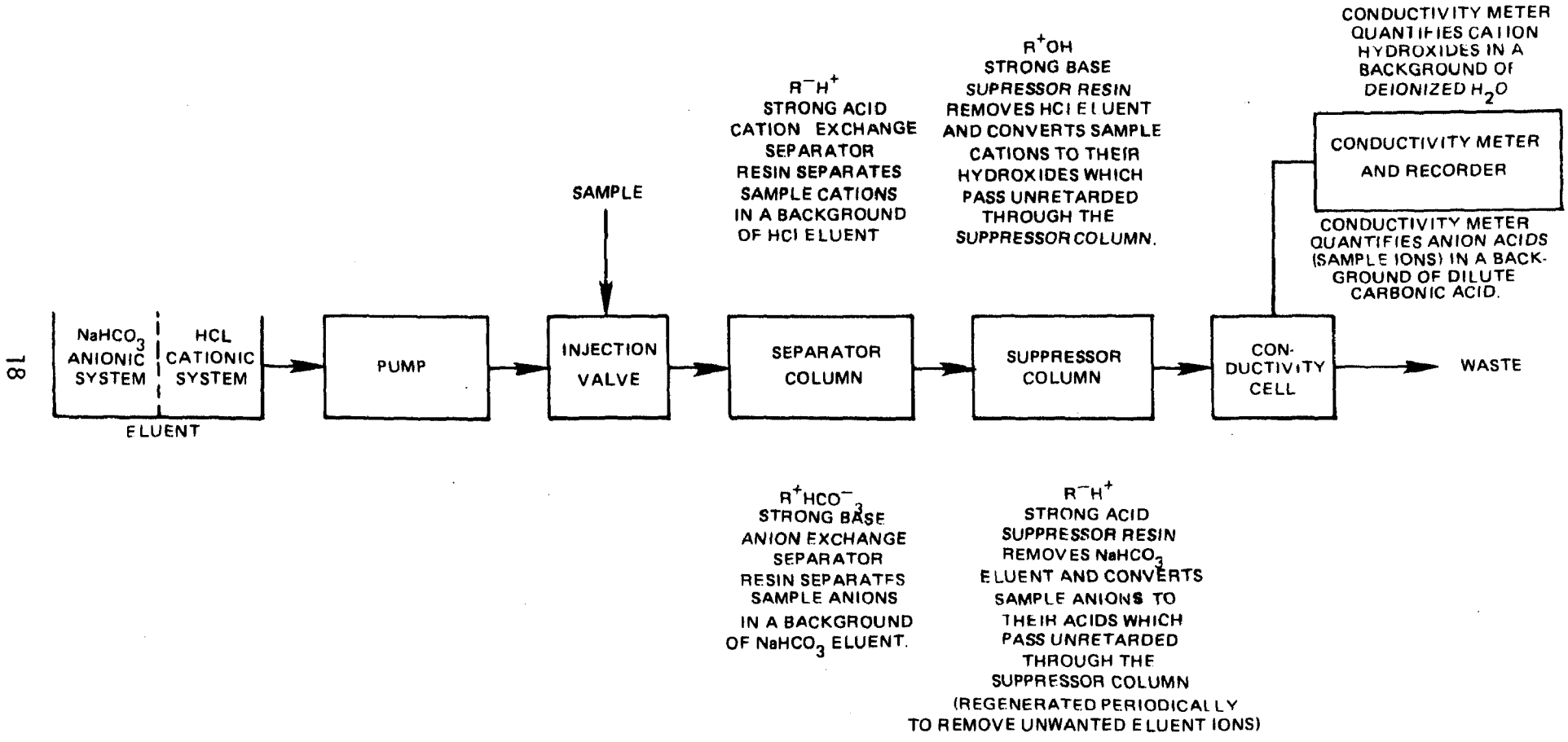


Figure 2.1 ION CHROMATOGRAPHY FLOW SCHEME

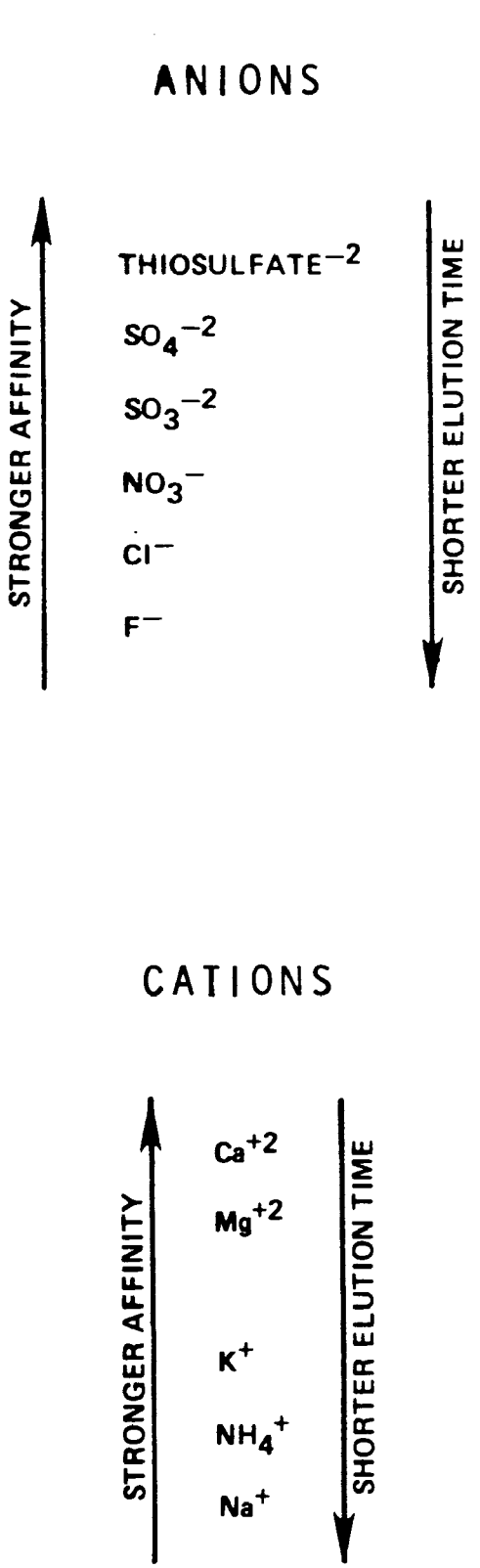


Figure 2.2 NORMAL ELUTION SEQUENCE FOR SOME COMMON IONS USING ION CHROMATOGRAPHY

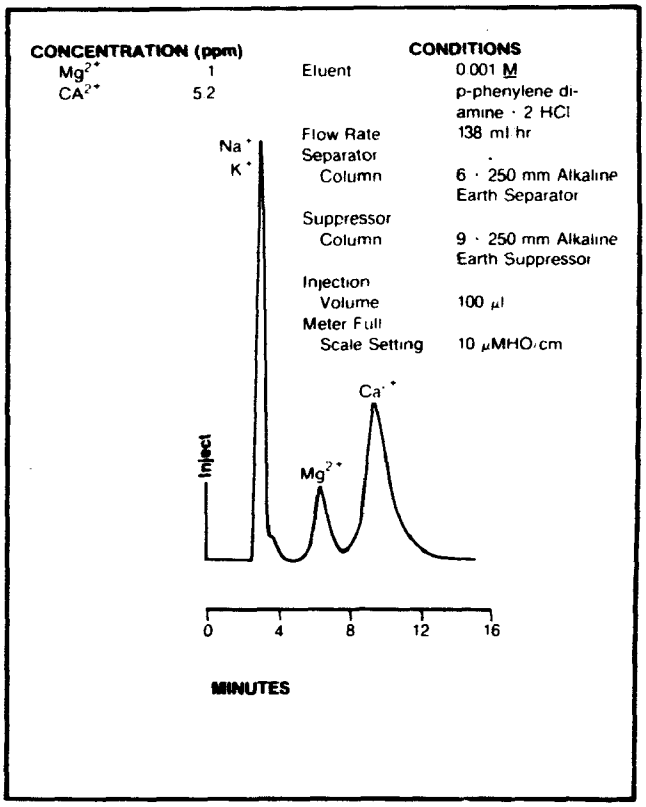


Figure 2.3 Sample Cationic Analysis Chromatogram

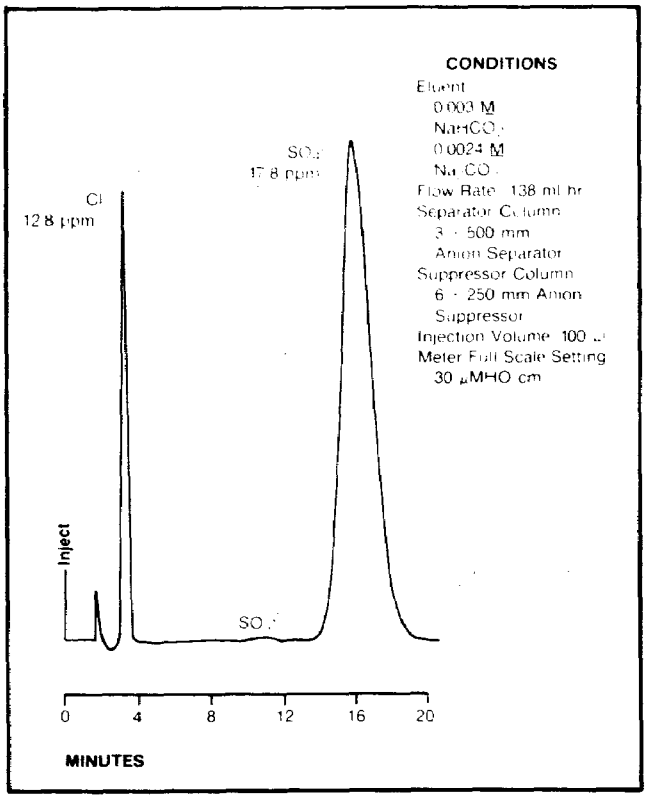


Figure 2.4 Sample Anionic Analysis Chromatogram

Section 3

WET CHEMICAL METHODS

Method 1

Suspended Solids

1. Discussion

Suspended solids in a solution or slurry sample are filtered and then dried to a constant weight in a microwave oven. Alternately, the sample may be dried for 3-4 hours at 83-85°C in a conventional oven. The resultant solids may be used for solids analysis.

Note: SAMPLE PREPARATION AND SEPARATION

Solids taken from slurries are used as a measure of suspended solids content in the slurry as well as for solids composition determinations. When liquor analyses are also required from the slurry sample, two samples should be collected because sample volume requirements for suspended solids measurement and for liquor analyses are not compatible.

2. Apparatus

a. Membrane filter apparatus

b. Drying oven, 84 $\pm$ 1°C or microwave oven

c. Vacuum pump with trap

d. Resealable plastic storage bags

e. Glass fiber filter discs, Whatman GFC, 4.25 cm diameter

f. Plastic weighing boats

g. Desiccator

h. Bottles, wide-mouth, polyethylene, 16 oz, 4 oz and 1 oz

3. Reagents

a. Calcium sulfate solution, saturated; add 3 g calcium sulfate dihydrate (gypsum) to 1 liter tap water at room temperature, mix well and allow solids to settle out before using supernate as wash solution.

b. Isopropyl alcohol, reagent grade

4. Procedure

All weighings should be made to 0.001 g.

4.1 Suspended Solids in Slurries

a. Weigh a clean, dry 1 oz bottle with cap and record weight as B1.

b. Collect slurry sample in bottle then cap the bottle.

c. Rinse solids off of bottle, dry then weigh and record weight as B2.

d. Weigh a weighing boat containing a dry filter disc. Record the weight as B3.

e. Assemble the filtration apparatus with the weighed filter disc. Do not turn on vacuum.

f. Wash the slurry sample out of the bottle and into the filter with about 25 ml of saturated $CaSO_4$ solution. Apply vacuum to the filter. In order to avoid possible channeling and inefficient washing, it is extremely important that the liquid level not be allowed to go beneath the surface of the solids in this step and the next.

g. Rinse the bottle with another 25 ml of $CaSO_4$ wash solution and then transfer to the filter just as the liquid level in the filter reaches the top of the solids bed.

h. Wash the solids with about 25 ml of isopropyl alcohol.

i. Transfer the filter disc and solids to the weighing boat which has been weighed with the filter disc in it. Transfer any solids clinging to the filter apparatus to the boat.

j. Dry the sample, filter disc and boat to constant weight in the microwave oven at HI setting (usually 3 minutes) or in a conventional oven at 84 ± 1°C.

k. Remove the boat, let cool in a desiccator for 2 minutes and weigh. Record weight as B4.

m. Transfer solids to a labeled plastic bag for storage.

4.2 Suspended Solids in Solutions

a. Weigh a weighing boat containing a dry filter disc.

b. Collect sample in a 16 oz bottle.

c. Thoroughly mix the sample by shaking.

d. Quickly pour out 250 ml of well-mixed sample into a 250 ml graduated cylinder.

e. Assemble the filtration apparatus with the weighed filter disc and apply vacuum.

f. Pour the cylinder contents into the filter being careful not to let the filter go dry.

g. Continue with steps 4.1.f. through k. except wash the graduated cylinder with each portion of wash water used in steps 4.1.f and g.

4.3 Liquor from Slurries

a. Collect sample in a 4 oz bottle.

b. Assemble the filtration apparatus with a filter disc and a clean filter flask.

c. Decant about 20 ml of liquor into the filter and apply vacuum. Turn off vacuum and disassemble the filter apparatus.

d. Swirl filtrate in filter flask then discard.

e. Reassemble filter apparatus with a new filter disc.

f. Decant remainder of the sample liquor into the filter and apply vacuum. Do not wash.

g. Transfer filtrate to a clean, dry plastic bottle and label.

5. Calculations

5.1 Suspended Solids in Slurries

$$\text{Suspended Solids (wt\%)} = \frac{B4 - B3}{B2 - B1} \times 100\%$$

where:

B1 = Weight of empty sample bottle, g

B2 = Weight of sample bottle containing sample, g

B3 = Weight of weighing boat plus filter disc, g

B4 = Weight of weighing boat plus filter disc plus dried solids, g

5.2 Suspended Solids in Solutions

$$\text{Suspended Solids (mg/l)} = \frac{B4 - B3}{V} \times 10^6$$

where:

B3 = Weight of weighing boat plus filter disc, g

B4 = Weight of weighing boat plus filter disc plus dried solids, g

V = Volume of sample used in step 4.2d., ml

10^6 = Factor to convert g to mg and ml to l

6. References

a. Shawnee Test Facility, Laboratory Procedures Manual, March 1976, % Solids in Slurry and Drying Solids, with microwave oven, unpublished.

b. "Chemical Analysis Procedures for Dual Alkali Process Stream Samples," Arthur D. Little, Inc., No. 75833, 4/22/76, Methods 1 and 2.

Method 2

Total Dissolved Solids

1. Discussion

Total dissolved solids may be defined as that material capable of passing through a standard glass fiber filter and dried to constant weight in a microwave oven. Alternatively, the filtered sample may be dried at 84°C in a conventional oven. Preservation of the sample is not recommended; analysis of the sample should begin as soon as possible.

Liquor may contain calcium, magnesium, chloride, sulfite and sulfate. Salts of these species may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying.

2. Apparatus

a. Glass fiber filter discs, Whatman GFC, 4.25 cm diameter
b. Membrane filter apparatus
c. Evaporating dish, glass or porcelain, small
d. Steam bath
e. Drying oven, 84 $\pm$ 1°C or microwave oven
f. Desiccator
g. Vacuum pump with trap

3. Procedure

a. Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water.

b. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

c. Preparation of evaporating dishes: Dry the clean dish for 3 minutes at HI in the microwave oven. Cool in desiccator and store until needed. Weigh immediately before use.

d. Assemble the filtering apparatus with a clean, dry filter flask and begin suction. Shake the sample vigorously and rapidly transfer about 50 ml to the funnel.

e. Filter the sample through the filter disc and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

f. Pipet 5.00 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

g. Dry the evaporated sample to constant weight at HI in the microwave oven or at 84 $\pm$ 1°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 1 mg.

4. Calculation

$$\text{TDS mg/l} = \frac{(A - B) \times 1000}{C}$$

where:

A = Weight of dried residue + dish, mg

B = Weight of dish, mg

C = Volume of filtrate used, ml

1000 = Factor to convert ml to l

5. Reference

U.S. Environmental Protection Agency "Methods for Chemical Analysis of Water and Wastes", EPA-625/6-74-003a (1976).

Method 3

Percent HCl Insoluble Solids

1. Discussion

This method is used to determine the HCl insoluble fraction of slurry solids, process filter cake and scale samples and to prepare the samples for further chemical analyses.

Samples are dissolved in acid and separated from undissolved material by filtration. An analytical mill is employed for scale samples to insure that all HCl solubles are dissolved.

Solids samples are normally analyzed for Ca and Mg subsequent to this procedure.

This method may also be used to prepare process filter cake samples for sodium analysis (see Method 4 discussion).

2. Apparatus

a. Membrane filter apparatus
b. Glass fiber filter discs, Whatman GFC, 4.25 cm diameter
c. Analytical mill
d. Magnetic stirrer
e. Drying oven, 84 $\pm$ 1°C or microwave oven
f. Vacuum pump with trap
g. Desiccator
h. Hotplate

i. Watchglasses, about 25 mm and 65 mm diameters

j. Plastic weighing boats

3. Reagents

a. Hydrochloric Acid, 1N; dilute 85 ml concentrated HCl to one liter with deionized water.

4. Procedure

a. Scale samples should be milled according to laboratory practice prior to further treatment. This step is not required for slurry solids or process filter cake samples.

b. Dry sample in a weighing boat to constant weight at HI in a microwave oven (usually 3 minutes) or at 84 ± 1°C in a conventional oven and cool in a desiccator. Process filter cake samples must be dried in a preweighed weigh boat. Weigh the boat plus filter cake sample before and after drying to determine moisture content.

c. Weigh approximately 0.2 g of sample to 0.001 g and transfer to a 250 ml Erlenmyer flask containing about 50 ml of deionized water and a magnetic stirring bar.

d. Slowly add 30 ml of 1N HCl while stirring. Cover with a small watchglass and boil for about 1 minute on a hotplate then remove from hotplate and stir for an additional 30 minutes (see Note).

e. Filter through a preweighed filter disc into a clean filter flask. Rinse Erlenmyer into filter with deionized water making sure that all solids are transferred to the membrane.

f. Dry the filter disc on a watchglass to a constant weight in a microwave oven (3 minutes at HI) or at 84 ± 1°C, cool in a desiccator and weigh.

g. Quantitatively transfer the contents of the filter flask into a 100 ml volumetric flask using a funnel.

h. Dilute to the mark with deionized water, mix by inversion, transfer to a clean, dry plastic bottle and label.

5. Calculation

5.1 HCl Insoluble Solids

$$\text{HCl Insoluble Solids (wt\%)} = \frac{B - A}{W} \times 100\%$$

where:

A = Weight of filter disc, g

B = Weight of filter disc plus dried residue, g, from 4.f.

W = Weight of sample, g, from 4.c.

5.2 Moisture in Process Filter Cake

$$\text{Moisture (wt\%)} = \left(1 - \frac{B1 - B}{B2 - B} \right) \times 100\%$$

where:

B = Weight of weigh boat, g

B1 = Weight of weigh boat plus dry sample, g

B2 = Weight of weigh boat plus sample as received, g

6. Note: If solids sample is to be analyzed for total sulfur by Turbidimetry (Method 12) add 10 ml H_2O_2 and stir 15 min prior to step d.

7. Reference

Shawnee Test Facility, "Laboratory Procedures Manual", March 1976, Method 4.

Method 4

Solids in Process Filter Cake

1. Discussion

Process filter cake, as collected, is slurried with deionized water, filtered and washed. The solids are dried and weighed to obtain % solids in the original cake. The dried cake and the filtrate are saved for later analyses.

If there is a question about the completeness of removal of sodium by this procedure then the process filter cake should be dried without slurrying with deionized water then prepared for sodium analysis by HCl dissolution (Method 3). Moisture content must be determined in this case.

2. Apparatus

a. Membrane filter apparatus
b. Glass fiber filter discs, Whatman GFC, 4.25 cm diameter
c. Vacuum pump with trap
d. Drying oven, 84 $\pm$ 1°C or microwave oven
e. Plastic weighing boats
f. Resealable plastic bags
g. Desiccator
h. Magnetic stirrer

3. Procedure

a. Weigh a plastic weighing boat containing a dry filter disc.

b. Weigh 5 to 10 g of wet filter cake (as collected) to 0.001 g and place in a 100 ml beaker.

c. Slurry with about 25 ml of deionized water.

d. Assemble the filter apparatus with a clean filter flask and the weighed filter disc. Apply vacuum then quickly pour the slurry into the filter. In order to avoid channeling and inefficient washing, it is extremely important that the liquid level not be allowed to go beneath the surface of the solids.

e. Rinse the beaker with an additional 25 ml of deionized water and pour into the filter just as the liquid level in the filter reaches the top of the solids bed.

f. Repeat the wash in step e. once.

g. Transfer the filter disc with solids to the weighing boat. Be sure that any solids clinging to the filter apparatus are transfered to the boat.

h. Dry the weighing boat to constant weight in the microwave oven at HI or in a conventional oven at 84 $\pm$ 1°C.

i. Cool in a desiccator then weigh to 0.001 g.

j. Transfer to a labeled resealable plastic bag for storage.

k. Transfer the filtrate quantitatively to a 100 ml volumetric flask and dilute to volume with deionized water. Mix by inversion then transfer to a plastic bottle and label.

4. Calculation

$$\text{Solids in Cake (wt\%)} = \frac{B1 - B}{W} \times 100\%$$

where:

B = Weight of weigh boat plus filter disc, g, from 3.a.

B1 = Weight of weigh boat plus filter disc plus dried solids, g, from 3.i.

W = Weight of sample as collected, g, from 3.a.

