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National Surface Water Survey Stream Survey (Pilot, Middle-Atlantic Phase I, Southeast Screening, and Middle-Atlantic Episode Pilot)

Analytical Methods Manual

NATIONAL SURFACE WATER SURVEY
STREAM SURVEY (PILOT, MIDDLE-ATLANTIC PHASE I, SOUTHEAST SCREENING, AND MIDDLE-ATLANTIC EPISODE PILOT)

ANALYTICAL METHODS MANUAL

by

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NOTICE

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ABSTRACT

The National Surface Water Survey of the National Acid Precipitation Assessment Program is a three-phase project to evaluate the current water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program to study changes in aquatic resources.

The U.S. Environmental Protection Agency requires that data collection activities be based on a program which ensures that the resulting data are of known quality and are suitable for the purpose for which they are intended. In addition, it is necessary that the data obtained be consistent and comparable. For these reasons, the same reliable, detailed analytical methodology must be available to and used by all analysts participating in the study.

This manual provides details of the analytical methods and internal quality control used to process and analyze samples for the National Stream Survey (NSS). The determinations and methods described are the following:

Parameter	Method
1. Base-Neutralizing Capacity	Titration with Gran analysis
2. Acid-Neutralizing Capacity	Titration with Gran analysis
3. Aluminum, total	202.2 AAS (furnace)
4. Aluminum, total extractable	Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace)
5. Aluminum, Nonexchangeable Pyrocatechol Violet (PCV) Reactive and Total PCV Reactive	Automated Colorimetric Pyrocatechol Violet (PCV)
6. Ammonium, dissolved	Automated colorimetry (phenate)
7. Calcium, dissolved	AAS (flame) or ICPES
8. Chloride, dissolved	Ion chromatography
9. Fluoride, total dissolved	Ion-selective electrode and meter
10. Inorganic carbon, dissolved	Instrument (acidification, CO_2 generation, IR detection)
11. Iron, dissolved	AAS (flame) or ICPES
12. Magnesium, dissolved	AAS (flame) or ICPES
13. Manganese, dissolved	AAS (flame) or ICPES
14. Nitrate, dissolved	Ion chromatography
15. Organic carbon, dissolved	Instrument (uv-promoted oxidation, CO_2 generation, IR detection)
16. pH	pH electrode and meter
17. Phosphorus, total dissolved	Automated colorimetry (Molybdate blue)
18. Potassium, dissolved	AAS (flame)

Parameter	Method
19. Silica, dissolved	Automated colorimetry (molybdate blue)
20. Sodium, dissolved	AAS (flame)
21. Sulfate, dissolved	Ion chromatography
22. Specific conductance	Conductivity cell and meter
23. True color	Comparison to platinum-cobalt color standards
24. Turbidity	Instrument (nephelometer)

ACKNOWLEDGMENT

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1.0 INTRODUCTION

The National Surface Water Survey (NSWS) is part of the National Acid Precipitation Assessment Program (NAPAP). One of the responsibilities of NAPAP is to assess the extent and severity to which aquatic resources within the U.S. are at risk because of effects of acid deposition.

The NSWS was initiated at the request of the Administrator of EPA when it became apparent that existing data could not be used to quantitatively assess the present chemical and biological status of surface waters of the U.S. Extrapolation of existing data, largely compiled through individual studies, to the regional or national scale was limited because studies were often biased in terms of site selection. Additionally, many previous studies were incomplete with respect to the chemical variables of interest, inconsistent relative to sampling/analytical methodologies, or highly variable in terms of data quality.

1.1 Background of the National Stream Survey

The NSWS is divided into two major components (Figure 1.1), the National Lake Survey (NLS) and the National Stream Survey (NSS), each of which has three phases. This document pertains to Phase I of the NSS (NSS-I) and a Phase I pilot survey that was conducted as a trial prior to the full NSS-I sampling effort.

The NSS-I involves a synoptic chemical survey of streams in the Eastern U.S. and was designed to alleviate uncertainty in making regional assessments based on existing data by:

(1) providing data from a subset of streams which are characteristic of the overall population of streams within a region;

(2) using standardized methods in collection of chemical data;

(3) measuring a complete set of variables thought to influence or be influenced by surface-water acidification;

(4) providing data which can be used to statistically investigate relationships among chemical variables on a regional basis; and

(5) providing reliable estimates of the chemical status of streams within a region of interest.

The U.S. Environmental Protection Agency (EPA) requires that data collection activities be based on a program which ensures that the resulting data are of known quality and are suitable for the purpose for which they are intended. The goals of the EPA in designing the NSS-I were to clearly identify NSS-I objectives; identify intended uses and users of the data;

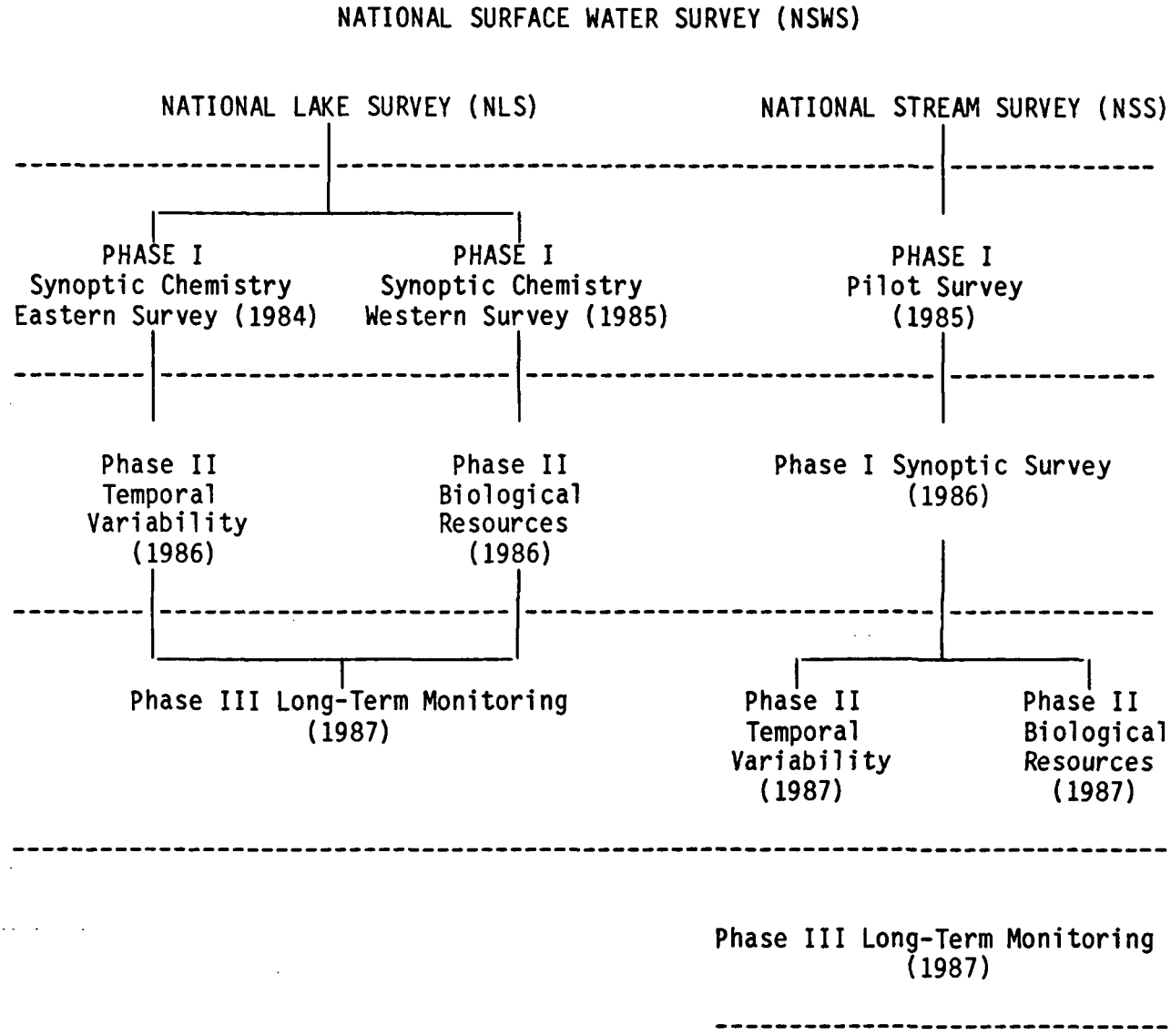


Figure 1.1. Organizational diagram of the National Surface Water Survey and the years during which field activities are to be initiated.

develop an overall conceptual and practical approach to meeting the objectives; develop an appropriate survey design; identify the quality of data needed; develop analytical protocols and quality assurance/quality control (QA/QC) procedures; test the approach through a "pilot" or feasibility study; and revise and modify the approach and methodology as needed.

By using these criteria as guidelines, NSS-I was designed to provide statistically comparable data which could be extrapolated with a known degree of confidence to a regional or national scale. The conceptual approach to the survey emphasized that the data would not be used to ascribe observed effects to acidic deposition phenomena. Rather, the intent of the survey was to provide information for the development of correlative, not cause-and-effect, relationships through large-scale monitoring activities.

The Quality Assurance Plan (Drouse et al., 1986) provides details of the extensive external and internal QA and QC activities for the Phase-I Pilot and NSS-I.

This manual provides details of the analytical methods and internal QC used to process and analyze the stream samples. Details of the actual sampling and on-site stream analyses are provided in the field operations manual (Hagley et al., 1986).

1.2 Physical Parameters and Analytes Measured

The constituents and parameters to be measured, along with a rationale for each, are listed below. Table 1.1 lists the required detection limits, relative precision goals, and expected ranges.

1.2.1 Base-Neutralizing Capacity (BNC)

CO_2 BNC is the BNC of a sample due to dissolved CO_2, hydronium, and hydroxide. In conjunction with ANC, this measurement is useful in refining calculations for both ANC and BNC. (An iterative calculation procedure is performed. During each iteration, improved values for ANC and BNC are generated).

1.2.2 Acid-Neutralizing Capacity (ANC)

ANC is a measure of all bases in a sample and is an indication of buffering capacity. Negative ANC is an indication of mineral BNC (mineral BNC = - ANC).

1.2.3 Aluminum, Total Extractable

Total extractable aluminum is an estimate of dissolved aluminum and includes most mononuclear aluminum species. Aluminum is considered to be highly toxic especially to fish. Knowing its

TABLE 1.1. REQUIRED MINIMUM ANALYTICAL DETECTION LIMITS, EXPECTED RANGES, AND INTRALAB RELATIVE PRECISION

Parameter[a]	Units	Required Detection Limit	Expected Range	Relative Intralab Precision Goal (%)[b]
BNC	µeq/L	5	10-150	10
ANC	µeq/L	5	-100-1000	10
Al, Total Extractable	mg/L	0.005	0.005-1.0	10(Al>0.01),20(Al<0.01)
Al Total	mg/L	0.005	0.005-1.0	10(Al>0.01),20(Al<0.01)
Al, Nonexchangeable and Total PCV Reactive	mg/L	0.010	0.010-0.800	10(Al>0.01),20(Al<0.01)
Ca	mg/L	0.01	0.5-20	5
Cl	mg/L	0.01	0.2-10	5
DIC	mg/L	0.05	0.1-20	10
DOC	mg/L	0.1	0.1-50	5(DOC>5),10(DOC<5)
F, Total dissolved	mg/L	0.005	0.01-0.2	5
Fe	mg/L	0.01	0.01-5	10
K	mg/L	0.01	0.1-1	5
Mg	mg/L	0.01	0.1-7	5
Mn	mg/L	0.01	0.01-5	10
Na	mg/L	0.01	0.5-7	5
NH_4	mg/L	0.01	0.01-2	5
NO_3	mg/L	0.005	0.01-5	10
P, Total dissolved	mg/L	0.002	0.005-0.07	10(P>0.01),20(P<0.01)
pH, Field	pH units	-	3-8	±0.1[c]
pH, Lab	pH units	-	3-8	±0.05[c]
SiO_2	mg/L	0.05	2-25	5
SO_4	mg/L	0.05	1-20	5
Specific Conductance	µS/cm	[d]	5-1000	1
True Color	PCU units[e]	0	0-200	±5[c]
Turbidity	NTU	2	2-15	10

[a]Dissolved ions and metals are being determined except where noted.
[b]Unless otherwise noted, this is the relative precision at concentrations above 10 times instrumental detection limits.
[c]Absolute precision goal is in terms of applicable units.
[d]Blank must be <0.9 µS/cm.
[e]PCU = platinum-cobalt units.

concentration is important in assessing the biological environment of a stream.

1.2.4 Aluminum, Total

Total aluminum is an estimate of the potential aluminum pool available to the biological environment.

1.2.5 Aluminum, Nonexchangeable Pyrocatechol Violet (PCV) and Total PCV Reactive

Exchangeable PCV reactive aluminum, measured as the difference between total reactive and nonexchangeable reactive, is that fraction of soluble aluminum species biologically available and considered toxic to fish. It is therefore important to know the relative amount of the exchangeable species to assess the biological environment of a stream.

1.2.6 Dissolved Inorganic Carbon

The field determination of dissolved inorganic carbon (DIC) is necessary in determining the degree of dissolved CO_2 saturation in a stream. Both the field and lab determinations of DIC (combined with pH) are useful in QA/QC calculations.

1.2.7 Dissolved Ions (Na, K, Ca, Mg, Fe, Mn, NH_4, F, Cl, SO_4, NO_3)

These are determined in order to chemically characterize the stream especially for mass ion balance and buffering capacity. Fluoride is also important as an aluminum chelator.

1.2.8 Dissolved Organic Carbon

Dissolved organic carbon (DOC) determination is necessary to establish a relationship with color and to estimate the concentration of organic acids. Also, DOC is important as a natural chelator of aluminum.

1.2.9 Dissolved Silica (SiO_2)

The absence or existence of dissolved silica is an important factor controlling diatom blooms, and it assists in identifying trophic status. It is also an indication of mineral weathering.

1.2.10 pH

pH is a general and direct indication of free hydrogen ion concentration.

1.2.11 Specific Conductance

The conductance of stream water is a general indication of its ionic strength and is related to buffering capacity.

1.2.12 Total Dissolved Phosphorus

This is an indicator of potentially available nutrients for phytoplankton productivity and overall trophic status.

1.2.13 True Color

True color, measured in PCU (platinum-cobalt units), is an indicator of organic acids and DOC. Substances which impart color may also be important natural chelators of aluminum.

1.2.14 Turbidity

Turbidity is a measure of suspended material in a water column and is measured in nephelometric turbidity units (NTU).

1.3 References

Drousé, S. K., D. C. Hillman, L. W. Creelman, and S. J. Simon, 1986. National Surface Water Survey - Stream Survey (Pilot, Middle-Atlantic Phase I, Southeast Screening, and Middle-Atlantic Episode Pilot) Quality Assurance Plan.

Hagley, C. A., C. M. Knapp, C. L. Mayer, and F. A. Morris, 1986. The National Surface Water Survey Stream Survey (Pilot, Middle-Atlantic Phase I, Southeast Screening, and Middle-Atlantic Episode Pilot) Field Training and Operations Manual.

2.0 FIELD OPERATIONS

Field operations are based at fully equipped mobile processing laboratories (MPL) in Las Vegas (for the pilot study the MPL were in the field). A list of equipment contained in the MPL is given in Table 2.1. Stream samples, collected by sampling crews, are sent by Federal Express to the MPL for preliminary analysis, processing, and shipment to analytical laboratories for more detailed analysis.

The activities of the MPL crew are described in this section. Sampling crew activities are described elsewhere (Hagley et al., 1986).

2.1 Personnel

The MPL is staffed by a crew consisting of a coordinator, supervisor, chemist, and analysts. Coordinators are responsible for the overall operation of the MPL including coordination with the sampling crews, sample tracking and logistics, data forms, and safety. The supervisor with the assistance of the chemist and analysts is responsible for MPL measurements and sample processing.

2.2 Daily Operations

The MPL operates each day that samples arrive. The daily MPL activities are outlined in Figure 2.1 and are divided into activities that are conducted before sample arrival (Section 2.2.1) and activities that are conducted following sample arrival (Section 2.2.2).

2.2.1 Activities Before Sample Arrival

Prior to sample arrival, the reagents for determining DIC, pH, and PCV Al, and for preparing aliquot 2 (total extractable Al) are prepared as described in sections 2.3, 2.4, 2.7, and 2.8, respectively. Also, the carbon analyzer, pH meter, nephelometer, and the flow injection analyzer (FIA) are calibrated as described in sections 2.3, 2.4, 2.5, and 2.7, respectively.

2.2.2 Activities Following Sample Arrival

After samples are delivered by the carrier, the steps outlined in Figure 2.1 are performed. The first step, performed by the coordinator, involves organizing the samples into a batch. The next six steps (aliquot preparation and pH, DIC, color, PCV Al and turbidity determinations) are performed simultaneously by the supervisor and analysts. Finally, after all measurements and processing are finished, the data forms are completed, the samples are packed, and the forms and samples are shipped to their destinations. These steps are detailed in sections 2.2.2.1 through 2.2.2.4.

TABLE 2.1. MOBILE PROCESSING LABORATORY EQUIPMENT LIST

1. Mobile Lab Equipped with

   a. Electrical and water inputs
   b. Water outlet
   c. Source of water meeting ASTM Type I specifications (such as Barnstead NANOpure/ROpure 40 or Millipore Milli-RO/Super-Q System)
   d. Heating/cooling system
   e. Freezer
   f. Laminar-flow hood delivering class 100 air
   g. Solvent storage cabinet
   h. Standard laboratory countertops and sink
   i. Analytical balance and plastic weighing boats

2. Centrifuge (capable of holding four 50-mL tubes) - 1

3. Clean 4-L Cubitainers - 30/day

4. Clean Nalgene Amber Wide-Mouth Bottles

   a. 500-mL (Nalgene No. 2106-0016) - 30/day
   b. 250-mL (Nalgene No. 2106-0008) - 60/day
   c. 125-mL (Nalgene No. 2106-0004) - 90/day

5. Total Extractable Aluminum Supplies

   a. Clean 50-mL graduated centrifuge tubes with sealing caps (Fisher No. 05-538-55A) - 30/day
   b. 10-mL polypropylene test tubes (Elkay No. 000-2024-001 - 30/day
   c. Plug Tite sealing caps (Elkay No. 127-0019-200) - 30/day
   d. HPLC-grade methyl isobutyl ketone (MIBK) - 180 mL/day
   e. Sodium acetate (Alfa ultrapure) - 80 g/month
   f. 8-hydroxyquinoline (99+ percent purity) - 30 g/month
   g. NH_4OH (30 percent - Baker Instra-Analyzed grade) - 750 mL/month
   h. Clean 1-L, 500-mL, and 100-mL volumetric flasks - 5 of each
   i. Glacial acetic acid (Baker Instra-Analyzed grade) - 100 mL/month
   j. Hydrochloric acid (12 M - Baker Instra-Analyzed grade) - 500 mL/month
   k. Phenol-red indicator solution (0.04 percent w/v - American Scientific Products 5720) - 1 L
   l. 2.00-mL Repipet dispenser - 2/station
   m. 3.00-mL Repipet dispenser top for 1-gallon bottle - 2/station
   n. 5.00-mL Repipet dispenser - 2/station
   o. 100-mL reagent bottle with dropper (Nalgene 2411-0060) - 2/station
   p. Polystyrene graduated cylinders (25-, 100-, 250-mL sizes) - 2 each/station

(continued)

TABLE 2.1. (Continued)

6.	Color Determination Kit (Hach Model CO-1)	- 2
7.	Color Kit Spare Supplies	
	a. Color disc (Hach No. 2092-00)	- 2
	b. Color viewing tube (Hach No. 1730-00)	- 10
	c. Hollow polyethylene stoppers (Hach No. 14480-74)	- 10
8.	Filtration Apparatus and Supplies	
	a. Membrane filters, 0.45 µm, 47-mm diameter (Gelman No. 60173) (package of 100)	- 7 pkg/week
	b. Teflon or plastic forceps	- 5
	c. Fisher filtrator - low form (Fisher 09-788)	- 3
	d. Acrylic vacuum chambers (custom made)	- 6
	e. Clean filter holder (Nalgene No. 310-4000)	- 12
	f. Spare rubber stoppers (Fisher No. 09-788-2)	- 6
	g. Vacuum pump with regulator (Millipore No. xx5500000)	- 1
9.	Disposable Gloves (talc-free)	- 2 pkg/week
10.	Preservation Supplies	
	a. Repipet Jr. (0.1 mL)	- 2
	b. Indicating pH paper (Whatman Type CS No. 2626-990 range 1.8 - 3.8)	- 6 packs/week
	c. HNO_3 and H_2SO_4 (Baker Ultrex grade or Seastar Ultrapure grade)	- 50 mL/week
11.	Frozen Freeze Gel Packs - daily use (reuseable)	- 25/day
	- shipping	- 30/40 sample batch
12.	Styrofoam-Lined Shipping Containers	- 4/day
13.	Field Data Forms, Shipping Forms, Batch Forms, etc.	
14.	Color Blindness Test Kit	- 1
15.	DIC Determination Supplies	
	a. Dohrman DC-80 carbon analyzer	- 1
	b. 50-mL polypropylene syringes - station use	- 50
	- field use	- 1/sample
	c. Mininert syringe valves - station use	- 20
	- field use	- 70

(continued)

TABLE 2.1. (Continued)

d. Zero-grade nitrogen gas	- 1 cylinder/ month
e. Anhydrous Na_2CO_3 (ACS Primary Standard Grade)	- 500 g
f. Syringe membrane filters (Gelman Acrodisc 4218, 0.45 µm)	- 1/sample
g. Spare carbon analyzer parts (nuts, ferrules, tubing, etc.)	
16. MPL pH Supplies	
a. pH meter (Orion Model 611)	- 2
b. Orion Ross epoxy body combination pH electrode	- 6
c. Filling solution for Ross combination pH electrode (pack of 6 bottles)	- 2
d. pH sample chamber	- 2
e. Certified 0.100 N H_2SO_4	- 2 L
f. Ringstand (to hold pH apparatus) and clamps	- 2
g. NBS-traceable pH buffers (pH 4 and 7)	- 2 L of each/ month
h. 50-mL disposable beakers	- 200
17. Turbidimeter (Monitek Model 21)	- 1
18. Turbidimeter Supplies	-
a. 5-, 10-, 20-, 50-, 100-, 200-NTU standards	- 1 L of each
b. Cuvettes	- 10
19. Class 100 Air Filtration Filters	- 6
20. Spare Water Treatment Cartridges	- 6
21. Coolers	- 4
22. Clean 20-L Cubitainers with Spigots	- 5
23. Digital Micropipets (5-40 µL, 40-200 µL, 200-1,000 µL, 1,000-5,000 µL)	- 1 of each
24. Micropipet Metal-Free Pipet Tips (in four sizes corresponding to micropipet sizes in item 23)	- 2 cases (1,000 tips/case) of each size
25. Reagents for PCV Aluminum Procedure	
a. Hydrochloric acid (Ultrex grade or equivalent)	
b. 1,10-Phenanthroline	

(continued)

TABLE 2.1. (Continued)

c. Hydroxylammonium chloride
d. Pyrocatechol violet
e. Hexamethylenetetraamine
f. Ammonium hydroxide
g. Aluminum standard
h. Ion-exchange resin
i. Nucleopore polycarbonate filters
j. Syringe filter holder
k. Nitric acid (Ultrex grade or equivalent)
l. Polystyrene divinyl benzene beads
26. Flow injection analyzer (Lachat)

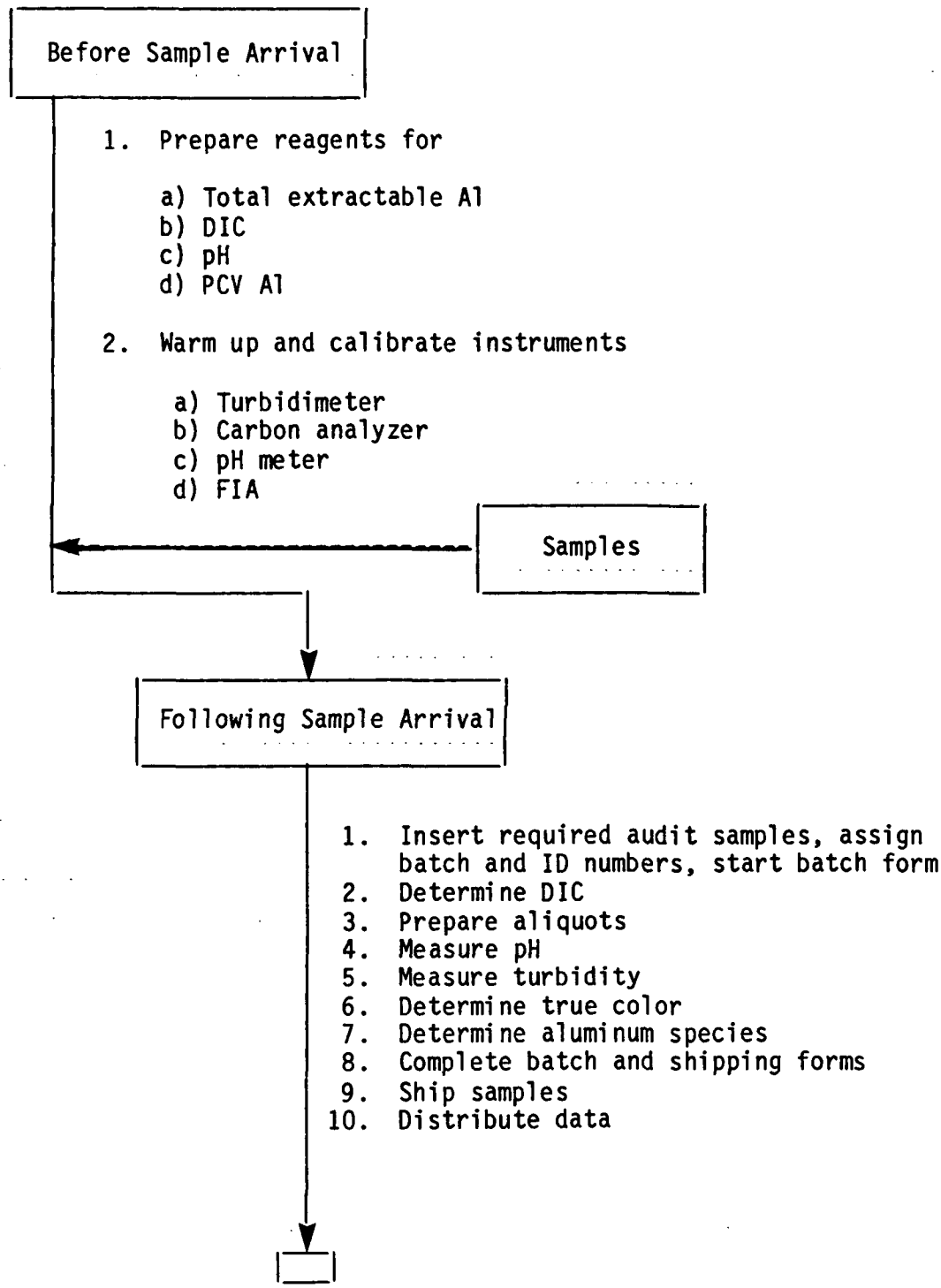


Figure 2.1. Flow scheme of daily mobile processing laboratory activities.