5. Reference

"Chemical Analysis Procedures for Dual Alkali Process Stream Samples," Arthur D. Little, Inc., No. 75833, 4/22/76, Methods 4 and 81.

Method 5

pH by pH Meter/Glass Electrode

1. Discussion

A pH meter with a combination glass electrode is used to measure solution and slurry pH. Sample pH values are measured at the time and point of sampling after calibrating pH meter at sample temperature.

2. Apparatus

a. pH meter

b. Combination electrode, Broadley-James

c. Thermometer

3. Reagents

a. Standard buffer solutions, pH 4, 7, 10

b. Storage solution, 2M KCl; dissolve 15 g of KCl in 100 ml of deionized water.

c. Reference electrode filling solution

4. Procedure

a. Calibrate pH meter with electrode in hot (40°C) pH 7 buffer with the pH meter temperature compensator set to buffer temperature.

b. Use the slope control to set pH meter with a hot (40°C) buffer at a pH near the system pH. Allow sufficient electrode immersion time to obtain a steady pH reading whether reading slurry, solution or buffer pH.

   Use the buffer pH value for 40°C as listed in the table on the buffer bottle rather than the pH at 25°C.

c. As soon as possible after sampling add enough sample to a beaker to cover the lower portion of the glass electrode. Measure the sample temperature and set the pH meter temperature compensator to the sample temperature. Read the pH.

d. Rinse the electrode with deionized water after each reading.

e. Replace buffer solution with fresh buffer at the beginning of each day.

5. Glass electrode performance evaluation

A glass electrode is considered unreliable and should be replaced if either of the following tests are failed:

a. If the pH meter cannot be set to the correct buffer pH value by turning the standardization control.

b. If a pH value is radically different from previous values or from an in-line meter value, the electrode should be compared with two "lab-standard" electrodes that are known to be reliable. If the pH value obtained with the questionable electrode is different by more than 0.2 pH units from the values obtained with the standard electrodes in a slurry sample, the questionable electrode should be discarded. Note that a defective electrode will sometimes give an accurate answer in a buffer but not in a slurry.

6. Reference

"pH Study at the Shawnee Test Facility," Air Quality Group, Research and Engineering, Bechtel Corporation, September 1976.

Method 6

Diluted Conductivity

1. Discussion

The specific conductance of a scrubber liquor sample diluted 1:500 is measured. This value is used as a check of analytical results. The diluted sample is saved for further analyses.

2. Apparatus

a. Conductivity meter, YSI Model 31

b. Thermometer

3. Reagents

Potassium Chloride; make up concentrations shown in the following table as needed for checking conductivity meter. Use deionized water with conductivity ≤ 1 μmho/cm for dilutions:

Concentrations In:		Specific Conductance @ 25°C
Molarity	Grams/Liter	μmho/cm
0.001	0.074	147.0
0.005	0.373	717.8
0.01	0.745	1,413
0.02	1.491	2,767
0.05	3.727	6,668
0.10	7.455	12,900
0.20	14.910	24,820

4. Procedure

a. Pipet 1.00 ml of absorber solution or freshly filtered slurry liquor into a 500 ml volumetric flask, dilute to volume with deion-

ized water with conductivity ≤ 1 μmho/cm and mix by inversion.

b. Set Function switch to Line. Allow 5 minutes for warm-up.

c. Rinse conductivity cell, and place in sample solution. Tap the cell, and dip it two or three times to remove trapped air (see Notes).

d. Set "Sensitivity" control to minimum by turning knob as far as possible counterclockwise.

e. Rotate "Range Switch" to obtain maximum shadow. "Shadow" is the area of the electron tube not lighted. Turn "Drive" to obtain maximum shadow. If dial indication is above 20.0 or below 2.0, turn "Range Switch" to next higher or lower setting.

f. Set "Sensitivity" to maximum (turn fully clockwise).

g. Turn "Drive" to obtain maximum shadow. If you cannot obtain a clear, well defined shadow, set the "Function" switch to 1 KHz.

h. Read the conductance by multiplying the reading on the dial by multiplier. Multiply this result by 500.

i. Save sample for sodium analysis.

5. Standardization

Standardize the conductivity meter daily with 0.001M or 0.005M KCl standard. The meter should indicate the specific conductance listed in the table $\pm$ 5%. If the variation is greater than $\pm$ 5% and is consistently either high or low, a factor should be used in determining actual conductivities. Calculate the factor as follows:

$$\text{factor} = C = \frac{\text{Conductivity of KCl Theoretical}}{\text{Conductivity of KCl Measured}}$$

at 25°C or temperature compensated

Multiply this factor times conductivity reading to get corrected result.

6. Notes

a. The cell must be clean before making any measurement. The cell should be rinsed with deionized water after each sample and before storing.

b. When taking a measurement, the cell's vent slots should be submerged. The electrode chamber should be free of any trapped air.

c. The cell should be at least 1/4" away from any other object, including the walls or bottom of the solution container.

d. Electric fields present from stirrer motors, heaters, etc., may affect readings.

e. If pH of the diluted solution is between 6 and 9 there should be a consistent relationship between conductivity and total dissolved solids for each sample type. Variation indicates analytical problems.

f. The conductivity should be approximately equal to the summation of the anion concentrations in meq/l x 100, if pH of the diluted sample is between 6 and 9. Presence of hydroxyl ion raises the conductivity relative to anion concentrations. Variation from this relationship indicates analytical problems.

g. Other KCl standard solutions should be checked when working with samples with higher conductivities.

7. Reference

Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp. 35-36, 71-75, (1975).

Method 7

Calcium and Magnesium by EDTA Titration

1. Discussion

Calcium in solution is titrated with a complexing agent, EDTA, at a high pH. An indicator changes color when all calcium has been complexed. Calcium plus magnesium is titrated with EDTA at pH 10. In liquor samples, magnesium concentration can be calculated by subtracting the calcium concentration (meq/l) from the calcium plus magnesium (hardness) concentration (meq/l) since the two concentrations are comparable. This is not the case in D/A solids samples where the concentration of magnesium is very low compared to the calcium concentration. Magnesium concentration in solids must be measured by I.C. or atomic absorption.

2. Apparatus

a. Buret, automatic, 10 ml

b. Measuring spoon (scoop), 0.1 g

c. Magnetic stirrer

3. Reagents

a. Ethylenediamine tetra-acetic acid, disodium salt (EDTA), standard solution, 0.02N

b. Potassium Hydroxide, 8N; carefully dissolve 45 g of KOH then dilute to 100 ml with deionized water in a volumetric flask while cooling under a stream of tap water.

c. Calcium Indicator, Hach Chemical Co. CalVer II, Cat. #852-99

d. Calcium standard solution, 1,000 mg/l

e. Buffer solution; carefully add 55 ml conc HCl to 400 ml deionized water and then, slowly and with stirring, add 310 ml 2-aminoethanol. Add 5.0 g of the magnesium salt of EDTA and dilute to 1 liter with deionized water.

f. Hardness Indicator; mix 0.5 g Eriochrome Black T with 100 g NaCl.

g. Magnesium Chloride solution, 1%; dissolve 1 g of $MgCl_2$ and dilute to 100 ml.

4. Procedure

4.1 Calcium in Liquor

a. Pipet 20.0 ml of slurry filtrate into a 250 ml Erlenmyer flask.

b. Dilute to about 100 ml with deionized water and start stirring.

c. Add 1 ml of 8N KOH. Immediately continue with next two steps.

d. Add 0.1 g of CalVer II with a scoop.

e. Titrate with 0.02N EDTA, slowing the titration near the endpoint, until the color just changes to pure blue.

4.2 Calcium in Solids

a. Pipet 5.00 ml of HCl dissolved solids from Method 3 into a 250 ml Erlenmyer flask. A solution of lime or limestone prepared as in Method 3 can be used in place of dissolved slurry solids except use 2.00 ml of dissolved lime solution instead of 5.00 ml.

b. Proceed with steps 4.1.b. through e. of this method.

4.3 Hardness in Liquor

a. Carry out steps 4.1.a. and 4.1.b.

b. Add 1 ml of hardness buffer. See note c.

c. Add 0.1g of hardness indicator.

d. Carry out step 4.1.e.

5. Calculation

5.1 Calcium (mg/l) in liquor = $\frac{400 \times V}{S1}$ = 20V for S1 = 20 ml

where:

V = volume of 0.02N EDTA, ml, from 4.1.e.

S1 = volume of liquor, ml, from 4.1.a.

5.2 Calcium (wt%) in solids = $\frac{4 \times V}{W \times S2}$ = $\frac{0.8 \times V}{W}$ for S2 = 5 ml

where:

V = volume of 0.02N EDTA, ml, from 4.1.e.

W = weight of solids dissolved, g, from Method 3, step 4.c.

S2 = volume of solids solution, ml, from 4.2.a.

5.3 Magnesium (mg/l) in liquor = $\frac{243 \times (Vt - V)}{S1}$ = 12.2 x (Vt - V) for S1 = 20 ml

where:

V = volume of 0.02N EDTA, ml, from 4.1.e.

Vt = volume of 0.02N EDTA, ml, from 4.3.d.

S1 = volume of liquor, ml, from 4.3.a.

and aliquots for the calcium and total hardness analyses are the same volume.

6. Notes

a. If an endpoint is indistinct, interferences may be present. Use a smaller aliquot and add more water before titrating.

b. Magnesium must be present for a sharp endpoint with CalVer II. If endpoint is not sharp, add a drop of 1% $MgCl_2$ in step 4.1.b.

c. If pH in step 4.3.b. is not 10 $\pm$ 0.1, repeat step 4.3.a. then adjust pH to about 10 with HCl or NaOH before adding hardness buffer.

7. Reference

Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp. 189-190 and 202-206, (1975).

Method 8

Sodium by Specific Ion Electrode

1. Discussion

A sample of 1:500 diluted liquor is mixed with conditioning solution and sodium concentration is measured directly with a specific ion meter. There are no known intereferences to this method in D/A samples diluted 1:500.

2. Apparatus

a. Specific ion meter, Orion Model 407 A/F

b. Sodium electrode, Orion Model 94-11-00

c. Single junction reference electrode, Orion Model 90-01-00

d. Magnetic stirrer

e. Beakers, plastic, 100 ml

f. Drying oven, 140°C or microwave oven

3. Reagents

a. Sodium Chloride, standard solution, 100 ppm sodium, Orion 94-11-07 or dissolve 254.2 mg NaCl dried in a microwave oven or at 140°C and dilute to 1,000 ml with doubly deionized water.

b. Ionic Strength Adjustor (ISA); dissolve 20 g NH_4Cl in 50 ml doubly deionized water, add 5.0 ml concentrated NH_4OH and dilute to 100 ml.

c. Filling Solution, for reference electrode, Orion 90-00-19.

d. Electrode rinse stock solution, 1M ammonium bifluoride; dissolve 5.7 g of reagent grade $NH_4F \cdot HF$ in 100 ml deionized water. Store in a plastic bottle.

4. Procedure

a. Pipet 5.00 ml of 100 ppm sodium standard into a 100 ml plastic beaker. Add 45 ml of doubly deionized water and a clean stirring bar. Place on an asbestos mat on a magnetic stirrer.

b. Add 1.0 ml of ISA and start stirring slowly.

c. Turn Function Switch to X+, wait for the reading to stabilize and adjust the meter needle to "1" (center scale) on the red logarithmic scale with the "CALIB" control.

d. Rinse electrodes, blot dry and place in a second plastic beaker containing 50 ml of 100 ppm sodium standard, 1.0 ml of ISA and a clean stirring bar. Start stirring slowly.

e. After reading is stable, turn the "Temp °C" knob until the meter needle reads "10" (full-scale right) on the red, logarithmic scale. Turn the clear "% Slope" dial until the white arrow on the "Temp °C" points to the temperature of the standards. If the slope is not in the range of 90 to 100%, consult trouble shooting check list in the electrode manual.

f. Transfer 50 ml of slurry liquor diluted 1:500 from Method 6 to another plastic beaker, add 1.0 ml ISA and a clean stirring bar.

g. Rinse electrodes, blot dry and place in sample. Stir thoroughly and read ppm sodium by multiplying meter reading on logarithmic scale by 10. See note a.

5. Calculations

mg/l Na in liquor = 500 x ppm Na in test solution

6. Notes

a. If the needle goes off-scale right in step 4.g., rinse electrodes, blot dry and place in the beaker containing 100 ppm sodium standard. Adjust the "CALIB" control until the needle points to "1" (center scale) on the red logarithmic scale. Rinse the electrode, blot dry and replace in sample. Multiply meter reading for sample by 100.

b. Store electrodes upright in a beaker containing a dilute sodium solution.

c. Never touch the membrane of the sodium electrode or the ground surface of the reference electrode.

d. The sodium electrode response may become slow due to hydration of the membrane. If this occurs, transfer 10 ml of electrode rinse stock solution into a 150 ml beaker, add about 100 ml of deionized water and place the tip of the sodium electrode in the solution. Swirl for about 30 seconds. Rinse well and soak in deionized water for an hour.

e. Problems with the reference electrode may be due either to improper flow of electrolyte or contamination of the filling solution. These problems may be handled as follows:

- The Filling Solution level in the electrode should be at least one inch above the level of the solution being measured.
- Push back the reference electrode sleeve so that a drop of Filling Solution collects at the tip of the electrode then release sleeve. Do this before every series of measurements.
- Whenever electrode response becomes erratic, change the reference electrode Filling Solution. Flush several times with Filling Solution before finally filling the electrode.

7. Verification

a. Pipet 5.0 ml of 100 ppm sodium standard, 1.0 ml of ISA and 45 ml of 1:500 diluted slurry liquor into a 100 ml plastic beaker and stir slowly.

b. New reading should be 0.9 times reading obtained in step 4g. plus 10.0 ppm.

c. If interference is suspected, repeat analysis using Method of Known Addition as outlined in electrode manual.

8. Reference

Instruction Manual for Sodium Electrode, Orion Research, Inc., Cambridge, Massachusetts.

Method 9

Chloride by $Hg(NO_3)_2$ Titration

1. Discussion

Chloride ions are titrated with mercuric nitrate to form soluble, slightly dissociated mercuric chloride at a pH near 2.5. Diphenylcarbazone forms a purple complex with excess mercuric ions to indicate the endpoint of the titration. Sulfite interference is removed by oxidation with hydrogen peroxide.

2. Apparatus

a. Buret, automatic, 10 ml

b. Magnetic stirrer

3. Reagents

a. Phenolphthalein indicator solution, 0.1% in alcohol.

b. Sodium hydroxide solution, 1N.

c. Hydrogen peroxide solution, 30%.

d. Manganese chloride solution, 10 mg/l; dissolve 0.04 g $MgCl_2 \cdot 4H_2O$ in 1000 ml of distilled water.

e. Bromocresol green indicator solution, 0.4% in alcohol, neutralized.

f. Nitric acid 1N; dilute 64 ml of 70-72% nitric acid to 1 liter.

g. Sodium hydroxide solution, 1N; carefully dissolve 40 g of NaOH and dilute to one liter with deionized water.

h. Diphenylcarbazone Buffer powder pillows, Hach Cat. #836-99

i. Mercuric nitrate solutions 0.141N and 0.0141N

j. Chloride Standard Solution, 1,000 ppm; dissolve 1.648 g of NaCl (dried at 140°C) in chloride-free deionized water and dilute to 1,000 ml in a volumetric flask.

4. Procedure

4.1 Liquor

a. Pipet a 2.00 ml aliquot of sample into a 250 ml Erlenmeyer flask. Add 20 ml of deionized water.

b. Add 2 drops of phenolphthalein indicator solution and sufficient 1N NaOH to give a red color.

c. Add 2 ml 30% H_2O_2, mix and let stand for 10 minutes.

d. Add 1 ml of 10 mg/l manganese solution. (The amount of chloride added is neglible, equivalent to only 4 x 10^{-5}M chloride in the sample.)

e. Heat solution and boil gently for approximately 15 minutes to destroy the peroxide, adding more deionized water if necessary to maintain liquid level. Absence of peroxide is indicated by a change in the boiling (gas evolution) character.

f. Cool the solution to room temperature, add 3-4 drops of bromocresol green indicator and bring just to the green color with 1N HNO_3.

g. Add contents of a diphenylcarbazone buffer powder pillow and titrate with 0.141N $Hg(NO_3)_2$ solution until color just changes to a permanent light pink.

4.2 Lime, Limestone or Soda Ash

a. Weigh out 0.2 to 0.3 g (weighed to ± 0.001 g) of dry, well-mixed sample, and transfer into a 250 ml Erlenmyer flask containing 50 ml of deionized water plus 3-4 drops of bromocresol green indicator solution. Start magnetic stirring.

b. Add 1N HNO_3 acid (4-8 ml) to dissolve all solids, and continue dropwise addition of the acid until the indicator turns green.

c. Adjust the indicator color to yellow-green by dropwise addition of 1N HNO_3 or 1N NaOH.

d. Add contents of a diphenycarbazone indicator buffer powder pillow and titrate with 0.0141N $Hg(NO_3)_2$ solution until color just changes to a stable light pink.

5. Calculation

5.1 Chloride (moles/l) in liquor = $\frac{V \times N}{S}$

where:

V = volume of $Hg(NO_3)_2$ titrant used, ml

N = normality of $Hg(NO_3)_2$ titrant

S = volume of sample used, ml, from 4.1.a.

5.2 Chloride (millimole/g) in lime or limestone = $\frac{V \times N}{W}$

where:

W = weight of sample used, g, from 4.1.a.

6. Titrant Standardization

Titrate a 25 ml aliquot of 1,000 ppm Cl^- solution, for 0.141N $Hg(NO_3)_2$ titrant using the procedure outlined above. Use 2 ml of 1000 ppm Cl^- solution to standardize 0.0141N $HgNO_3$.

N of titrant = $0.0282 \times \frac{S}{V}$

where:

V = volume of $Hg(NO_3)_2$ titrant used, ml

S = volume of 1000 ppm Cl^- solution used, ml

7. Notes

a. A small amount of undissolved indicator/buffer powder remaining in a sample will not affect results.

b. To analyze chloride in slurry solids, perform steps 4.2.a. and 4.2.b. then steps 4.1.b. through 4.1.f. and finally step 4.2.d. Calculations are the same as for chloride in lime or limestone.

8. References

a. "Chemical Analysis Procedures for Dual Alkali Process Stream Samples," Arthur D. Little, Inc., No. 75833, 4/22/76, Methods 19, 61, 63 and 69.

b. Standard Methods for the Examination of Water and Wastewater, 14th edition, pp 304-306, (1975).

Method 10

Fluoride by Specific Ion Electrode

1. Discussion

A sample of slurry liquor is mixed with conditioning solution and fluoride concentration is read directly with a specific ion meter. Interferences are removed in the procedure.

2. Apparatus

a. Specific Ion Meter, Orion Model 407 A/F

b. Fluoride Electrode, Orion Model 94-09-00

c. Single Junction Reference Electrode, Orion Model 90-01-00

d. Magnetic Stirrer

e. Beakers, plastic, 100 ml

f. Micropipet

3. Reagents

a. Fluoride Standard Solution, 100 ppm, Orion 94-09-07 or dissolve 221.0 mg NaF and dilute to 1,000 ml with deionized water

b. Total Ionic Strength Adjustment Buffer, Orion 94-09-11 diluted with deionized water as indicated on bottle

c. Filling Solution, for reference electrode, Orion 90-00-01

d. Hydrochloric Acid, concentrated

4. Procedure

a. Transfer 49.5 ml deionized water into a beaker and add 0.50 ml of 100 ppm fluoride standard with a micropipet.

b. Pipet 5.0 ml of TISAB into the beaker and stir slowly with magnetic mixer.

c. Turn Function Switch to X-, wait for reading to stabilize and adjust the meter needle to "1" (center scale) on the red logarithmic scale.

d. Rinse electrodes, blot dry and place in a second beaker containing 5.0 ml of fluoride standard, 5.0 ml of TISAB and 45.0 ml of deionized water. Start stirring slowly.

e. After reading is stable, turn the Temperature Compensator Knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.

f. Transfer 50 ml of decanted slurry liquor to another beaker, add 5.0 ml TISAB and start stirring slowly.

g. Rinse and blot dry pH meter electrode then place in sample. If pH is not $\leq$ 5.5, adjust pH to <5.5 with measured, dropwise addition of concentrated HCl. Remove pH electrode without rinsing into sample.

h. Rinse fluoride and reference electrodes, blot dry and place in sample. Read fluoride concentration directly. If HCl addition $\geq$ 0.5 ml, correct results by multiplying:

$$\frac{55 + \text{ml HCl}}{55} \times (\text{meter reading})$$

5. Verification

a. Transfer 0.50 ml of 100 ppm fluoride standard with a syringe into the sample measured in step 4h.

b. New reading should be exactly 1.0 ppm higher than reading for sample alone.

c. If interference is suspected, repeat analysis using Method of Known Addition as outlined in electrode manual.

6. References

a. Instruction Manual for Fluoride Electrode, Orion Research, Inc., Cambridge, Massachusetts.

b. Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp 391-393, (1975).

Method 11

Nitrate by Chromotropic Acid

1. Discussion

Solutions containing nitrate are first treated to eliminate interferring ions. A yellow reaction product is then formed with chromotropic acid and the nitrate concentration is determined spectrophotometrically. As written, the procedure measures only nitrate nitrogen; see note for including ammonia and nitrite nitrogen in the determination. Concentration range is 0.1 to 5 mg/l nitrate nitrogen (NO_3-N).