2.2.2.1 Sample Identification and Batch Organization--Three types of samples (routine, duplicate, and blank) are collected and delivered to the MPL. The sample type is indicated on the sample label (Figure 2.2). The samples collected on a given day are organized into a batch consisting of the routine, duplicate, and blank samples collected on that day as well as audit samples (inserted daily at the MPL).

After organization, a unique batch ID number is assigned to each batch and is recorded on the labels (and corresponding aliquot labels) of all samples in the batch. Next, an ID number is randomly assigned to each sample as follows:

Routine Samples - Five sample containers are filled at each stream, namely, four syringes (for DIC, pH, PCV Al determination) and a cubitainer. One ID number is assigned to all five containers and is recorded on each container label.

Duplicate and Blank Samples - ID numbers are assigned in the same manner as for the routine samples. (Note: There are no syringe samples for the blank.)

Field Audit Samples - One 2-L field audit sample (received each day from a central source) is inserted into each day's batch of samples. The field audit sample is assigned an ID number in the same manner as a routine sample, and the number is recorded on the label (Figure 2.3a).

Lab Audit Samples - One lab audit sample (received from a central source) is included in each day's batch. A single lab audit sample consists of a set of seven aliquots. Each aliquot has a temporary label (Figure 2.3b) listing the aliquot number, audit sample code, preservative amount, and shipping date. The lab audit sample is then assigned batch and sample ID numbers in the same manner as for a routine sample. An aliquot label (Figure 2.3c) is attached to each aliquot, and the batch and sample ID numbers are recorded on the label as are the date and amount of preservative added.

After the batch and sample ID numbers have been assigned and recorded on each sample label, the same information is recorded on Form 5, Batch/QC Field Data (Figure 2.4). Codes necessary to complete the form are given in Table 2.2.

NOTE 1: The ID numbers are randomly assigned to all samples in a batch. Furthermore, ID numbers run consecutively from 1 to the number of samples in the batch. Audit samples must not always be assigned the same ID number.

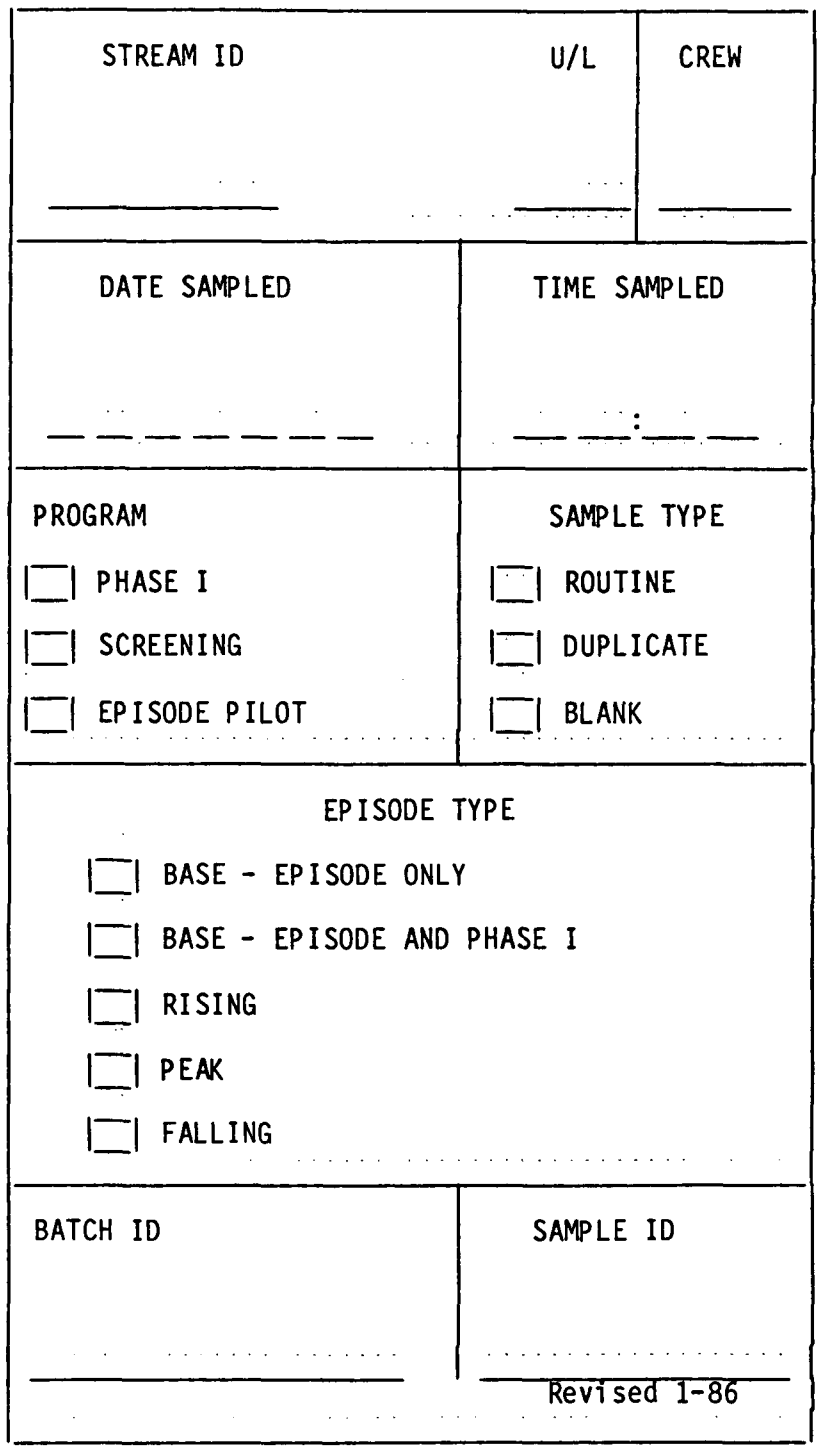
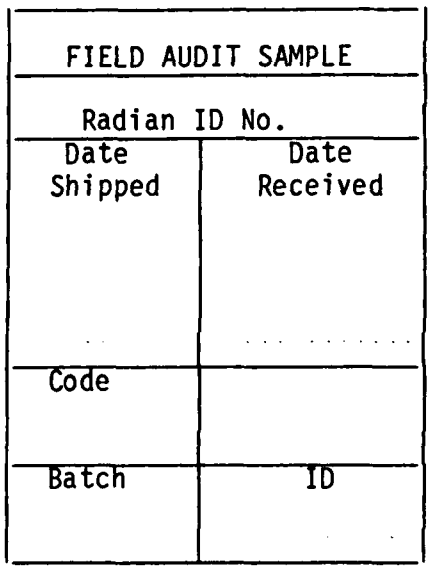
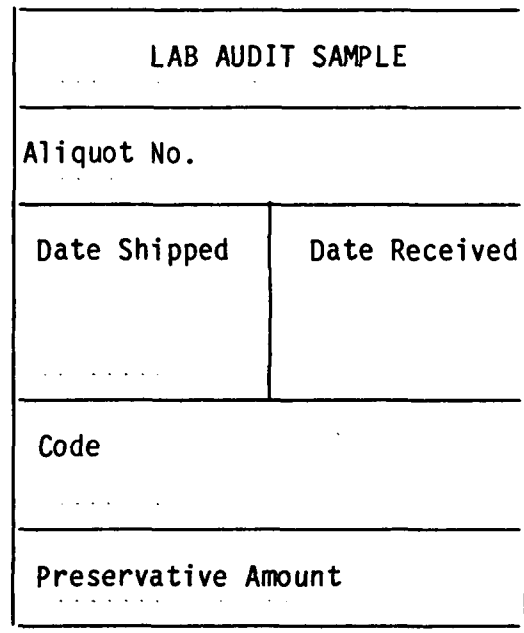


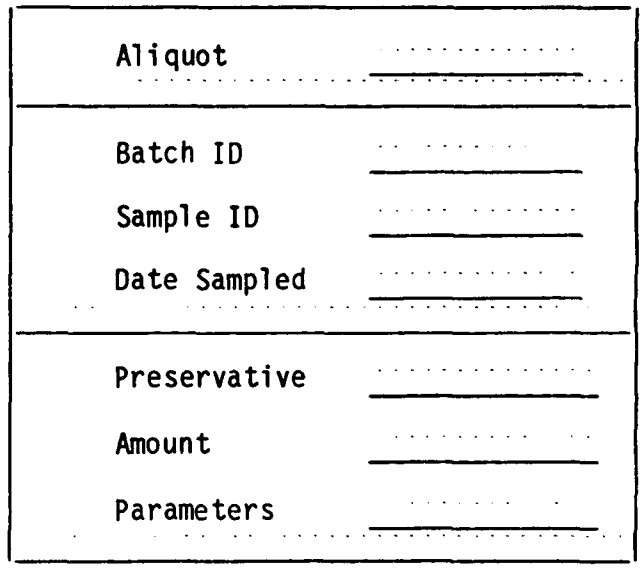
Figure 2.2. Field sample label.



a. Field Audit Sample Label



b. Lab Audit Sample Label



Note: The aliquot no., preservative, and parameters are preprinted on the seven aliquot labels.

c. Aliquot Label

Figure 2.3. Aliquot and Audit Sample Labels.

NATIONAL SURFACE WATER SURVEY
BATCH/QC FIELD DATA FORM

DATE RECEIVED BY DATA MGT. ____________
ENTERED ____________
RE-ENTERED ____________

☐ **FORM 2 LAKES**
OR
☐ **FORM 5 STREAMS**

BATCH ID ______	LAB TO WHICH BATCH SENT ______	DATE PROCESSED ______	BASE SITE ID ______
NO. SAMPLES IN BATCH ______	DATE SHIPPED ______	AIR-BILL NO ______	LAB CREW ID ______
			MOBILE LABORATOPY SUPERVISOR ______

SPLIT	SAMPLE ID	LAKE OR STREAM ID	SITE OR TYPE	SAMPLE CODE	DIC (mg/L) QCCS LIMITS UCL — 2.2 LCL — 1.8		STATION pH QCCS LIMITS UCL — 4.1 LCL — 3.9		TURBIDITY (NTU) QCCS LIMITS UCL — 5.5 LCL — 4.5		COLOR (PC UNITS)	CONDUCTIVITY (uS cm⁻¹)		PCV ALUMINUM (ppm) UCL — LCL — DISSOLVED		PCV ALUMINUM (ppm) UCL — LCL — ORGANIC	
					VALUE	QCCS	VALUE	QCCS	VALUE	QCCS	VALUE	VALUE	QCCS	VALUE	QCCS	VALUE	QCCS
	QCCS			QCCS													
	[illegible]																
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COMMENTS   DATA QUALIFIERS X, Y and Z ARE AVAILABLE FOR USE ON THIS FORM.

SAMPLE ID	QUALIFIER	COMMENT
______	X	______
______	X	______
______	X	______
______	Y	______
______	Y	______
______	Y	______
______	Z	______
______	Z	______
______	Z	______

WHITE – ORNL COPY   YELLOW – FIELD COPY   PINK – EMSL-LV COPY

[illegible] REVISION 1-86

Figure 2.4. NSWS Form 5 - Batch/QC Field Data.

TABLE 2.2. LIST OF SAMPLE CODES

Sample Type	Code	Description
Normal[a]	R	Routine Stream Sample
	D	Duplicate Stream Sample
	B	Field Blank Sample
	TD	Trailer Duplicate
Audit	F L 1-001	
		Radian I.D. Number
		Concentrate lot number
		Concentration Level
		L = low, N = Natural
		Type of Audit Sample (F = FIELD, L = LAB)
Episodic	EB	Episodic sample, base hydrograph
	ER	Episodic sample, rising hydrograph
	EP	Episodic sample, peak hydrograph
	EF	Episodic sample, falling hydrograph
	M1	Initial Middle Atlantic Phase I Sample
	M2	Final Middle Atlantic Phase I Sample
	S	Southeast Screening Sample

[a]Normal samples require a Stream ID.

NOTE 2: Field audit samples are processed exactly like routine stream samples. Lab audit samples receive no field treatment other than labeling and shipping.

NOTE 3: Seven (eight for the Pilot Study) different aliquots are prepared from each field sample (routine, duplicate, or blank). Each aliquot is assigned the same batch and ID number as the sample from which it is prepared.

NOTE 4: After Form 5 is completed, the temporary label on the lab audit sample (seven aliquots) is removed and placed in the lab audit logbook.

2.2.2.2 Determination of DIC, pH, Turbidity, True Color, and PCV Al--These parameters are measured as described in sections 2.3, 2.4, 2.5, 2.6, and 2.7, respectively.

2.2.2.3 Aliquot Preparation--Seven aliquots (eight for the Stream Study Pilot) are prepared from each sample, each with the same batch and sample ID numbers. The details for preparing each aliquot are provided in section 2.8.

2.2.2.4 Form Completion, Sample Shipment, and Data Distribution--After a batch has been completely processed, the supervisor records all analytical data on Form 5 (Figure 2.4). The coordinator then reviews and signs the form. Next, each aliquot is sealed in a plastic bag and is packed in a Styrofoam-lined shipping container along with 7 to 10 frozen freeze-gel packs (to maintain aliquots at 4°C). A shipping form (Figure 2.5) is then completed and enclosed with each container, and the containers are shipped by overnight delivery to its destination. Finally, copies of Forms 1 (a form completed by the sampling crew for each sample), 3, and 5 are sent to the locations indicated in Figure 2.6.

2.3 Determination of DIC

2.3.1 Scope and Application

This method is applicable to the determination of DIC in natural surface waters and is written specifically for the NSWS. DIC is determined in NSWS mobile processing laboratories by using a Dohrman DC-80 Carbon Analyzer. For this reason, the method has been written with the assumption that the DC-80 is being used (Xertex - Dohrman Corp., 1984). The method detection limit (MDL) for DIC determined from replicate analyses of a calibration blank (approximately 0.1 mg/L DIC) is 0.1 mg/L DIC. A 1.00-mL sample volume was used to determine the MDL. The applicable analyte concentration range is 0.1 to 50 mg/L DIC.

NATIONAL SURFACE WATER SURVEY
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818
ALEXANDRIA, VA 22314

NSWS
FORM 3

RECEIVED BY _____
IF INCOMPLETE IMMEDIATELY NOTIFY:
SAMPLE MANAGEMENT OFFICE
(703) 557-2490

SHIPPING

FROM (STATION ID):	TO (LAB):	BATCH ID	DATE SAMPLED	DATE SHIPPED / AIR-BILL NO.	DATE RECEIVED

SAMPLE ID	ALIQUOTS SHIPPED (FOR STATION USE ONLY)							SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY)
	1	2	3	4	5	6	7	
01								
02								
03								
04								
05								
06								
07								
08								
09								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								

QUALIFIERS:
V: ALIQUOT SHIPPED
M: ALIQUOT MISSING DUE TO DESTROYED SAMPLE

WHITE - FIELD COPY
PINK - LAB COPY
YELLOW - SMO COPY
GOLD - LAB COPY FOR RETURN TO SMO

Figure 2.5. NSWS Form 3 - Shipping.

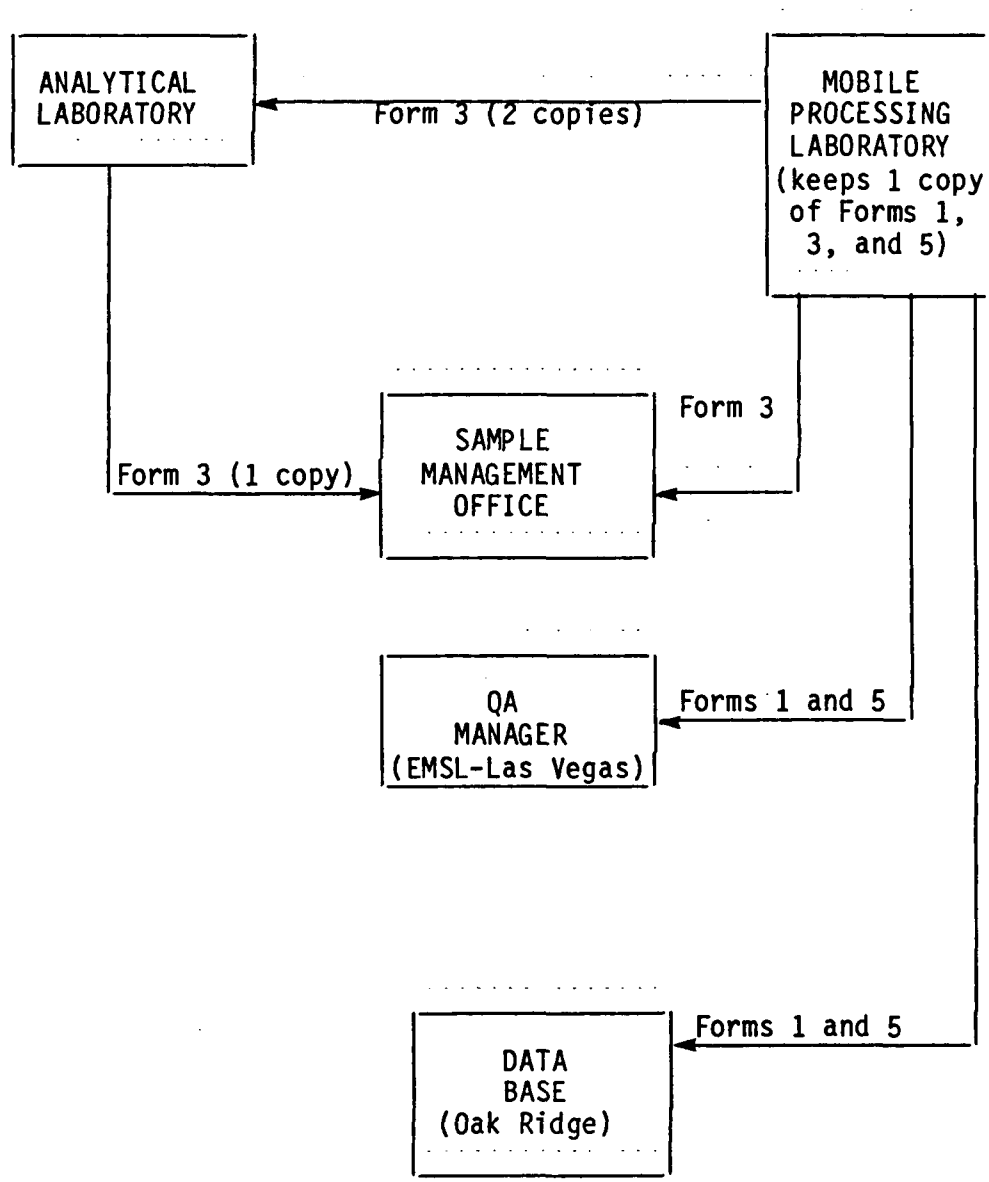


Figure 2.6. Data flow scheme.

2.3.2 Summary of Method

Samples for DIC determination are collected and sealed at the stream sites in syringes. At the MPL, a syringe filter is attached to the syringe, and sample is filtered into the sample loop of the DC-80. The sample is subsequently injected into a reaction chamber containing 5 percent phosphoric acid. The carbonates (DIC) in the sample react with the acid to form CO_2 which is sparged from the reaction chamber with a nitrogen gas carrier stream. The CO_2 in the carrier stream is then detected and quantified (in terms of DIC) by an infrared (IR) CO_2 analyzer.

2.3.3 Interferences

No interferences are known.

2.3.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling concentrated phosphoric acid.

The nitrogen cylinder must be secured in an upright position. The line pressure must be kept below 40 psi.

2.3.5 Apparatus and Equipment

2.3.5.1 Dohrman DC-80 Carbon Analyzer equipped with High Sensitivity Sampler (1.00-mL loop).

2.3.5.2 Reagent bottles for DIC standards (equipped with three-valve cap to permit storage under a CO_2-free atmosphere, Rainin No. 45-3200).

2.3.5.3 0.45-μm syringe filters (Cellulose nitrate).

2.3.5.4 60-mL plastic syringes.

2.3.5.5 Luer-Lok syringe valves.

2.3.6 Reagents and Consumable Materials

2.3.6.1 Nitrogen Gas (99.9 percent)--CO_2-free.

2.3.6.2 Phosphoric Acid (5 percent v/v)--Carefully add 50 mL concentrated phosphoric acid (H_3PO_4, sp gr 1.71) to 500 mL water. Mix well and dilute to 1,000 mL with water.

2.3.6.3 Stock DIC Quality Control Sample Solution--Weekly, open a fresh ampule of anhydrous, primary standard grade sodium carbonate (Na_2CO_3) and dissolve 8.825 g in water, then dilute to 1.000 L. Store at 4°C in a special reagent bottle under a CO_2-free atmosphere.

2.3.6.4 Stock DIC Calibration Standard Solution--Biweekly, open a fresh ampule of anhydrous, primary standard grade Na_2CO_3 and dissolve 8.825 g in water, then dilute to 1.000 L. Store at 4°C in a special reagent bottle under a CO_2-free atmosphere.

2.3.6.5 Water--Water used in all preparations must conform to ASTM specifications for Type I water (ASTM, 1984). Such water is obtained from the Millipore Milli-Q water system.

2.3.7 Sample Collection, Preservation, and Storage

Samples are collected and sealed in 60-mL plastic syringes. They are stored at 4°C until use.

2.3.8 Calibration and Standardization

2.3.8.1 Set up and operate the DC-80 according to the manufacturer's instructions.

2.3.8.2 Calibration Standard (10.00 mg/L DIC)--Prepare the calibration standard daily by diluting 5.000 mL of the stock DIC calibration standard to 500.00 mL with fresh water. Store in a special reagent bottle under a CO_2-free atmosphere.

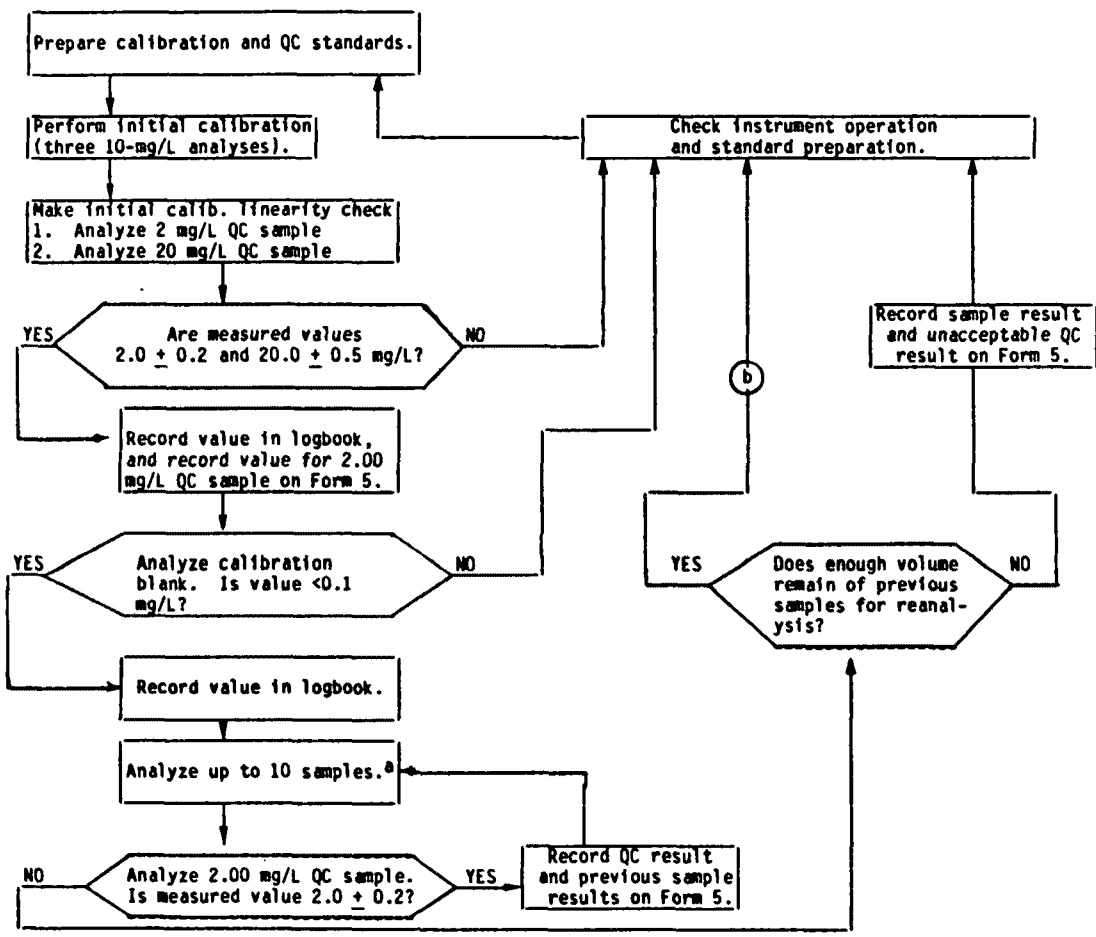
2.3.8.3 Erase previous calibration. Load the sample loop with the 10.00-mg/L DIC calibration standard by flushing with 7 to 10 mL solution. Inject and start the analysis. When the analysis is complete, repeat the process twice more.

2.3.8.4 Calibrate the analyzer by pushing the calibrate button. This completes the calibration. Sample results are output directly in mg/L DIC.

2.3.9 Quality Control

QC procedures are outlined in Figure 2.7 and are described in sections 2.3.9.1 through 2.3.9.5.

2.3.9.1 Initial Calibration Verification and Linearity Check--Immediately after calibration, analyze two QC samples to ensure the calibration validity and linearity.



[a]Analyze one sample per batch in duplicate.
[b]Reanalyze sample associated with unacceptable QC result.

Figure 2.7. Flow scheme for DIC determination.

Daily, prepare a 2.00-mg/L and a 20.00-mg/L DIC QC sample by diluting 1.000 and 10.00 mL of the stock DIC QC sample, respectively, to 500.00 mL with fresh water. Store each DIC QC sample in a special reagent bottle under a CO_2-free atmosphere.

Analyze the QC samples. The results must be 2.0 ± 0.2 and 20.0 ± 0.5 mg/L DIC. If the results do not fall within these ranges, a problem exists in the calibration, standard preparation, or QC sample preparation. The problem must be resolved prior to sample analysis, and the QC samples must be reanalyzed. Acceptable results must be obtained before continuing.

2.3.9.2 Continuing Calibration Verification--To check for calibration drift, analyze the 2.00-mg/L DIC QC sample after every 10 samples and after the last sample. The measured value must be 2.0 ± 0.2 mg/L DIC. If it is not, repeat the calibration and reanalyze all samples analyzed since the last acceptably analyzed QC sample.

2.3.9.3 Calibration Blank Analysis--After the initial calibration, analyze a fresh calibration blank. It must contain less than 0.1 mg/L DIC. If it does not, check the water system and repeat the calibration procedure (including preparation of standards).

2.3.9.4 Duplicate Analysis--To determine the analytical precision, analyze one sample per batch in duplicate.

2.3.9.5 Detection Limit Determination--Determine the detection limit by analyzing 20 blank samples. The detection limit is defined as three times the standard deviation.

2.3.10 Procedure

2.3.10.1 Check that the DC-80 is equilibrated and that a stable baseline has been achieved.

2.3.10.2 Prepare calibration standard and calibrate the analyzer.

2.3.10.3 Perform the necessary QC analyses. Proceed with sample analysis if acceptable results are obtained.

2.3.10.4 Place a syringe valve on the sample syringe and filter 7 to 10 mL of sample directly into the sample loop. Inject the sample and start the analysis. Discard the syringe filter after a single use.

2.3.10.5 Thirty seconds after injection, switch the valve to the load position and load the next sample. The analysis time for a single sample is 3 to 4 minutes.

2.3.10.6 At the end of the day, rinse the sample loop with water. Keep the power to the IR analyzer on at all times.

2.3.11 Calculations

No calculations are necessary. Sample results are output on the printer directly in mg/L DIC.

2.3.12 Reporting

Record the batch and sample ID numbers directly on the printer output. Similarly identify QC samples. Attach the printout to the logbook. Record the sample and QC data on Form 2.

2.4 Determination of pH

2.4.1 Scope and Application

This method is applicable to the determination of pH in surface waters of low ionic strength and is written specifically for the NSWS. For the NSWS, pH is determined in the MPL using an Orion Model 611 pH meter and an Orion Ross combination pH electrode. As a result, the method has been written assuming that the Orion meter and electrode are used (Orion, 1983). The applicable pH range is 3 to 11.

2.4.2 Summary of Method

Samples for pH determination are collected and sealed in syringes at the stream site. At the field station, pH is measured in a closed system to prevent atmospheric exposure. The measurement is performed by attaching the sample syringe to the pH sample chamber (Figures 2.8 and 2.9), by injecting sample, and by determining pH by using a pH meter and electrode.

2.4.3 Interferences

No interferences are known.

2.4.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling sulfuric acid.

2.4.5 Apparatus and Equipment

2.4.5.1 Orion Model 611 pH meter

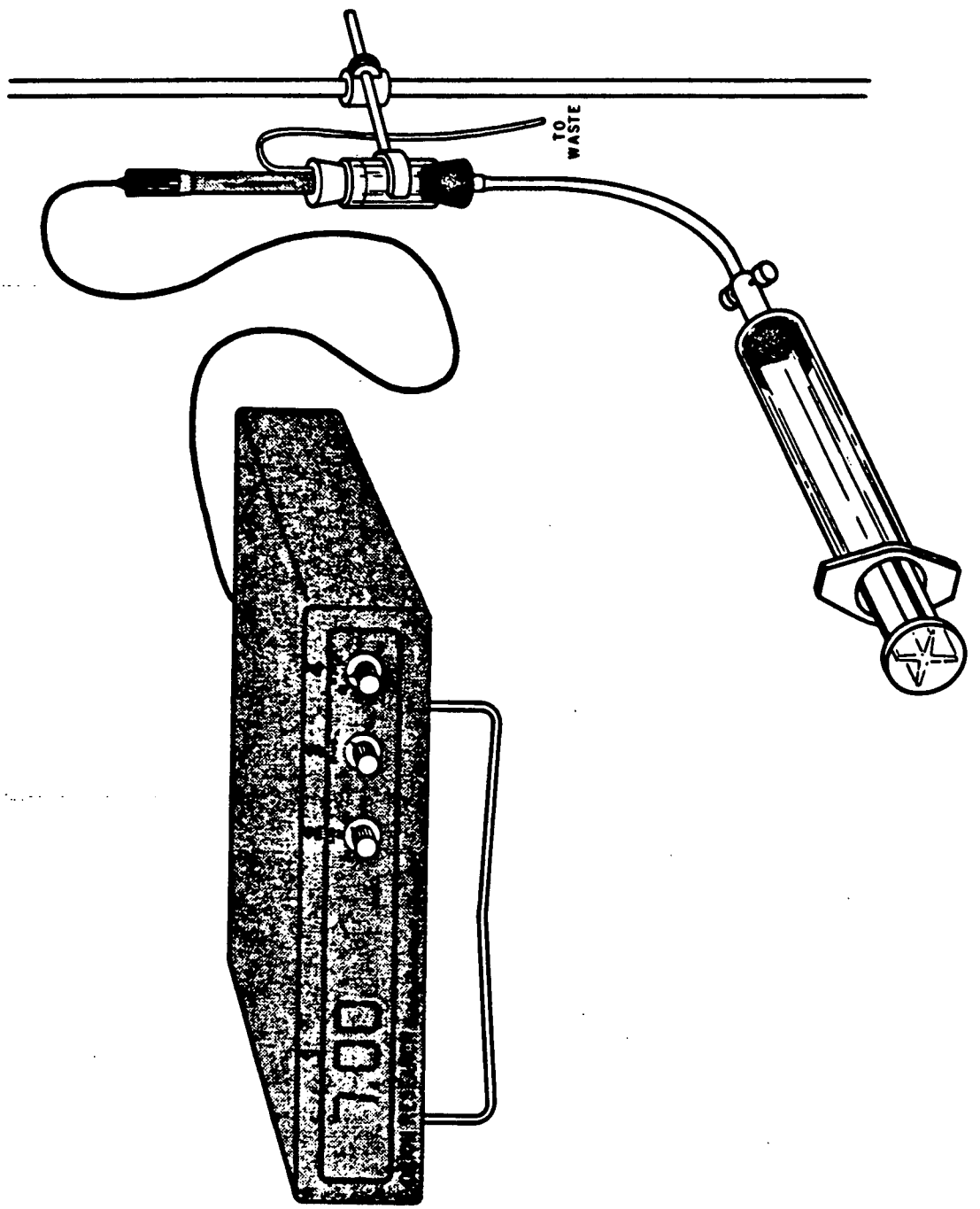


Figure 2.8. Schematic of pH measurement system.

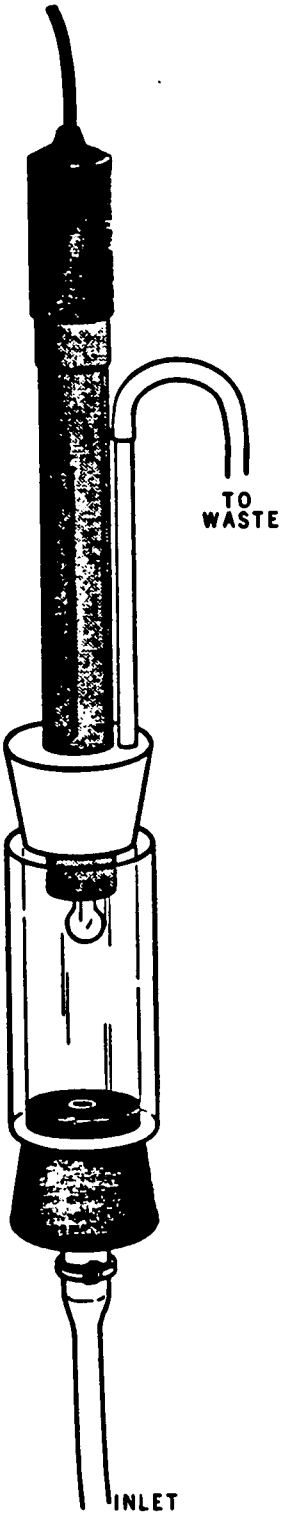


Figure 2.9. pH sample chamber.

2.4.5.2 Orion Ross combination pH electrode

2.4.5.3 pH sample chamber

2.4.5.4 60-mL plastic syringes

2.4.5.5 Luer-Lok syringe valves

2.4.6 Reagents and Consumable Materials

2.4.6.1 pH Calibration Buffers (pH 4 and 7)--Commercially available pH calibration buffers (NBS-traceable) at pH values of 4 and 7.

2.4.6.2 Potassium Chloride (3 M)--Dissolve 75 g KCl in 1 L of water.

2.4.6.3 Stock pH Quality Control Sample Solution (0.100N H_2SO_4)--Commercially available certified standard sulfuric acid at a concentration of 0.100N.

2.4.6.4 Water--Water used in all preparations must conform to ASTM specifications for Type I water ASTM D 1193 (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.

2.4.7 Sample Collection, Preservation, and Storage

Samples are collected and sealed in 60-mL plastic syringes. They are stored at 4°C until used.

2.4.8 Calibration and Standardization

2.4.8.1 Weekly, calibrate the temperature function of the pH meter and electrode using a two-point calibration (4°C and room temperature) following the instructions.

2.4.8.2 Daily, calibrate the pH function of the pH meter and electrode using a two-point calibration (pH 7 and 4) following the instructions.

2.4.8.3 Copiously rinse the electrode with water. Immerse in 20 mL pH 7 buffer and stir for 30 to 60 seconds. Discard and replace with an additional 40 mL pH 7 buffer. While the solution is gently stirred, measure and record the pH.

2.4.8.4 Repeat the preceding step using the pH 4 buffer.

2.4.8.5 Compare the pH values obtained for the pH 7 and 4 buffers to their certified values. If either observed value differs from the certified value by more than ±0.02 pH units, repeat the electrode calibration.

If acceptable results cannot be obtained, replace the electrode.

2.4.9 Quality Control

QC procedures are outlined in Figure 2.10 and are as follows:

2.4.9.1 pH QC Check Sample--Daily, prepare a pH QC check sample (pH QCCS) by diluting 1.000 mL of the 0.100N H_2SO_4 to 1.000 L with water.

2.4.9.2 Initial pH QC Check--Immediately after calibration, analyze the pH QCCS by using the procedure described in section 2.4.8. The observed pH must be 4.0 ± 0.1 pH unit. If it is not, repeat the calibration process, then repeat the measurement on a fresh pH QCCS. If an acceptable result is still not obtained, consult the troubleshooting guide which is provided by the manufacturer for the meter and electrode. Samples must not be analyzed until an acceptable value for the pH QCCS is obtained.

2.4.9.3 Continuing pH QC Check--In order to check for calibration drift, the pH QCCS sample is analyzed after every five samples and after the last sample. The measured valve must be 4.0 ± 0.1 pH unit. If it is not, recalibrate the electrode and meter and reanalyze all samples analyzed since the last acceptably analyzed pH QCCS.

2.4.9.4 Duplicate Analysis--To determine the analytical precision, analyze one sample per batch in duplicate.

2.4.10 Procedure

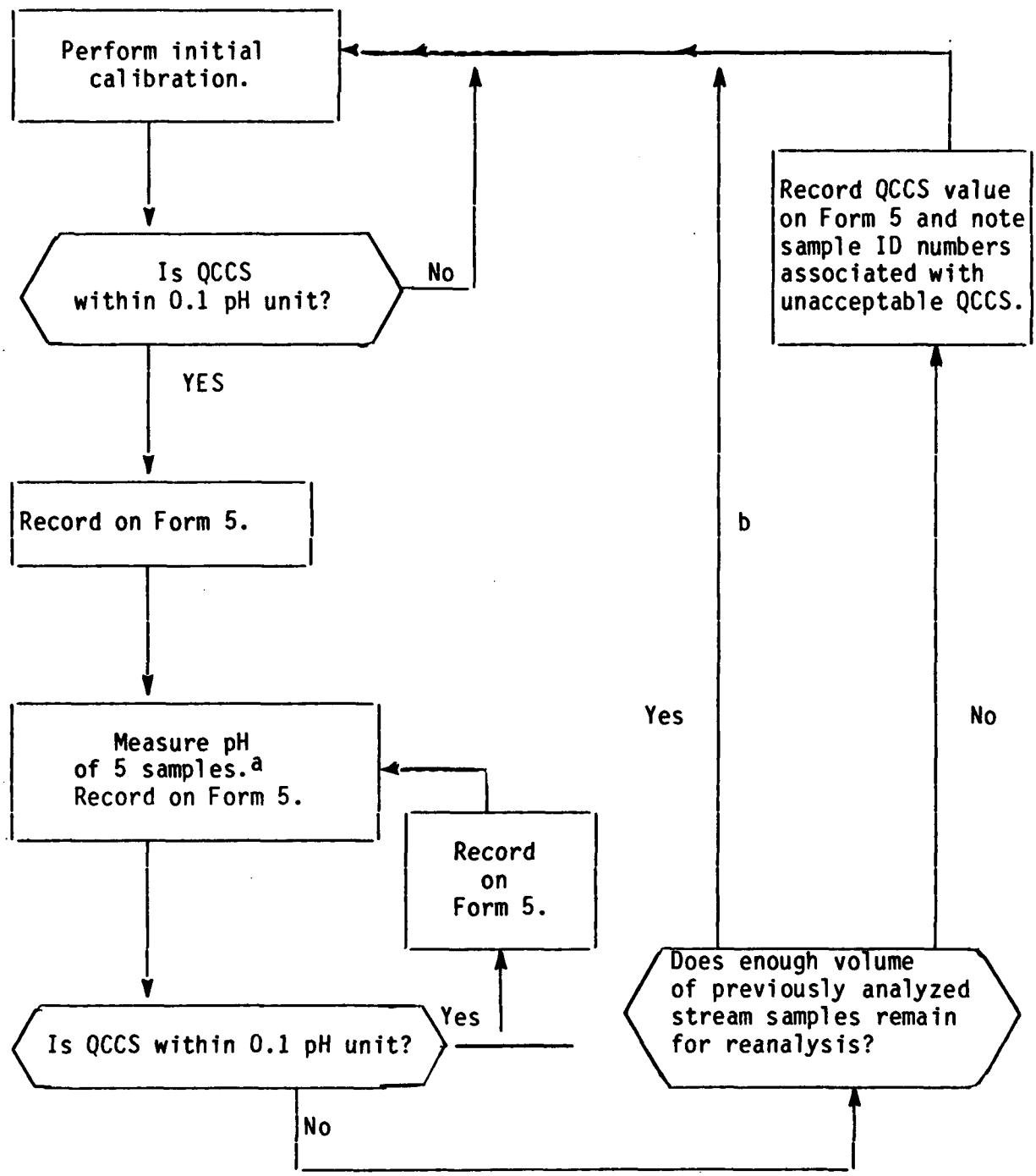
2.4.10.1 Calibrate the pH meter and electrode.

2.4.10.2 Perform the required QC analysis. Proceed with sample analyses if acceptable results are obtained.

2.4.10.3 Clamp a pH sample chamber to a ringstand. Rinse thoroughly with water.

2.4.10.4 Equilibrate the sample syringes to room temperature.

2.4.10.5 Attach a sample syringe to the sample chamber. Fill the chamber with sample. Rinse the electrode in the top of the chamber for 15 to 30 seconds. Drain the chamber and repeat. Refill the chamber with sample and loosely insert the electrode. Flush with 5 to 10 mL sample to expel air bubbles, then lightly seal the chamber. Measure and record the sample pH and temperature. Monitor the pH reading. Record the reading when it stabilizes (± 0.01 pH unit/minute, usually about 1 to 5 minutes). Slowly inject 5 mL sample over a 60-second period. Measure the pH and record when stable. Repeat the 5-mL injections until successive pH readings are within 0.03 pH units.



[a]Measure 1 sample per batch in duplicate (same syringe).
[b]Previous samples must be reanalyzed after unacceptable QCCS is obtained.

Figure 2.10. Flow scheme for pH determinations.

2.4.10.6 Rinse the sample chamber and electrode copiously with water between samples.

2.4.10.7 At the end of the day, store the electrode in 3 M KCl.

2.4.11 Calculations

No calculations are required.

2.4.12 Reporting

Record the raw data in the pH logbook, and record the final sample pH value on Form 5. Also record the initial and continuing QC results on Form 5.

2.5 Determination of Turbidity

2.5.1 Scope and Application

This method is applicable to the determination of turbidity in natural surface waters and is written specifically for the NSWS. Turbidity is determined in the MPL by using a Monitek Model 21 nephelometer. As a result, the method has been written with the assumption that the Monitek nephelometer is used (Monitek, 1977). The applicable turbidity range is 0 to 200 NTU.

2.5.2 Summary of Method

Samples are collected at the stream site in Cubitainers. At the MPL the sample turbidity is measured directly in NTU by using a calibrated nephelometer.

2.5.3 Interferences

Air bubbles in the sample cuvette interfere with the determination and cause a positive bias.

2.5.4 Safety

2.5.4.1 The calibration standards and sample types pose no hazard to the analyst.

2.5.5 Apparatus and Equipment

2.5.5.1 Monitek Model 21 nephelometer and sample cuvettes

2.5.6 Reagents and Consumable Materials

2.5.6.1 Turbidity Calibration Standard (10 NTU)--Commercially available certified turbidity standard.

2.5.6.2 Turbidity Quality Control Samples (1.7, 5, 20, 50, 100, and 200 NTU)--Commercially available certified turbidity standards.

2.5.7 Sample Collection, Preservation, and Storage

Stream samples are collected in plastic Cubitainers and are stored at 4°C until use.

2.5.8 Calibration and Standardization

2.5.8.1 Turn on the nephelometer power and lamp. Allow to warm up for 15 to 30 minutes.

2.5.8.2 Set the nephelometer range switch to 20. Zero the instrument with the zero knob.

2.5.8.3 Place the 10.0-NTU calibration standard in the instrument. Calibrate by setting the reading to 10.0 with the calibrate knob.

2.5.9 Quality Control

QC procedures are outlined in Figure 2.11 and are as follows:

2.5.9.1 Initial Calibration Verification and Linearity Check--Immediately after calibration, analyze the 1.7-, 5.0-, and 20.0-NTU QC samples to ensure the calibration validity and linearity. The measured values must be 1.7 ± 0.3, 5.0 ± 0.5, and 20.0 ± 1.0. If the measured values are unacceptable, the calibration must be repeated. Ensure that the instrument is warmed up and that the cuvettes are clean. Acceptable results must be obtained prior to sample analysis.

2.5.9.2 Continuing Calibration Check--After every eight samples and after the last sample, reanalyze the 5.0-NTU QC sample. The measured value must be 5.0 ± 0.5 NTU. If it is not, recalibrate the instrument and re-analyze all samples analyzed since the last acceptably analyzed QC sample.