2. Apparatus

a. Spectrophotometer for use at 410 nm with 1 cm or longer light path

b. 1 cm cells for use in spectrophotometer

c. Magnetic stirrer

d. Hotplate

3. Reagents

a. Stock Nitrate Solution; dissolve 721.8 mg dried anhydrous potassium nitrate or 606.9 mg dried anhydrous sodium nitrate and dilute to 1000 ml with doubly-deionized water in a volumetric flask. 1 ml = 0.1 mg NO_3-N.

b. Standard Nitrate Solution; pipet 50.0 ml of stock nitrate solution into a 500 ml volumetric flask and dilute to the mark with doubly-deionized water. 1 ml = 10 μg NO_3-N/l

c. Antimony Reagent; heat 500 ml antimony metal in 80 ml conc H_2SO_4 until all the metal has dissolved. Cool and cautiously add 20 ml of doubly-deionized water which has been cooled to near 0°C in an ice bath. If crystals separate upon standing overnight, redissolve them by heating.

d. Chromotropic acid reagent: Purify the chromotropic acid (4, 5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt) in the following manner. Boil 125 ml deionized water in a beaker and gradually add 15 g 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt with constant stirring. To the solution add 5 g activated decolorizing charcoal. Boil the mixture for about 10 minutes. Add deionized water to make up the loss due to evaporation. Filter the hot solution through cotton wool. Add 5 g activated charcoal to the filtrate and boil for 10 more minutes. Filter, first through cotton wool and then through a filter paper, to remove the charcoal completely. Cool the solution and slowly add 10 ml nitrate-free conc H_2SO_4. Boil the solution until about 100 ml are left in the beaker. Allow the solution to stand overnight. Transfer the crystals of chromotropic acid to a Buchner funnel and wash thoroughly with 95% alcohol until the crystals are white. Dry the crystals at 80°C.

   Dissolve 100 mg purified chromotropic acid in 100 ml conc H_2SO_4 and store in a brown bottle. Prepare every 2 weeks. A colorless reagent solution signifies the absence of nitrate contamination from the sulfuric acid.

e. Urea reagent; dissolve 5 g urea in doubly-deionized water and dilute to 100 ml.

f. NaOH, 0.1N; carefully dissolve 4 g of NaOH pellets and dilute to 1 liter with doubly-dionized water.

g. H_2SO_4, 0.1N; carefully add 2.8 ml of conc H_2SO_4 to doubly-deionized water and dilute to 1 liter.

h. $MnCl_2$, 10 mg Mn/l; dissolve 0.04 g $MnCl_2 \cdot 4H_2O$ in 1000 ml of deionized water.

i. $AgNO_3$, 1.4N; dissolve 24 g $AgNO_3$ in deionized water and dilute to 100 ml. 1 ml is equivalent to about 50 mg Cl. Store in a brown bottle.

j. Phenolphthalein Indicator Solution; 0.1% in alcohol.

k. H_2O_2, 30%

l. H_2SO_4, concentrated, nitrate-free

m. Source of air or nitrogen for sparging

4. Procedure

a. Pipet 25.0 ml of sample into a 125 ml Erlenmyer flask.

b. Add a drop of phenolphthalein solution and if the solution is pink, add sufficient 0.1N H_2SO_4 to make the solution colorless plus an additional ml.

c. Add 0.5 ml of $AgNO_3$ solution for every 1,000 mg/l Cl in the sample as determined in Method 9. Mix. See note C.

d. Add a few drops more of phenolphthalein and sufficient 0.1N NaOH to make the solution pink.

e. Sparge the solution with a stream of air or N_2 while gently boiling to remove NH_3. Add doubly-deionized water to keep volume near 2.5 ml. Sparging is complete when a piece of pH indicator paper, dampened with deionized water and held in the fumes from the flask, indicates a neutral pH. Cool solution to near room temperature.

f. Add 2 ml of 30% H_2O_2, mix and allow to react for 10 minutes.

g. Add a ml of 10 mg/l manganese solution and boil for about 15 minutes to destroy the peroxide. Absence of peroxide is indicated by a change in the boiling (gas evolution) character. During this period, allow the volume to be reduced to about 10 ml but do not allow the solution to go to dryness. Add additional doubly-deionized water during boiling, if needed.

h. Cool, then quantitatively transfer the contents of the flask to a 25 ml volumetric flask using doubly-deionized water to rinse and dilute to volume. Mix by inversion.

i. Filter with a filter funnel into a clean test tube. Do not rinse.

j. Pipet 2.5 ml of the filtrate into a dry 10 ml volumetric flask.

k. Add 1 drop of urea reagent.

l. Place the flask in a small beaker containing cold (10 to 20°C) water and carefully add 2 ml antimony reagent. Swirl the flask during addition of each reagent. Leave the flask in the bath for about 4 minutes before continuing.

m. Add 1 ml chromotropic acid reagent and swirl flask again. Leave the flask in the bath for an additional 3 minutes.

n. Add conc H_2SO_4 to the mark, stopper and mix by inverting four times.

o. Allow the flask to stand for 45 minutes at room temperature then again adjust the volume to the 10 ml with conc H_2SO_4. Mix by inversion very gently to avoid introducing gas bubbles.

p. Set zero on the spectrophotometer at 410 nm using deionized water in a 1 cm cell.

q. Rinse the sample cell with sample solution then fill carefully, to avoid trapping bubbles, by holding the cell in a slanting position and pouring the solution very slowly down the side of the cell. Be careful not to get any of the solution on fingers or clothes and neutralize any spills with sodium bicarbonate and water.

r. Read the absorbance at 410 nm 15 minutes or more after the last volume adjustment.

s. Determine the corresponding μg NO_3-N from the standard curve.

5. Standard NO_3-N Curve Preparation

a. Pipet into marked, 100 ml volumetric flasks 0, 1.0, 5.0, 15, 25, 35 and 50 ml of standard nitrate solution and dilute to the mark with doubly-deionized water. Mix. These flasks contain 0, 10, 50, 150, 250, 350 and 500 g NO_3-N respectively.

b. Pipet 25.0 ml of each standard into labled 125 ml Erlenmyer flask and add 1 ml 0.1 N H_2SO_4 and 0.5 ml of $AgNO_3$ solution to each.

c. Carry out steps d., f. through h. and j. through r. of the above procedure for each.

d. Plot absorbance on the ordinate against mg N on the abscissa for each standard.

6. Calculation

$$\text{mg/l nitrate N} = \frac{\mu\text{g nitrate N}}{\text{ml sample (from step 4.j.)}}$$

$$\text{mg/l } NO_3 = \text{mg/l nitrate N} \times 4.43$$

7. Notes

a. The procedure as written determines only nitrate N. To include nitrite N, delete step 4.k. To include ammonia N, delete step 4.e.

b. If sample contains more than 5 mg/l NO_3-N, make an appropriate dilution of the sample before starting procedure. Dilution factor must then be included in the calculation.

c. If sample chloride concentration is less than 2,000 mg/l steps 4.b., c. and i. may be deleted.

8. References

a. "Chemical Analysis Procedures for Dual Alkali Process Stream Samples", Arthur D. Little, Inc. No. 75833, Method 21, 4/22/76.

b. Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp 429-431, (1975).

Method 12

Total Sulfur and Sulfate by Turbidimetry

1. Discussion

Sulfate (or sulfate plus sulfite which has been oxidized by H_2O_2 to the sulfate form) is converted to a uniform barium sulfate suspension. The resulting turbidity is measured spectrophotometrically and compared to a standard curve.

2. Apparatus

a. Spectrophotometer, for use at 420 nm, with 25 mm light path

b. Matched 1" test tubes for use in spectrophotometer

c. Vortex type test tube stirrer

d. Hotplate

3. Reagents

a. Hydrogen peroxide, 30%

b. Standard sulfate solution, 50 mg/l, Hach Cat #2578-11 or dissolve 147.9 mg dried anhydrous sodium sulfate, Na_2SO_4, in deionized water and dilute to 1,000 ml in a volumetric flask (1.00 ml = 100 mg $SO_4^=$). Dilute 50 ml to 100 ml in a volumetric flask for 50 mg/l.

c. SulfaVer IV powder pillows, Hach Cat. #12065-99

4. Procedure

4.1 Preparation of Standard Absorption Curve

a. Pipet 2.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of 50 mg/l standard sulfate solution into matched test tubes. This represents 0.10,

0.25, 0.50, 0.75, 1.00 and 1.25 mg of $SO_4^{=}$ ion.

b. Dilute each solution to 25.0 ml with deionized water.

c. Add 25 ml of deionized water to another matched test tube for a blank.

d. Empty one SulfaVer IV powder pillow into each test tube and mix on a vortex mixer for 15 seconds.

e. At least 5 minutes but before 10 minutes after mixing, set zero on the spectrophotometer at 420 nm with the blank, then read the absorbance for each test tube.

f. Prepare a standard absorption curve by plotting absorbance against mg $SO_4^{=}$ for each reading.

4.2 Total Sulfur in Liquor

a. Pipet 20.0 ml of 1:500 diluted slurry filtrate from Method 6 into a 100 ml volumetric flask.

b. Add 1 ml of 30% H_2O_2, heat gently and swirl for 3 minutes.

c. Cool, then dilute to 100 ml with deionized water and mix by inversion.

d. Transfer 25 ml of this solution into a matched test tube.

e. Pipet 10.0 ml of 50 mg/l standard sulfate solution into another matched test tube and dilute to exactly 25.0 ml with deionized water.

f. Add 25 ml of deionized water to another matched test tube for a blank.

g. Empty one SulfaVer IV powder pillow into each test tube and mix on a vortex-mixer for 15 seconds.

h. At least five minutes but before 10 minutes after mixing, set zero on the spectrophotometer at 420 nm with the blank, then read the absorbance for each test tube. See Note b.

4.3 Total Sulfur in Solids

a. Pipet 2.0 ml of HCl/H_2O_2 dissolved solids solution from Method 3 step 4.h. into a 100 ml volumetric flask.

b. Dilute to 100 ml with deionized water and mix by inversion.

c. Transfer 25 ml of this solution into a matched test tube.

d. Proceed with steps 4.2.e. through i. of this Method.

4.4 Sulfate in Liquor

a. Pipet 5.00 ml of freshly prepared 1:500 diluted slurry filtrate from Method 6 into a matched test tube. Dilute to 25.0 ml.

b. Proceed with steps 4.2.e. through i. of this Method.

4.5 Sulfate in Solids

a. Pipet 5.00 ml of slurry solids solution from Method 3 into a matched test tube. Dilute to 25.0 ml.

b. Proceed with steps 4.2.e. through i. of this Method.

5. Calculation

5.1 Total Sulfur (as g/l $SO_4^=$) in liquor = $\frac{\text{mg } SO_4^= \text{ (from curve)}}{A} \times 2 \times 10^3$

where:

A = ml of 1:500 diluted filtrate used in 4.2.a.

2×10^3 = dilution factor for A:500 dilution and 25:100 dilution

5.2 Total sulfur (in millimoles/g) in solids = $\frac{\text{mg } SO_4^= \text{ (from curve)}}{B \times W_1} \times 4.17$

where:

B = ml of solution used in 4.3.a.

W_1 = weight of solids used in step 4.c. of Method 3

4.17 = dilution factor for B:100 dilution and 25:100 dilution/MW (SO_4)

5.3 Sulfate (in g/l) in liquor = $\frac{\text{mg } SO_4^= \text{ (from curve)}}{C} \times 1.25 \times 10^4$

where:

C = ml of 1:500 diluted filtrate used in 4.4.a.

1.25×10^4 = dilution factor for 1:500 dilution and C:25 dilution

5.4 Sulfate (in millimoles/g) in solids = $\frac{\text{mg } SO_4^{=} \text{ (from curve)}}{D \times W_2} \times 1.04$

where:

D = ml of solution used in 4.5.a.

W_2 = weight of solids used in step 4.c. of Method 3 (Solids Dissolution), g

1.04 = dilution factor for D:100 dilution/MW (SO_4)

6. Notes

a. If the result for the standard sulfate solution is not 0.50 mg $SO_4^{=}$ ± 0.025 mg, then the standard absorption curve should be checked and the analysis repeated, if necessary.

b. If the absorbance value measured is not within the range of 0.05 to 0.8, the analysis must be repeated using a suitably adjusted aliquot in step 4.2.a. for liquor or 4.3.c. for solids.

c. The matched test tubes must be washed shortly after each set of analyses to prevent the deposition of a white film on the inside of the tubes.

7. References

a. Shawnee Test Facility, Turbidimetric Determination of Total Sulfur, unpublished.

b. Methods for Chemical Analysis of Water and Wastes, EPA-625-16-74-003, p 277, (1974).

c. Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp 496-498, (1975).

Method 13

Total Oxidizable Sulfur and Thiosulfate by Iodate/Thiosulfate Titration

1. Discussion

Excess iodate is added to a sample, then the sample is acidified and excess iodine is backtitrated with thiosulfate. To determine thiosulfate, sulfite is complexed with formaldehyde so that only thiosulfate is free to react with added iodate.

2. Apparatus

a. Buret, automatic, 10 ml

b. Magnetic stirrer

3. Reagents

a. Sodium Thiosulfate, 0.1N, standardize daily against 0.1N Iodide-Iodate

b. Iodide-Iodate solution, 0.1N, dissolve 3.566 g KIO_3 (dried for two hours at 120°C), 2.5 g $NaHCO_3$ and 34.8 g KI in about 500 ml of deionized water then dilute to 1,000 ml in a volumetric flask.

c. Starch solution, 0.5%

d. Hydrochloric Acid, 10% or 1N

e. Formaldehyde, 37%

4. Procedure

4.1 Total Oxidizable Sulfur

a. Pipet 2.00 ml of freshly filtered slurry liquor into a 250 ml

Erlenmyer flask or place 0.1 to 0.12 g slurry solids dried to constant weight in a microwave oven (or at 84 ± 1°C in a conventional oven), cooled and weighed to 0.001 g, in a flask. Add about 50 ml of deionized water to the flask.

b. Start magnetic stirring, then pipet in iodate solution. Use 10.0 ml of 0.1N iodate solution for a liquor sample or 20.0 ml of 0.1N iodate solution for a solids sample.

c. Add 10 ml of 1N HCl.

d. Titrate with 0.1N thiosulfate until a pale yellow color is evident then add a ml of starch solution and continue titrating slowly until the solution just turns from blue to colorless.

e. Run a blank repeating steps 4.1.a. through d. using 10.00 ml of 0.1N iodate solution and no sample.

4.2 Thiosulfate

a. Use a graduated cylinder to measure 50.0 ml of freshly filtered slurry liquor into a 250 ml Erlenmyer flask or place 1.0 g of dry (75°C or microwave), finely-ground slurry solids, weighed to 0.001 g, and 50 ml of deionized water in the flask.

b. Place flask in a mixture of ice and water contained in a large beaker on top of a magnetic stirrer.

c. Start stirring. Add 10 ml of formaldehyde and cool solution to below 15°C. Remainder of analysis must be carried out with solution temperature < 15°C to maintain bisulfite-formaldehyde complex.

d. Add 10.0 ml of 0.1N iodate solution with a pipet.

e. Proceed with steps 4.1.c. through 4.1.e.

5. Calculation

5.1 $$N = \frac{10}{B} \times N\ IO_3$$

where:

N = normality of thiosulfate titrant

B = volume of thiosulfate titrant used for blank, ml, from 4.1.e.

$N\ IO_3$ = normality of thiosulfate titrant used for blank, ml, from 4.1.e.

5.2 TOS as mg $SO_3^{=}$/l in liquor = $\frac{(B - S) \times N \times (40{,}000)}{V1}$

where:

S = volume of thiosulfate titrant used for sample, ml, from 4.1.d.

V1 = volume of liquor sample used, ml, from 4.1.a.

40,000 = $\frac{mg}{meq}$ SO_3 x 1000 $\frac{ml}{l}$

5.3 TOS in meq/g in solids = $\frac{(B - S) \times N}{W1}$

where:

W1 = weight of solids sample used, g, from 4.1.a.

5.4 Thiosulfate in mg/l in liquor = $\frac{(B - S) \times N \times (112{,}000)}{V2}$

where:

V2 = volume of liquor sample used, ml, from 4.2.a.

112,000 = $\frac{mg}{meg}$ S_2O_3 x 1000 $\frac{ml}{l}$

5.5 Thiosulfate in ppm in solids = $\frac{(B - S) \times N \times (112{,}000)}{W2}$

where:

W2 = weight of solids sample used, g, from 4.2.a.

6. Note

To minimize errors associated with sulfite oxidation in the sample, sample bottles should be filled to overflowing then capped and analysis should be performed within an hour of sample collection.

7. References

a. "Chemical Analysis Procedures for Dual Alkali Process Stream Samples," Arthur D. Little, Inc., No. 75833, 4/22/76, Methods 11 and 51.

b. Snell, F.D., Biffen, F.M., Commercial Methods of Analysis, McGraw-Hill Book Co., Inc., New York, pp. 174-175, (1944).

Method 14

Available Alkalinity by HCl Titration

1. Discussion

The available alkalinity in lime or limestone is determined by titration with HCl to the phenolphthalein endpoint. The value found for lime is available alkalinity but the value found for limestone must be doubled for available alkalinity.

2. Apparatus

a. Buret, automatic

b. Magnetic stirrer

3. Reagents

a. Hydrochloric acid, standard 0.1N

b. Phenolphthalein indicator solution, 0.1% in alcohol

c. Drying oven, 105°C or microwave oven

d. Desiccator

4. Procedure

a. Dry lime or limestone sample to constant weight and cool in a desiccator. Weigh out about 0.4 g of sample to 0.001 g and transfer to a 250 ml Erlenmeyer flask containing about 100 ml of deionized water.

   Alternatively, thoroughly mix a lime slurry sample by shaking the sample bottle then quickly pour out about 2 g of lime slurry into a preweighed sample boat. A lime slurry sample is then treated in the same manner as a dry sample.

b. Add a drop of phenolphthalein indicator solution and titrate with 0.1N HCl to the permanent disappearance of the pink color. The solution should remain colorless for at least 3 minutes while stirring is continued to dissolve all the solids.

5. Calculation

5.1 Lime

$$\text{Total Alkalinity (millimoles OH/g)} = \frac{(\text{ml HCl}) \times (\text{N of HCl})}{\text{g sample}}$$

$$\text{Alkalinity (as wt\% } Ca(OH)_2) = \frac{(\text{ml HCl}) \times (\text{N of HCl}) \times (3.7)}{\text{g sample}}$$

where:

$$3.7 = \frac{37 \text{ mg}}{\text{meq}} \; Ca(OH)_2 \times \frac{1 \text{g}}{1000 \text{ mg}} \times 100\%$$

5.2 Limestone

$$\text{Total Alkalinity (millimoles OH/g)} = \frac{(\text{ml HCl}) \times (\text{N of HCl}) \times (2)}{\text{g sample}}$$

$$\text{Alkalinity (as wt\% } CaCO_3) = \frac{(\text{ml HCl}) \; (\text{N of HCl}) \; (10)}{\text{g sample}}$$

$$\text{where } 10 = 2 \times \frac{50 \text{ mg}}{\text{meq}} \; CaCO_3 \times \frac{1 \text{ g}}{1000 \text{ mg}} \times 100\%$$

6. Reference

"Chemical Analysis Procedures for Dual Alkali Process Stream Samples", Arthur D. Little, Inc., No. 75833, Methods 58 and 65, 4/22/76.

Method 15

Hydroxide by HCl Titration

1. Discussion

Hydroxide concentration is determined directly by titration with hydrochloric acid, using thymolphthalein as an indicator.

2. Apparatus

a. Buret, automatic

b. Magnetic stirrer

3. Reagents

a. Calcium chloride solution; dissolve 2.5 g of $CaCl_2 \cdot 2H_2O$ in 100 ml deionized water

b. Thymolphthalein indicator solution, 0.05% in ethanol

c. Hydrochloric acid, standard solution, 0.1N

4. Procedure

a. Pipet 10.0 ml of solution sample into a 250 ml Erlenmyer flask or place about 0.5 g of dried solids, weighed to 0.001 g, in the flask.

b. Add about 50 ml of deionized water, 10 ml of $CaCl_2$ solution and 3-4 drops of thymolphthalein solution.

c. If solution is not blue, report $\leq$ 0.001 moles OH^-/l in a solution sample or $\leq$ 0.02 millimoles OH^-/g in a solids sample.

d. If solution is blue, titrate with HCl to the disappearance of the blue color. If the blue color reappears on continued stirring, continue titration until blue color is absent for at least one minute. See Note a.

5. Calculation

$$\text{Hydroxide in solution (moles/l)} = \frac{(\text{ml HCl}) \times (\text{N HCl})}{10}$$

$$\text{Hydroxide in solids (millimoles/g)} = \frac{(\text{ml HCl}) \times (\text{N HCl})}{\text{g sample}}$$

6. Notes

a. If too much indicator has been added, the endpoint is seen as a marked decrease in the intensity of the blue color.

b. For increased sensitivity (lower detection limit) use a larger aliquot or less concentrated HCl titrant.

7. Reference

"Chemical Analysis Procedures for Dual Alkali Process Stream Samples", Arthur D. Little, Inc., No. 75833, Methods 13 and 53, 4/22/76.

Method 16

Carbonate in Solids by CO_2 Evolution

1. Discussion

Sample is made alkaline and $SO_3^=$ is oxidized with H_2O_2. It is then acidified in an air tight system and the volume of CO_2 evolved is measured.

2. Apparatus (see Figure 3.1)

   a. Leveling bulb (250 ml)
   b. Tygon tubing
   c. Gas buret (100 ml)
   d. T-connector
   e. Stopcock
   f. Reaction flask (250 ml Erlenmeyer) with two hole stopper
   g. Buret
   h. 2 Ring stands with clamps
   i. Magnetic stirrer
   j. Asbestos mat

3. Reagents

   a. Sodium Hydroxide, 0.1N
   b. Hydrochloric Acid, concentrated
   c. Hydrogen Peroxide, 30%
   d. Phenolphthalein Indicator Solution
   e. 10% H_2SO_4 + methyl red indicator

4. Procedure

a. Set up the apparatus as shown in Figure 3.1, except do not stopper. The leveling bulb and gas buret contain 10% H_2SO_4. Buret g should be filled with concentrated HCl.

b. Transfer about 1.5 g of dry slurry solids or lime (weighed to 0.001 g) into the reaction flask. Use about 0.1 g of limestone or soda ash.

c. Add 10 ml of deionized water, and a magnetic stirring bar. Steps d. and e. should be omitted for lime and limestone samples.

d. Add 2 drops of phenolphthalein solution and then add 0.1N NaOH dropwise while stirring until a permanent faint pink color is seen in solution.

e. Add 5 ml of 30% H_2O_2, stopper the flask and stir for at least ten minutes.

f. Stop stirring, and check that the flask is tightly stoppered.

g. With stopcock open, lower leveling bulb 20-30 cm and raise until both liquid levels are at the zero reading. Close stopcock.

h. Again lower the leveling bulb as before and raise to the zero mark to check for possible leaks in the system. Repeat until a zero reading is maintained.

i. Start stirring again then add exactly 1.00 ml HCl from buret g. As the CO_2 is evolved, keep the leveling bulb below the liquid level in the buret to lower pressure and allow the CO_2 to escape freely.

j. Measure the volume of gas liberated by raising the leveling bulb to the point where liquid levels are equal. Repeat until a constant value is obtained. Read the volume of gas collected, subtract 1.00 ml for the volume of HCl added and record this value as the volume of gas evolved.

5. Calibration

Place 0.100 g of reagent grade, dry $CaCO_3$ into the reaction flask with 10 ml of deionized water. Continue with steps f. through j. of the procedure. It is essential that the time allowed for CO_2 evolution in step i. be the same for the standard as for the sample in order to avoid errors from

temperature effects on gas volume due to heat of reaction.

6. Calculations

$$\text{Carbonate (mmol/g)} = \frac{Vs}{Vst \times W}$$

where:

Vs = volume of gas evolved from sample, ml

Vst = volume of gas evolved from 0.100 g of $CaCO_3$, ml

W = weight of sample used in analysis, g

0.100 g of $CaCO_3$ standard = 1.00 mmol

$$\text{weight \% Carbonate as } CaCO_3 = \frac{Vs}{Vst} \times \frac{10}{W}$$

where:

$$10 = \frac{100 \text{ mg}}{\text{mmol}} \; CaCO_3 \times \frac{1 \text{g}}{1000 \text{ mg}} \times 100\%$$

7. Reference

"Methods of Soil Analysis," American Society of Agronomy, Inc., Madison, Wisconsin, Method 91-6, 1965.

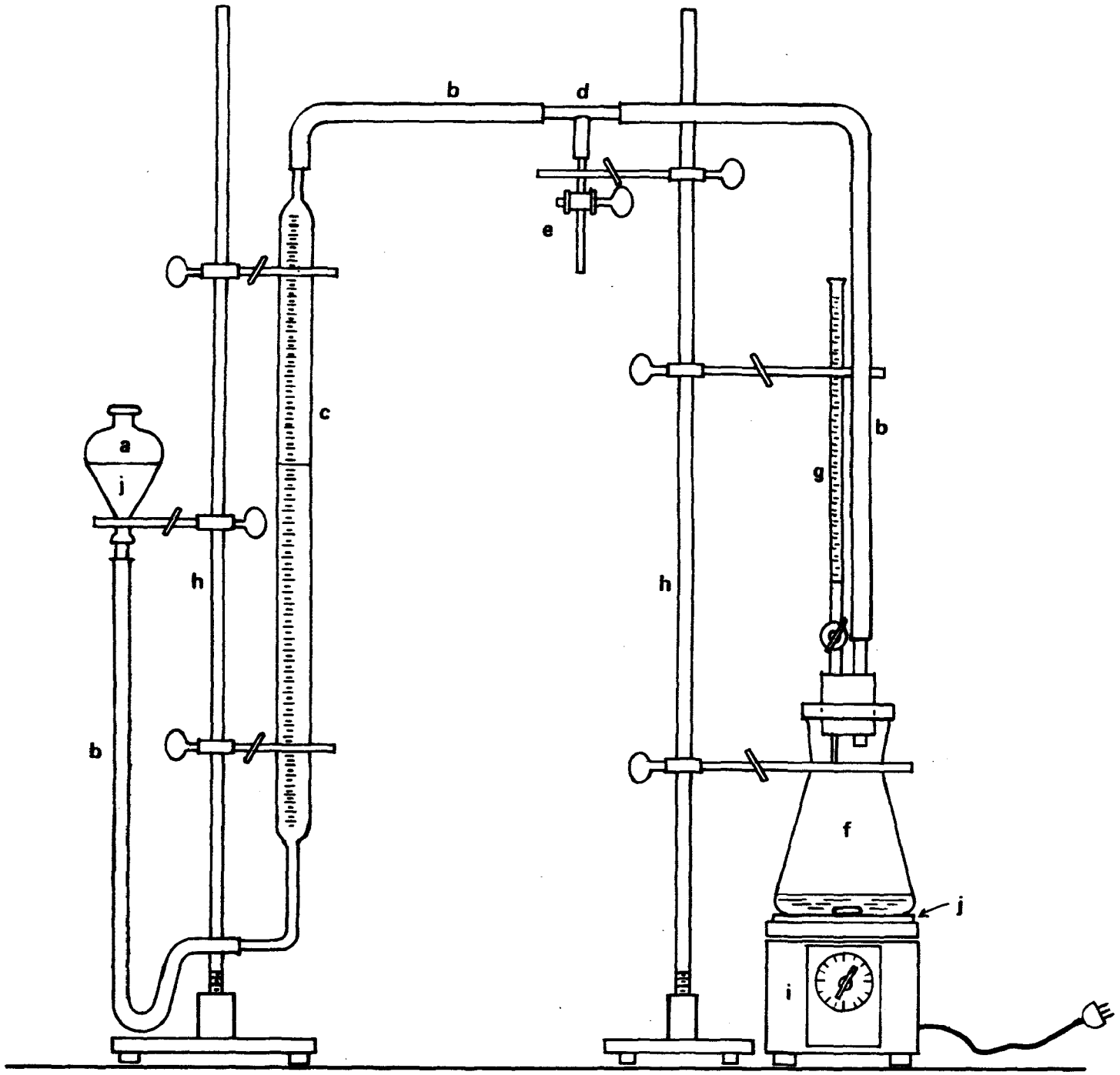


FIGURE 3.1

CARBONATE DETERMINATION APPARATUS

Method 17

Carbonate by HCl Titration

1. Discussion

Carbonate in liquor samples is determined by preliminary titration with hydrochloric acid followed by backtitration with sodium hydroxide. Sulfite interference is removed by alkaline oxidation with hydrogen peroxide.

2. Apparatus

a. 2 Burets, automatic

b. Magnetic stirrer

c. Hotplate

3. Reagents

a. Sodium hydroxide, standard solution, 0.1N

b. Phenolphthalein indicator solution, 0.1% in alcohol

c. Hydrogen peroxide solution, 30%

d. Manganese chloride solution; dissolve 0.04 g of $MnCl_2 \cdot 4H_2O$ in 1000 ml distilled water

e. Hydrochloric acid, standard solution, 0.1N

f. Bromocresol green indicator solution, 0.4% in alcohol, neutralized

4. Procedure

Note: Once the determination is started, it must be carried through Step q. (acid to bromocresol green) in order to avoid error from absorption of atmospheric CO_2.

a. Transfer 25 ml of 0.1N NaOH into a 250 ml Erlenmeyer flask and add 1 drop of phenolphthalein indicator solution.

b. Pipet a 25.0 ml aliquot of sample solution into the sodium hydroxide. Record this volume as "S".

c. If the phenolphthalein color disappears immediately, add an additional 10 ml of NaOH solution. The pink (alkaline) indicator color should persist for at least 30 seconds.

d. Add 5 ml of 30% hydrogen peroxide, mix well and allow to stand for 10 minutes. Add 1 ml of manganese chloride solution, and boil until effervescence ceases.

e. Cool quickly in water bath. If pink color has faded, add 1 drop of the the phenolphthalein solution to determine if the solution is still alkaline.

f. Titrate with 0.1N HCl to disappearance of pink color.
Note: If too much indicator has been added, the endpoint is seen as a marked decrease in intensity of the red color. Record the volume (level) of 0.1N HCl in the buret as "A".

g. Add 3-4 drops of bromocresol green indicator solution to the titration solution, and continue titration with 0.1N HCl until a permanent yellow color is seen. Then add 3 ml of titrant in excess. Record the reading of the HCl buret as "B".

h. Quantitatively transfer the titrated solution to a 150 ml beaker and gently boil (uncovered) for 10 minutes.
Note: It may be necessary to add small amounts of distilled water during the boiling in order to avoid spattering losses.

i. Cool the solution, and backtitrate with standard 0.1N NaOH to a green endpoint. Record this volume as "C".

j. Run blank determination with all reagents.

5. Calculation

$$\text{Millimoles carbonate} = [(B - A) \times N\ HCl] - [C \times N\ NaOH]$$

$$\text{Carbonate (moles/l)} = \frac{(\text{millimoles } CO_3 \text{ in sample}) - (\text{millimoles } CO_3 \text{ in blank})}{S}$$

where: N HCl = normality of HCl

N NaOH = normality of NaOH (to bromocresol green endpoint)

6. Notes

a. The size of the aliquot used in step b. should be adjusted as necessary so that only a few ml of 0.1N HCl (step g.) are needed to backtitrate the 25 ml (or less) of 0.1N NaOH (step a.) for routine samples.

b. The 0.1N NaOH used in steps a. and c. need not be a standardized solution. The normality of the NaOH used in step i. must be known exactly.

7. Reference

"Chemical Analysis Procedures for Dual Alkali Process Stream Samples", Arthur D. Little, Inc., No. 75833, Method 15, 4/22/76.

Method 18

Liquid Density

1. Discussion

Liquid densities are determined by the use of a hydrometer (for clear liquors) or by weighing a known volume (for slurries).

2. Apparatus

a. Hydrometer set, capable of measuring specific gravities between 0.900 and 2.000

b. Volumetric flask, 50 ml capacity

c. Thermometer

d. Triple beam balance 1000 g capacity, sensitive to 0.1 g

3. Procedure

3.1 Using hydrometers: For clear liquids and very slow-settling slurries

a. Use cylinder of sufficient diameter for hydrometer to float freely without touching walls. Read value for specific gravity from the graduated scale at the meniscus. It may be necessary to try several hydrometers before the one most suited to the particular sample is found.

b. Record temperature of the sample. Convert specific gravity to density or vise versa, as shown under calculations.

3.2 Weighing a known volume: For slurries

a. Weigh a clean, dry 50 ml volumetric flask to 0.1 g. Record weight as "F".

b. Measure temperature of sample and record as "T".

c. Mix sample thoroughly by shaking in sample bottle.

d. Quickly pour through a funnel into the volumetric flask slightly less than 50 ml.

e. Mix sample again then quickly withdraw some sample with a medicine dropper and transfer exactly enough sample to the flask to bring volume to 50.0 ml.

f. Wipe outside of flask then weigh to 0.1 g. Record weight as S.

4. Calculations

Note: Report 3 significant figures for these calculations.

4.1 Density of liquids

$$D_4^T = \frac{1}{\text{Sp. Gr.}}$$

where:

D_4^T = Density of liquid at temperature T, °C, referred to water at 4°C, g/ml

Sp. Gr. = Specific gravity read from hydrometer

4.2 Density of slurries

$$D_4^T = \frac{S - F}{50}$$

where:

S = Weight of flask plus sample, g

F = Weight of flask, g

50 = Volume of flask, ml

5. Reference

Shawnee Test Facility, "Laboratory Procedures Manual," March 1976, Method 3.

Method 19

Settling Test Procedure

1. Discussion

Well-stirred slurry or slurry dilutions are introduced into a graduated cylinder. Liquid interface versus time data are collected. Thickener sizing factors are calculated.

2. Special Equipment

a. Graduated cylinders, 2000 ml and 1000 ml.

b. Stop watch or,

c. Clock with second hand.

d. Yardstick; opaque cardboard background.

e. Gallon containers for slurry samples.

f. Thickening test stirrer, 0.02 rpm (Dorr-Oliver).

g. Beakers, 500 ml and 1000 ml.

h. Pipets, 50 ml and 100 ml.

3. Procedure

3.1 Characterization of Slurry

a. Shake container of slurry well. Pour slurry into cylinder. The test stirrer should be in operation. Observe solid/liquid interface and note whether the interface is distinct or diffuse. Observe if slurry settles fast or slowly. Cylinder size is based on settling characteristics of the slurry.

b. Record position of solid/liquid interface at 0, 5, 10, 15, 30, and 60 minutes after pouring slurry into cylinder.

3.2 Tests on Concentrated Slurry and Diluted Slurry.

a. Shake container of slurry well, pour into test cylinder and turn on stirrer. Repeat observations as described above.

b. Decant sufficient clear liquid from the settling slurry to increase concentration to 1.5 times original.

c. Repeat step 3.1.

d. Decant sufficient clear liquid from the settled slurry to increase concentration to 1.5 times original.

e. Repeat step 3.1.

f. Decant sufficient clear liquid from the settled slurry to increase concentration to 4.0 times original.

g. Repeat step 3.1.

h. Add sufficient water to bring concentration to 1/2 that of original sample.

i. Repeat step 3.1.

3.3 Settling Tests with Coagulant Addition

Mix slurry well with the amount of coagulant prescribed by the test conditions. Pour into test cylinder and observe solid/liquid interface. Test stirrer should be in operation. Record time required for settling as described in 3.1, above.

3.4 Tests on Slowly Settling Slurry

a. Repeat 3.1 above but allow 16 hours per set of 6 points because of slow settling.

b. Repeat 3.3 above but allow 16 hours per set of 6 points because of slow settling.

3.5 Second Order Settling Tests for "Thin" Slurry (<1% suspended solids)

a. Arrange six 500 ml beakers and six 50 ml pipets on the laboratory bench. Clamp the pipets so that the tips are uniformly 2" below the liquid surface in each of the beakers. Bring the slurry to room temperature. Beaker and pipet sizes are determined by slurry characteristics.

b. Mix slurry well and pour to equal heights in each of the beakers. Use yardstick to measure exact height.

c. Withdraw slurry samples from the respective beakers sequentially at 0, 5, 10, 15, 30, and 60 minutes. Determine and record % solids at each settling time. Provide illumination (lamp) and opaque background (black or white cardboard) for observation of solid/liquid interface.

4. Alternate Laboratory Test Method

Place a measured quantity of slurry at a known density in a beaker or glass cylinder. Attach a narrow strip of paper on one side of the container. Mix slurry thoroughly. Draw a line on the paper at the top of the slurry and mark "0" minutes. For five minutes, at one-minute intervals, mark the point to which the solids have settled. This determines the free settling rate of solids at the initial density.

Usually readings should be taken at three different densities of the slurry corresponding approximately to densities which will exist in the various zones in the thickener.

Decant sufficient clear water or solution to establish a slurry with intermediate density. For instance, if initial slurry density was 1:4, solids to water, the removal of one-fourth of the water would establish a density of 1:3. Mix thoroughly. Repeat readings of settlement as above.

Then decant again to obtain a slurry at the third density. The slurry just

tested was at 1:3 dilution, so decanting one-third of the water will give a 1:2 dilution, solids to water. Mix thoroughly. Repeat settling measurements at one-minute intervals for five minutes.

The settling rate per minute should be uniform during the testing at each dilution until compression is reached, at which time the amount of settling will decrease during each succeeding minute. Measure the settling marks in inches, thus determining the settling rate in inches per minute for each slurry density, and convert this to feet per hour.

Determining Final Density

Final density is then determined. Thoroughly mix the slurry remaining after the test at 1:2 dilution and allow to settle for 19 hours. Mark the position of settled solids and let stand for a few hours to see if final density was reached. If the solids continue to settle mark its position at hourly intervals until settling stops. Decant off all clear water or solution. Then determine moisture content of the solids by weighing and drying.

5. Calculating Thickener Area

Thickener area required is calculated by applying above determined data in the following formula:

$$A = \frac{1.333\ (F - D)}{R}$$

A = Thickener area in square feet per ton of dry solids thickened in 24 hours.

F = Initial density (Parts Water to Solids by weight).

D = Final density at which solids will settle or density at which you want to discharge solids from the thickener.*

R = Settling rate in feet per hour.

Calculations of indicated thickener area from each of the three settling rates obtained in tests will indicate any change in settling rate in the different zones of the thickener, and the largest area obtained from the three calculations should be used.

Assume the following data was obtained from the above tests:

At 1:4 dilution R = 0.50 feet per hour

At 1:3 dilution R = 0.30 feet per hour

At 1:2 dilution R = 0.15 feet per hour

Final density D = 1.1

Applying this data to above formula, you obtain:

$$A = \frac{1.33\ (4-1)}{.50} = 7.98 \text{ FT2/TPD}$$

$$A = \frac{1.33\ (3-1)}{.30} = 8.86 \text{ FT2/TPD}$$

$$A = \frac{1.33\ (2-1)}{15} = 8.87 \text{ FT2/TPD}$$

A computer program has been developed by Bechtel that reduces the data. The output is thickener size data, in square feet of thickener area per ton/day of solids (FT2/TPD).

---

* Usually it is desired to discharge solids from the thickener at its final density as shown in the above test. However, if you want the discharge to be more diluted than the actual final density, the density desired should be used in above formula rather than the final density to which the solids will settle.

6. Reference

Shawnee Test Facility, "Laboratory Procedures Manual," March 1976, Method 20.

Method 20

Particle Size Distribution

1. Discussion

Slurry solids are sized with a wet screen technique for particle size ranges greater than 37 μm. For more definition of size ranges below 75 μm, a sub-sieve analysis utilizing an hydrometer can be used. These procedures are discussed in order below:

A. Wet Sieve Analysis

2. Apparatus

a. 3" O.D. x 2" high brass sieves, lid and bottom pan. Tyler screen sizes 48, 100, 200, 325 and 400 mesh equivalent to 300, 150, 75, 45 and 37 μm respectively.

b. Porcelain Buchner funnel, 75 mm plate with fitted rubber stopper

c. Filter paper, 7 cm dia., Whatman #1

d. Vacuum pump with water trap

e. Filter-flask, 1 liter

f. Rubber tubing, heavy-duty

g. Brush for cleaning sieves

h. Drying oven, 105°C

i. Hand-operated, pump-type spray bottle with adjustable spray for washing particles through screens

j. Ladle, stainless steel, 1 oz. capacity

3. Reagent

Calcium Sulfate solution, saturated; mix $CaSO_4 \cdot 2H_2O$ with tap water (room temperature) at the rate of 3 g per liter, mix well and allow solids to settle out before using supernate.

4. Procedure

a. Weigh the dry, clean sieves, bottom pan and a 250 ml beaker. Also weigh a dry filter paper.

b. Thoroughly mix the slurry sample by shaking and inverting the sample bottle. Be sure that no solids remain clumped on the bottom of the bottle.

c. Quickly pour all of the mixed sample into a large beaker.

d. Stir the slurry with the ladle and ladle out a representative sample containing about 25 g of suspended solids into the tared, 250 ml beaker.

e. Assemble the Buchner funnel apparatus and connect to the vacuum pump through a trap. Place tared filter paper in funnel, wet and smooth, apply vacuum and check that there are no leaks.

f. Assemble the sieves in order of decreasing mesh size and push the bottom sieve of the stack into the Buchner funnel.

g. Pour sample into the top sieve and carefully wash out the beaker into the sieve with saturated $CaSO_4$ solution using the hand sprayer.

h. Rinse top sieve with sprayer until all undersized particles are washed through and wash water is clear. See note.

i. Remove top screen and rinse next screen, etc. until all screens have been rinsed. Stack rinsed screens in original order on bottom pan.

j. When all wash water has passed through the filter paper, remove paper and transfer to bottom pan. Recover all solids remaining in the Buchner funnel by brushing into the bottom pan, if solids are dry, or use a stream of <u>deionized</u> water from a wash bottle to complete transfer.

k. Reassemble the sieves and pan in original order and dry at 105°C to constant weight.

l. Place the lid on the top screen, cool and hand-sieve by means of a lateral and vertical motion of the sieves accompanied by a jarring action in order to transfer remaining, under-size material.

m. Weigh each sieve and the pan and record as gross weights.

5. Calculations

Subtract the filter paper weight from the pan weight. Determine net weight of each fraction by subtracting the tare weight from the gross weight of each sieve and the pan. Calculate percent passing or percent retained by each sieve and tabulate results against screen size. The sum of the individual fraction weights should be near net weight of beaker times percent suspended solids divided by 100.

6. Note

In steps g. and h., control $CaSO_4$ solution addition so that none of the sieves or the filter funnel overflow. The process can be sped up by tapping each of the sieves in the stack. If solids appear in the filter flask, discard the run.

B. Sub-Sieve Analysis by Hydrometer Method

2. Apparatus

a. Hydrometer, ASTM 151 H, 0.995-1.050 Specific Gravity

b. Graduated cylinder, 1,000 ml

c. Thermometer, -20 to 110°C

d. Constant temperature bath, 20°C, e.g., a styrofoam ice chest

e. Volumetric flask, 100 ml marked so as to be distinguishable from other 100 ml flasks in lab

f. Syringe, 1 ml

g. Stopwatch

h. Parafilm

3. Reagent

Calcium Sulfate solution, saturated; see A.3. above.

4. Procedure

4.1 Specific Gravity (based on ASTM D854, Test for Specific Gravity of Soils)

a. Adjust the temperature of the water bath to 20°C with hot water or ice.

b. Weigh out 10 to 15 g of dried slurry solids prepared as in the procedure for Total Suspended Solids from the sample to be sub-sieve analyzed. Record weight as W1.

c. Transfer to the marked, 100 ml flask which has been completely dried.

d. Add about 50 ml of saturated $CaSO_4$ solution at 20°C and mix by inversion.

e. Rinse down any solids adhering to the neck of the flask above the 100 ml mark by adding additional 20°C $CaSO_4$ solution until liquid is about 2 cm below mark.

f. Cap flask and place in 20°C bath for one hour.

g. If any air bubbles are present after one hour, remove by rolling flask or application of vacuum.

h. Carefully dry inside of flask neck above 100 ml mark with a rolled up filter paper or by other means.

i. Recap flask, replace in 20°C bath for 15 minutes.

j. Carefully add additional $CaSO_4$ solution to make exactly 100 ml using the syringe.

k. Recap the flask, dry thoroughly and weigh. Record as W2.

l. Occasionally repeat steps e. through k. with no sample. In

step k. record the weight as P, the weight of the flask plus 100 ml of saturated $CaSO_4$ solution at 20°C.