2.5.9.3 Duplicate Analysis--In order to determine the analytical precision, analyze one sample per batch in duplicate.

2.5.10 Procedure

2.5.10.1 Warm up the nephelometer.

2.5.10.2 Calibrate the nephelometer.

2.5.10.3 Analyze the QC samples. Proceed with the following sample analysis if acceptable results are obtained.

2.5.10.4 Allow the sample Cubitainer to reach room temperature. Gently swirl sample Cubitainers to mix and distribute any particles which may have settled out during sample transport. Care must be taken to avoid agitation-induced air bubbles which interfere with the measurement. Rinse the nephelometer cuvette with two 5-mL portions of sample, then fill (approximately 25 mL sample). Wipe the cuvette with a Kimwipe, insert the cuvette into the nephelometer, and measure the turbidity on range 20. (Note: Fingerprints, bubbles, smudges, etc., must be avoided because they will affect the accuracy of the system.) The turbidity of a sample is not expected to exceed 20 NTU; however, if this occurs, the sample must be analyzed on range 200. In this case, a QC sample with a turbidity greater than the sample must be analyzed (50, 100, or 200-NTU QC samples are available). Acceptable results for the QC samples are 50 ± 2.5, 100 ± 5, and 200 ± 10, respectively. If an acceptable QC value is not obtained, the turbidimeter must be recalibrated on range 200 by using a 100-NTU QC standard, and the sample must be reanalyzed. If the sample turbidity exceeds 200 NTU, the sample must be diluted 1:10 with filtered sample and must be reanalyzed on range 200 as stated above. The turbidity of the original sample is calculated by multiplying the turbidity of the dilute sample by the dilution factor.

2.5.10.5 Rinse cuvette thoroughly with water between samples.

2.5.11 Calculations

No calculations are required.

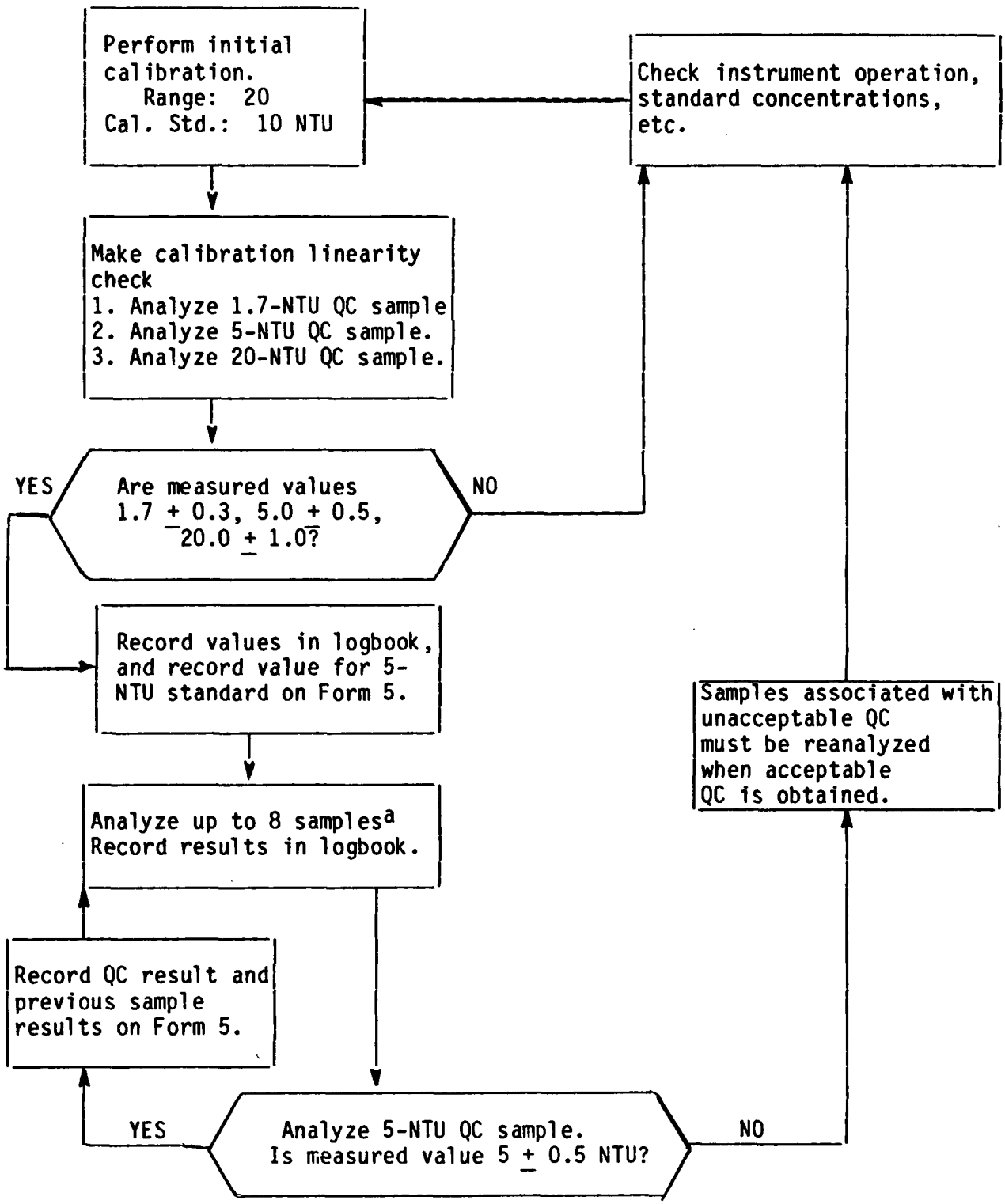
2.5.12 Reporting

Record the sample and QC data in the turbidity logbook and on Form 5. Report only the QC data for the 5.0-NTU QC sample on Form 5.

2.6 Determination of True Color

2.6.1 Scope and Application

This method is applicable to the determination of true color in natural surface waters and is written specifically for the NSWS. True color is determined in the MPL by using a Hach Color Determination Kit. As a result, the method has been written with the assumption that the Hach Color Determination Kit is used. The applicable color range is 0 to 200 PCU.



[a]Analyze one sample per batch in duplicate.

Figure 2.11. Flow scheme for turbidity determinations.

2.6.2 Summary of Method

Samples are collected at the stream site in Cubitainers. At the MPL, the true color is determined after centrifuging a sample and after comparing its color to APHA PCU color standards.

2.6.3 Interferences

No interferences are known.

2.6.4 Safety

The sample types pose no hazard to the analyst.

2.6.5 Apparatus and Equipment

2.6.5.1 Hach Model CO-1 Color Determination Kit with sample cuvette.

2.6.6 Reagents and Consumable Materials

2.6.6.1 Water--Water used to rinse cuvettes must conform to ASTM specifications for Type I water ASTM D 1193 (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.

2.6.7 Sample Collection, Preservation, and Storage

Streams samples are collected in plastic Cubitainers and are stored at 4°C until use.

2.6.8 Calibration and Standardization

The color kit contains permanent color standards. No calibration is necessary.

2.6.9 Quality Control

Duplicate Analysis--To determine the analytical precision, analyze one sample per batch in duplicate.

2.6.10 Procedure

2.6.10.1 Allow the samples to reach room temperature.

2.6.10.2 Centrifuge a 50-mL sample to remove turbidity. Rinse a sample cuvette with three 5-mL portions of centrifuged sample. Fill the cuvette with sample and cap it. Determine the color by using the color kit and by following the instructions provided by the manufacturer.

2.6.10.3 Rinse the sample cuvette thoroughly with water between samples.

2.6.11 Calculations

No calculations are necessary.

2.6.12 Reporting

Record the sample data in the color logbook and on Form 5.

2.7 Determination of Nonexchangeable Pyrocatechol Violet (PCV) Reactive and Total PCV Reactive Aluminum

2.7.1 Scope and Application

This method is applicable to the determination of total reactive and nonexchangeable reactive aluminum species in natural surface waters.

Detection Limits (MDLs) are to be determined. The method is presently in the developmental stage, and only limited data are available on its application. A similar manual method was found to have a detection limit of 3.0 µg Al/L (Dougan and Wilson, 1974). Rogeberg and Henriksen, 1985, reported a minimum detection limit of 10 µg Al/L when use was made of an automated segmented flow system similar to the one in the present study. This MDL is identical to that reported for an automated flow injection analyzer. The method is applicable for determining the various Al species over the concentration range 0.01 to 0.80 mg Al/L.

This method does not distinguish various inorganic monomeric aluminum species from each other nor does it distinguish the various neutral organic complexes of aluminum from each other. Furthermore, the definitions of total monomeric and nonlabile monomeric organic aluminum are operationally based upon commonly accepted usage. Actually, some charged, organically complexed aluminum may be measured as inorganic aluminum, and some strongly complexed aluminum may not be measured in either fraction.

2.7.2 Summary of Method

Samples are collected in syringes. The aluminum species in each sample are subsequently determined by flow injection analysis (FIA). Samples are loaded into the FIA system manually, directly from the syringe, and are then injected. The sample, carried by a deionized flow stream, is mixed with hydroxylammonium/1,10-phenanthroline solution to eliminate iron interference. The sample is next reacted with a pyrocatechol violet solution. The pH of the solution is then adjusted to pH 6.1 with buffer. The Al is subsequently quantitated by measuring the absorbance

of the PCV-Al complex at 580 nm. The Al so measured is termed total PCV reactive Al.

Another portion of sample undergoes the same reaction sequence; however, it is first passed through a strong cation-exchange column prior to reaction with PCV. The column removes inorganic monomeric Al. The Al measured after the cation-exchange procedure is termed nonexchangeable PCV reactive Al. Other organic complexes of aluminum are very stable and do not react with PCV and are not measured. This fraction is believed to be nontoxic to fish.

2.7.3 Definitions

Total PCV reactive aluminum (total monomeric aluminum) is defined as the fraction of aluminum which reacts with pyrocatechol violet without preliminary acidification. This includes aluminum in the free ionic form and aluminum which is weakly complexed (compared to pyrocatechol violet) by inorganic and organic ligands.

Nonexchangeable PCV reactive aluminum is operationally defined as the fraction of total monomeric aluminum which is not removed by cation-exchange resins but is reactive with PCV. This fraction includes weakly complexed organo-aluminum species (organic monomeric aluminum).

It is theoretically nontoxic and is subtracted from total reactive aluminum to estimate the inorganic monomeric aluminum concentration which is believed to be toxic to fish.

2.7.4 Interferences

Holding time and storage methods affect the aluminum speciation in water samples. Samples should be analyzed as soon as possible after collection. Samples should be stored at 4°C in the dark during transit. Changes in temperature and pH may drastically alter aluminum speciation.

Iron (III) interferes with the determination of aluminum when use is made of this method. The interference is eliminated by reducing Fe (III) to Fe (II) with hydroxylammonium chloride and subsequently chelating with 1,10-phenanthroline.

2.7.5 Safety

The calibration standards and most chemical reagents encountered in this method pose no hazard to the analyst when good laboratory practices are followed. Protective clothing (safety glasses, gloves, lab coat) should be worn when handling concentrated acids and bases.

2.7.6 *Apparatus and Equipment*

2.7.6.1 Automated Dual Channel Flow-Injection Analyzer--A microprocessor-controlled system is used for automatic injection of samples, mixing of the required chemicals for the pyrocatechol violet reaction, and detection of the aluminum-catechol complex.

2.7.6.2 Cation-Exchange Column--An Amberlite IR 120 (14 to 50 mesh) exchange resin is used to separate the organic monomeric aluminum from the inorganic monomeric aluminum, by using a 100 mm x 3 mm ID Teflon column with fritted Teflon inserts containing the resin.

2.7.6.3 Clean-Air Laminar-Flow Hood--

2.7.6.4 Nucleopore/Polyearbonate Filters--

2.7.6.5 Polystyrene Divinyl Benzene Beads (14 to 50 mesh)--

2.7.7 Reagents and Consumable Materials

2.7.7.1 Water--All water used in preparing reagents and cleaning labware must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

2.7.7.2 Stock Reagents--

Ethanol - 95 percent (Reagent).

Hydrochloric acid (HCl) - concentrated (Baker Ultrex grade or equivalent).

Sodium Chloride - crystal (ACS reagent grade).

Ammonium hydroxide (NH_4OH) - concentrated (Baker Instra-Analyzed or equivalent).

Nitric Acid - concentrated (Ultrex grade or equivalent).

0.1 M HCl - slowly add 8.3 mL concentrated HCl acid to 500 mL water and dilute to 1.00 L mark.

Cleaning solution (0.1 N HCl in 10 percent ethanol) - Slowly add 8.3 mL concentrated HCl to 500 mL D.I. water in a 1-L graduated cylinder. Then add 100 mLs ethanol and bring to a final volume of 1.00 L with D.I. water. Prepare under fume hood.

10 percent nitric acid (1.6 N) - Slowly add 10 mL concentrated Ultrex nitric acid to 50 mL of water. Dilute to 100 mL with water.

Sodium chloride solution (0.001 M NaCl) - Dissolve 0.058 g sodium chloride (ACS reagent grade) in water and dilute to 1.00 L.

2.7.7.3 Working Reagents--

Reagent R1 (masking solution) - dissolve 7.6 g hydroxylammonium chloride and 0.56 g 1,10-phenanthroline in 600 mL water and dilute to 1.000 L. Degas and store in clean polyethylene bottle.

Reagent R2 (pyrocatechol violet solution) - dissolve 0.375 g pyrocatechol violet in 400 mL water. Let solution stand for about 5 minutes with occasional shaking, then dilute to 1.00 L. Store in acid-washed, water-rinsed polyethylene bottle. Degas before use.

Reagent R3 (buffer) - dissolve 78 g hexamethylenetetraamine in 750 mL water and dilute to 1 L. Mix well, degas, and transfer the solution to a polyethylene bottle.

Ion-exchange resin - mix the sodium form of the Amberlite IR 120 (14 to 52 mesh) resin with 1 percent of the corresponding hydrogen form. Wash the resin twice with water and then with 0.001 M NaCl until the supernatant is clear. Pack column daily with fresh Amberlite resin.

NOTE: Reagents R1, R2, and R3 must be prepared daily.

2.7.7.4 Aluminum Calibration Standards--

Stock aluminum calibration solution (1,000 mg Al/L) - Commercially available certified standard.

Dilute stock aluminum calibration solution (10 mg Al/L) - Add, using a volumetric pipet, 10.0 mL of the 1,000 mg Al/L solution to 750 mL water containing 1.0 mL 10 percent nitric acid in a 1.0 liter volumetric flask, then dilute to the mark with water.

Dilute calibration standards - Daily, prepare the calibration standards listed in the table by diluting the appropriate volume of 10.0 mg Al/L standard solution to 100 mL. Dispense using volumetric pipets.

Low Calibration		High Calibration	
Standard Concentration (mg/L)	mL 10.0 mg Al/L Required	Standard Concentration (mg/L)	mL 10.0 mg Al/L Required
0.0000	0.000		
0.0250	0.250	0.3500	3.500
0.1000	1.000	0.5000	5.000
0.2000	2.000	0.7500	7.500
0.3500	3.500	1.0000	10.000

NOTE: Prepare the blank (0.000 mg Al/L) by adding 0.020 mL 10 percent nitric acid to 50 mL water in a 100-mL volumetric flask. Dilute to 100 mL with water.

2.7.7.5 Aluminum Quality Control Samples--

Stock aluminum QC solution (1,000 mg Al/L) - Commercially available certified standard from a source independent of the calibration standard.

Dilute QC stock aluminum solution (10 mg Al/L) - Prepare as in section 2.7.7.4.

Detection limit QC sample (0.020 mg Al/L) - Daily, add 0.0200 mL 1,000 mg Al/L QC solution to 100 mL water then dilute to 1.000 L.

Routine QC sample (0.0750 mg Al/L) - Daily, add 3.75 mL 10.00 mg Al/L QC solution to 100 mL water then dilute to 500.00 mL.

2.7.7.6 Syringe Filters--

Acid-wash sufficient 25-mm Swin-Lok filter holders with 5 percent nitric acid. Rinse thoroughly with water.

Using clean Teflon forceps, remove a 25-mm Nucleopore polycarbonate filter from the package. Dip filter into beaker of water to prewet the filter.

Place filter on the filter base. Place filter base with filter on syringe attachment. Center o-ring on filter and place filter top on o-ring. Compress o-ring by screwing exit port onto syringe attachment.

Attach a syringe containing 5 percent nitric acid onto the Luer-Lok fitting. Inject 1 to 2 mL through the filter unit. Attach another syringe containing water and inject three separate aliquots of 10 to 15 mL through the filter unit.

Repeat the above procedure to prepare adequate filter units for daily batch analysis. Store acid-washed syringe filters in self-sealing bags until needed.

2.7.8 Sample Collection, Preservation, and Storage

Samples are collected in 60-mL syringes with syringe lock valves to prevent CO_2 degassing or adsorption.

Samples are stored at 4°C in the dark.

2.7.9 Calibration and Standardization

Channel 1 (Reactive Aluminum)--Analyze the low and high calibration standards (including the 0.00 mg/L standard) before each shift. A

calibration curve is generated by plotting standard response versus standard concentration. Alternatively, the best fit line of response versus concentration is calculated (by the data system of the FIA) by linear regression.

Channel 2 (Nonexchangeable Reactive Aluminum)--Replace the ion-exchange column in the FIA system channel 2 with a blank column containing polystyrene divinyl benzene resin beads (same mesh size as ion-exchange resin). Analyze the low and high standards and generate a calibration curve as in the Channel 1 calibration.

2.7.10 Quality Control

Internal Quality Control--

MPL Duplicate - analyze one sample per batch in duplicate. The RSD for duplicate results must be less than or equal to 10 percent. If it is not, the reason for the poor precision must be found and eliminated prior to continuing sample analysis.

Detection Limit Quality Control Check Sample - analyze the detection limit QCCS immediately after calibration and prior to sample analysis. The measured concentration must be within 20 percent of the actual concentration. If not, the reason for the poor accuracy must be found and eliminated prior to sample analysis.

Routine Quality Control Check Sample - analyze the routine QCCS after the detection limit QCCS, after every fifth sample, and after the final sample. The observed concentration should be within 10 percent of the actual concentration. If this is not the case, the reason for the poor accuracy must be found and eliminated before continuing sample analysis. If necessary, the FIA must be recalibrated. All samples analyzed since the last acceptable QCCS must be reanalyzed.

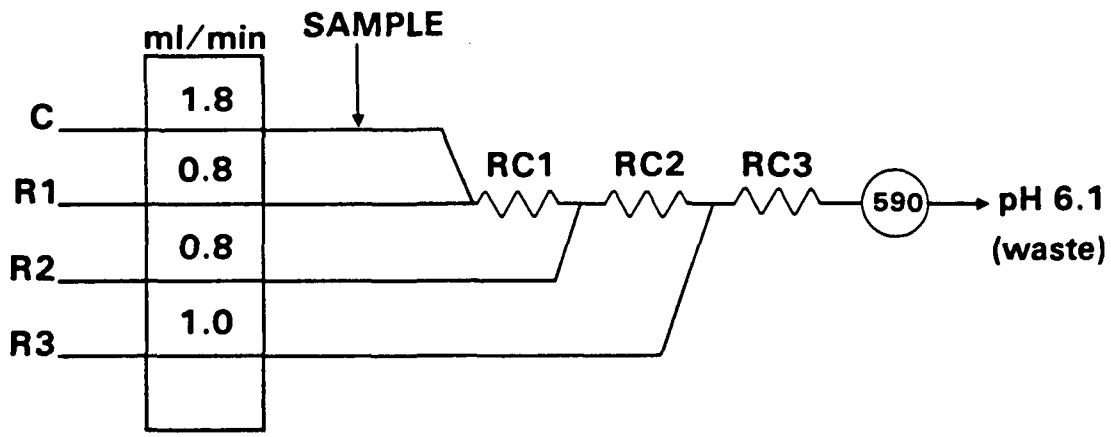
2.7.11 Procedure

2.7.11.1 System Preparation--Set up both channels of the FIA system as illustrated in Figures 2.12 and 2.13. Program the computer according to instructions provided by the manufacturer.

2.7.11.2 Fill unused syringes with the calibration standards and QC samples.

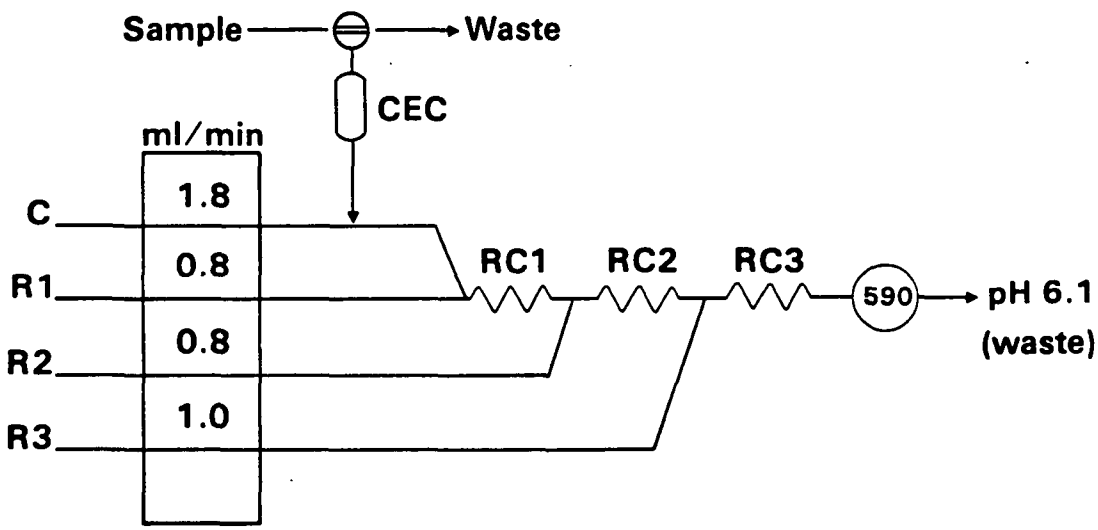
2.7.11.3 Sample Analysis--

Standard and QC sample analysis (channel 1 - Reactive Al) - manually load the sample injection loop and then inject to start the FIA analysis.



Key: Carrier:Deionized water (or 0.1 M HCl)
R1 - Masking solution : Hydroxylammonium chloride and 1,10 Phenanthroline chloride
R2 - Color reagent : Pyrocatecholviolet
R3 - Buffer solution : Hexamethylenetetramine and NaOH
RC1 - Reaction coil, 10 cm (0.5 mm i.d.)
RC2 - Reaction coil, 30 cm (0.5 mm i.d.)
RC3 - Reaction coil, 60 cm (0.5 mm i.d.)

Figure 2.12. Channel one schematic for total PCV reactive Al.



Key: Carrier:Deionized water (or 0.1 M HCl)
R1 - Masking solution : Hydroxylammonium chloride and 1,10 Phenanthroline chloride
R2 - Color reagent : Pyrocatecholviolet
R3 - Buffer solution : Hexamethylenetetramine and NaOH
RC1 - Reaction coil, 10 cm (0.5 mm i.d.)
RC2 - Reaction coil, 30 cm (0.5 mm i.d.)
RC3 - Reaction coil, 60 cm (0.5 mm i.d.)
CEC - Cation exchange column

Figure 2.13. Channel two schematic for nonexchangeable PCV reactive Al.

Standard and QC sample analysis (channel 2 - Nonexchangeable Al) - manually load the sample injection loop, then inject to start the FIA analysis.

Routine sample analysis - place a 0.4-µm polycarbonate syringe filter on the sample syringe. Eject 5.0 mL sample through the filter into a waste container. Next, load the sample injection loop with filtered sample and inject to start the FIA analysis.

2.7.11.4 Analyze the routine QC sample every five samples and after the last sample. Results must be within the specifications listed in section 2.7.10.

2.7.11.5 If a sample concentration exceeds the calibrated range, inject a smaller sample volume (consult the operating manual for details on techniques to reduce sample volume).

2.7.11.6 Replace the ion-exchange cartridge after every 50 samples injected.

2.7.11.7 After a day's analysis, flush the FIA system with water for 5 minutes and then flush with air for 2 minutes.

2.7.12 Calculations

Calculate concentration by comparing the peak heights with the calibration curve. Report results as µg Al/L for both species of aluminum.

2.7.13 Precision and Accuracy

For surface water samples containing 10 to 350 µg Al/L, the average standard deviation was ±3.1 µg Al/L.

Accuracy (recovery) was reported by Rogeberg and Henriksen, 1985, for surface waters spiked with 150 and 580 µg Al/L. The recovery was found to be to be 99 percent and 105 percent, respectively.

2.8 Aliquot Preparation

2.8.1 Summary

Stream samples are collected in 4-L Cubitainers. From each sample, the aliquots are prepared. Each aliquot is processed in a different manner according to which analytes will be determined in the aliquot.

A brief description of the aliquots is given in Table 2.3.