4.2 Sub-Sieve Analysis (based on ASTM D422, Particle Size Analysis of Soils)

a. Thoroughly mix the slurry sample by shaking and inverting the sample bottle. Be sure that no solids remain clumped on the bottom of the bottle.

b. Quickly pour all the mixed sample into a large beaker.

c. Stir the slurry with a ladle and ladle out a representative sample containing about 50 g of suspended solids into a tared beaker. (See note a).

d. Weigh the beaker with sample and record the difference between the gross and tare weights of the beaker as W, the weight of the slurry sample.

e. Transfer the sample to 1000 ml graduated cylinder rinsing with 20°C $CaSO_4$ solution.

f. Dilute to 1,000 ml with 20°C $CaSO_4$ solution.

g. Cover the cylinder mouth with Parafilm and vigorously mix the contents by shaking and inversion. Place the cylinder in the water bath, start the stopwatch and remove the Parafilm.

h. Take hydrometer readings at 2, 5, 10, 15, 30, 60, 120, 240, 360 and 1440 minutes (see Note a.). Read hydrometer at top of meniscus. Insert the hydrometer 20 to 25 seconds before each reading is due to approximately the depth it will have when the reading is taken. After each reading is taken immediately remove the hydrometer and place in a cylinder of 20°C $CaSO_4$ solution with a spinning motion. Adjust temperature of water bath to 20°C about 15 minutes before each reading is due. Record hydrometer reading and time from start of settling period.

i. Hydrometers are graduated to be read at the bottom of the meniscus and calculations in section 5. are based on using water with a specific gravity of 1.000 instead of saturated $CaSO_4$ solution. To correct for these factors, fill the 1,000 ml graduated cylinder to 1,000 ml with $CaSO_4$ solution, adjust to 20°C in the water bath and record the specific gravity as read at the top of the meniscus. The correction factor is this value minus 1.000.

5. Calculations

5.1 Slurry Solid Specific Gravity $= \dfrac{W1}{W1 - (W2 - P)}$

where:

W1 = weight of 105°C or microwave dried slurry sample solids

W2 = weight of the volumetric flask with $CaSO_4$ solution and sample solids at 20°C

P = weight of the volumetric flask with $CaSO_4$ solution only at 20°C

5.2 Solids Remaining in Suspension (%) = $\frac{100,000}{Ws} \times \frac{G}{G-1} \times R$

where:

Ws = weight of slurry sample, W, from B.4.2.d. x % Total Suspended Solids in sample divided by 100, g

G = slurry solids specific gravity

R = hydrometer reading minus correction factor from B.4.2.i.

5.3 Diameter of a particle corresponding to the percentage indicated by a given hydrometer reading, D,

$$= \frac{0.30}{980 \times (G - 1)} \times \frac{L}{T}$$

where:

D = diameter of particle, mm

L = distance from the surface of the suspension to the level at which the density is being measured from Table 3-1, cm

T = interval of time from beginning of sedimentation to the taking of the reading, minutes

G = slurry solids specific gravity

Table 3-1

EFFECTIVE DEPTH OF HYDROMETER READING

Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	1.020	11.0
1.002	15.8	1.022	10.5
1.004	15.2	1.024	10.0
1.006	14.7	1.026	9.4
1.008	14.2	1.028	8.9
1.010	13.7	1.030	8.4
1.012	13.1	1.032	7.8
1.014	12.6	1.034	7.3
1.016	12.1	1.036	6.8
1.018	11.5	1.038	6.2

6. Reporting

Make a plot of particle diameters on a logarithmic abscissa against percentages smaller than the corresponding diameter on an arithmetic ordinate. Results can also be tabulated as for the wet-sieve analysis.

7. Notes

a. Weight of sample used and the time intervals between hydrometer readings can be adjusted to obtain reasonable changes in specific gravity values between readings.

b. A computer or programmable calculator can be used to advantage for these calculations.

c. See ASTM D422 for details of determining particle size ranges below 75 μm in dry samples or at temperatures other than 20°C.

8. Reference

American Society for Testing and Materials, Philadelphia, Pennsylvania, Methods D854 and D422.

Method 21

Sodium by Flame Photometer

1. Discussion

A diluted liquid sample is aspirated in an LPG/oxygen flame. Emitted light is passed through a filter to isolate the radiation characteristic of sodium. The intensity of the light is measured by a phototube and is approximately proportional to the sodium concentration. The relationship of the intensity measured to sodium concentration is not linear so that a standard curve must be utilized.

The calcium to sodium concentration ratios in D/A absorber liquors and in samples of soda ash or process filter cake dissolved in water is small and calcium is not an interference in these samples. However, if HCl-dissolved process filter cake samples are to be analyzed by this method, standards must contain the same concentration of calcium as samples since the relatively high level of calcium in the samples would otherwise be an interference.

A non-ionic surfactant is used in samples and standards to assure proper aspiration. Samples which contain suspended solids must be filtered to prevent burner clogging.

2. Apparatus

a. Flame photometer, Coleman Model 51 with accessories
b. Regulators for oxygen and LPG supply
c. Drying oven, 140°C or microwave oven
d. Micropipet, 100 microliter volume

e. Bottles, plastic, 125 ml

3. Reagents

a. Sodium standard solution, 1000 mg/l Na, dissolve 2.542 g of NaCl dried in a microwave oven (or at 140°C) in deionized water and dilute to the mark in a one liter volumetric flask.

b. Calcium, 1,160 mg/l Ca; place 2.896 g $CaCO_3$ in a one liter volumetric flask, add 50 ml deionized water then dissolve the $CaCO_3$ by dropwise addition of a minimum amount of conc HCl. Dilute to the mark with deionized water and mix by inversion.

c. Sterox, 1% solution.

4. Procedure

4.1 Photometer operation

a. Turn power switch to On. Be sure "FILTER" switch is set to sodium.

b. Run aspirator cleaning tool wire through the aspirator capillary several times. Insert from the bottom of the capillary--never insert from the top.

c. Start O_2 flow and set regulator pressure to 13 psi, if necessary. Shut off O_2 with needle valve.

d. Open LPG tank valve and adjust regulator pressure to 6 inches of water, if necessary. Shut off LPG with tank valve.

e. Hold down "IGNITE" button for about 5 seconds then open LPG tank valve. When flame ignites, immediately release the "IGNITE" button and start O_2 flow by opening needle valve.

f. Allow flame and electronics to "warmup" for 10 minutes.

g. Transfer prepared samples to small plastic sample cups being careful not to touch the inside or rim of the cups. Place cups in the 20-position sample tray and then mount the tray on the rotating sample holder beneath flame compartment. Rotate each sample and standard in turn to the position beneath aspirator and then lift sample holder to start aspiration. Sample holder will not rotate while in the raised position.
Note: Readings must be taken while liquid level in sample cup is between the two lines inscribed on the cup.

Discard cups after use.

h. Set photometer as follows:
For liquor or water dissolved samples of soda ash or process filter cake

- Aspirate 100 mg/l Na standard and set reading with "CALIBRATE" control to exactly 10 on 0-10 scale.
- Aspirate 10 mg/l Na standard (no Ca) and set reading to exactly 1 with "ZERO" control.
- Repeat above two steps until readings are consistent--be sure that liquid level in sample cup is above bottom inscribed line when reading is taken.

For HCl-dissolved process filter cake samples with normal sodium concentration

- Aspirate 50 mg/l Na standard (Low Ca) and set reading with "CALIBRATE" control to exactly 10 on 0-10 scale.
- Aspirate 5 mg/l Na standard (Low Ca) and set reading to exactly 1 with "ZERO" control.
- Repeat above two steps until readings are consistent--be sure that liquid level in sample cup is above bottom line inscribed on cup when reading is taken.

For HCl-dissolved process filter cake samples with low sodium concentration

- Aspirate 50 mg/l Na standard (High Ca) and set reading with "CALIBRATE" control to exactly 10 on 0-10 scale.
- Aspirate 5 mg/l Na standard (High Ca) and set reading to exactly 2 with "ZERO" control.
- Repeat above two steps until readings are consistent--be sure that liquid level in sample cup is above bottom line inscribed on cup when reading is taken.

4.2 Preparation of standard curve

Prepare 100 ml Na standards for use with liquor or soda ash samples (no calcium) as follows:

a. Label six 100 ml volumetric flasks with the Na concentration indicated for each.

b. Pipet 2.00 ml of 1% Sterox into each flask.

c. Pipet the following amounts of 1,000 mg/l Na standard into the flasks.

Sodium Concentration (mg/l)	ml of 1,000 mg/l Na Standard in 100 ml
10	1.00
20	2.00
40	4.00
60	6.00
80	8.00
100	10.0

d. Add sufficient deionized water to each flask to make exactly 100 ml of solution then mix by inversion. Transfer to clean, dry 125 ml plastic bottles and label. Include on the labels the statement "No Calcium".

e. Prepare a second set of standards for HCl-dissolved process filter cake samples by following steps a. through d. above with the following exceptions:

- Pipet 100 ml of 1,160 mg/l Ca solution into each flask.
- Include on the labels the statement "Low Calcium (116 mg/l)".
- Use the following table for sodium standard addition in step c.

Sodium Concentration (mg/l)	ml of 1,000 mg/l Na Standard in 100 ml
5	0.50
10	1.00
20	2.00
30	3.00
40	4.00

f. Prepare a third set of standards as in the step e. with the following exceptions:

- Pipet 50.0 ml of 1,160 mg/l Ca solution into each flask.
- Include on the labels the statement "High Calcium (580 mg/l)".

g. Set instrument according to 4.1.h. above with "No Calcium" standards then take readings of the first set of standards. Reset instrument with "Low Calcium" standards then take readings of the "Low Calcium" set of standards. Reset with "High Calcium" standards and take readings of the "High Calcium" set of standards.

h. Plot three standard curves, one for low calcium samples, one for HCl-dissolved process filter cake samples with high sodium content (>1%), and one for HCl-dissolved filter cake with low sodium content (<1%). Plot meter reading on the y-axis against sodium concentration (mg/l) on the x-axis then draw a smooth curve through the points for each set of standard readings. The standard curves containing calcium are good only for process filter cake samples containing about 29% Ca in the dried sample and which are prepared for analysis as indicated in 4.3 below.

4.3 Sample Analyses

a. Prepare sample dilutions in volumetric flasks as indicated in Table 3-1 on page 3-21-6. Label flasks with the sample log numbers.

b. Transfer a maximum of 10 diluted samples plus a duplicate and a spike of one sample to sample cups then place the cups in the sample tray and record the tray location for each sample. Do not place samples containing differing concentrations of calcium in the same batch of sodium analyses.

c. Transfer a low sodium concentration standard and a high sodium concentration standard in sample cups to the tray for setting the instrument. Use the standards with calcium concentrations appropriate to the samples being analyzed as indicated by in Table 3-1.

d. Analyze samples as directed in 4.1 and record the reading obtained for each sample.

e. Use the standard curve appropriate to the calcium concentration to determine the sodium concentration in mg/l corresponding to the reading obtained for each sample.

5. Calculations

5.1 Sodium in Liquor

$$\text{Sodium (g/l)} = C \times \frac{1\text{g}}{1000\text{ mg}} \times \frac{100\text{ ml}}{0.1\text{ml}}$$

$$= C$$

where:

C = Na concentration from standard curve, mg/l

Table 3-2

SAMPLE PREPARATION FOR SODIUM ANALYSIS BY FLAME PHOTOMETER

Sample Type	Initial Dilution for Solids Sample Dissolution	Additional Dilution Requried for Na Analysis	Volume of 1% Sterox Requrired in Na Dilution	Na Standards Used for Water-Dissl'd Samps	Na Standards Used for HCl-Dissl'd Samps
Liquor (Absorber, Secondary Reactor, Thickener)	-------	0.1 ml:100 ml	2.00 ml	No Ca	
Soda Ash	~5 g:250 ml	0.1 ml:25 ml	0.5 ml	No Ca	
Process Filter Cake (> 1% Na in dry cake)	~0.5 g:100 ml	2 ml:25 ml	0.5 ml	No Ca	*Low Ca
Process Filter Cake (< 1% Na in dry cake)	~0.5 g:100 ml	10 ml:25ml	0.5 ml	No Ca	*High Ca

*Note: The standards indicated may be used for sodium analysis of HCl-dissolved process filter cake containing between 28 and 30 wt% calcium in the dry cake. If sample calcium concentration is outside of this range, then new standards must be utilized containing [Ca]/29 times the amount of 1,160 mg/l calcium solution (in 100 ml of standard) indicated in Section 4.2 for low or high calcium standard preparation where [Ca] = Calcium concentration (wt%) in the dry process filter cake sample.

5.2 Sodium in Solids

$$\text{Sodium (wt\% in dry solids)} = C \times \frac{V}{W} \times \frac{VF}{AF} \times \frac{1g}{1000\ mg} \times \frac{1l}{1000\ ml} \times 100\%$$

$$= C \times \frac{V}{W} \times \frac{VF}{AF} \times 10^{-4}$$

where:

C = Na concentration from standard curve, mg/l
V = Volume of dissolved solids sample, ml
W = Weight of solids in dissolved sample, g
VF = Volume of final dilution, ml
AF = Aliquot volume of dissolved solids sample used in final dilution, ml

6. References

a. Coleman Model 51 Flame Photometer Instrument Manual, Coleman Instruments Division of Perkin Elmer Corporation, Maywood, Illinois.

b. Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp. 250-253, (1975).

Method 22

Active Sodium by Titration

1. Description

This is a tentative method proposed by Arthur D. Little, Inc. for analysis of active sodium in Dual Alkali absorber liquor.

Total active sodium concentration is defined as follows:

$$[Na+]active = 2 \times ([Na_2SO_3] + [Na_2CO_3]) + [NaHSO_3] + [NaOH] + [NaHCO_3]$$

In this procedure the anions associated with active sodium are titrated with standard acid to the bromocresol green endpoint.

The sample is boiled with excess acid, during the analysis, to expel SO_2 and CO_2. Other cations than sodium could be an interference (actually, the alkaline anions associated with these cations) if present in significant concentrations but in D/A absorber streams their concentrations are very small compared to the concentration of sodium. Sulfate and chloride do not interfere.

2. Apparatus

a. Burets, automatic

b. Magnetic stirrer

c. Hotplate

3. Reagents

a. Hydrochloric acid, standard solution, 0.1N

b. Sodium hydroxide, standard solution, 0.1N

c. Bromocresol green indicator solution, 0.4% in alcohol, neutralized

4. Procedure

a. Pipet 2.00 ml of filtered sample into an Erlenmyer flask.

b. Add about 50 ml of deionized water and 2-3 drops of bromocresol green indicator solution.

c. Titrate with 0.1N HCl to a yellow endpoint and add 5 ml excess acid. Record the exact total volume added.

d. Bring solution to a boil on a hotplate and continue to boil for 10 minutes. Add additional deionized water, as necessary, to maintain volume. See note.

e. Cool flask then titrate to a green endpoint with 0.1N NaOH.

5. Calculations

$$\text{Active sodium (moles/l)} = \frac{A \times N\ HCl - B \times N\ NaOH}{V}$$

where:

A = Volume of HCl added in 4.c., ml

B = Volume of NaOH added in 4.e., ml

V = Volume of sample used in 4.a., ml

N HCl = Normality of HCl

N NaOH = Normality of NaOH

6. Note

If sample turns green while boiling in 4.d., start analysis with a new sample aliquot and add 10 ml excess HCl in 4.c.

7. Reference

Letter, S. P. Spellenberg (A. D. Little) to C. Hardt (Louisville Gas & Electric), dated May 31, 1979.

Method 23

Total Sulfur by LECO

1. Discussion

A solids sample is burned at high temperature in a stream of oxygen to convert sulfur to SO_2. Iron and tin accelerators are added to the sample before combustion to provide required inductive mass. The combustion products are carried into a dilute acid solution containing iodate, iodide and starch indicator. As the blue iodine/starch complex is bleached by SO_2, more iodate solution is added to return the solution color to the original intensity. The color intensity is measured by a lamp and photocell with output displayed on a microammeter.

Since the conversion of sulfur to SO_2 is not complete, a "furnace factor" is developed by analyzing sulfur standards. The amount of standard iodate consumed during a sample combustion is used with the furnace factor to compute total sulfur in the sample as wt% sulfate.

2. Apparatus

LECO Sulfur Determinator including oxygen purifying train, induction furnace and semi-automatic titrator.

3. Reagents

a. Iodate solution; add 4.44 g KIO_3, 5 g KI and 6 pellets of KOH to about 500 ml of deionized water in a 1 liter volumetric flask. Dissolve the salts then dilute to the mark with deionized water and mix by inversion.

b. Hydrochloric acid; carefully add 15 ml of concentrated HCl to about 500 ml of deionized water in a 1 liter graduated cylinder. Dilute to 1,000 ml with deionized water and mix.

c. Starch solution; use commercially prepared stabilized, starch indicator solution and add 10 g of KI per liter. Dissolve and mix. Replace when endpoint produced is not a distinct blue with no reddish tinge.

d. Tin metal accelerator; LECO Cat. #501-076.

e. Iron powder accelerator; LECO Cat #501-077.

4. Procedure

a. Turn on filament voltage (located beneath the green indicator light on the lower right side of the induction furnace).

b. Turn on titrator power switch (located in the lower right side of the titrator face).

c. Allow 5 minutes for warmup.

d. Accurately weigh about 0.07 grams of dried sample into a porous cup and record exact weight of sample.

e. Add to the cup in the following order:

(1) One glass scoop of tin metal accelerator.
Note: Shake the tin metal into the cup so that the sample is covered by the tin.

Caution: Three scoops or two heavily heaped scoops of iron powder may over-load the furnace resulting in a circuit breaker trip on the furnace. If this occurs, remove the cup and set up again using less iron. Reset the breaker and restart the procedure.

(2) Two slightly rounded glass scoops of iron powder accelerator (see note under [1]). Place porous cover on cup.

The sample is ready for analysis.

f. Drain the reaction vessel by opening the glass stopcock at the bottom of the reaction vessel on the titrator.

g. Close the stopcock.

h. Place a finger over the hole on the manifold button located on the lower left side of the titrator and press the button down. Squeeze the rubber bulb until the fluid level in the reaction chamber reaches the bottom black line on the reservoir.

i. Add 3-4 drops of starch solution to the reaction vessel.

j. Raise the porous cup holder (without porous cup) into the glass reaction chamber on the induction furnace and lock into place.

k. Open the valve on the oxygen bottle and set the flow rate at 1 liter/minute (flow rate is controlled by needle valve on the left side of oxygen purifying train and by the regulator control on the oxygen tank).

l. Briefly press the "FINE" button on the lower right side of titrator. Note: At this point, a blue color will develop in the titration vessel.

m. Cover the hole of the manifold button on the left side of the titrator (do not press down), then squeeze the rubber bulb till the buret is filled. Uncover the hole and the buret will self-zero.

n. Set microammeter pointer to 10 with "CALIBRATE" knob.

o. Lower the cup holder on the induction furnace and place porous sample cup with sample in position.

p. Turn on the high voltage switch (located below the red indicator light on the lower left side of the induction furnace).

q. Return cup holder and sample cup to operating position.

r. Check to see if bubbles of gas are being evolved from the titration reaction vessel. If not, lower cup holder and check to see if sample cup is in proper position.

s. When SO_2 is evolved the microammeter reading will decrease. Keep the reading between 10 and 12 by depressing the "COARSE" and "FINE" buttons as required. When reading no longer changes, adjust reading to exactly 10 with "FINE" button. Titration is complete.

Things that should occur during combustion:

(1) An orange light will appear over the sample cup.

(2) After about 2 minutes the sample cup will begin to emit orange light.

(3) A white gas will be evolved from the titration vessel until near the end of the titration.

(4) The plate current will increase until all SO_2 in evolved, then decrease.

(5) The grid current will decrease as the plate current increases.

t. Carefully lower the cup holder.

u. Read and record the buret reading.

v. Drain the titration vessel and refill as before the further analyses.

w. Remove the sample cup with tongs or test tube holder.

5. Furnace Factor Determination:

a. Obtain a sample of known sulfur concentration, dry to constant weight.

b. Weigh at least 3 samples of the known into 3 sample cups. Record the weights.

c. Run the samples as described for routine samples.

6. Calculations

6.1 Total Sulfur

$$\text{Total Sulfur (wt\% as } SO_4^{=}) = \frac{30 \times V \times FF}{W}$$

Where:

V = volume of iodate titrant used, ml
W = weight of solids sample, g
FF = furnace factor
30 = conversion factor for $SO_4^{=}$ equivalent weight and percent

6.2 Furnace Factor

$$FF = \frac{S \times W}{30V}$$

where:

FF = Furnace Factor
S = Sulfur content of standard, wt% as $SO_4^{=}$
V = volume of iodate titrant used, ml

Use the average furnace factor found with the replicate standard analyses.

7. Note

The volume of titrant added by pushing the "FINE" button may be adjusted with the "SENSITIVITY" control on the rear of the titrator unit.

8. Reference

LECO Semi-Automatic Sulfur Determinator Instruction Manuals, LECO Corporation, St. Joseph, Michigan.

Section 4

QUALITY ASSURANCE PROGRAM

4.1 INTRODUCTION

This quality assurance program details procedures for establishing a laboratory quality control (QC) program and also gives the quality assurance procedures which will be used for monitoring the QC program. The purpose of the QC program is to systematically insure that the precision and accuracy of all analytical data meet required limits of acceptability for proper evaluation of project results. The QC program will monitor and document the quality of data produced by both the on-site laboratory and subcontractors. Quality assurance procedures will be used to ensure the effectiveness of the QC program.