TABLE 2.3. ALIQUOT DESCRIPTIONS

Aliquot	Container Description	Description
1	250 mL (acid-washed)	Filtered sample acidified with HNO_3 to a pH <2
2	10 mL (acid-washed)	MIBK-Hydroxyquinoline extract
3	250 mL (not acid-washed)	Filtered sample
4	125 mL (acid-washed)	Filtered sample acidified with H_2SO_4 to a pH <2
5	500 mL (not acid-washed)	Raw unfiltered sample
6[a]	125 mL (acid-washed)	Filtered sample acidified with H_2SO_4 to a pH <2
7	125 mL (acid-washed)	Unfiltered sample acidified with HNO_3 to a pH <2
8[b]	10 mL	MIBK-Hydroxyquinoline extract

[a]Unfiltered for Pilot study.
[b]For Streams Pilot only. See 2.8.5.5.

2.8.2 Safety

The sample types and most reagents used in preparing aliquots pose little hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling concentrated sulfuric, nitric, hydrochloric, and glacial acetic acids and concentrated ammonium hydroxide. The use of hydrochloric and acetic acids and of ammonium hydroxide should be restricted to the hood.

MIBK is a highly flammable organic solvent and must be kept away from ignition sources. Also, MIBK vapor is irritating to the eyes, nose, and throat. Exposure to the vapor may cause temporary irritation.

Liquid MIBK is also an irritant. If spilled on skin or in eyes, wash affected area thoroughly with water until irritation stops. The use of MIBK should be restricted to the hood. If it must be used outside of the hood, organic vapor masks should be worn.

2.8.3 Apparatus and Equipment

Filtration Apparatus--Includes filter holder, vacuum chamber, and vacuum pumps.

2.8.4 Reagents and Consumable Materials

2.8.4.1 Ammonium Hydroxide (1 M)--Carefully add 20 mL concentrated ammonium hydroxide (NH_4OH, 5 M, Baker Instra-Analyzed grade or equivalent) to 80 mL water.

2.8.4.2 Glacial Acetic Acid--Baker Instra-Analyzed grade or equivalent.

2.8.4.3 8-hydroxyquinoline Solution (10 g/L)--Dissolve 5 g 8-hydroxyquinoline (99 percent plus purity) in 12.5 mL glacial acetic acid (HOAc, Baker Instra-Analyzed grade or equivalent), then dilute to 500 mL with water.

2.8.4.4 8-hydroxyquinoline/Sodium Acetate Reagent (HOx Reagent)--Prepare daily by mixing in order, 30 mL 1.0 M NaOAc, 150 mL water, and 30 mL 8-hydroxyquinoline solution.

2.8.4.5 Buffer Solution (pH 8.3)--Carefully add 56 mL glacial acetic acid (Baker Instra-Analyzed grade or equivalent) to 75 mL NH_4OH (5 M, Baker Instra-Analyzed grade or equivalent). Dilute to 250 mL with water. Adjust the pH to 8.3 with NH_4OH or HOAc (whichever is necessary, testing the pH with indicating pH paper). Add an additional 16 mL NH_4OH, then dilute to 500 mL with water.

2.8.4.6 Nitric Acid (HNO_3, 12 M, Baker Ultrex grade or equivalent).

2.8.4.7 Phenol Red Indicator Solution (4 percent w/v).

2.8.4.8 Sodium Acetate (NaOAc, 1.0 M)--Dissolve 8.20 g sodium acetate (Alfa ultrapure grade or equivalent) in water, then dilute to 100 mL.

2.8.4.9 Sulfuric Acid (H_2SO_4, 18 M, Baker Ultrex grade or equivalent).

2.8.4.10 Water--Water used in all preparations must conform to ASTM specifications for Type I water ASTM D 1193 (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.

2.8.4.11 Aliquot Bottles--Clean aliquot bottles are required for the aliquots prepared from each sample. The bottles are cleaned (by using the procedure in Appendix A) and are supplied by an outside contractor.

2.8.4.12 Indicating pH Paper (Range 8 to 9 and 1 to 3)

2.8.4.13 Membrane Filters (0.45-μm pore size)

2.8.5 Procedure

Preparation of the aliquots is described in this section. All filtrations and aliquot 2 preparation are performed in the laminar-flow clean work station.

2.8.5.1 Preparation of Aliquots 1, 4, and 6 (Unfiltered for Pilot Study)

Complete aliquot labels for aliquots 1, 4, and 6 and attach to containers. Assemble the filtration apparatus with a waste container as a collection vessel. Thoroughly rinse the filter holder and membrane filter in succession with 20 to 40 mL water, 20 mL 5 percent HNO_3 (Baker Instra-Analyzed grade), and 40 to 50 mL water.

Rinse the filter holder and membrane with 10 to 15 mL of the sample to be filtered.

Replace the waste container with the aliquot 1 container. Reapply vacuum (vacuum pressure must not exceed 12 in. Hg), and filter 10 to 15 mL of sample. Remove the vacuum. Rinse the aliquot 1 container with the 15 mL of filtered sample by slowly rotating the bottle so that the sample touches all surfaces. Discard the rinse sample and replace the container under the filter holder.

Filter sample into the container until full.

Transfer filtered sample into the aliquot 4 and 6 containers (previously labeled) after first rinsing the containers with 10 to 15 mL filtered sample.

Return the aliquot 1 container to the filtration apparatus and collect additional filtered sample until the container is full.

If it is necessary to replace a membrane (because of clogging) before adequate filtered sample has been obtained, rinse the new membrane with 15 to 20 mL water, 10 to 15 mL 5 percent HNO_3, 40 to 50 mL water, and 10 to 15 mL sample prior to collecting additional sample.

Between samples, remove the membrane and thoroughly rinse the filter holder with water.

Preserve by adding concentrated HNO_3 to aliquot 1 and concentrated H_2SO_4 to aliquots 4 and 6 in 0.100-mL increments until the pH <2 (U.S. EPA, 1983). Check the pH by placing a drop of sample on indicating pH paper, using a clean plastic pipet tip. Record on the aliquot label the volume of acid added.

Store aliquots 1, 4, and 6 at 4°C until ready to ship.

2.8.5.2 Preparation of Aliquot 2 - Total Extractable Aluminum

Obtain a filtered portion of sample from the analyst performing filtrations.

Rinse a clean, plastic 50-mL graduated centrifuge tube with three 10-mL portions of the filtered sample, then fill to the 25.0-mL mark.

Add two to three drops phenol red indicator, 5.0 mL HOx reagent, and 2.0 mL NH_4^+/NH_3 buffer. Shake for 5 seconds. This should adjust the pH to 8.3, and the solution should turn red. If it does not turn red, rapidly adjust the pH by dropwise addition of 1 M NH_4OH until the solution color changes to red. Add 10.0 mL MIBK, cap, and shake vigorously for 10 seconds by using a rapid, end-to-end motion. (Note: Successful extraction depends on good agitation.) This entire process should take about 15 to 20 seconds. Open tube carefully after shaking because pressure builds up.

Centrifuge the sample to hasten separation of the aqueous and organic layers, then transfer the MIBK layer with a 5-mL micropipet to a 10-mL centrifuge tube. Securely cap tube.

Complete a label for aliquot 2 and attach label to the container.

Store the 10-mL tube containing aliquot 2 at 4°C in the dark until ready to ship.

Discard the 50-mL centrifuge tube after a single use.

2.8.5.3 Preparation of Aliquot 3--Filtered sample for aliquot 3 is obtained similarly to that for aliquots 1, 4, and 6, except that the filter holder used to filter aliquot 3 is never allowed to come into contact with nitric acid. This is CRUCIAL in preventing nitrate contamination. Previous experience indicates that even the most scrupulous water rinses did not remove all traces of a nitric acid rinse. Blanks still contained measurable nitrate.

Soak filter holders for 24 hours in deionized water prior to first use.

Complete an aliquot 3 label and attach label to the aliquot bottle.

Assemble the filtration apparatus with a waste container as a collection vessel. Thoroughly rinse the filter holder and membrane filter with three 25-mL portions water, followed by 10 to 15 mL sample to be filtered.

Replace the waste container with the aliquot 3 container and filter an additional 15 mL sample. Remove the container and rinse by slowly rotating the bottle so that the sample touches all surfaces. Discard the rinse sample and replace the container under the filter holder.

Filter sample into the container until full.

If it is necessary to replace a membrane (because of clogging), rinse the membrane with three 20-mL portions water followed by 15 mL sample before collecting additional sample.

Store at 4°C until ready to ship.

Between samples, remove the membrane and thoroughly rinse the filter holder with water.

2.8.5.4 Preparation of Aliquots 5 and 7--Aliquots 5 and 7 are unfiltered aliquots.

Complete aliquot 5 and 7 labels and attach to the appropriate aliquot bottles. Transfer 15 to 20 mL sample to aliquot bottle and rinse by slowly rotating bottle so that sample touches all surfaces. Discard rinse.

Fill aliquot bottle with unfiltered sample. Fill aliquot 5 bottle so that no headspace exists.

Preserve by adding concentrated HNO_3 to aliquot 7 in 0.100-mL increments until pH <2 (U.S. EPA, 1983). Check the pH by placing a drop of sample on indicating pH paper, using a clean plastic pipet tip.

Record the volume of acid added on the aliquot label.

Store at 4°C until ready to ship.

2.8.5.5 Aliquot 8 Preparation (Extractable Organic Aluminum) Stream Pilot Only--

Aliquot 8 is prepared as soon as possible. Furthermore, it is only prepared for samples with an initial pH <6 (as determined from field data). As with Aliquot 2, Aliquot 8 must be prepared in the laminar-flow hood.

Prepare the resin column by pouring the resin slurry into a column until there is a 10-mL resin bed. Top up the column with 3×10^{-4} M NaCl and connect the column to the peristaltic pump.

Pump 3×10^{-4} M NaCl through the column and adjust the flow rate to 40.0 mL/min. Flush the column with 50 mL of the eluent. Check the eluent pH. It must be 5.0 ± 0.5. If not, reprepare the resin slurry and column.

Pump 50 mL of sample through the column, collecting the column effluent in a waste container. Pump an additional 25 to 30 mL sample through the column, collecting the effluent in a clean 50-mL centrifuge tube.

Adjust the volume in the tube to 25.0 mL. Extract the 25.0 mL by using the same procedure as for Aliquot 2. Attach an Aliquot 8 label, recording the necessary information. Store at 4°C until ready to ship.

Flush the column with 50 mL of eluent. Check the effluent pH. It must be 5.0 ± 0.5. If not, reprepare the column before processing another sample.

NOTE: Keep resin covered with liquid. Avoid the introduction of air into the column.

2.9 References

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3.0 ANALYTICAL LABORATORY OPERATIONS

3.1 Summary of Operations

Samples are shipped from the MPL to the contract analytical laboratories for analysis. Each sample consists of seven (eight for Stream Pilot) aliquots, each processed in a different manner depending on the analytes for which the aliquot will be analyzed. A brief description of each aliquot and of corresponding analytes are given in Table 3.1.

After receipt, the analytes in each sample are quantified. The analyses must occur within the prescribed holding times (Table 3.2) or a penalty is assessed against the lab. Strict QC requirements must be followed throughout the analyses. Finally, the sample results must be reported in the proper format, on a timely basis, for entry in the NSWS data base.

3.2 Sample Receipt and Handling

Samples are shipped to the contract laboratory by overnight delivery service. Upon receipt, measure the temperature inside the shipping container and record the temperature on the shipping form. Log in samples and ensure that the samples listed on the shipping form have actually been received. Note anything unusual (such as leaking samples) on the shipping form.

Store sample aliquots 2, 3, 4, 5, and 6 in the dark at 4°C when not in use. The samples must be stored at 4°C for 6 months or until notified by the QA manager.

Clean all labware that comes into contact with the sample (such as autosampler vials, beakers, etc.) as described in Appendix A.

3.3 Sample Analysis

The analytes to be determined in each sample and corresponding measurement techniques are listed in Table 3.3, and the method protocols are provided in sections 4 through 13. Each analyte must be determined within the holding times listed in Table 3.2.

3.4 Internal Quality Control Requirements

QC is an integral part of sample analysis. Method QC requirements common to all methods are detailed in this section. QC requirements specific to a single method are detailed in the description for that method.

TABLE 3.1. LIST OF ALIQUOTS, CONTAINERS, PRESERVATIVES, AND CORRESPONDING PARAMETERS TO BE MEASURED

Aliquot[a]	Container	Preservative and Description	Parameters
1	250 mL	Filtered, pH <2 with HNO_3	Ca, Mg, K, Na, Mn, Fe
2	10 mL	MIBK-HQ extract	Total extractable Al
3	250 mL	Filtered	Cl, F, SO_4, NO_3, SiO_2
4	125 mL	Filtered, pH <2 with H_2SO_4	DOC, NH_4
5	500 mL	Unfiltered	pH, BNC, ANC, specific conductance, DIC
6[b]	125 mL	Filtered, pH <2 with H_2SO_4	Total dissolved P
7	125 mL	Unfiltered, pH <2 with HNO_3	Total Al
8[c]	10 mL	MIBK-HQ extract	Extractable organic Al (ion exchanged)

[a]Aliquots 2, 3, 4, 5, and 6 must be stored at 4°C in the dark.
[b]Unfiltered for Pilot Study.
[c]Aliquot 8 is used for the Pilot Study only.

TABLE 3.2. LIST OF HOLDING TIMES

Maximum Holding Time	Parameter
7 days	NO_3,[a] pH[b], Total extractable Al
14 days	ANC, BNC, specific conductance, DIC, DOC
28 days	Total P, NH_4, Cl, SO_4, F, SiO_2
6 months[c]	Ca, Mg, K, Na, total Al, Mn, Fe

[a]Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (un-acidified) be determined within 48 hours of collection, evidence exists (Peden, 1981 and APHA et al., 1985) that nitrate is stable for 2 to 4 weeks if stored in the dark at 4°C.

[b]Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for up to 15 days if stored at 4°C and sealed from the atmosphere. The pH is also measured in a sealed sample at the field station within 12 hours of sample collection.

[c]Although the EPA (U.S. EPA, 1983) recommends a maximum 6-month holding time for these metals, this study requires that all of the metals be determined within 28 days. This is to ensure that significant changes do not occur and to obtain data in a timely manner.

TABLE 3.3. LIST OF PARAMETERS AND CORRESPONDING MEASUREMENT METHODS

Parameter	Method
1. BNC	Titration with Gran analysis
2. ANC	Titration with Gran analysis
3. Aluminum, total	202.2 AAS (furnace)
4. Aluminum, total extractable	Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace)
5. Aluminum, Nonexchangeable and Total PCV Reactive	Automated Colorimetric Pyrocatechol Violet (PVC)
6. Ammonium, dissolved	Automated colorimetry (phenate)
7. Calcium, dissolved	AAS (flame) or ICPES
8. Chloride, dissolved	Ion chromatography
9. Fluoride, total dissolved	Ion-selective electrode and meter
10. Inorganic carbon, dissolved	Instrument (acidification, CO_2 generation, IR detection)
11. Iron, dissolved	AAS (flame) or ICPES
12. Magnesium, dissolved	AAS (flame) or ICPES
13. Manganese, dissolved	AAS (flame) or ICPES
14. Nitrate, dissolved	Ion chromatography
15. Organic carbon, dissolved	Instrument (uv-promoted oxidation, CO_2 generation, IR detection)
16. pH	pH electrode and meter
17. Phosphorus, total dissolved	Automated colorimetry (molybdate blue)
18. Potassium, dissolved	AAS (flame)
19. Silica, dissolved	Automated colorimetry (molybdate blue)
20. Sodium, dissolved	AAS (flame)
21. Sulfate, dissolved	Ion chromatography
22. Specific conductance	Conductivity cell and meter

3.4.1 Method Quality Control

Each method contains specific QC steps which must be performed to ensure data quality. Table 3.4 is a brief summary of the required QC checks as well as control limits and corrective actions for QC checks outside control limits. QC steps common to all (or most) of the methods are detailed in sections 3.4.1.1 through 3.4.1.5, while QC steps specific to a single method are detailed in the method protocol.

3.4.1.1 Calibration Verification QC Check Sample--After performing the calibration step for a method, verify the calibration (to ensure proper standard preparation, etc.) prior to sample analysis by analyzing a calibration QC check sample (QCCS). The QCCS is a known sample containing the analyte of interest at a concentration in the low- to mid-calibration range. Furthermore, the QCCS must be independent of the calibration standards.

For each batch of samples, analyze the calibration QCCS immediately after calibration, after every 10 sample analyses, and after the final sample analysis. Plot the measured analyte concentration in the QCCS on a control chart and develop the 95 percent and 99 percent confidence intervals. The 99 percent confidence interval must be within the limits given in Table 3.5. (The limits in Table 3.5 may be used as initial limits until enough data are obtained to generate a control chart.) If the 99 percent confidence interval is not within those limits, a problem exists with the experimental technique or the QCCS itself.

The measured analyte concentration in the QCCS must be within the 99 percent confidence interval. An acceptable result must be obtained prior to continuing sample determinations. If unacceptable results are obtained, repeat the calibration step and reanalyze all samples analyzed since the last acceptably analyzed QCCS.

3.4.1.2 Detection Limit Determination and Verification--Determine the detection limit weekly for all parameters (except pH and specific conductance for which the term detection limit does not apply). For the NSWS, the detection limit is defined as three times the standard deviation of 10 nonconsecutive reagent or calibration blank analyses. In the case where a signal is not obtained for a blank analysis (such as in ion chromatographic analyses or autoanalyzer analyses), a low-concentration standard (concentration about three to four times the detection limit) is analyzed rather than a blank. Detection limits must not exceed the values listed in Table 1.1. If a detection limit is not met, refine the analytical technique and optimize any instrumentation variables until the detection limit is achieved.

TABLE 3.4. SUMMARY OF INTERNAL METHOD QUALITY CONTROL CHECKS

Parameter or Method	QC Check	Control Limits	Corrective Action[a]
BNC, ANC, pH	1. Titrant standardization cross-check.	1. Relative difference <5%.	1. Restandardize titrants.
	2. Electrode calibration (Nernstian response check).	2. Slope = 1.00 ± 0.05.	2. Recalibrate or replace electrode.
	3. pH QCCS (pH 4 and 10) analysis.	3. pH 4 = 4.00 ± 0.05. pH 10 = 10.00 ± 0.05.	3. Recalibrate electrode.
	4. Blank analysis (salt spike).	4. |Blank| ≤10 μeq/L.	4. Prepare fresh KCl spike solution.
	5. Duplicate analysis.	5. RSD ≤10%.	5. Refine analytical technique. Analyze another duplicate.
	6. Protolyte comparison.	6. See method (Section 4).	6. See method (Section 4).
Ions (Cl, F, NH_4, NO_3, SO_4), Metals (Al, Ca, Fe, K, Mg, Mn, Na), SiO_2, Total dissolved P, DIC, DOC Specific Conductance	1a. Initial QCCS analysis (calibration and verification).	1a,b. The lesser of the 99% CI or value given in Table 3.5.	1a. Prepare new standards and recalibrate.
	b. Continuing QCCS analysis (every 10 samples).		b. Recalibrate. Reanalyze associated samples.
	2a. Detection limit determination (weekly).	2a. DL < values in Table 1.1.	2a,b. Optimize instrumentation and technique.
	b. DL QCCS analysis (daily, metals and total P only).	b. %Recovery = 100 ±20%.	
	3. Blank analysis.	3a. Blank ≤2 x DL (except sp. cond.).	3a,b. Determine and eliminate contamination source. Prepare fresh blank solution. Reanalyze associated samples.
		b. Blank ≤0.9 μS/cm (sp. cond. only).	
	4. Duplicate analysis.	4. Duplicate precision (RSD) < values given in Table 1.1.	4. Investigate and eliminate source of imprecision. Analyze another duplicate.
	5. Matrix spike (except total ext. Al, DIC, and sp. cond.).	5. %Recovery = 100 ± 15%.	5. Analyze 2 additional spikes. If one or both outside control limits, analyze sample batch by method of standard additions.
	6. Resolution test (IC only).	6. Resolution ≥60%.	6. Clean or replace separator column. Recalibrate.

[a]Assuming QC check is outside control limits.

TABLE 3.5. MAXIMUM CONTROL LIMITS FOR QUALITY CONTROL SAMPLES

Parameter	Maximum Control Limit for QC Sample (% Deviation from Theoretical Concentration of QC Sample)
Al, total extractable	±20%
Al, total	±20%
Ca	±5%
Cl	±5%
DIC	±10%
DOC	±10%
F, total dissolved	±5%
Fe	±10%
K	±5%
Mg	±5%
Mn	±10%
Na	±5%
NH_4	±10%
NO_3	±10%
P, total dissolved	±20%
SiO_2	±5%
SO_4	±5%
Specific conductance	±2%

To verify the detection limit for the determination of metals and total dissolved P daily, analyze a detection limit QCCS after calibration and prior to sample analysis. The detection limit QCCS must contain the analyte of interest at two to three times the detection limit. The measured concentration must be within 20 percent of the true concentration. If it is not, the detection limit is questionable.

3.4.1.3 Blank Analysis--Once per batch analyze a calibration blank as a sample. The calibration blank is defined as a "0" mg/L standard (contains only the matrix of the calibration standards). The measured concentration of the calibration blank must be less than twice the instrumental detection limit. If not, the blank is contaminated, or the calibration is in error at the low end. Prior to sample analysis, investigate and eliminate any contamination source and repeat the calibration.

Prepare and analyze a reagent blank for the three methods which require sample preparation (dissolved SiO_2, total dissolved P, and total Al). A reagent blank contains all the reagents (in the same quantities) used in preparing a real sample for analysis. Process in the same manner (digestions, etc.) as a real sample. The measured concentration of the reagent blank must be less than twice the required detection limit (Table 1.1). If it is not, the reagent blank is contaminated. Investigate and eliminate the contamination source. Prepare and analyze a new reagent blank and apply the same criteria. Reanalyze all samples associated with the contaminated blank when the contamination is eliminated. Contact the QA manager if a contaminated reagent blank problem cannot be rectified.

Prepare one reagent blank with each set of samples processed at one time. For example, if two sample batches are processed together, only one reagent blank is necessary. Report the concentration of the single reagent blank for both batches. On the other hand, if a sample batch is split into groups that are processed at different times, a reagent blank is necessary for each group. In this case, report all reagent blank values for the batch. (Identify in a cover letter which reagent blank values are associated with which samples.)

3.4.1.4 Duplicate Sample Analysis--Prepare and analyze one sample per batch in duplicate. If possible, for duplicate analysis choose a sample containing analyte at a concentration greater than five times the detection limit. Calculate the relative standard deviation (RSD) between duplicates. The duplicate precision (RSD) must not exceed the value given in Table 1.1. If duplicate RSD values fall outside the values given in Table 1.1, a problem exists (such as instrument malfunction, calibration drift, etc.). After finding and resolving

the problem, analyze a second sample in duplicate. Acceptable duplicate sample results must be obtained prior to continuing sample analysis.

$$\%RSD = \frac{S}{\bar{x}} \times 100$$

$$S = \left(\frac{\Sigma(\bar{x} - x)^2}{n-1} \right)^{1/2}$$

3.4.1.5 Matrix Spike Analysis (Stream Pilot only)--Prepare one matrix spike with each batch by spiking a portion of a sample with a known quantity of analyte. The spike concentration must be the larger of two times the endogenous level or ten times the required detection limit. Also, the volume of the spike added must be negligible (less than or equal to 0.001 of the sample aliquot volume). Calculate the percent recovery of the spike as follows:

$$\% \text{ spike recovery} = \frac{\left(\begin{array}{c}\text{measured} \\ \text{concentration} \\ \text{of sample} \\ \text{plus spike}\end{array} - \begin{array}{c}\text{measured} \\ \text{concentration} \\ \text{of unspiked} \\ \text{sample}\end{array} \right)}{(\text{actual concentration of spike added})} \times 100$$

The spike recovery must be 100 ± 15 percent. If the recovery is not acceptable, spike and analyze two additional, different samples. If either recovery is unacceptable, analyze the entire batch by the method of standard additions. The method of standard addition involves analyzing the sample, sample plus a spike at about the endogenous level, and sample plus a spike at about twice the endogenous level.

NOTE: Matrix spikes for graphite furnace atomic absorption spectroscopy (GFAA) analyses may not be added directly in the furnace.

The concentration of the matrix spike must not exceed the instrument linear dynamic range. For this reason, the matrix spike concentration for furnace analyses must be chosen judiciously and may be different than suggested above.

Similarly, care must be taken to avoid exceeding the linear range when performing standard additions for GFAA analyses. The samples may be diluted, and the spike levels may be adjusted so that the linear range is not exceeded.

3.4.2 Overall Internal Quality Control

Once each parameter in a sample has been determined, two procedures exist for checking the correctness of analyses. These procedures are outlined in sections 3.4.2.1 and 3.4.2.2.

3.4.2.1 Anion-Cation Balance--Theoretically, the acid neutralizing capacity (ANC) of a sample equals the difference between the concentration (eq/L) of cations and the anions in a sample (Kramer, 1982). In practice, this is rarely true because of analytical variability and because of ions that are present but not measured. For each sample, calculate the percent ion difference (%ID) as follows:

$$\% \text{ Ion Difference} = \frac{\text{ANC} + \Sigma \text{ anions} - \Sigma \text{ cations}}{\text{TI}} \times 100$$

$$\text{TI (Total ion strength)} = \Sigma \text{ anions} + \Sigma \text{ cations} + \text{ANC} + 2\,[H^+]$$

$$\Sigma \text{ anions} = [Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}]$$

$$\Sigma \text{ cations} = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+]$$

$$\text{ANC} \cong [ALK]$$

$$[H^+] = (10^{-pH}) \times 10^6 \ \mu eq/L$$

All concentrations are expressed as microequivalents/liter (µeq/L). Table 3.6 lists factors for converting mg/L to µeq/L for each of the parameters.

The %ID must not exceed the limits given in Table 3.7. An unacceptable value for %ID indicates the presence of unmeasured ions or an analytical error in the sample analysis. For the surface waters sampled, the ions included in the %ID calculation are expected to account for 90 to 100 percent of the ions in a sample. Note that the ANC term in the calculation accounts for protolyte ions that are not specifically determined (such as organic acids and bases).

Examine the data from samples that do not meet the %ID criteria for possible causes of unacceptable %ID. Often, the cause is improper data reporting (misplaced decimal point, incorrect data reduction,

TABLE 3.6 FACTORS TO CONVERT mg/L TO µeq/L

Ion	Factor (µeq/L per mg/L)
Ca^{2+}	49.9
Cl^-	28.2
F^-	52.6
K^+	25.6
Mg^{2+}	82.3
Na^+	43.5
NH_4^+	55.4
NO_3^-	16.1
SO_4^{2-}	20.8

switched sample ID's, etc.). After examining the data, redetermine any parameter that is suspect. If an explanation for the poor %ID cannot be found and if the problem cannot be corrected, contact the QA manager at EMSL-Las Vegas for further guidance.

3.4.2.2 Conductivity Balance--Estimate the specific conductance of a sample by summing the equivalent conductances for each measured ion. Calculate the equivalent conductance for each ion by multiplying the ion concentration by the appropriate factor in Table 3.8. Calculate the percent conductance difference (%CD) as follows:

$$\% \text{ Conductance Difference} = \frac{\text{calculated cond.} - \text{measured cond.}}{\text{measured conductance}} \times 100$$

The %CD must not exceed the limits listed in Table 3.7. As with the %ID calculation, an unacceptable value for %CD indicates either the presence of unmeasured ions or an analytical error in the sample analysis. For the surface waters sampled, the ions included in the

TABLE 3.7. CHEMICAL REANALYSIS CRITERIA

A. Anion-Cation Balance

Total Ion Strength (μeq/L)	Maximum % Ion Difference[a]
<50	60
≥50<100	30
≥100	15

B. Specific Conductance

Measured Conductance (μS/cm)	Maximum % Conductance Difference[a]
<5	50
≥5<30	30
≥30	20

[a]If the absolute value of the percent difference exceeds these values, the sample is reanalyzed. When reanalysis is indicated, the data for each parameter are examined for possible analytical error. Any suspect results are then redetermined, and the above percent differences are recalculated (Peden, 1981). If the differences are still unacceptable or if no suspect data are identified, the QA manager should be contacted for guidance.

TABLE 3.8. CONDUCTANCE FACTORS OF IONS[a]

Ion	Specific Conductance (μS/cm at 25°C) per mg/L	Ion	Specific Conductance (μS/cm at 25°C) per mg/L
Ca^{2+}	2.60	Na^{+}	2.13
Cl^{-}	2.14	NH_4^{+}	4.13
CO_3^{2-}	2.82	SO_4^{2-}	1.54
H^{+}	3.5×10^5 (per mole/L)	NO_3^{-}	1.15
HCO_3^{-}	0.715	K^{+}	1.84
Mg^{2+}	3.82	OH^{-}	1.92×10^5 (per mole/L)

$$[H^+] \text{ moles/L} = 10^{-pH}$$

pH = pH determined at V=0 of the BNC titration.

$$[OH^-] = \frac{Kw}{[H^+]}$$

$$HCO_3^- = \frac{5.080\,[DIC(mg/L)]\,[H^+]\,K_1}{[H^+]^2 + [H^+]\,K_1 + K_1\,K_2}$$

$$CO_3^{2-} = \frac{4.996\,[DIC(mg/L)]\,K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1\,K_2}$$

$$K_1 = 4.4463 \times 10^{-7} \quad K_2 = 4.6881 \times 10^{-11}$$

[a]APHA et al., 1985; Weast, 1972.

%CD calculation are expected to account for 90 to 100 percent of the ions in a sample. However, in contrast to the %ID calculation, there is no term in the %CD calculation to account for protolytes not specifically determined.

Examine the data from samples that do not meet the %CD criteria for possible causes of the unacceptable %CD, such as improper data reporting or analysis. The presence or absence of unmeasured protolytes can be tested by the procedures described in section 4. Note that the absence of unmeasured protolytes is positive evidence that the %CD exceeds the maximum difference because of analytical error. Redetermine any parameter that is identified as suspect. If an explanation for the poor %CD cannot be found and if the problem cannot be corrected, contact the QA manager at EMSL-Las Vegas for further guidance.

3.5 Data Reporting

Record the results from each method on the data form indicated in Table 3.9 (blank data forms are included in Appendix B). Report results to the number of decimal places in the actual detection limit. However, report no more than four significant figures. Sample results from reanalyzed samples (occasionally samples are reanalyzed for QC reasons) are annotated by the letter R. Results obtained by standard additions are annotated by the letter G. These and other data qualifiers are listed in Table 3.10. After the forms are completed, the laboratory manager must sign them to indicate that he has reviewed the data and that the samples were analyzed exactly as described in this manual. All deviations from the manual require the authorization of the QA manager prior to sample analysis.

3.6 References

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1985. Standard Methods for the Examination of Water and Wastewater, 16th Ed. APHA, Washington, D.C.

Kramer, J. R., 1982. ANC and BNC. In: R. A. Minear, L. H. Keith (eds.), Water Analysis. Vol. 1. Inorganic Species, Part 1. Academic Press, Orlando, Florida.

McQuaker, N. R., P. D. Kluckner, and D. K. Sandberg, 1983. Chemical Analysis of Acid Precipitation: pH and BNC Determinations. Environ. Sci. Technol., v. 17 n. 7, pp. 431-435.

Peden, M. E., 1981. Sampling, Analytical, and Quality Assurance Protocols for the National Atmospheric Deposition Program. Paper presented at October 1981 ASTM D-22 Symposium and Workshop on Sampling and Analysis of Rain. ASTM, Philadelphia, Pennsylvania.

TABLE 3.9. LIST OF DATA FORMS

Data Form	Description
11	Summary of sample results
13	ANC and BNC results
14[a]	QC data for ANC and BNC analysis
15[a]	Specific conductance (measured and calculated)
16[a]	Anion-cation balance calculations
17	Ion chromatography resolution test form
18	QA (detection limits)
19	Sample holding times summary
20	Blank and QCCS results
21	Dilution factors
22	Duplicate results

[a]Form is not required but is recommended for internal lab use.

Copies of raw data must be submitted as requested by the QA manager. All original raw data must be retained by the lab until notified otherwise. Raw data include data system printouts, chromatograms, notebooks, QC charts, standard preparation data, and all information pertinent to sample analysis.

TABLE 3.10. NATIONAL SURFACE WATER SURVEY DATA QUALIFIERS

Qualifier	Indicates
F	Result outside criteria with consent of QA manager
G	A typical result; already reanalyzed and confirmed by the laboratory manager
H	Holding time exceeded criteria (Form 19 only)
J	Result not available; insufficient sample volume shipped
K	Result not available; entire aliquot not shipped
L	Result not available; analytical interference
M	Result not available; sample lost or destroyed by lab
N	Not required
P	Result outside criteria, but insufficient volume for reanalysis
Q	Result outside QA criteria
R	Result from reanalysis
S	Contamination suspected
T	Leaking container
U	Result not required by procedure
V	Anion-cation balance outside criteria because of DOC
W	% Difference (%D) calculation (Form 14) outside criteria because of high DOC.
Y	Available for miscellaneous comments
Z	Available for miscellaneous comments

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

Weast, R. C. (ed.), 1972. CRC Handbook of Chemistry and Physics, 53rd Ed. CRC Press, Cleveland, Ohio.

4.0 DETERMINATION OF BASE-NEUTRALIZING CAPACITY, ACID-NEUTRALIZING CAPACITY, AND pH

4.1 Scope and Application

This procedure is applicable to the determination of pH, ANC, and BNC in weakly buffered natural waters of low ionic strength. The terms ANC and BNC refer to the acid-neutralizing capacity (ANC) and base-neutralizing capacity (BNC) of systems which are based on the carbonate ion system. (The soluble reacting species are H_2CO_3, HCO_3^-, and CO_3^{2-}.) For calculation purposes, it is assumed that the streams in this survey are represented by a carbonate ion system; hence, the ANC and BNC definitions are made in relation to the carbonate ion species (Kramer, 1982; Butler, 1982).

4.2 Summary of Method

Samples are titrated with standardized acid and base while monitoring and recording the pH. The BNC and ANC are determined by analyzing the titration data by using a modified Gran analysis technique (Kramer, 1982; Butler, 1982; Kramer, 1984; Gran, 1952).

The Gran analysis technique defines the Gran functions F_1 and F_2 based upon the sample volume, the acid or base volume added, and the carbonate dissociation constants. The Gran functions are calculated for several data pairs of titrant volume added (either acid or base) and the resulting pH. The data pairs are chosen so that they cross the ANC and BNC equivalence points. When the Gran functions are plotted versus volume of titrant added, the linear portion of each curve can be interpolated to the equivalence point.

The pH is determined prior to the start of the titrations with the electrode used during the titration. (U.S. EPA, 1983; McQuaker et al., 1983; NBS, 1982).

The air-equilibrated pH is determined similarly after equilibrating the sample with 300 ppm CO_2 in air. Air equilibration is expected to normalize pH values by factoring out the day-to-day and seasonal fluctuations in dissolved CO_2 concentrations.

4.3 Interferences

No interferences are known.

4.4 Safety

The standards, sample types, and most reagents pose little hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling concentrated acids and bases.

Gas cylinders must be secured in an upright position.

4.5 Apparatus and Equipment

4.5.1 pH/mV Meter--A digital pH/mV meter capable of measuring pH to ±0.01 pH unit, potential to ±1 mV, and temperature to ±0.5°C must be used. It must also have automatic temperature compensation capability.

4.5.2 pH Electrodes--High-quality, low-sodium glass pH and reference electrodes must be used. (Gel-type reference electrodes must not be used.) A combination electrode is recommended (such as the Orion Ross combination pH electrode or equivalent), and the procedure is written assuming one is used.

4.5.3 Buret--A microburet capable of precisely and accurately delivering 10 to 50 µL must be used (relative error and standard deviation less than 1 percent).

4.5.4 Teflon Stir Bars

4.5.5 Variable Speed Magnetic Stirrer

4.5.6 Plastic Gas Dispersion Tube

NOTE: Glass dispersion tubes must not be used because they can add ANC to a sample. Plastic dispersion tubes are available in most fish-aquarium supply stores.

4.5.7 Titration System--Alternatively to items 4.5.1 through 4.5.3, a commercial titration instrument meeting the same specifications may be used.

4.6 Reagents and Consumable Materials

4.6.1 Carbon Dioxide Gas (300 ppm CO_2 in Air)--Certified Standard Grade

4.6.2 Hydrochloric Acid Titrant (0.01N HCl)--Add 0.8 mL concentrated hydrochloric acid (HCl, 12N, ACS reagent grade or equivalent) to 500 mL water, then dilute to 1.00 L with water. Standardize as described in section 4.8.1.

4.6.3 Nitrogen Gas (N_2)--CO_2-free

4.6.4 Potassium Chloride Solution (0.10 M KCl)--Dissolve 7.5 g KCl (Alfa Ultrapure or equivalent) in water, then dilute to 1.00 L with water.

4.6.5 Potassium Hydrogen Phthalate (KHP)--Dry 5 to 10 g KHP (ACS-certified primary standard grade or equivalent) at 110°C for 2 hours, then store in a desiccator.

4.6.6 pH Calibration Buffers (pH 4, 7, and 10)--NBS-traceable pH buffers at pH values of 4, 7, and 10.

4.6.7 pH QC Samples (pH 4 and 10)--pH 4 QC sample - dilute 1.00 mL standardized 0.01N HCl titrant to 100.00 mL with water. The theoretical pH is calculated by:

$$pH = -\log\left(\frac{N_{HCl}}{100}\right)$$

4.6.8 pH 10 QC sample - Dilute 1.00 mL of the standardized 0.01N NaOH titrant to 100.00 mL with water. The theoretical pH is calculated by:

$$pH = 14 + \log\left(\frac{N_{NaOH}}{100}\right)$$

4.6.9 Sodium Carbonate (Na_2CO_3)--Dry 5 to 10 g Na_2CO_3 (ACS certified primary standard grade or equivalent) at 110°C for 2 hours, then store in a desiccator.

4.6.10 Sodium Hydroxide Stock Solution (50 percent w/v NaOH)--Dissolve 100 g NaOH (ACS reagent grade or equivalent) in 100 mL water. After cooling and allowing any precipitate to settle (may be hastened by centrifugation), transfer the supernatant to a polyethylene bottle. Store tightly capped and avoid atmospheric exposure.

4.6.11 Sodium Hydroxide Titrant (0.01 N NaOH)--Dilute 0.6 to 0.7 mL 50 percent NaOH to 1.0 L with water. Standardize as described in section 4.8.2.

4.6.12 Water--Water used to prepare reagents and standards must conform to ASTM D 1193 specifications for Type I water (ASTM, 1984).

4.7 Sample Collection, Preservation, and Storage

The sample for which BNC, ANC, and pH is to be determined is delivered to the lab in a 500-mL amber polyethylene bottle (aliquot 5). Store at 4°C and minimize atmospheric exposure.

4.8 Calibration and Standardization

4.8.1 Standardization of HCl Titrant

4.8.1.1 Weigh about 1 g anhydrous Na_2CO_3 to the nearest 0.1 mg, dissolve in water, then dilute to 1.000 L. Calculate the concentration by the following equation.

$$N_{Na_2CO_3} = \frac{\text{Wt. } Na_2CO_3 \text{ g}}{\frac{106.00 \text{ g}}{\text{mole}} \times \frac{1 \text{ mole}}{2 \text{ eq}}} \times \frac{1}{1L}$$

NOTE: This solution is to be freshly prepared just before use.

4.8.1.2 Calibrate the pH meter and electrode as recommended by the manufacturer.

4.8.1.3 Pipet 1.00 mL standard Na_2CO_3 plus 40.00 mL CO_2-free deionized water into a clean, dry titration vessel. Add a Teflon stir bar and stir at a medium speed (no visible vortex).

4.8.1.4 Immerse the pH electrode and record the pH when a stable reading is obtained.

4.8.1.5 Add a known volume of the HCl titrant and record the pH when a stable reading is obtained. Use the following table as a guide to the volume of titrant that should be added in different pH ranges:

pH	Maximum Volume Increment of HCl Titrant (mL)
>7.5	0.2
7.5-4	0.1
<4	0.2

Continue the titration until the pH <4. Obtain at least seven data points in the range pH 4 to 7.

4.8.1.6 Calculate F_{1b} for each data pair (volume acid added, pH) with pH in the range 4 to 7:

$$F_{1b} = (V_s + V)\left[\frac{V_s C}{(V_s + V)}\left(\frac{[H^+]K_1 + 2\,K_1\,K_2}{[H^+]^2 + [H^+]K_1 + K_1\,K_2}\right) + \frac{K_w}{[H^+]} - [H^+]\right]$$

F_{1b} = Gran function

V_s = Initial sample volume = 41.00 mL

V = Volume of HCl added in mL

C = N Na_2CO_3/(2 x dilution factor)

$$[H^+] = 10^{-pH}$$

$$K_1 = 4.4463 \times 10^{-7}$$

$$K_2 = 4.6881 \times 10^{-11}$$

$$K_w = 1.01 \times 10^{-14}$$

4.8.1.7 Plot F_{1b} versus V. Using the points on the linear portion of the plot, perform a linear regression of F_{1b} on V to obtain the coefficients of the line:

$$F_{1b} = a + bV$$

The correlation coefficient should exceed 0.999. If it does not, reexamine the plot to make sure only points on the linear portion are used in the linear regression.

4.8.1.8 Calculate the equivalence volume, V_1, by:

$$V_1 = -a/b$$

then calculate the HCl normality by:

$$N_{HCl} = \frac{N\ Na_2CO_3 \times V\ Na_2CO_3}{V_1}$$

4.8.1.9 Repeat the titration and calculation three times (steps 4.8.1.3 through 4.8.1.8). Calculate an average N_{HCl} and standard deviation. The RSD must be less than 2 percent. If it is not, the entire standardization must be repeated until it is less than 2 percent.

4.8.1.10 The concentration of every new batch of HCl titrant must be cross checked by using the procedure described in section 4.8.2.2.

4.8.1.11 Store in a clean polyethylene bottle. Although the HCl titrant is stable, it must be restandardized monthly (sections 4.8.1.1 through 4.8.1.9).

NOTE: An example of an HCl standardization is given in Appendix C-1.0.

4.8.2 Standardization of NaOH Titrant

Every batch of NaOH titrant is initially standardized against KHP (section 4.8.2.1), and the standardization is cross-checked against

standardized HCl titrant (section 4.8.2.2). Thereafter, it is restandardized daily against the HCl titrant (section 4.8.2.3).

4.8.2.1 Initial NaOH standardization

Weigh about 0.2 g KHP to the nearest 0.1 mg, dissolve in water, then dilute to 1.000 L. Calculate the normality of the solution by the following equation.

$$N_{KHP} = \frac{\text{wt. KHP g}}{\frac{204.22\ \text{g}}{\text{eq}}} \times \frac{1}{1\ \text{L}}$$

Calibrate the pH electrode and meter as recommended by the manufacturer.

Purge the titration vessel with CO_2-free nitrogen, then pipet 5.00 mL standard KHP solution and 20.00 mL CO_2-free water into the vessel. Maintain a CO_2-free atmosphere above the sample throughout the titration.

Add a Teflon stir bar and stir at a medium speed (no visible vortex).

Immerse the pH electrode and record the reading when it stabilizes.

Titrate with the 0.01N NaOH by using the increments specified in the table below. Record the volume and pH (when stable) between additions. Continue the titration until the pH >10. Obtain at least four data points in the pH range 5 to 7 and four data points in the pH range 7 to 11.

pH	Maximum Volume Increment of NaOH Titrant (mL)
<5	0.10
5 to 9	0.05
>9	0.2

Calculate F_{3b} for each data pair (volume added, pH) with a pH 5 to 10.

$$F_{3b} = (V_s + V)\left[\frac{V_s C}{(V_s + V)}\left(\frac{[H^+]K_1 + 2[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1 K_2}\right) + [H^+] - \frac{K_w}{[H^+]}\right]$$

F_{3b} = Gran function

V_s = Initial sample volume = 25.00 mL

V = Volume of NaOH added (mL)

C = N KHP corrected for initial dilution = N KHP/5

$[H^+]$ = 10^{-pH}

K_1 = 1.3×10^{-3}

K_2 = 3.9×10^{-6}

K_w = 1.01×10^{-14}

Plot F_{3b} versus V. Using the points on the linear portion of the plot, perform a linear regression of F_{3b} on V to obtain the coefficients of the line:

$$F_{3b} = a + bV$$

The correlation coefficient should exceed 0.999. If it does not, examine the plot to ensure that only points on the linear portion are used in the linear regression.

Calculate the equivalence volume, V_3, by:

$$V_3 = -a/b$$

then calculate the NaOH normality by:

$$N_{NaOH} = \frac{N_{KHP} \times V_{KHP}}{V_3}$$

Repeat the titration and calculation a total of three times. Calculate an average N_{NaOH} and standard deviation. The RSD must be less than 2 percent. If not, the entire standardization must be repeated until the RSD is less than 2 percent.

4.8.2.2 NaOH-HCl Standardization Cross-Check

Purge a titration vessel with CO_2-free nitrogen, then pipet 0.500 mL of 0.01N NaOH and 25.00 mL of CO_2-free water into the vessel. Maintain a CO_2-free atmosphere above the sample.

Add a Teflon stir bar and stir at a medium speed.

Immerse the pH electrode and record the reading when it stabilizes.

Titrate with the standardized 0.01N HCl by using the increments specified in the table below. Record the volume and pH (when stable) between additions. Continue the titration until the pH is less than 3.5. Obtain at least seven data points in the pH range 4 to 10.

pH	Maximum Volume Increment of HCl Titrant (mL)
>10	0.2
10 to 4	0.05
<4	0.2

Calculate F_1 for each data pair (V, pH) with a pH 4 to 10.

$$F_1 = (V_s + V)\left(\frac{K_w}{[H^+]} - [H^+]\right)$$

F_1 = Gran function

V_s = Initial sample volume = 25.5 mL

V = Volume of HCl added (mL)

K_w = 1.01×10^{-14}

$[H^+]$ = 10^{-pH}

Plot F_1 versus V. Using the points on the linear portion of the plot, perform a linear regression of F_1 on V to obtain the coefficients of the line:

$$F_1 = a + bV$$

The correlation coefficient should exceed 0.999. If not, reexamine the plot to ensure that only points on the linear portion are used in the linear regression.

Calculate the equivalence volume, V_1, by:

$$V_1 = -a/b$$

then calculate the HCl normality (designated as N'_{HCl}) by:

$$N'_{HCl} = \frac{N_{NaOH} \times V_{NaOH}}{V_1}$$

$V_{NaOH} = 0.500$

Calculate the absolute relative percent difference (RPD) between N'_{HCl} and N_{HCl} (normality determined in section 4.8.1) by:

$$RPD = \left| \frac{N'_{HCl} - N_{HCl}}{0.5\ (N'_{HCl} + N_{HCl})} \right| \times 100$$

The absolute RPD must be less than 5 percent. If it is not, then a problem exists in either the acid or the base standardization or both (bad reagents, out-of-calibration burets, etc.). The problem must be identified, and both procedures 4.8.1 and 4.8.2 repeated until the RPD calculated above is less than 5 percent.

4.8.2.3 Daily NaOH Standardization

Calibrate the pH meter and electrode as recommended by the manufacturer.

Purge the titration vessel with CO_2-free nitrogen, then pipet 1.000 mL NaOH titrant plus 25.00 mL CO_2-free water into the vessel. Maintain a CO_2-free nitrogen atmosphere above the sample. (Smaller volumes of NaOH may be used. A known volume of CO_2-free water should be added to bring solution to a convenient volume.)

Add a Teflon stir bar and stir at a medium speed.

Immerse the pH electrode and record the reading when it stabilizes.

Titrate with the standardized HCl titrant by using the increments specified in the table below. Record the volume and pH (when stable) between additions. Continue the titration until the pH <4. Obtain at least seven data points in the pH range 4 to 10.

pH	Maximum Volume Increment of HCl Titrant (mL)
>10	0.2
10 to 4	0.05
<4	0.2

Calculate F_1 for each data pair (volume acid added, pH) with a pH 4 to 10:

$$F_1 = (V_s + V) \frac{K_w}{[H^+]} - [H^+]$$

F_1 = Gran function

V_s = Initial sample volume = 26.00 mL

V = Volume of HCl added

K_w = 1.01×10^{-14}

$[H^+]$ = 10^{-pH}

Plot F_1 versus V. Using the points on the linear portion of the plot, perform a linear regression of F_1 on V to obtain the coefficients of the line:

$$F_1 = a + bV$$

The correlation coefficient should exceed 0.999. If it does not, reexamine the plot to make sure that only points on the linear portion are used in the linear regression.