The quality assurance program will consist of three phases. During Phase I, the project Quality Control Coordinator will ensure that the QC program is established. During Phase II he will ensure the QC program is being implemented effectively. Round robin samples prepared by an outside laboratory will be utilized and a quality assurance audit will be carried out. In Phase III, after completion of project field activities, a written evaluation of the project quality control effectiveness will be prepared.

4.2 ORGANIZATION

The organizational structure shown in Appendix C on page 158 illustrates the basic QC functions of the project personnel.

The project Quality Control Coordinator (QCC) will coordinate the quality control program and quality assurance procedures with operations personnel to insure that the quality control program is properly functioning throughout the project. In addition to responsibility for the overall functioning of the QC program, specific duties of the QCC will include performance of the QC audit(s) and maintenance of the round-robin reference sample program. The QCC will report to the project manager.

4.3 QUALITY ASSURANCE PLAN

The quality control for the project will be developed and executed under a three phase QA program.

Phase I

Phase I consists of an initial period of laboratory start-up and on-site evaluation of instruments and methods for precision and accuracy. QC charts will be prepared for each analytical procedure. Instructions for constructing these charts are listed in Section 4.7.1, Development of Quality Control Charts. A QC notebook will be initiated at this time. Contents of the QC notebook will include the following:

Item	Reference
QC Charts	Section 4.7
QC Memos	Appendix C, page 159

Item	Reference
Lab Notebook Audits	Appendix C, pages 160 and 161
Copies of calibration curves with check standard values and acceptance limits	

Other log books and notebooks that will be initiated during Phase I include:

Item	Reference
Analytical Balance QC Log	Appendix C, page 162
Sample Log Book	Section 4.6
Instrument Service and Repair Notebook	Section 4.4
Reagent Log Book	Section 4.4
Lab Notebook for each analyst	Appendix C, pages 160 and 161

Description of these items may be found under the associated references. Some of the items may be combined into a single notebook.

Phase II

Phase II covers routine laboratory operation. During routine operations, at least one duplicate and one spiked sample (if appropriate) will be determined per day for each analysis run. If samples in a batch exceed 10 in number, a second duplicate and spike will be included for every multiple of 10 samples. These duplicate and spike results will be monitored with modified Shewart charts as specified in Section 4.7, Quality Control Data Aquisition and Data Handling. Samples will be logged in accordance with the procedure outlined in Section 4.6, Sample Handling, Shipping, and Storage. Any samples which are submitted to a subcontractor for analyses will be handled as described in Section 4.6. Modified Shewhart charts will be used to monitor the

quality of data obtained from subcontractors by documenting the results obtained on blind duplicates and spiked samples or standards. Whenever results from either the site laboratory or a subcontractor exceed control limits, results of that analytical run will be considered invalid. The investigation into the problem and the remedies instituted will be the responsibility of the laboratory supervisor. He will document the investigation with a Quality Control Memo (Appendix C, page 159) which will be submitted to the QCC for final review.

Also during phase II, the overall effectiveness and performance of the data aquisition and handling system will be continually evaluated. Standards will be routinely submitted to the on-site laboratory and to outside laboratories for analyses and the analytical results will be documented. A major audit by the Quality Control Coordinator will be performed on the quality control system. As part of the audit, notebooks and logs will be evaluated utilizing the notebook audit sheet (Appendix C, pages 160 and 161).

Phase III

At the completion of the project a comprehensive quality assurance report including the documents, memo's, and charts generated during the project will be prepared. Any evaluations and suggestions for improvement that develop from the system audit(s) will be included.

4.4 CALIBRATION AND CONTROL

Instruments

An Instrument Service and Repair Notebook will be maintained by the on-site

laboratory supervisor. All major analytical instruments will be described including accessories. For example, a pH meter will be identified by manufacturer, model, serial number, and number and type of electrodes. The date the instrument and/or accessory is put into service will be recorded. Any routine maintenance and calibration procedures required will be documented along with a schedule and check-off sheet to indicate that the work has been completed. Service and repair performed by authorized repairmen will be documented by inserting copies of their reports in the notebook.

Instruments will be calibrated according to manufacturer recommendations or as described in the written procedures in Section 3 of this manual.

The analytical balance calibration will be verified weekly and any time the balance is moved or subjected to rough handling. If at any time, standard Class S weights cannot be weighed to $\pm$ 1 mg of their stated value, the balance will be recalibrated by a service engineer. A form for weekly verification of the analytical balance calibration is shown in Appendix C, page 162. A daily calibration of each pH meter will be made and recorded in the Instrument Service and Repair Notebook. A daily reading of a conductivity standard will likewise be recorded for the conductivity meter.

Reagents

All reagent chemicals will be dated upon receipt and stored properly in accordance with safety regulations. A "first-in, first-out" storage procedure will be used.

A reagent log-book will be maintained in the laboratory. Entries will document the manufacturer and lot number of the reagent or stock solution,

date of preparation, technician, the concentration of the solution, and the expiration date (if appropriate). A label containing this information will be affixed to the reagent bottle.

4.5 DOCUMENT CONTROL

All written analytical procedures will state the date at which the procedure becomes effective and any subsequent revision will be given an effective date. Procedure revisions will be sent to all affected parties.

Instrument manuals will be stored in specified locations convenient to the respective instruments. All notebooks and logs will be stored in specified locations within the laboratory.

4.6 SAMPLE HANDLING, SHIPPING, AND STORAGE

The following outline describes in chronological order the QC procedures to be followed for sample handling, storing, and shipping. More specific sampling instructions are given in Section 1 of this manual.

1. When samples are received in the lab, they will be identified with a numbering code.
2. This information will be recorded in a sample log along with date, sampling location, and other related information (see Figure 1.2).
3. Samples will be preserved when required.
4. Samples will next be segregated into those to be analyzed at the site laboratory and those to be sent to outside labs.
5. Those analyses such as sulfite which require immediate attention will be started at this point.
6. All shipped samples will be packaged consistent with the physical abuse they may receive during shipment. Samples will be shipped

and packed in a manner which insures that the required preservation-handling requirements are met and maintained during the entire period of shipment.

7. An inventory of the samples by I.D. number and analyses required will be recorded in the Sample Shipment Letter. A separate form will be prepared for each shipping container. One copy of the Sample Shipment Letter will be included in the shipping box, one copy will be sent to the project manager and one to the shipment destination. The original will be maintained at the field facility.

8. Upon delivery for shipment, field personnel will telephone the outside laboratory and inform them of the estimated time of arrival of the samples, the carrier, the number of shipping containers, and whether the samples will be held for pick-up or will be delivered.

9. When the outside laboratory receives the shipment, they will sign and date the letter, note any discrepancies on it and forward a copy of the letter to the Project Manager.

4.7 QUALITY CONTROL DATA AQUISITION AND DATA HANDLING

The procedures discussed in Sections 4.4 through 4.6 are designed to enable the laboratory to produce reliable analytical data. Analytical data quality is monitored by a continuing statistical evaluation of analytical precision and accuracy.

Analytical precision and accuracy are defined in the following paragraphs and then a listing of the procedures to be followed for monitoring these parameters is given.

Precision

Precision refers to the reproducibility of replicate analyses. If an analysis is performed many times on the same sample, results will not be the same but will vary around an average value. The width of this group of results is a property of the given procedure. The narrower the grouping, the closer each individual

measurement is to the average, the more precise the method is said to be. Conversely, the more disperse the grouping, the less precise it is.

In a properly designed analytical procedure, this scatter of results is due to the accumulated effects of all the indeterminate random errors associated with the procedure. The width of this grouping is specified by a parameter called the standard deviation. The distribution of individual results of a properly designed analysis are specified by knowledge of the mean and the standard deviation provided the distribution law is known. This specification allows the establishment of consistent criteria for the acceptance or rejection of data.

Precision control charts based on these acceptance criteria are used to establish and monitor the reproducibility of analytical procedures.

Accuracy

Accuracy refers to the agreement between a determined constituent concentration and the true or known concentration. Accuracy in the laboratory is established and monitored with accuracy control charts which are similar in construction to precision control charts.

Poor accuracy is caused by systematic errors. These errors are always in one direction, either high or low relative to the "true" value, and are determinate. This deviation is often called laboratory bias.

It is much more difficult to monitor accuracy than it is to monitor precision. Analyses of samples with an unknown matrix, containing an unknown quantity of some substance which may be in an unknown form cannot always be judged to have high accuracy when an added amount of "spike" gives a good yield.

Unusual matrices must be carefully monitored and accuracy data for unusual samples should generally be evaluated separately from established control charts. For example, a $\pm$ 10% accuracy control limit for water sample analyses cannot be expected to apply to analyses of fly ash.

Consideration must also be given to whether or not the spike addition will respond in the same manner as the element in question already in the sample will respond. The spike will be free and available to treatment in most cases, while the naturally occurring element may be found in the matrix or may be present in a volatile or insoluble form, etc.

4.7.1 Development Of Quality Control Charts

The data necessary for establishment of both precision and accuracy control charts will be generated simultaneously. To develop this data for an analytical procedure, the following steps will be followed.

1. Select twenty samples which are similar to the routine laboratory samples which will be analyzed with the analytical procedure.
2. Analyze each sample in duplicate.
3. Add known amounts of standard ("spike") to an aliquot of each sample. The final concentration in each spiked sample aliquot must be within the concentration range of the analytical procedure and should be within the middle one-third of the range. For each sample aliquot, use the following equation to determine the amount of spike to be added (see Table 4-1 for an example).

$$Amts = \frac{Amtos\ (Cncss - Cncos)}{Cncs - Cncss}$$

where: Amts = Amount of standard to be added

Amtos = Original sample aliquot size

Cncss = Constituent concentration required in spiked sample

Cncos = Average constituent concentration found in original sample

Cncs = Constituent concentration in standard

Note: Amounts (Amts and Amtos) are expressed in ml for liquid samples and in grams for solids samples.

Concentrations (Cncss, Cncos and Cncs) are expressed in mg/l for liquid samples and in weight % for solid samples.

4. Analyze each of the spiked samples.

TABLE 4-1

EXAMPLE CALCULATION OF SPIKE AMOUNT REQUIRED
FOR TOS IN SOLIDS ANALYSIS

		TOS Concentration (wt% as $SO_3^=$)			
Sample	Duplicate	Found	Average (Cncos)	Required (Cncss)	Amts*
1	A1 A2	47.72 47.12	47.42	50.0	0.211
2	A1 A2	45.68 45.98	45.83	47.5	0.113
3	A1 A2	47.01 46.59	46.80	52.0	0.507
-	- -	- -	-	-	-
-	- -	- -	-	-	-
20	A1 A2	43.78 44.13	43.96	46.0	0.126

$$*Amts = \frac{Amtos\ (Cncss - Cncos)}{Cncs - Cncss}$$

Amts = Amount of Na_2SO_3 to be added, g

Amtos = Original sample aliquot size = 1.000 g (or as required)

Cncss = $SO_3^=$ concentration required in spiked sample, wt%

Cncos = Ave. $SO_3^=$ concentration found in original sample, wt%

Cncs = $SO_3^=$ concentration in standard Na_2SO_3, wt%

$$= \frac{MWSO_3^=}{MWNa_2SO_3} \times 100\% \times PNa_2SO_3 = \frac{80.06}{126.04} \times 100\% \times .980 = 62.25\ wt\%$$

PNa_2SO_3 = Na_2SO_3 Purity = $\frac{98.0\%}{100\%}$ = .980 (for this example)

for Sample 1: $$Amts = \frac{1.000\ g \times (50.0\ wt\% - 47.42\ wt\%)}{62.25\ wt\% - 50.0\ wt\%} = 0.211\ g$$

Notes:
1. The required $SO_3^=$ concentration values are arbitrarily selected within the normal working concentration range.
2. The amount of spike required depends on the original sample aliquot size. 1.000 g was arbitrarily used for the original sample aliquot size in this example.

Precision Control Charts

Data obtained from the duplicate analyses of the 20 unspiked samples are used to calculate the control limit for an analytical precision control chart. The following procedure is used (see Table 4-2 for an example).

1. Calculate the precision statistic, I, for each pair of duplicates:

$$I = \frac{/A1 - A2/}{A1 + A2} \times 10^3$$

where: A1 = Analytical result for first duplicate
A2 = Analytical result for second duplicate
/A1 - A2/ = Absolute value of the difference between A1 and A2

2. Calculate the average value, $\bar{I}$, of the I statistic:

$$\bar{I} = \frac{\Sigma I}{n}$$

where: ΣI = Sum of I values
n = Number of I values

3. Calculate the precision upper control limit:

Upper Control Limit, UCL = $3.27\bar{I}$

4. At least 50% of the I values used to calculate the UCL must be $\leq$ UCL/3 and none of these I values may exceed the UCL. Data that do not meet these criteria cannot be used for establishing control charts.

5. Prepare the precision control chart as shown in Figure 4-1.

Accuracy Control Charts

Data obtained from analyses of the 20 samples before and after spiking are used to calculate control limits for an analytical accuracy control chart. The following procedure is used:

1. Calculate the yield, Y, for each spiked sample:

$$Y = \frac{Cncf}{Cncss} \times 100\%$$

where: Cncf = Constituent concentration found in spiked sample
Cncss = Theoretical constituent concentration in spiked sample

2. Calculate the average yield, $\bar{Y}$, and the standard deviation of the yield, σ_Y:

$$\bar{Y} = \frac{\Sigma Y}{n}$$

$$\sigma_Y = \sqrt{\frac{\Sigma(\bar{Y} - Y)^2}{n - 1}}$$

where: ΣY = Sum of Y values
n = Number of Y values

3. At least 50% of the Y values must fall within the range of $\bar{Y} \pm \sigma_Y$ and all Y values must fall within the range of $\bar{Y} \pm 3\ \sigma_Y$. Data that do not meet these criteria cannot be used for establishing control charts.

4. Calculate the accuracy control limits:

Upper Control Limit, UCL = $\bar{Y} + 3\sigma_Y$

Lower Control Limit, LCL = $\bar{Y} - 3\sigma_Y$

5. Prepare the accuracy control chart as shown in Figure 4-2.

Table 4-2

EXAMPLE CALCULATION OF CONTROL LIMITS FOR PRECISION AND ACCURACY CONTROL CHARTS FOR TOS IN SOLIDS ANALYSIS

TOS Concentration (wt% as $SO_3^=$)

	Original Sample			Spiked Sample		I	Y
	Duplicate		Average	Calc.	Found	$(= \frac{/A1 - A2/}{A1 + A2} \times 10^3)$	$(= \frac{Cncf}{Cncs} \times 100\%)$
Sample	A1	A2	(Cncos)	(Cncss)	(Cncf)		
1	47.72	47.12	47.42	50.00	48.42	6.33	96.84
2	45.68	45.98	45.83	47.50	47.23	3.27	99.43
3	47.01	46.59	46.80	52.00	50.95	4.49	97.98
4	47.76	47.04	47.40	49.25	49.48	7.59	100.47
5	45.88	46.27	46.08	48.35	47.02	4.23	97.25
6	46.53	45.44	45.99	50.05	50.10	11.85	100.10
7	47.00	46.83	46.92	48.85	48.32	1.81	98.92
8	47.96	47.00	47.48	49.80	48.21	10.11	96.81
9	48.40	48.08	48.24	52.55	51.38	3.32	97.77
10	46.45	46.72	46.59	48.75	48.56	2.90	99.61
11	45.44	46.40	45.92	47.80	48.02	10.45	100.46
12	47.48	47.52	47.50	49.20	46.76	0.42	95.04
13	46.68	46.12	46.40	48.60	48.59	6.03	99.98
14	47.48	47.82	47.65	51.25	51.41	3.57	100.31
15	50.96	51.13	51.05	55.50	54.87	1.67	98.86
16	47.08	46.80	46.94	49.65	50.02	2.98	100.74
17	48.02	49.08	48.55	51.00	50.30	10.92	98.63
18	39.86	40.51	40.19	42.25	41.45	8.09	98.10
19	43.01	43.50	43.26	44.65	43.57	5.66	97.58
20	43.78	44.13	43.96	46.00	46.26	3.98	100.57

Precision Control Limit

$$\bar{I} = \frac{\Sigma I}{n} = 5.48$$

Upper Control Limit, UCL = $3.27\bar{I}$ = 17.9

Accuracy Control Limits

$$\bar{Y} = \frac{\Sigma Y}{n} = 98.77\%$$

$$\sigma_Y = \sqrt{\frac{\Sigma(\bar{Y} - Y)^2}{n-1}} = 1.57\%$$

Upper Control Limit, UCL = $\bar{Y} + 3\sigma_Y$ = 103.5%

Lower Control Limit, LCL = $\bar{Y} - 3\sigma_Y$ = 94.0%

4.7.2 Use of Quality Control Charts

After quality control charts have been established for each method, they will be used for routine monitoring of analytical precision and accuracy. The following procedures will be used for monitoring the analytical data.

1. Each set of analyses must include at least one duplicate and one spiked sample (or standard). If the set includes more than 10 samples, then at least one duplicate and one spike must be run for each multiple of 10 samples. If this is not possible, a notation should be made in the analyst's laboratory notebook explaining the conditions that make it impossible (e.g., "Duplicates could not be run due to insufficient volume of sample").

2. After calculating concentrations in the normal manner, compute the precision statistic, $I = \frac{/A1-A2/}{A1+A2} \times 10^3$ where A1 is the first duplicate result and A2 is the second.

3. Record the calculated value along with the date, sample identification, initials, matrix, etc., in the appropriate section of the Quality Control Notebook.

4. Plot the I statistic value on the appropriate precision graph. Page 163 of Appendix C can be photocopied to provide blank QC charts.

5. Calculate the yield, $Y = \frac{Cncf}{Cncss} \times 100\%$, where Cncss is the calculated concentration of the spiked sample or standard, and Cncf is the concentration found.

6. Repeat step 3. for spiked samples then plot the Y statistic values on the appropriate accuracy graph.

7. If any I or Y value falls outside the associated control limit or if any seven successive Y values fall on the same side of the average Y value line then notify the Laboratory Supervisor. Analytical results determined since the last in-control check was made are suspect and should not be reported until verified. Further analyses using the method in question must be suspended until the problem is identified and resolved. A Quality Control Memo should be used to document the investigation. A Quality Control Memo form is shown in Appendix C, page 159.

8. After all the QC data has been transferred to the QC chart, the analyst should write "QC" at the top of his lab notebook page. If no QC data appears on the page, "No QC" is written at the top of the page.

4.7.3 Other Methods For Monitoring Analytical Quality

Following are some additional procedures which will be used for monitoring the quality of sample analyses.

Ionic Imbalance

The ionic imbalance of a complete sample analysis can be computed as shown on the calculation form in Table 4-3. The ionic imbalance is calculated here as the difference between the total cation and anion concentrations divided by the average of the cation and anion concentrations and multiplied by 100% when analytical results for liquors are expressed in milliequivalents/liter (meq/l) and for solids in milliequivalents/gram (meq/g).

Since the sulfate plus total oxidizable sulfur concentrations together make up the total sulfur determined in the total sulfur analysis, the sulfate plus total oxidizable sulfur concentrations or the total sulfur concentration can be used in calculating the sum of anion concentrations for a sample analysis.

When thiosulfate is present in a liquor sample, the thiosulfate concentration in mg/l is multiplied by 0.0089 and this value is added to the total oxidizable sulfur (TOS) concentration (meq/l) when calculating the sum of the anions (ΣAnions). This is required because two equivalents of thiosulfate, in terms of ionic strength, represent only one equivalent in terms of reaction with iodine in the TOS analysis.

All TOS is present as thiosulfate in the quality assurance liquor standard used. For these samples, the TOS concentration should be doubled (and the thiosulfate concentration ignored) when calculating ΣAnions. That is, for quality assurance liquor standards only,

$$\Sigma\text{Anions} = 2 \times [\text{TOS}] + [SO_4^{=}] + [Cl^-] + [\text{Total Alkalinity}]$$

where [ ] is the concentration in meq/l.

For solids samples containing thiosulfate, the thiosulfate concentration in wt% (10^{-4} x ppm thiosulfate) is added to the TOS concentration (meq/g) when calculating ΣAnions.

If it is desired to compute ΣAnions using the total sulfur concentration instead of the total oxidizable sulfur plus sulfate concentrations, a related adjustment must be used. Here, one equivalent of thiosulfate in terms of ionic strength represent two equivalents in terms of oxidation to sulfate in the total sulfur analysis. Therefore, the meq/l or meq/g of thiosulfate calculated as described above is subtracted from the total sulfur concentration when calculating ΣAnions with the total sulfur concentration.

To summarize, ΣAnions can be calculated in either of two ways:

$$\Sigma\text{Anions} = [\text{TOS}] + [SO_4^{=}] + [Cl^-] + [OH^-] + [CO_3^{=}] + \text{Thiosulfate conc}$$

or $$\Sigma\text{Anions} = [\text{TS}] + [Cl^-] + [OH^-] + [CO_3^{=}] - \text{Thiosulfate conc}$$

where [ ] is concentration in meq/l for liquors or in meq/g for solids and thiosulfate concentration is in mmol/l for liquors or in mmol/g for solids. Use the Ionic Imbalance Calculation Sheet shown in Table 4-3 for these calculations.

Ionic imbalances should be monitored with control charts similar to the accuracy control charts described in Section 4.7.1. The value for the ionic imbalance itself is used in place of the Y value for the control chart. Twenty solids analysis ionic imbalance results are used to calculate control limits which are then used to construct a solids analysis ionic imbalance control chart as described under Accuracy Control Charts in Section 4.7.1. Twenty liquor analysis ionic imbalance values are used to construct a liquor analysis ionic imbalance control chart. Ionic imbalance results are then plotted on the appropriate chart for every complete analysis performed and if an ionic imbalance exceeds a control limit or if seven consecutive values fall on one side of the average ionic imbalance line then the laboratory supervisor will be notified.