Calculate the equivalence volume, V_1, by:

$$V_1 = -a/b$$

then calculate the NaOH normality by:

$$N_{NaOH} = \frac{N_{HCl} \times V_1}{V_{NaOH}}$$

Repeat the titration and calculation twice more. Calculate an average N_{NaOH} and standard deviation. The RSD must be less than 2 percent. If it is not, the entire standardization must be repeated until the RSD is less than 2 percent.

Because the NaOH titrant can readily deteriorate through exposure to the air, every effort must be made to prevent its exposure to the air at all times. Furthermore, it must be standardized daily or before every major work shift. Store the NaOH titrant in a linear polyethylene or Teflon container with a CO_2-free atmosphere, e.g., under CO_2-free air, nitrogen, or argon.

NOTE: An example of NaOH standardization is given in Appendix C.

4.8.3 Calibration and Characterization of Electrodes

Separate electrodes must be used for the acid and base titrations. Each new electrode pair must be rigorously evaluated for Nernstian response by using the procedure described in section 4.8.3.1 prior to analyzing samples. After the initial electrode evaluation, the electrodes are calibrated daily by using the procedure in section 4.8.3.2.

4.8.3.1 Rigorous Calibration Procedure--This procedure calibrates and evaluates the Nernstian response of an electrode. Also, it familiarizes the analyst with the characteristic response time of the electrode.

Following the instructions of the manufacturer, calibrate the electrode and meter used for acid titrations with pH 7 and 4 buffer solutions and calibrate the electrode used for base titrations with pH 7 and 10 buffer solutions.

Prepare a blank solution by pipetting 50.00 mL CO_2-free water and 0.50 mL 0.10M KCl into a titration vessel.

Add a Teflon stir bar and stir at a medium speed by using a magnetic stirrer.

Titrate the blank with standardized 0.01N HCl by using the increments specified in the table below. Continue the titration until the pH is 3.3 to 3.5. Record the pH between each addition, noting the time required for stabilization. Obtain at least seven data points that have a pH less than 4.

pH	Maximum Volume Increment of HCl Titrant (mL)
>4	0.050
<4	0.3

Prepare a fresh aliquot of water and 0.1M KCl as in 4.8.3.1.2.

Under a CO_2-free atmosphere, titrate the blank with standardized 0.01N NaOH by using the increments specified in the table below.

Continue the titration until the pH is 10.5 to 11. Record the pH between each addition. Obtain at least 10 data points between pH 9 and 10.5.

pH	Maximum Volume Increment of NaOH Titrant (mL)
<10	0.10
>10	0.20

For each titration, calculate the pH for each data by point using pH* = -log [H+]. [H+] is calculated by:

acid titration

$$[H^+] = \frac{V_A C_A}{V_S + V_A}$$

base titration

$$[H^+] = \frac{K_W}{\left(\frac{V_B C_B}{V_S + V_B}\right)}$$

V_A = acid volume

C_A = HCl concentration in eq/L

V_S = sample volume = 50.5 mL

k_w = 1.01×10^{-14}

V_B = base volume

C_B = NaOH concentration in eq/L

For each titration, plot the measured pH versus the calculated pH (designated as pH*). Perform a linear regression on each plot to obtain the coefficients of the line:

$$pH = a + b(pH^*)$$

The plots must be linear with b = 1.00 ± 0.05 and r > 0.999. Typically, some nonlinearity exists in the pH region 6 to 8. This is most likely because of small errors in titrant standardization, impure salt solutions, or atmospheric CO_2 contamination. The nonlinear points should not be used in the linear regression.

If the plots are not linear and do not meet the specifications above, the electrode should be considered suspect. The electrode

characterization must then be repeated. If unacceptable results are still obtained, the electrode must be replaced.

The plots for both titrations should be coincident. Combine the data from both titrations and perform a linear least squares analysis on the combined data to obtain new estimates for the coefficients of the equation:

$$pH = a + b(pH^*)$$

The electrodes are now calibrated. Do not move any controls on the meter.

If the two plots are not coincident (i.e., the coefficients a and b do not overlap), the characterization must be repeated. If the plots are still not coincident, the electrode must be replaced.

4.8.3.2 Daily Calibration Procedure--Generally, the calibration curve prepared above is stable from day to day. This daily calibration is designed to verify the calibration on a day-to-day basis.

Copiously rinse the electrode with water. Immerse it in 20 mL of pH 7 buffer and stir for 1 to 2 minutes. Discard the buffer and replace with an additional 40 mL of pH 7 buffer. While the solution is gently stirred, measure the pH. Adjust the pH meter calibration knob until the pH is equal to the theoretical pH of the buffer.

Record the theoretical pH and the final, measured pH reading. (The two values should be identical).

Copiously rinse the electrode with water. Immerse it in 20 mL of pH 4 QC sample and stir for 1 to 2 minutes. Discard the sample and replace it with an additional 40 mL pH 4 QC sample. While the solution is stirred, measure and record the pH. From the calibration curve of pH versus pH*, determine the pH* for the observed pH. Compare pH* to the theoretical pH of the QC sample. The two values must agree within ±0.05 pH unit. If the two values do not agree, the rigorous calibration procedure (section 4.8.3.1) must be performed prior to sample analysis.

Repeat the above step with the pH 10 QC sample. This sample must be kept under a CO_2-free atmosphere when in use, or acceptable results may not be obtained.

4.9 Quality Control

4.9.1 Duplicate Analysis

Analyze one sample per batch in duplicate. The duplicate precision (expressed as an RSD) must be less than or equal to 10 percent. If the duplicate precision is unacceptable (RSD >10 percent), then a problem exists in the experimental technique. Determine and eliminate the cause of the poor precision prior to continuing sample analysis.

4.9.2 Blank Analysis

Determine the ANC in one blank per batch. The absolute value of the ANC must be less than or equal to 10 µeq/L. If it is not, contamination is indicated. Determine and eliminate the contamination source (often the source will be the water or KCl) prior to continuing sample analysis. Blank values are calculated as described in 4.11.1 and Appendix C-4.0.

4.9.3 pH QCCS

Prior to analysis of the first sample in a shift and every five samples thereafter, the appropriate pH QC sample (pH 4 QC for acid titrations and pH 10 QC for base titrations) must be analyzed by using the following procedure. Copiously rinse the electrode with deionized water. Immerse it in 20 mL of QC sample and stir it for 30 to 60 seconds. Discard the sample and replace it with an additional 40 mL of QC sample. While the solution is gently stirred, measure and record the pH. From the calibration curve of pH versus pH*, determine the pH*. If the pH* and theoretical pH of the QC sample differ by more than ±0.05 pH unit, stop the analysis and repeat the rigorous electrode calibration (section 4.8.3.1). Previously analyzed samples (up to last acceptable QC sample) must be reanalyzed. Acceptable values of pH* are reported on Form 20.

4.9.4 Comparison of Initial Titration pH Values

The values for measured pH at $V_{titrant} = 0$ (before KCl spike) of the acid and base titrations should be within ±0.1 pH unit. If they are not, check operation to ensure that cross-contamination is not occurring.

4.9.5 For a sample with ANC $\leq$ -15 µeq/L, calculate a value for ANC as follows:

$$[ANC]_{CO} = 10^{6} \times 10^{-pH^*} \text{ (pH at } V = 0)$$

(The pH at $V_{titrant} = 0$ is taken from the acid titration.) If ANC differs from $[ANC]_{CO}$ by more than ±10 µeq/L, then check the electrode operation and calibration.

4.9.6 Comparison of Calculated ANC and Measured ANC

A value for ANC can be calculated from the DIC concentration and the pH of a sample. Two sets of pH and DIC values are obtained in the lab: (1) pH* at V=0 of the base titration and the associated DIC concentration and (2) pH of the air-equilibrated sample and the associated DIC concentration. Each set can be used to calculate a value for ANC. The calculated values for Alk can then be compared to the measured value of ANC. The comparison is useful in checking both the validity of assuming a carbonate system and the possibility of analytical error. ANC is calculated from pH and DIC as follows:

$[ANC]_{C1}$ = calculated ANC from initial pH and DIC at time of base titration

$[ANC]_{C2}$ = calculated ANC from air-equilibrated pH and DIC

$$[ANC]_C\ (\mu eq/L) = \left[\frac{DIC}{12{,}011}\left(\frac{[H^+]K_1 + 2\,K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}\right) + \frac{K_w}{[H^+]} - [H^+]\right] \times 10^6$$

DIC = DIC in mg/L (the factor 12,011 converts mg/L to moles/L)

$[H^+] = 10^{-pH}$

$K_1 = 4.4463 \times 10^{-7}$ at 25°C

$K_2 = 4.6881 \times 10^{-11}$ at 25°C

$K_w = 1.01 \times 10^{-14}$ at 25°C

$[ANC]_{C1}$ and $[ANC]_{C2}$ are compared as follows:

For $[ANC]_{C1} \leq 100$ µeq/L, the following condition applies:

$$\left|[ANC]_{C1} - [ANC]_{C2}\right| \leq 15\ \mu eq/L$$

For $[ANC]_{C1} > 100$ µeq/L, the following condition applies:

$$\left|\frac{[ANC]_{C1} - [ANC]_{C2}}{([ANC]_{C1} + [ANC]_{C2})/2} \times 100\right| \leq 10\%$$

If either of the above conditions is not satisfied, then the pH and DIC values are suspect and must be remeasured. It is very important that the pH and DIC be measured as closely together in time as possible. If they are not measured closely in time, acceptable agreement between $[ANC]_{C1}$ and $[ANC]_{C2}$ may not be obtained. When acceptable values for $[ANC]_{C1}$ and $[ANC]_{C2}$ are obtained, their average is compared to the measured ANC as described below.

For $[ANC]_{C\text{-}avg} \leq 100$ µeq/L, then the difference "D" and the acceptance window "w" are:

$$D = [ANC]_{C\text{-}avg} - ANC, \text{ and } w = 15 \text{ µeq/L}$$

For $[ANC]_{C\text{-}avg} > 100$ µeq/L, then:

$$D = \frac{[ANC]_{C\text{-}avg} - ANC}{[ANC]_{C\text{-}avg}} \times 100, \text{ and } w = 10\%$$

If $|D| \leq w$, it is valid to assume a carbonate system. If $D < -w$, then the assumption of a pure carbonate system is not valid, and the sample contains noncarbonate protolytes (soluble reacting species) such as organic species. If $D > w$, then an analytical problem exists in the pH determination, DIC determination, or acid titration (such as titrant concentration). In this case the problem must be identified, and the sample must be reanalyzed.

4.9.7 Comparison of Calculated BNC and Measured BNC

Just as for ANC, pH and DIC values can be used to calculate a BNC value. Since the BNC of a sample changes with changing DIC, only the initial pH and DIC values measured at the beginning of the base titration are used to calculate an BNC value. This calculated BNC is then compared to the measured BNC value. BNC is calculated by:

$$[BNC]_C \text{ (µeq/L)} = \left[\frac{DIC}{12{,}011}\left(\frac{[H^+]^2 - K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}\right) + [H^+] - \frac{K_w}{[H^+]}\right] \times 10^6$$

$[BNC]_C$ is compared to BNC as described below.

For $[BNC]_C \leq 100$ µeq/L, then:

$$D = [BNC]_C - BNC, \text{ and } w = 10 \text{ µeq/L}$$

For $[BNC]_C > 100$ µeq/L, then:

$$D = \frac{[BNC]_C - BNC}{[BNC]_C} \times 100, \text{ and } w = 10\%$$

If $|D| \leq w$, then it is valid to assume a carbonate system. If $D < -w$, the assumption of a pure carbonate system is not valid, and the sample contains noncarbonate protolytes such as organic species.

If $D > w$, then an analytical problem exists in the pH determination, DIC determination, or base titration (such as titrant concentration). In this case the problem must be identified, and the sample must be reanalyzed.

4.9.8 Comparison of Calculated Total Carbonate and Measured Total Carbonate

If the assumption of a carbonate system is valid, the sum of ANC plus BNC is equal to the total carbonate. This assumption can be checked by calculating the total carbonate from the DIC, then comparing the calculated total carbonate to the measured estimate of total carbonate (the sum of ANC plus BNC). The total carbonate is calculated by:

$$C_C \text{ (µmole/L)} = \text{DIC (mg/L)} \times 83.26 \text{ (µmole/mg)}$$

C_C is compared to (ANC + BNC) as follows:

For $C_C \leq 100$ µmole/L, then:

$$D = C_C - (ANC + BNC), \text{ and } w = 10 \text{ µmole/L}$$

For $C_C > 100$ µmole/L, then:

$$D = \frac{C_C - (ANC + BNC)}{C_C} \times 100, \text{ and } w = 10\%$$

If $|D| \leq w$, the assumption of a carbonate system is valid. If $D < -w$, the assumption is not valid, and the sample contains noncarbonate protolytes. If $D > w$, an analytical problem exists. It must be identified, and the sample must be reanalyzed.

4.10 Procedure

An acid titration (section 4.10.1) and a base titration (section 4.10.2) are necessary to determine the BNC and ANC of a sample. As part of each titration, the sample pH is determined. The air-equilibrated pH is determined in a separate sample portion (section 4.10.3).

4.10.1 Acid Titration

4.10.1.1 Allow a sealed sample (aliquot 5) to reach ambient temperature.

4.10.1.2 Copiously rinse the electrode with deionized water, then immerse in 10 to 20 mL sample. Stir for 30 to 60 seconds.

4.10.1.3 Pipet 40.00 mL of sample into a clean, dry titration flask.

4.10.1.4 Add a clean Teflon stir bar and place on a magnetic stirrer. Stir at a medium speed (no visible vortex).

4.10.1.5 Immerse the pH electrode and read pH. Record pH on Forms 11 and 13 when the reading stabilizes (1 to 2 minutes). This is the initial measured pH at $V_{titrant} = 0$.

4.10.1.6 Add 0.40 mL 0.1M KCl. Read and record the pH on Form 13. This is the initial measured pH at $V_{titrant} = 0$ after addition of KCl spike.

4.10.1.7 Add increments of 0.01N HCl as specified in the table below. Record the volume of HCl added and the pH when a stable reading is obtained. Adjust the volume increment of titrant so that readings can be taken at pH values of 4.5 and 4.2. Continue the titration until the pH is between 3.3 and 3.5. Obtain at least six data points that have a pH less than 4.

pH	Maximum Volume Increment of HCl Titrant (mL)
>9	0.1
9.0 to 7.0	0.025
7.0 to 5.5	0.1
5.5 to 4.5	0.05
4.5 to 3.75	0.1
<3.75	0.3

4.10.2 Base Titration

4.10.2.1 Take a portion of aliquot 5 at this time for DIC determination. If the DIC is not determined immediately, the sample must be kept sealed from the atmosphere. A simple way to do this is to withdraw the sample for DIC by using a syringe equipped with a syringe valve. By closing the valve, the sample is sealed from the atmosphere (syringe valves that fit standard Luer-Lok syringes are available from most chromatography supply companies).

4.10.2.2 Purge the titration vessel with CO_2-free air, N_2, or Ar.

4.10.2.3 Copiously rinse the electrode with deionized water, then immerse in 10 to 20 mL sample for 30 to 60 seconds.

4.10.2.4 Pipet 40.00 mL sample into the CO_2-free titration vessel. Maintain a CO_2-free atmosphere above the sample. Do not bubble the N_2 (or other CO_2-free gas) through the sample. Add a clean Teflon stir bar to the vessel and place it on a magnetic stirrer. Do not turn stirrer on at this point.

4.10.2.5 Immerse the pH electrode, read pH, and record pH on Forms 11 and 13 when pH stabilizes. This is the initial measured pH at $V_{titrant} = 0$.

4.10.2.6 Add 0.40 mL 0.10M KCl. Stir for 10 to 15 seconds. Read pH, and record pH on Form 13.

4.10.2.7 Add 0.025 mL of 0.01N NaOH and begin gentle stirring (no visible vortex). Record the NaOH volume and pH when it stabilizes. Continue the titration by adding increments of NaOH as specified below until the pH >11. Record the volume of NaOH added and the pH after each addition. Obtain at least 10 data points in the pH region 9 to 10.5. If the initial sample pH is less than 7, obtain at least 5 data points below pH 8.

pH	Maximum Volume Increment of NaOH Titrant (mL)
<5	0.025
5 to 7	0.050
7 to 9	0.025
9 to 10	0.10
10 to 10.5	0.30
>10.5	1.00

4.10.3 Air-Equilibrated pH Measurement

4.10.3.1 Allow the sealed sample (aliquot 5) to reach ambient temperature.

4.10.3.2 Copiously rinse the electrode with deionized water, then immerse in 10 to 20 mL sample. Stir for 30 to 60 seconds.

4.10.3.3 Pipet 20 to 40 mL sample into a clean, dry titration flask.

4.10.3.4 Add a clean Teflon stir bar and place on a magnetic stirrer. Stir at a medium speed.

4.10.3.5 Bubble standard gas containing 300 ppm CO_2 through the sample for 20 minutes. Measure and record the pH.

4.10.3.6 Take a subsample at this time for DIC determination. The subsample must be kept sealed from the atmosphere prior to analysis. The DIC should be measured as soon as possible.

4.11 Calculations

During the titrations, any substance which reacts with the acid or base is titrated. However, for calculations, it is assumed that the samples represent carbonate systems and that the only reacting species are H^+, OH^-, H_2CO_3, HCO_3^-, and CO_3^{2-}. When use is made of this assumption, the two parameters

"ANC" and "CO_2-BNC" are calculated. The validity of the assumption is checked as described in sections 4.9.6 through 4.9.8.

The theory behind the calculations is available elsewhere (Kramer, 1982; Butler, 1982; Kramer, 1984). Examples of the calculations are given in Appendix C.

4.11.1 Initial Calculations

4.11.1.1 From the calibration curve of measured pH versus calculated pH (pH*), determine pH* for each pH value obtained during both the acid and base titrations. Next, convert all pH* values to hydrogen ion concentrations by using the equation:

$$[H^+] = 10^{-pH^*}$$

4.11.1.2 Using the acid titration data, calculate the Gran function F_{1a} for each data pair (V_a, pH*) in which pH* <4:

$$F_{1a} = (V_s + V_a)\,[H^+]$$

V_s = Total initial sample volume (40.00 + 0.400)mL
V_a = Cumulative volume of acid titrant added

Plot F_{1a} versus V_a. The data should be on a straight line with the equation:

$$F_{1a} = a + bV_a$$

Perform a linear regression of F_{1a} on V_a to determine the correlation coefficient (r) and the coefficients a and b. The coefficient r should exceed 0.999. If it does not, examine the data to ensure that only data on the linear portion of the plot were used in the regression. If any outliers are detected, repeat the regression analysis. Calculate an initial estimate of the equivalence volume (V_1) by:

$$V_1 = -a/b$$

TABLE 4.1. LIST OF CALCULATION PROCEDURES FOR COMBINATIONS OF INITIAL V_1 AND pH*

Sample Description		Calculation Procedure	Section No.
Initial V_1	Initial pH*		
<0	-	A	4.11.2
>0	$\leq$7.6	B	4.11.3
>0	>7.6	C	4.11.4

NOTE: For blank analyses, calculate ANC by ANC = V_1 C_a/V_{sa}. Further calculations are not necessary.

Further calculations are based on this initial estimate of V_1 and the initial sample pH*. Table 4.1 below lists the appropriate calculation procedure for the various combinations of V_1 and initial sample pH*.

4.11.1.3 Throughout the calculations, there are several equations and constants that are frequently used. These are listed in Table 4.2.

4.11.2 Calculation Procedure A (Initial V_1 <0)

4.11.2.1 From the base titration data, determine which data set (V, pH*) has the pH* nearest (but not exceeding) a pH = 8.2. As an initial estimate, set the equivalence volume V_2 equal to the volume of this data set. Next, calculate initial estimates of ANC, BNC, and C by:

$$ANC = \frac{V_1 C_a}{V_{sa}}$$

C_a = concentration of acid titrant

V_{sa} = original sample volume (acid titration)

$$BNC = \frac{V_2 C_b}{V_{sb}}$$

TABLE 4.2. LIST OF FREQUENTLY USED EQUATIONS AND CONSTANTS

No.	Equation
1	$F_{1c} = (V_s + V)\left[\frac{C([H^+]K_1 + 2K_1K_2)}{[H^+]^2 + [H^+]K_1 + K_1K_2} + \frac{K_w}{[H^+]} - [H^+]\right]$
2	$F_{2c} = (V_s + V)\left[\frac{C([H^+]^2 - K_1K_2)}{[H^+]^2 + [H^+]K_1 + K_1K_2} + [H^+] - \frac{K_w}{[H^+]}\right]$

Constants and variable:
- V_s = Total initial sample volume
- V = Cumulative volume of titrant added
- C = Total carbonate expressed in moles/L
- $[H^+]$ = Hydrogen ion concentration
- $K_1 = 4.4463 \times 10^{-7}$ at 25 C
- $K_2 = 4.6881 \times 10^{-11}$ at 25 C
- $K_w = 1.01 \times 10^{-14}$ at 25 C

C_b = concentration of base titrant

V_{sb} = original sample volume (base titration)

C = total carbonate = ANC + BNC

4.11.2.2 Calculate the Gran function F_{1c} for the first 7 to 8 points of the base titration by using equation 1, Table 4.2. Plot F_{1c} versus V_b. Perform a linear regression with the points lying on the linear portion of the plot. Determine the coefficients of the line $F_{1c} = a + bV$. The coefficient r should exceed 0.999. If it does not, examine the plot to ensure that only points on the linear portion are used. From the coefficients, calculate a new estimate of V_1 by:

$$V_1 = -a/b$$

Next, calculate the Gran function F_{2c} (equation 2, Table 4.2) for data from the base titration across the current estimate of V_2. (Use the first 4 to 6 sets with a volume less than V_2 and the first 6 to 8 sets with a volume greater than V_2.) Plot F_{2c} versus V_b. The data should lie on a straight line with the equation $F_{2c} = a + bV$. Perform a linear regression of F_{2c} on V_b and determine the coefficients of the line. If $r < 0.999$ reexamine the data to ensure that only

points on the linear portion were used in the regression. Calculate a new estimate of V_2 by:

$$V_2 = -a/b$$

4.11.2.3 Calculate new estimates of ANC, BNC, and C by using the new estimates of V_1 and V_2 (an asterisk indicates a new value).

$$ANC^* = \frac{-V_1 C_b}{V_{sb}} ; \quad BNC^* = \frac{V_2 C_b}{V_{sb}} ; \quad C^* = ANC + BNC$$

4.11.2.4 Compare the latest two values for total carbonate. If

$$\left|\frac{C - C^*}{C + C^*}\right| > 0.001$$

then calculate a new estimate for C by:

$$C(new) = (C + C^*)/2$$

Using the new value for C, repeat the calculations in 4.11.2.2 through 4.11.2.4. Continue repeating the calculations until the relative difference between C and C* is less than 0.001.