An ionic imbalance will be calculated whenever a complete analysis is made on a solids or liquor sample. Results will not be reported for any sample analysis with an ionic imbalance outside of the control limits.

Sulfur Analyses Balance

The sum of the sulfur concentrations found in the sulfate and total oxidizable sulfur analyses must be equivalent to the sulfur found in the total sulfur analysis. If there is not an equivalency, the analytical problem must be found and corrected.

The total oxidizable sulfur plus sulfate concentrations may be converted to the equivalent total sulfur concentration as follows:

$$TSE = SO_4 + TOS \times \frac{96.1}{80.1} + S_2O_3 \times \frac{96.1}{112.1}$$

$$= SO_4 + 1.2 \times TOS + 0.86 \times S_2O_3$$

where: TSE = Total Sulfur Equivalent (as SO_4)
SO_4 = Sulfate (as SO_4)
TOS = Total Oxidizable Sulfur (as SO_3)
S_2O_3 = Thiosulfate (as S_2O_3)

all liquor concentrations are in mg/l and
all solids concentrations are in wt%
(wt% = ppm x 10^{-4})

TABLE 4-3

IONIC IMBALANCE CALCULATION SHEET

	Liquor Sample ____			Solids Sample ____		
	mg/l	x factor	= meq/l	wt%	x factor	= meq/g
Na	____	0.0435	____	____	0.435	____
Ca	____	0.0499	____	____	0.499	____
Mg	____	0.0823	____	____	0.823	____
ΣCations			____			____
TOS (as SO_3)	____	0.0250*	____	____	0.250	____
SO_4	____	0.0208	____	____	0.208	____
Cl	____	0.0282	____	____	0.282	____
OH	____	0.0588	____	____	0.588	____
CO_3	____	0.0333	____	____	0.333	____
Total Alk			____			
ΣAnions			____			____
Ionic Imbalance	____			____		

$$\text{Ionic Imbalance} = \frac{\Sigma\text{Cations} - \Sigma\text{Anions}}{\Sigma\text{Cations} + \Sigma\text{Anions}} \times 200\%$$

* In the case of quality assurance liquor standards this factor should be 0.0500 instead of 0.0250. See 4.7.3, Ionic Imbalance.

pH and Conductivity Screening

The pH measured at the sample point (see Section 1.2) and undiluted conductivity found for slurry and liquor samples with Methods 5 and 6 should be used to screen samples brought to the laboratory for analyses. Routine samples collected at the same sample point should have similar pH values and conductivities from day to day. If the pH or conductivity has changed significantly and the reason is unknown, it is possible that the sample was improperly taken, or taken from the wrong sample point. Another possibility is an upset in process conditions.

When a pH or conductivity value is outside of the expected range, a new sample should be taken immediately.

5. Reference

Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019 (March 1979).

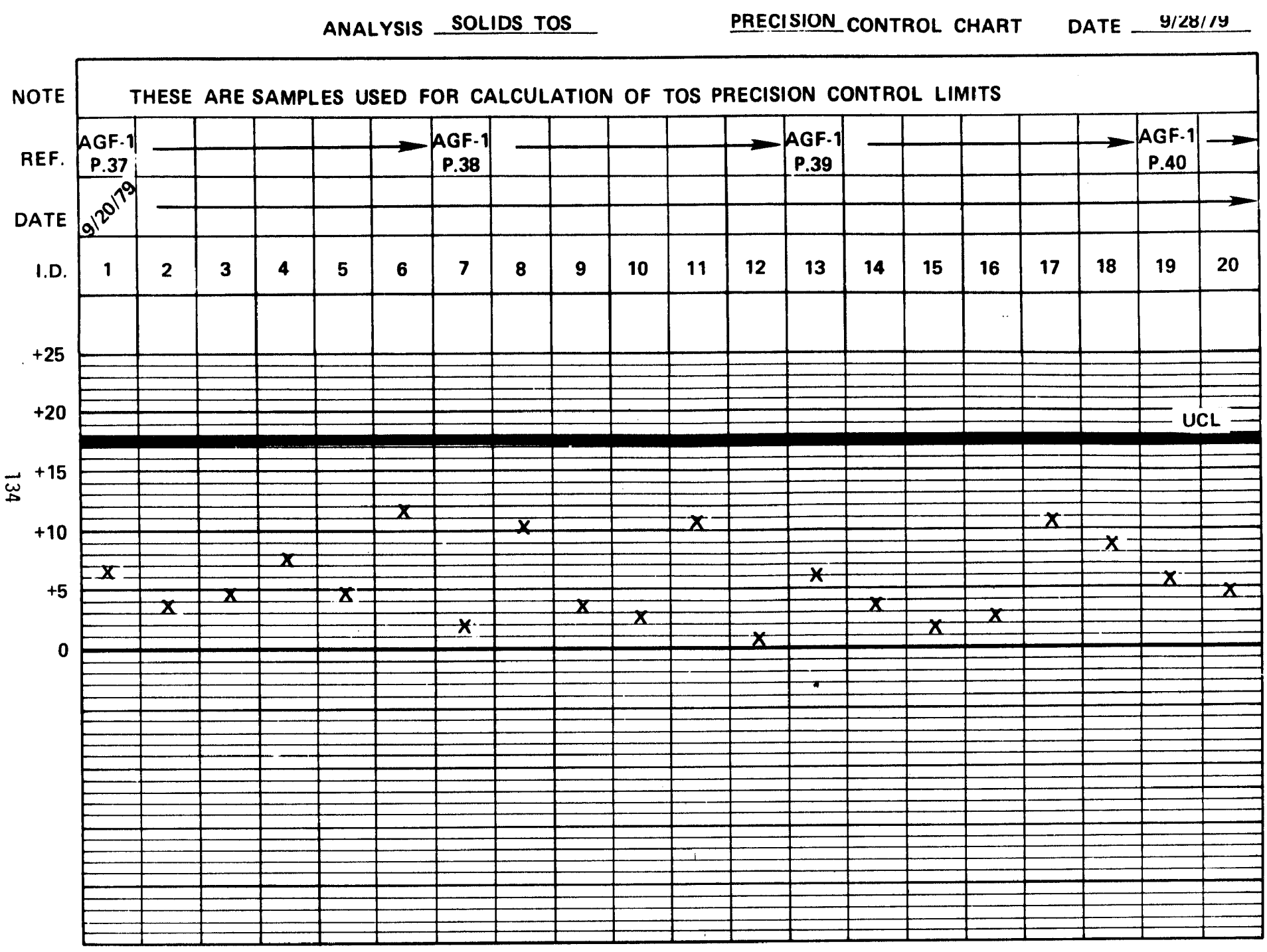


FIGURE 4.1 EXAMPLE PRECISION CONTROL CHART

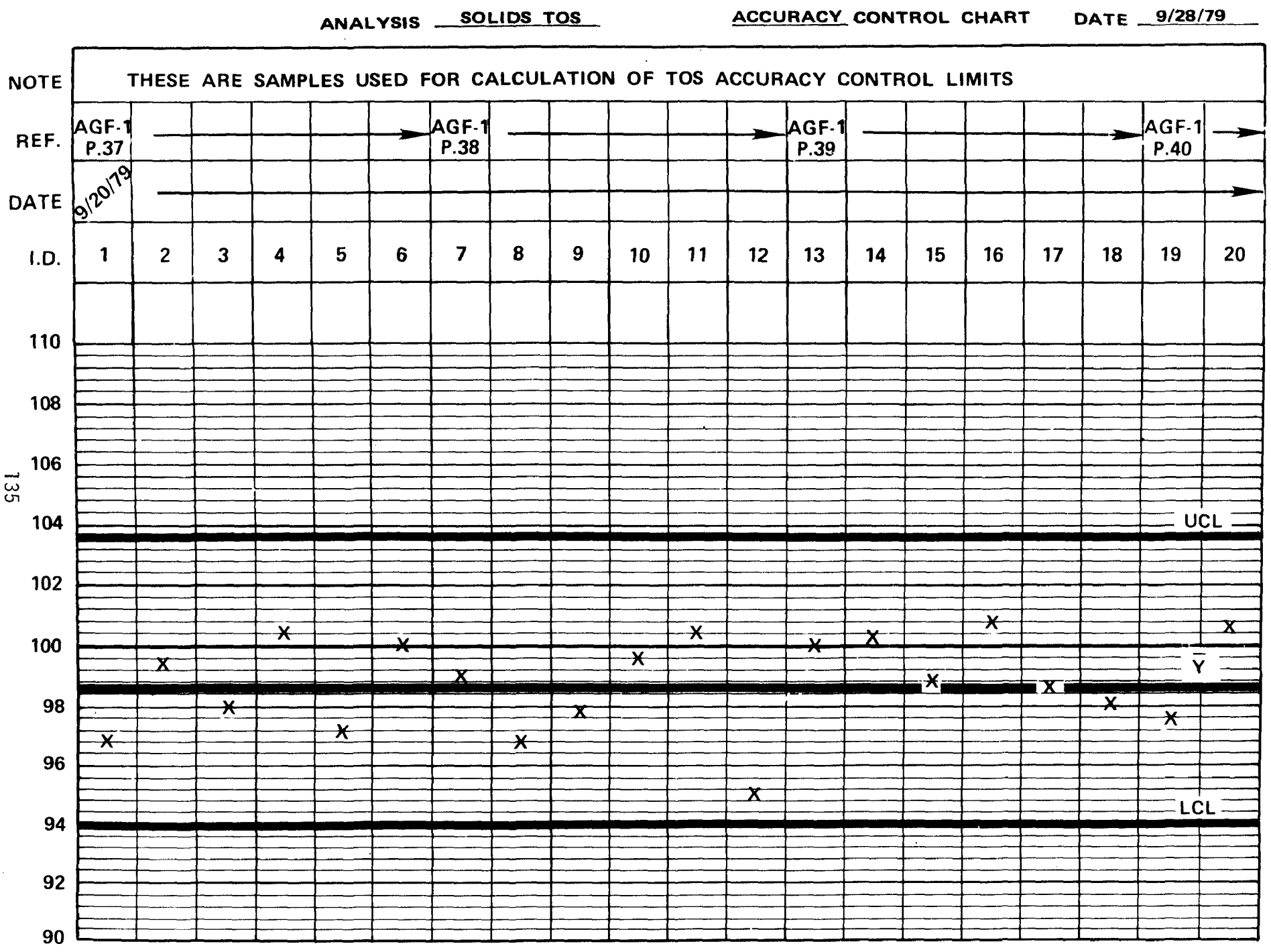


FIGURE 4.2 EXAMPLE ACCURACY CONTROL CHART

APPENDIX A

ION CHROMATOGRAPH MATERIAL REQUISITION

APPENDIX A

ION CHROMATOGRAPH MATERIAL REQUISITION

Item #	Quantity	Description	Catalog #
1.	1	Auto Ion System 12 Analyzer complete with provision for one Separator/ Suppressor column system, loop-type sample injection valve, high sensitivity conductimetric detector, eluent reservoirs, quick disconnect fittings, two constant volume pumps with adjustable flowrates, solid state programmable controller, and all other necessary accessories.	030002
2.	1	Autosampler - Holds 99+, 15 ml samples, manufactured by Gilson.	030009
3.	1	Master Starter Kit - Contains flanging tool, various tubing fittings, extra-buffer bottles and injection syringes and Milton-Roy Pump rebuild kit.	030190
4.	2	3x250 2% Brine Separator Columns	030364
5.	1	Anion/Cation Column Kit Ca, Mg, Na Includes 3x150 mm, 3x250 mm, 3x500 mm Anion Separator Columns, 6x250 Anion Separator, 3x150 mm, 6x250 mm Cation Separator and 9x250 mm Cation Suppressor.	030011
6.	1	Honeywell Dual Pen Recorder - AFB 200A1015 1 pen input selectable, variable speed.	030012

APPENDIX B

SHORT FORM PROCEDURES

Sequence

1. Start anion system on IC to obtain steady baseline.

2. Weigh a 1-oz bottle for % SS, and label this bottle and a 4-oz bottle for each sample.

3. Collect samples. See Method 1 for amount of sample to collect in the 1-oz bottle; fill the 4-oz bottle. Measure pH at sample point.

4. Log in samples, and place assigned numbers on each bottle.

5. Measure density, temperature, and conductivity on each sample in 4-oz bottle before filtration.

6. Filter the 4-oz samples without washing.

7. As soon as possible, run Total Oxidizable Sulfur on the unoxidized* filtrate.

8. To a 250 volumetric flask, add 1 ml of unoxidized filtrate from #6 above, and then add 1 ml of 30% H_2O_2; mix well to oxidize sulfite to sulfate (Total Sulfur). Dilute the Total Sulfur sample to 250 ml exactly.

9. Run the oxidized sample through the IC on auto mode. If you get a peak for SO_3, notify lab manager immediately.

10. While the IC is running, complete the % suspended solids samples.

11. Next, run calcium and magnesium (plus hydroxide and thiosulfate, if required) on the unoxidized filtrate from #6 above.

12. Dilute some of the remaining unoxidized liquid (filtrate) 1:500 for diluted conductivity and Na analysis by flame photometer.

13. Complete calculations for concentrations and ionic imbalance as presented in Sections 3 and 4 of the Laboratory Manual.

---

*Unoxidized = filtrate without H_2O_2 addition
Oxidized = filtrate with H_2O_2 added

Anion Analysis with Auto-Ion 12 Analyzer

Initial Startup

1. Check that:

   a. "Program Select" is set to 1.

   b. Eluent pump (front pump) vernier is set to 30.0.

   c. Detector Range switch is set to 5.

   d. "Gauge" switch is up.

   e. "B Samples/Cycle" is set to 99.

   f. "MANUAL AUTO" is set to AUTO.

2. Switch "PGM Auto Manual" to Manual.

3. Flip up "H_2O", "ELU", "SEP", and "3" (RECORDER) switches. Turn "Eluent Selection to E_1. Flip down "RGN" and "INJ" switches, then push "Write" button and hold down momentarily.

4. Flip "Pump" switch to ON. If gauge indicates greater than 700 psi or if maximum reading does not fall to 650 psi or less after 5 minutes, flip "Pump" switch off and notify lab supervisor.

5. Push and hold down "METER ZERO" button while setting blue and red pens to zero with the "BLUE" and "RED" recorder knobs.

6. When blue pen draws a steady line, unlock "OFFSET" control (side lever up) and set blue pen on zero with "OFFSET"; relock "OFFSET".

Sample Setup

1. Dilute each sample and an equal volume of 30% H_2O_2 1:250 with deionized water (e.g., add 1 ml sample + 1 ml H_2O_2 to a 250 volumetric flask and dilute to volume with deionized water). Mix well. Note that other dilutions may be required to obtain peaks within the working range.

2. Use the large automatic pipet to transfer samples to the automatic sampler sample tubes. Start with the first sample tube to the right of the sampler suction tube. Transfer standards and diluted samples in the following order:

   a. Mid-anion Standard

   b. Diluted samples, maximum of 10 (if there are more than 10 samples, repeat Steps a-d and f-k for each multiple of 10; Step e is performed only for the final group of samples)

c. Duplicate of the last diluted sample transferred

d. Mid-anion Standard

e. Sample of deionized water

Use the following procedure to transfer samples to sample tubes:

f. Wipe outside of the automatic pipet syringe with a Kim Wipe.

g. Depress pipet button completely, then slowly suck the sample into the syringe.

h. Dispense the syringe contents into a waste container.

i. Suck a new portion of the sample into the syringe, then dispense into the appropriate sample tube.

j. Record the sample description, dilution and sample tube number in your lab notebook. Leave room in notebook to record peak heights.

k. Repeat Steps f-j for each diluted sample and standard.

3. Set "Total Samples" to the total number of sample tubes filled. Set "A Samples/Cycle" to either 13 or to the total number of sample tubes filled minus one, whichever number is smaller.

Start of Operation

When depressing a button in the following steps, hold the button down momentarily to assure operation:

1. Push "Reset" button.

2. Switch "PGM Auto Manual" to Auto.

3. Push "Sub-program Load" button.

4. Push "Start/Step" button.

Results

Record peak heights for each sample as follow:

1. There will be a red peak and a blue peak (5 divisions after the red) for each component.

2. The order of elution in the standard is fluoride first, then chloride, and finally sulfate. The number of divisions

on the zero line between the injection pip and the highest point on each of the component peaks (i.e., retention times) must be the same for sample and standards; this is how sample peaks are identified (i.e., F^-, Cl^- or $SO_4^=$).

3. For each of the three components for each sample, record the blue peak maximum minus the blue baseline value if the blue peak maximum is less than 100. Otherwise, subtract the red baseline value from the red peak maximum and record this value multiplied by 10.

4. Transfer results to IC worksheets, and perform the indicated calculations.

Method #1

Suspended Solids

1. Pre-weigh a clean, dry, 1-oz bottle, and record as empty bottle weight.

2. Collect % SS sample from same sample point as sample for other analyses.

3. Collect enough sample to yield about 1/8" of solids when filtered through the filter disc:

   a. V-101 about 1/4" in bottle (4 to 7 g)
   b. 3001 bottle full (around 30 g)
   c. 3501 about 1/4" from top in bottle (around 20 g)

4. Dry the outside of the bottle, then record the weight of the sample bottle plus sample. This weight minus empty bottle weight = sample weight.

5. Pre-weigh a weight boat containing a dry GFC filter disc.

6. Place the filter disc in the filter holder and assemble filter.

7. Measure two 25 ml portions of saturated $CaSO_4$ solution* into two 30 ml beakers.

8. Transfer the slurry from the sample bottle to the filter apparatus.

9. Turn on vacuum pump.

10. Rinse the sample bottle and the filter cake twice with the 25 ml portions of $CaSO_4$ solution as follows: Swirl the $CaSO_4$ solution in the sample bottle, then quickly transfer to the filter just as the liquid level in the filter reaches the top of the filter cake. Note: In order to avoid channeling and inefficient washing, it is important that the liquid level not go beneath the surface of the solids at any time before filtering and washing are completed.

11. Follow the $CaSO_4$ washings by washing down the sides of the filter funnel and the filter cake with 20-25 ml of isopropyl alcohol from a squeeze bottle.

12. Carefully transfer all the filter cake and the filter disc into the pre-weighed weigh boat.

13. Dry in microwave oven on HIGH setting for 3 minutes.

14. Remove weigh boat, and place in desiccator. Weigh when cool. This weight minus the combined weight of filter disc and weigh boat = dry solids weight.

15. Calculate as follows: $$SS\ (wt\%) = \frac{\text{Weight of Dry Solids}}{\text{Original Sample Weight}} \times 100\%$$

*$CaSO_4$ solution must be free of all suspended solids. See Lab Manual, Method #1.

Method #3

% HCl Insoluble Solids

1. Weigh about 0.2 g of dried solids samples from Method 1 and transfer to an Erlenmyer flask. Record Weight.
2. Slowly add 30 ml of 1N HCl, swirl to mix and add about 50 ml of deionized water.
3. Boil for about one minute on a hotplate with a watchglass covering flask, then remove from hotplate and stir 30 minutes with a magnetic stirrer.
4. Pre-weigh a dry GFC filter disc.
5. Place the filter disc in the filter holder and assemble filter apparatus with a clean filter flask.
6. Turn on vacuum.
7. Transfer Erlenmyer contents to filter and rinse Erlenmyer into filter with deionized water.
8. Carefully transfer all the solids to the filter disc and place on a watchglass.
9. Dry in microwave oven on HI for 3 minutes.
10. Cool in desiccator then weigh filter disc plus solids. Record weight.
11. Transfer contents of filter flask into a 100 ml volumetric flask using a funnel. Rinse filter flask into funnel with deionized water.
12. Dilute to volume, mix by inversion and transfer to a clean, dry plastic bottle. Label bottle.
13. Calculate as follows:

$$\text{HCl Insoluble Solids (wt\%)} = \frac{(\text{Weight of Dry Solids plus filter disc} - \text{weight of filter disc}) \times 100\%}{\text{Original Sample Weight}}$$

Method #6

Diluted Conductivity

Sample Preparation

1. Use 1:500 diluted absorber solution or freshly filtered slurry liquor.

2. Measure the conductivity using the procedure described below or as indicated in the conductivity meter instruction manual.

Conductivity Measurement

1. Set "Function" switch to Line. Allow 5 minutes for warm-up.

2. Rinse Conductivity Cell, and place in sample solution. Tap the cell, and dip it two or three times to remove trapped air (see Notes).

3. Set "Sensitivity" control to minumum by turning knob as far as possible counter-clockwise.

4. Rotate "Range Switch" to obtain maximum shadow. "Shadow" is the area of the electron tube not lighted. Turn "Drive" to obtain maximum shadow. If dial indication is above 20.0 or below 2.0, turn "Range Switch" to next higher or lower setting.

5. Set "Sensitivity" to maximum (turn fully clockwise).

6. Turn "Drive" to obtain maximum shadow. If you cannot obtain a clear, well defined shadow, set the "Function" switch to 1 KHz.

7. Read the Conductance by multiplying the reading on the dial by multiplier. Multiply this result by 500.

8. Save sample for sodium analysis.

Notes:

1. The cell must be clean before making any measurement. The cell should be rinsed with deionized water after each sample and before storing.

2. When taking a measurement, the cell's vent slots should be submerged. The electrode chamber should be free of any trapped air.

3. The cell should be at least 1/4" away from any other object, including the walls on bottom of the solution container.

4. Electric fields present from stirrer motors, heaters, etc., may affect readings.

Method #7

Calcium by EDTA Titration

1. Pipet 20.0 ml of filtered, undiluted sample (use 5.00 ml for lime slurry) into an Erlenmeyer flask. For solids, pipet 5.00 ml of HCl-dissolved slurry from Method #3.

2. Dilute sample to about 50 ml with deionized water.

3. Add 1 ml of 8N KOH.

4. For solids samples, add 1 drop of 1% $MgCl_2$ solution.

5. Add 0.1 g of CalVer II with a scoop (color will be purple).

6. Titrate with 0.02N EDTA until color just changes from purple to pure blue.

7. Calculations

$$\text{Calcium (mg/l)} = \frac{400 \times V}{S}$$

where:

V = Volume of 0.02N EDTA, ml
S = Sample volume from 1. above

$$\text{Calcium (wt\%)} = \frac{4V}{WS}$$

where:

V = Volume of 0.02N EDTA, ml
W = Weight of solids dissolved, g
S = Sample volume

Note: 1. If endpoint is not sharp, use a smaller sample aliquot and dilute to about 100 ml with deionized water.

Method #7

Total Hardness (Magnesium) by EDTA Titration

1. Pipet 20.0 ml of sample into an Erlenmeyer flask.

2. Dilute to about 50 ml with deionized water.

3. Add 1 ml of Total Hardness Buffer.

4. Add about 0.1 g of Hardness Indicator with a scoop (color will be pink).

5. Titrate with 0.02N EDTA until color just changes from pink to pure blue.

6. Calculations

$$\text{Magnesium (mg/l)} = \frac{243 \times (V_t - V)}{S}$$

where:

V_t = Volume of 0.02N EDTA, ml
V = Volume of 0.02N EDTA, ml used in calcium determination
S = Volume of sample, ml

Note: Calculations are based on dilutions given in Section 3.

Method #8

Sodium by Specific Ion Electrode

1. Place 50 ml of the 10 ppm Na standard and 1 ml of Ionic Strength Adjuster (ISA) in a 100 ml plastic beaker.

2. Rinse electrode, blot dry, then place in solution. Start magnetic stirring.

3. Turn to "X^+" and use "CALIBRATE" knob to adjust needle to read "1" on the red scale.

4. Place 50 ml of the 100 ppm Na standard and 1 ml of ISA in another 100 ml beaker. Repeat Step 2.

5. Use "TEMP°C" knob to set needle to read "10" on the red scale. Turn outer ring to solution temperature. Slope should read between 90 and 100%.

6. Repeat 10 ppm and 100 ppm Na standards several times to assure calibration is accurate.

7. Check 30 ppm Na standard (should read "3" on the red scale) and 50 ppm Na standard (should read "5" on red scale). Instrument is now ready for use on unknown samples.

8. Use 50 ml of a 1:500 dilution of sample, and add 1 ml of ISA. Place electrode in sample, and read red scale.

9. Multiply result by dilution factor to obtain sample concentration.

Notes:

a. Specific Ion instrument is left on at all times, set on X^+. Electrode should be stored in a sample that contains sodium (not a sodium standard).

b. Between each sample or standard that is run, the electrodes should be rinsed with deionized water and then carefully dried with tissue.

c. Use a magnetic stirrer with an asbestos pad. Stir slowly.

d. Excessive needle drift may be stopped by cleansing the sodium electrode. Dip electrode in ammonium bifluoride for 30 seconds, followed by rinsing with deionized water and drying (see electrode manual). Recalibration will be necessary.

Method #9

Chloride by $Hg(NO_3)_2$ Titration

1. Pipet 2.00 ml of sample into a flask or beaker and add approximately 20 ml of deionized water.

2. Add 2 drops of phenolphthalein indicator solution and exactly enough drops of 1N NaOH to give a red color.

3. Add 2 ml of 30% H_2O_2 (stored in refrigerator), mix, and let stand for 10 minutes (solution will turn clear).

4. Add 1 dropperful of $MnCl_2$ solution.

5. Heat solution, and boil gently for approximately 15 mintues to destroy peroxide. Absence of peroxide is shown by a change in the boiling character. It will not fizz as much. Add deionized water if necessary for volume control.

6. Cool to room temperature (in an ice bath if desired), then add 3-4 drops of bromocresol green indicator (solution will turn blue).

7. Add 1N HNO_3 dropwise until solution just turns pale green or yellow.

8. Add 1/4 contents of a Hach diphenylcarbazone powder pillow, and titrate with 0.0141N $Hg(NO_3)_2$ until color just changes from yellow to light pink.

9. Calculation

$$\text{Chloride (moles/l)} = \frac{V \times N}{S}$$

where:

V = Volume of $Hg(NO_3)_2$ titrant, ml
N = Normality of $Hg(NO_3)_2$
S = Volume of sample

Method #13

Total Oxidizable Sulfur

1. Add about 50 ml of deionized water into a clean Erlenmeyer flask.

2. Pipet in 0.1N iodate solution. Use 10.0 ml for liquor samples or 20.0 ml for solids samples.

3. Add 5 ml of 1N HCl.

4. Pipet 2.00 ml of freshly filtered, undiluted sample into flask. For solids, place in flask 0.100 to 0.120 g of dry solids dried to constant weight in microwave oven (3 minutes at HI) or at 84°C and then cool in desiccator.

5. Titrate with 0.1N thiosulfate until a pale yellow color is present and then add several drops of starch solution (this will turn solution very dark blue).

6. Continue titrating slowly until solution just turns from dark blue to colorless, the final endpoint.

7. Also run a blank by using about 50 ml of deionized water and 10.0 ml of 0.1N iodate solution.

8. Calculations

$$\text{TOS } (mgSO_3^{=}/l) = \frac{(B - S) \times N \times (40{,}000)}{V}$$

$$\text{TOS } (meq/g) = \frac{(B - S) \times N}{W}$$

where:

B = Volume of titrant used for blank, ml
S = Volume of titrant used for sample, ml
N = Normality of thiosulfate
V = Volume of sample, ml
W = Weight of sample, g

Note: 1. Blank should require about 10 ml of titrant. Samples should require less titrant. Increasing SO_3 concentration will result in decreasing titrant used.

2. Calculations are based on dilutions given in Section 3.

Method #13

Thiosulfate

1. Add approximately 50 ml of deionized water into a 250 ml Erlenmeyer flask or 150 ml beaker.

2. Place container in an ice bath contained in a large beaker.

3. When temperature is below 15°C, add 10 ml of formaldehyde.

4. Add 10.0 ml of 0.1N iodate solution.

5. Add 5 ml of 1N HCl.

6. Using a graduated cylinder, measure 50.0 ml of filtered sample into the container that is in the ice bath. For solids, place in container about 1 g (weighed to 0.001 g) of dry (84°C or microwave for 3 minutes) sample.

7. Titrate with 0.1N Thiosulfate until color is pale yellow.

8. Add a few drops of starch solution (this will cause solution to turn dark blue) and continue titrating slowly until solution just turns from dark blue to colorless.

9. Run a blank using approximately 50 ml of deionized water and 10.00 ml of 0.1N iodate solution.

10. Calculations

$$\text{Thiosulfate (mg/l)} = \frac{(B - S) \times N \times 112{,}000}{V}$$

$$\text{Thiosulfate (ppm, solids)} = \frac{(B - S) \times N \times 112{,}000}{W}$$

where:

B = Volume of titrant used for blank, ml
S = Volume of titrant used for sample, ml
N = Normality of titrant
V = Volume of sample, ml
W = Weight of sample, g

Note: Calculations are based on dilutions given in Section 3.

Method #15

Hydroxide Determination by HCl Titration

1. Pipet 10.0 ml of solution sample, or place about 0.5 g (weighed to 0.001 g) of dried solids, into a beaker or Erlenmeyer flask.

2. Add approximately 50 ml of deionized water.

3. Add 10 ml of $CaCl_2$ solution.

4. Add 3-4 drops of thymolphthalein indicator solution. (Solution should turn blue; if not, then report $\leq$ 2 mg/l OH in a solution or $\leq$ 0.02 millimoles OH/g in a solid sample.)

5. Titrate blue solution with 0.1N HCl until blue color disappears and remains clear for at least one minute.

6. Calculations

$$\text{Hydroxide (moles/l)} = \frac{(\text{ml HCl}) \times (\text{N HCl})}{\text{Volume sample, ml}}$$

$$\text{Hydroxide (millimoles/g)} = \frac{(\text{ml HCl}) \times (\text{N HCl})}{\text{Weight sample, g}}$$

Method #23

Total Sulfur by LECO

1. Turn on Filament Voltage Switch. (Other two furnace switches should be off.)

2. Add about 0.07 g of dried sample weighed to 0.001 g to a green crucible.

3. Add 1-1/2 scoops of iron accelerator chips and one scoop of tin accelerator chips to the green crucible. Place lid on crucible.

4. Fill Titration Vessel to approximately 1-1/2" below the HCl inlet with diluted HCl (15 ml HCl/1000 ml) by pushing down on "Manifold" and squeezing Aspirator Bulb.

5. Add 3-4 drops of starch indicator to diluted HCl in Titration Vessel.

6. Purge gas line by inserting crucible holder (without crucible) into furnace and opening O_2 regulator. Set O_2 flow rate to between 1 and 1.5 liters/minute.

7. Add several drops of titration solution with "FINE" button until the HCl solution turns yellow. If solution turns dark blue, an excess of the KI-KIO_3 solution has been added; empty Titration Vessel by opening stopcock beneath vessel, close stopcock, and start again at Step 4.

8. Fill the buret with KI-KIO_3 solution by holding finger lightly on Manifold and squeezing Aspirator Bulb. Set the reading on the microammeter to 10 by adjusting the "CALIBRATE" control knob. Lower crucible holder.

9. Turn on High Voltage Switch.

10. Place crucible with sample and lid on crucible holder, raise holder into the furnace, and lock in place.

11. Keep the microammeter reading between 10 and 12 by depressing "COARSE" and "FINE" buttons as required. When reading no longer changes, adjust to exactly 10 with "FINE" button. Titration is complete.

12. Record the volume of KI-KIO_3 solution used, and calculate the sample sulfur concentration.

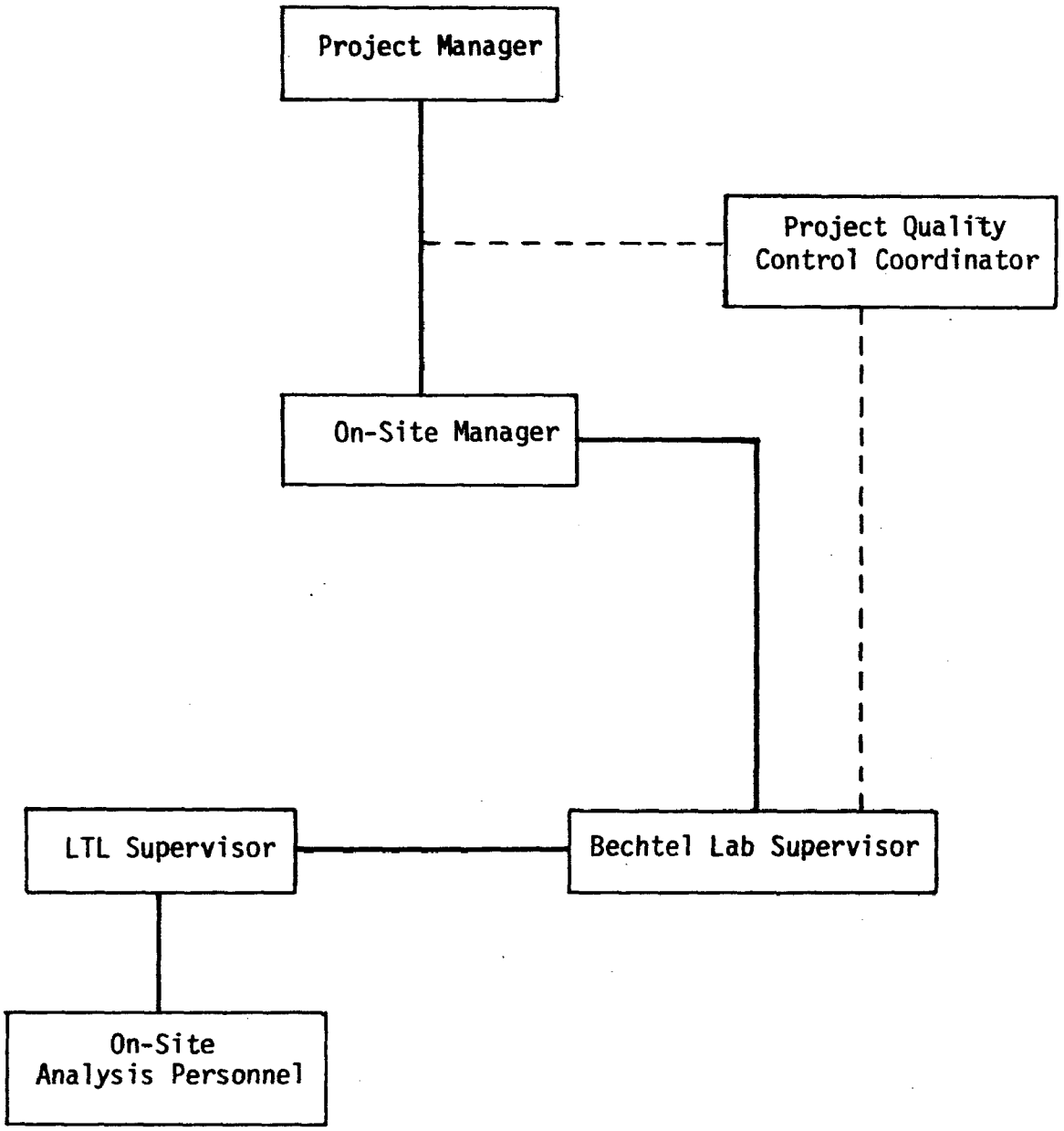
$$\text{Total Sulfur (as wt\% } SO_4) = \frac{\text{ml of KI-}KIO_3\text{ sol'n} \times 30 \times \text{Furnace Factor}}{\text{wt. sample}}$$

APPENDIX C

QUALITY ASSURANCE FORMS

DUAL ALKALI LABORATORY

ORGANIZATION CHART



QUALITY CONTROL MEMO

A Q.C. Review was performed on _____. The following items are brought to your attention for action or information.

TAKE ACTION INDICATED NOT LATER THAN	
Return to me	
See me personally	
Need not be returned	
Being sent for your information	
Furnish data requested	
Take action indicated	
Take up with _____ _____ _____	
Investigate and report to _____	
Express your judgement	
Set time when we may discuss this _____	

Date:_____ Q.C. Auditor _____

_____ Reply Below This Line _____

Date:_____ By _____

LABORATORY NOTEBOOK AUDIT

A. Neatness

1. Entries are legible.
2. Entries are not obscured or obliterated by smudges, acid holes, etc.
3. Erroneous entries are lined out with a single horizontal line. (Not obliterated).
4. Inappropriate pages are lined out with a single diagonal line.
5. Entries are in pen.

B. Completeness

1. There is sufficient information to reconstruct what was done during analysis, including calculations.
2. Entries are titled.
3. Entries are dated.
4. The method used in the analysis is identified or described.
5. Standards are identified adequately.
6. Samples are identified adequately.
7. Q.C. samples are identified adequately.
8. Aliquots and dilutions are identified adequately.
9. All columns are identified adequately.
10. Proper units are identified in the final result column.
11. There are sufficient notations and explanations in the event of unusual circumstances, i.e. interferences.
12. There are sufficient cross references (i.e., see Mud page 5 for DWF's) to permit review of calculation, etc.
13. There is either the original calibration curve graph, a cross reference to the location of the graph, or linear regression analysis parameters for the curve directly in the note book.

14. There are notations to indicate that the Q.C. data has been reported (Q.C. at the top of the page).

15. There are notations that the results have been transferred to the work-in-progress book (R at top of page).

16. There are initials of analyst and calculation checker at the bottom of the page.

17. If a standard method is referenced, any modifications or changes in the method as it was actually performed are noted.

C. Organization

1. There is either an up to date table of contents or an up to date index in the notebook.

2. The entries follow an easily determined pattern (i.e., the time sequence for sequential measurements indicated by vertical spacing).

3. Sufficient space is allotted such that analytical data are not crowded together.

D. Quality Assurance

1. Whenever feasible, at least one duplicate and one spiked sample are included in the analysis.

2. With larger groups of samples a duplicate and spike are included for every multiple of 10 samples.

3. The Q.C. data is calculated and recorded in the Q.C. book.

E. Initiative

1. Analyst takes pride in overall appearance and quality of his work.

2. Analyst constantly works to improve procedures and performance.

3. Analyst is alert to potential problems and communicates them to the Laboratory Supervisor.

4. Analyst records Q.C. data and indicates that data have been recorded.

Balance:_____

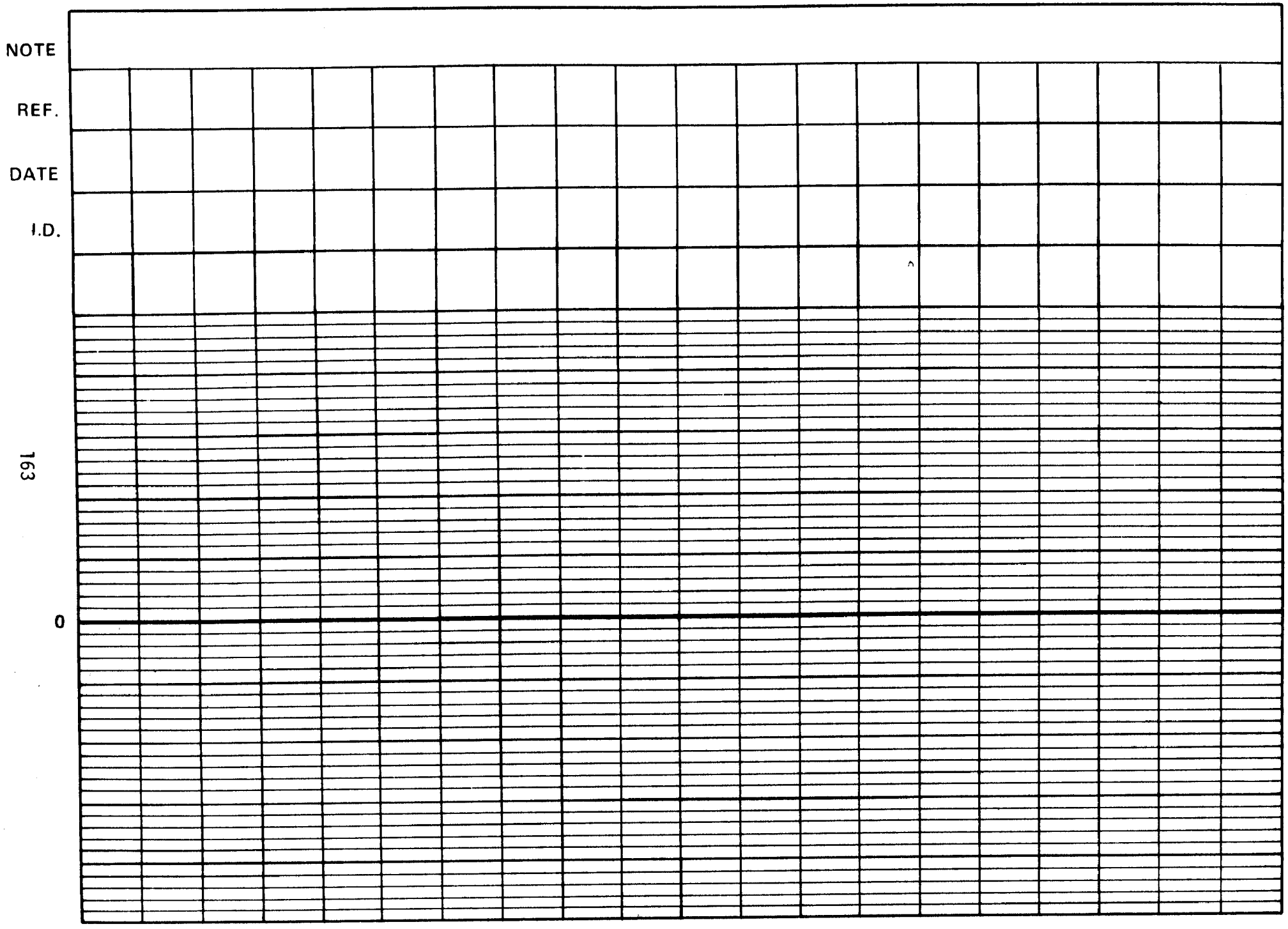
ANALYTICAL BALANCE QUALITY CONTROL LOG

Class S Weights (g)

Date	Time	1	10	50	Comments	Tech

Analytical Balance Quality Control Form

ANALYSIS _____ _____ CONTROL CHART DATE _____



TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
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4. TITLE AND SUBTITLE Laboratory Procedures: Analysis of Sodium-based Dual-alkali Process Streams		5. REPORT DATE March 1980 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. R. Donnelly, D. C. Shepley, T. M. Martin, and A. H. Abdulsattar		8. PERFORMING ORGANIZATION REPORT NO.
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15. SUPPLEMENTARY NOTES IERL-RTP project officer is Norman Kaplan, Mail Drop 61, 919/541-2556.

16. ABSTRACT The report gives procedures for chemical analysis of process streams of a flue gas desulfurization (FGD) system (utilizing the Combustion Equipment Associates/Arthur D. Little sodium-based dual-alkali process) at Louisville Gas and Electric's Cane Run Unit 6. The U.S. EPA has contracted with Bechtel to develop and implement a test program to characterize this FGD process. As part of this effort, Bechtel has established a laboratory at the site for routine chemical analyses of the process streams. The methods used for these chemical analyses comprise this laboratory procedures manual. The procedures were extracted from three principal sources: 'Chemical Analysis Procedures for Dual Alkali Process Stream Samples,' A. D. Little report No. 75833, 4/22/76; 'Laboratory Procedures Manual,' Shawnee Test Facility, Paducah, KY, prepared by Bechtel, 3/76; and 'Standard Methods for the Examination of Water and Wastewater,' 14th edition, 1975. Procedures were verified by on-site analyses in accordance with the quality assurance section of this report. In some cases, modifications adapted the standard procedures to the specific process conditions and to best utilize available resources.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Flue Gases	Stationary Sources	21B
Desulfurization	Dual-alkali Process	07A, 07D
Sodium		07B
Tests		14B
Analyzing		
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