When the expression is less than 0.001, convert the final values for ANC, BNC, and C to μeq/L by:

$$ANC\ (\mu eq/L) = ANC\ (eq/L) \times 10^6$$

$$BNC\ (\mu eq/L) = BNC\ (eq/L) \times 10^6$$

$$C\ (\mu eq/L) = C\ (eq/L) \times 10^6$$

4.11.3 Calculation Procedure B (Initial $V_1 > 0$, Initial pH* ≤ 7.6)

4.11.3.1 From the base titration data, determine which data set (V, pH*) has the pH* nearest but not exceeding 8.2. As an initial estimate, set the equivalence volume V_2 equal to the volume of this data set. Next calculate initial estimates of ANC, BNC, and C by:

$$ANC = \frac{V_1 C_a}{V_{sa}} ; \quad BNC = \frac{V_2 C_b}{V_{sb}} ; \quad C = ANC + BNC$$

4.11.3.2 Calculate the Gran function F_{1c} (equation 1) for data sets from the acid titration with volumes across the current estimate of V_1 (use the first 4 to 6 sets with volumes less than V_1 and the first 6 to 8 sets with volumes greater than V_1). Plot F_{1c} versus V_a. The data should lie on a line with the equation $F_{1c} = a + bV$. Perform a linear regression of F_{1c} on V_a and determine the coefficients of the line. If r does not exceed 0.999, reexamine the data to ensure that no outliers were used in the regression. Calculate a new estimate for V_1 by:

$$V_1 = -a/b$$

Next, calculate the Gran function F_{2c} (equation 2) for data sets from the base titration with volumes across the current estimate of V_2. (Use the first 4 to 6 sets with volumes less than V_2 and the first 6 to 8 sets with volumes greater than V_2). Plot F_{2c} versus V_b. The data should lie on a line with the equation $F_{2c} = a + bV$. Perform a linear regression of F_{2c} on V_b and determine the coefficients of the line. If r does not exceed 0.999, reexamine the data to ensure that only data on the linear portion were included in the regression. Calculate a new estimate for V_2 by:

$$V_2 = -a/b$$

4.11.3.3 Calculate new estimates of ANC, BNC, and C using the latest estimates of V_1 and V_2.

$$ANC^* = \frac{V_1 C_a}{V_{sa}} \quad ; \quad BNC^* = \frac{V_2 C_b}{V_{sb}} \quad ; \quad C^* = ANC + BNC$$

4.11.3.4 Compare the latest two values for total carbonate. If:

$$\left| \frac{C - C^*}{C + C^*} \right| > 0.001$$

then calculate a new estimate of C by:

$$C_{(new)} = (C + C^*)/2$$

Using the new value of C, repeat the calculations in 4.11.3.2 through 4.11.3.4. Continue repeating the calculations until the above expression is less than 0.001.

When the expression is less than 0.001, convert the final values for ANC, BNC, and C to μeq/L by:

$$\begin{aligned} \text{ANC } (\mu\text{eq/L}) &= \text{ANC (eq/L)} \times 10^6 \\ \text{BNC } (\mu\text{eq/L}) &= \text{BNC (eq/L)} \times 10^6 \\ \text{C } (\mu\text{eq/L}) &= \text{C (eq/L)} \times 10^6 \end{aligned}$$

4.11.4 Calculation Procedure C (Initial V_1 >0, Initial pH* >7.6)

4.11.4.1 Obtain an initial estimate of the equivalence volume V_2 by following the procedure in 4.11.4.1.1 if the initial sample pH* $\geq$8.2. If the initial sample pH* <8.2, then follow the procedure in 4.11.4.1.2.

From the acid titration data, determine which data set (V, pH*) has the pH* nearest but not exceeding 8.2. As an initial estimate, set the equivalence volume V_2 equal to the volume of this data set. Go to section 4.11.4.1.3.

Using data sets from the acid titration with pH* values across a pH = 7 (use 4 to 6 sets with a pH* $\leq$7 and 4 to 6 sets with a pH* $\geq$7), calculate the Gran function F_{2a} by:

$$F_{2a} = (V_1 - V_a)\,[H^+]$$

Plot F_{2a} versus V_a. The data should lie on a straight line with the equation $F_{2a} = a + bV$. Perform a linear regression of F_{2a} on V_a. The coefficient r should exceed 0.999. If it does not, reexamine the plot to ensure that only data on the linear portion were used in the calculation. Calculate a new estimate for V_2 by:

$$V_2 = -a/b$$

Calculate estimates of ANC, BNC, and C by:

$$\text{ANC} = \frac{V_1 C_a}{V_{sa}} \; ; \quad \text{BNC} = \frac{-V_2 C_a}{V_{sa}} \; ; \quad \text{C} = \text{ANC} + \text{BNC}$$

4.11.4.2 Calculate the Gran function F_{1c} (equation 1) for data sets from the acid titration with volumes across the current estimate of V_1 (use the first 4 to 6 sets with volumes less than V_1 and the first 6 to 8 sets with volumes greater than V_1). Plot F_{1c} versus V_a. The data should lie on a straight line with the equation $F_{1c} = a + bV_a$. Perform a linear regression of F_{1c} on V_a and determine the coefficients of the line. The coefficient r should exceed 0.999. If it does not, reexamine the plot to ensure that only data on the linear portion were included in the regression. Calculate a new estimate for V_1 by:

$$V_1 = -a/b$$

Next, calculate the Gran function F_{2c} (equation 2) for data sets from the acid titration with volumes across the current estimate of V_2 (use the first 4 to 6 sets with volumes less than V_2 and the first 6 to 8 sets with volumes greater than V_2). Plot F_{2c} versus V_a. The data should lie on a straight line with the equation $F_{2c} = a + bV$. Perform a linear regression of F_{2c} on V_a and determine the coefficients of the line. The coefficient r should exceed 0.999. If it does not, reexamine the plot to ensure that only data on the linear portion were included in the regression. Calculate a new estimate of V_2 by:

$$V_2 = -a/b$$

4.11.4.3 Calculate new estimates of ANC, BNC, and C by using the latest estimates of V_1 and V_2.

$$ANC^* = \frac{V_1 C_a}{V_{sa}} \quad ; \quad BNC^* = \frac{-V_2 C_a}{V_{sa}} \quad ; \quad C^* = ANC + BNC$$

4.11.4.4 Compare the latest two values for total carbonate. If:

$$\left| \frac{C - C^*}{C + C^*} \right| > 0.001$$

then calculate a new estimate of C by:

$$C_{(new)} = (C + C^*)/2$$

Using this new value of C, repeat the calculations in 4.11.4.2 through 4.11.4.4. Continue repeating the calculations until the above expression is less than 0.001.

When the expression is less than 0.001, convert the final values for ANC, BNC, and C to μeq/L by:

$$\begin{aligned} ANC\ (\mu eq/L) &= ANC\ (eq/L) \times 10^6 \\ BNC\ (\mu eq/L) &= BNC\ (eq/L) \times 10^6 \\ C\ (\mu eq/L) &= C\ (eq/L) \times 10^6 \end{aligned}$$

4.12 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Butler, J. N., 1982. Carbon Dioxide Equilibria and Their Applications. Addison-Wesley Publications, Reading, Massachusetts.

Gran, G., 1952. Determination of the Equivalence Point in Potentiometric Titrations. Part II. Analyst, v. 77, pp. 661-671.

Kramer, J. R., 1982. ANC and BNC. In: R. A. Minear and L. H. Keith (eds.), Water Analysis, Vol. 1. Inorganic Species, Part 1. Academic Press, Orlando, Florida.

Kramer, J. R., 1984. Modified Gran Analysis for Acid and Base Titrations. Environmental Geochemistry Report No. 1984-2. McMaster University, Hamilton, Ontario, Canada.

McQuaker, N. R., P. D. Kluckner, and D. K. Sandberg, 1983. Chemical Analysis of Acid Precipitation: pH and BNC Determinations. Environ. Sci. Technol., v. 17, n. 7, pp. 431-435.

National Bureau of Standards, 1982. Simulated Precipitation Reference Materials, IV. NBSIR 82-2581. U.S. Department of Commerce - NBS, Washington, D.C.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 150.1, pH. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

5.0 DETERMINATION OF AMMONIUM

5.1 Scope and Application

This method covers the determination of ammonia in natural surface waters in the range of 0.01 to 2.6 mg/L NH_4^+. This range is for photometric measurements made at 630 to 660 nm in a 15-mm or 50-mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

5.2 Summary of Method

Alkaline phenol and hypochlorite react with ammonia to form an amount of indophenol blue that is proportional to the ammonium concentration. The blue color formed is intensified with sodium nitroprusside (U.S. EPA, 1983).

5.3 Interferences

Calcium and magnesium ions may be present in concentration sufficient to cause precipitation problems during analysis. A 5 percent EDTA solution is used to prevent the precipitation of calcium and magnesium ions.

Sample turbidity may interfere with this method. Turbidity is removed by filtration at the field station. Sample color that absorbs in the photometric range used also interferes.

5.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents.

5.5 Apparatus and Equipment

5.5.1 Technicon AutoAnalyzer Unit (AAI or AAII) consisting of:

5.5.1.1 Sampler.

5.5.1.2 Manifold (AAI) or Analytical Cartridge (AAII).

5.5.1.3 Proportioning pump.

5.5.1.4 Heating bath with double-delay coil (AAI).

5.5.1.5 Colorimeter equipped with 15-mm tubular flow cell and 630- to 660-nm filters.

5.5.1.6 Recorder.

5.5.1.7 Digital printer for AAII (optional).

5.6 Reagents and Consumable Materials

5.6.1 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

5.6.2 Sulfuric Acid (5N) - Air Scrubber Solution

Carefully add 139 mL concentrated sulfuric acid to approximately 500 mL ammonia-free water. Cool to room temperature and dilute to 1 L with water.

5.6.3 Sodium Phenolate Solution

Using a 1-L Erlenmeyer flask, dissolve 83 g phenol in 500 mL water. In small increments, cautiously add with agitation 32 g NaOH. Periodically cool flask under flowing tap water. When cool, dilute to 1 L with water.

5.6.4 Sodium Hypochlorite Solution

Dilute 150 mL of a bleach solution containing 5.25 percent NaOCl (such as "Clorox") to 500 mL with water. Available chlorine level should approximate 2 to 3 percent. Clorox is a proprietary product, and its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Because of the instability of this product, storage over an extended period should be avoided.

5.6.5 Disodium Ethylenediamine-Tetraacetate (EDTA) (5 percent w/v)

Dissolve 50 g EDTA (disodium salt) and approximately six pellets NaOH in 1 L water.

5.6.6 Sodium Nitroprusside (0.05 percent w/v)

Dissolve 0.5 g sodium nitroprusside in 1 L deionized water.

5.6.7 NH_4^+ Stock Standard Solution (1,000 mg/L)

Dissolve 2.9654 g anhydrous ammonium chloride, NH_4Cl (dried at 105°C for 2 hours), in water, and dilute to 1,000 mL.

5.6.8 Standard Solution A (10.00 mg/L NH_4^+)

Dilute 10.0 mL NH_4^+ stock standard solution to 1,000 mL with water.

5.6.9 Standard Solution B (1.000 mg/L NH_4^+)

Dilute 10.0 mL standard solution A to 100.0 mL with water.

5.6.10 Using standard solutions A and B, prepare (fresh daily) the following standards in 100-mL volumetric flasks:

NH_4^+ (mg/L)	mL Standard Solution/100 mL
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

5.7 Sample Collection, Preservation, and Storage

Samples are collected, filtered, and preserved (addition of H_2SO_4 until pH <2) in the field. The samples must be stored at 4°C when not in use.

5.8 Calibration and Standardization

Analyze the series of ammonium standards as described in section 5.10.

Prepare a calibration curve by plotting the peak height versus standard concentration.

5.9 Quality Control

The required QC is described in section 3.4.

5.10 Procedure

5.10.1 Since the intensity of the color used to quantify the concentration is pH-dependent, the acid concentration of the wash water and the standard ammonium solutions should approximate that of the samples. For example, if the samples have been preserved with 2 mL concentrated H_2SO_4/L, the wash water and standards should also contain 2 mL concentrated H_2SO_4/L.

5.10.2 For a working range of 0.01 to 2.6 mg/L NH_4^+ (AAI), set up the manifold as shown in Figure 5.1. For a working range of 0.01 to 1.3 mg/L NH_4^+ (AAII), set up the manifold as shown in Figure 5.2. Higher concentrations may be accommodated by sample dilution.

5.10.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents by feeding distilled water through sample line.

5.10.4 For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII use a 60/hr 6:1 cam with a common wash.

5.10.5 Load sampler tray with unknown samples.

5.10.6 Switch sample line from water to sampler and begin analysis.

5.10.7 Dilute and reanalyze samples with an ammonia concentration exceeding the calibrated concentration range.

5.11 Calculations

Compute concentration of samples by comparing sample peak heights with calibration curve. Report results in mg/L NH_4^+.

5.12 Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), when use was made of surface-water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH_3-N/L, the standard deviation was ±0.005 (U.S. EPA, 1983).

In a single laboratory (EMSL-Cincinnati), when use was made of surface-water samples at concentrations of 0.16 and 1.44 mg NH_3-N/L, recoveries were 107 percent and 99 percent, respectively (U.S. EPA, 1983). These recoveries are statistically significantly different from 100 percent.

5.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 350.1, Ammonia Nitrogen. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

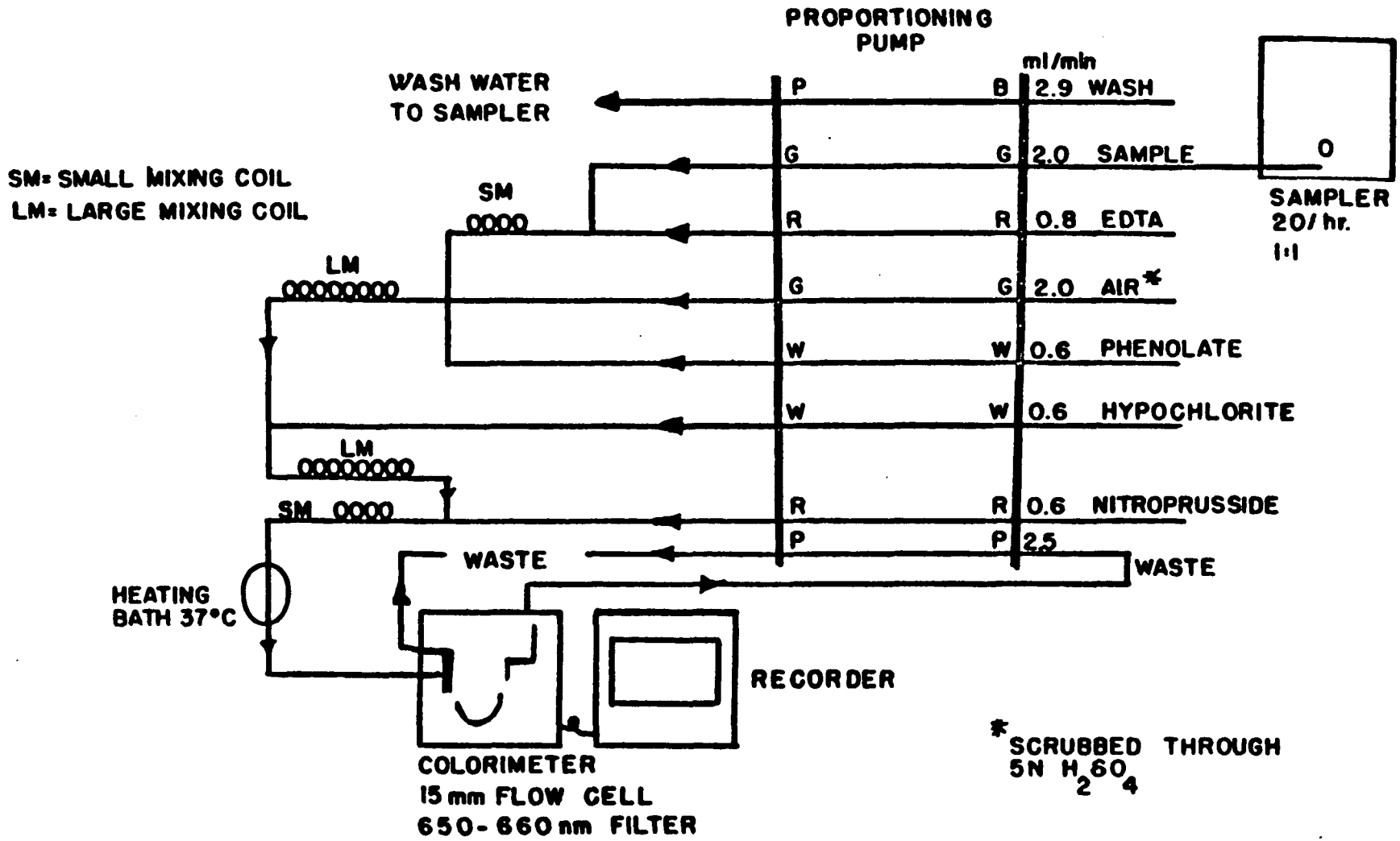

Figure 5.1. Ammonia manifold AAI.

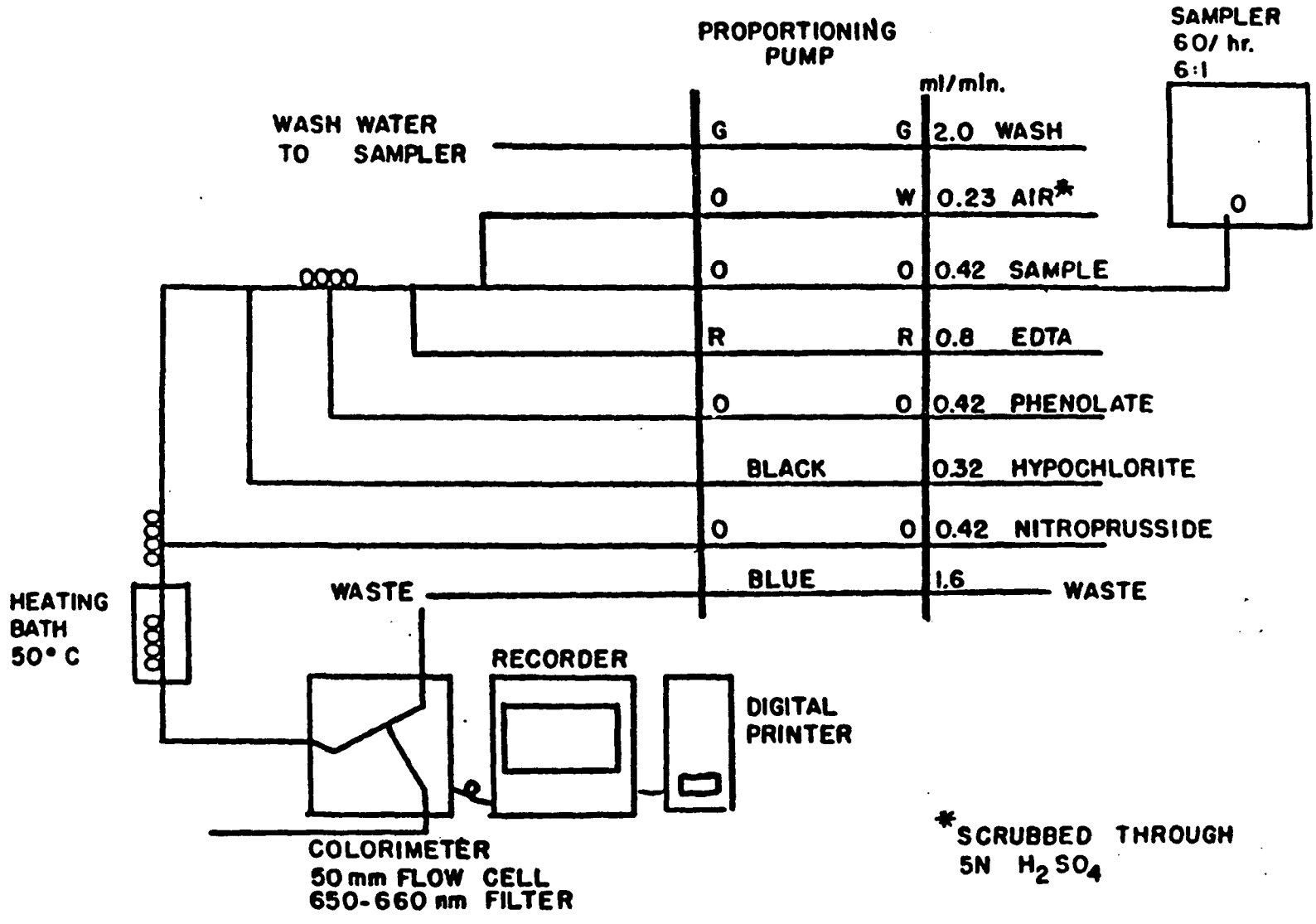

Figure 5.2. Ammonia Manifold AAII.

6.0 DETERMINATION OF CHLORIDE, NITRATE, AND SULFATE BY ION CHROMATOGRAPHY

6.1 Scope and Application

This method is applicable to the determination of chloride, nitrate, and sulfate in natural surface waters by ion chromatography (IC).

This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram.

6.2 Summary of Method

Samples are analyzed by IC. IC is a liquid chromatographic technique that combines ion exchange chromatography, eluent suppression, and conductimetric detection.

A filtered sample portion is injected into an ion chromatograph. The sample is pumped through a precolumn, separator column, suppressor column, and a conductivity detector. The precolumn and separator column are packed with a low-capacity anion exchange resin. The sample anions are separated in these two columns with the separation being based on their affinity for the resin exchange sites.

The suppressor column reduces the conductivity of the eluent to a low level and converts the sample anions to their acid form. Typical reactions in the suppressor column are:

$$\underset{\text{(high-conductivity eluant)}}{Na^+ HCO_3^- + R - H} \quad \longrightarrow \quad \underset{\text{(low conductivity)}}{H_2CO_3 + R - Na}$$

$$Na^+ A^- + R - H \quad \longrightarrow \quad HA + R - Na$$

Three types of suppressor columns are available: the packed-bed suppressor, the fiber suppressor, and the micromembrane suppressor. The packed-bed suppressor contains a high-capacity cation exchange resin in the hydrogen form. It is consumed during analysis and must be periodically regenerated off-line. The latter two suppressors are based on cation exchange membranes. These suppressors are continuously regenerated throughout the analysis. Also, their dead volume is substantially less than that of a packed-bed suppressor. For these two reasons, the latter two suppressors are prefered.

The separated anions in their acid form are measured by using a conductivity cell. Anion identification is based on retention time. Quantification is performed by comparing sample peak heights to a calibration curve generated from known standards (ASTM, 1984a; O'Dell et al., 1984; Topol and Ozdemir, 1981).

6.3 Interferences

Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. The stream samples are not expected to contain any interfering species. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution or spiking can be used to solve most interference problems.

The water dip or negative peak that elutes near and can interfere with the chloride peak can be eliminated by the addition of the concentrated eluant so that the eluant and sample matrix are similar.

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in ion chromatograms.

Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

6.4 Safety

Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. The calibration standards, samples, and most reagents pose no hazard to the analyst. Protective clothing and safety glasses should be worn when handling concentrated sulfuric acid.

6.5 Apparatus and Equipment

6.5.1 Ion Chromatograph

Analytical system complete with ion chromatograph and all accessories (conductivity detector, autosampler, data recording system, etc.).

6.5.2 Anion Pre- and Separator Columns

Dionex Series AG-4A and AS-4A are recommended for use with the 2000i ion chromatographs. AG-3 and AS-3 columns are recommended for older ion chromatographs.

6.5.3 Suppressor Column

Dionex AFS fiber suppressor or AMMS membrane suppressor is recommended.

6.6 Reagents and Consumable Materials

Unless stated otherwise, all chemicals must be ACS reagent grade or better. Also, salts used in preparation of standards must be dried at 105°C for 2 hours and stored in a desiccator.

6.6.1 Deionized Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984b).

6.6.2 Eluant Solution (0.0028M $NaHCO_3$/0.0020M Na_2CO_3)

Dissolve 0.94 g sodium bicarbonate ($NaHCO_3$) and 0.85 g sodium carbonate (Na_2CO_3) in water and dilute to 4 L. This eluant strength may be adjusted for different columns according to the recommendations provided by the manufacturer.

6.6.3 Fiber Suppressor Regenerant (0.025N H_2SO_4)

Add 2.8 mL concentrated sulfuric acid (H_2SO_4, Baker Ultrex grade or equivalent) to 4 L water.

6.6.4 Stock Standard Solutions

6.6.4.1 Sulfate Stock Standard Solution (1,000 mg/L SO_4^{2-})--Dissolve 1.8141 g potassium sulfate (K_2SO_4) in water and dilute to 1.000 L.

6.6.4.2 Chloride Stock Standard Solution (200 mg/L Cl^-)--Dissolve 0.3297 g sodium chloride (NaCl) in water and dilute to 1.000 L.

6.6.4.3 Nitrate Stock Standard Solution (200 mg/L NO_3^-)--Dissolve 0.3261 g potassium nitrate (KNO_3) in water and dilute to 1.000 L.

6.6.4.4 Fluoride Stock Standard Solution (1,000 mg/L F^-)--Dissolve 2.2100 g sodium fluoride (NaF) in water and dilute to 1.000 L.

6.6.4.5 Phosphate Stock Standard Solution (1,000 mg/L P)--Dissolve 4.3937 g potassium phosphate (KH_2PO_4) in water and dilute to 1.000 L.

6.6.4.6 Bromide Stock Standard Solution (1,000 mg/L Br^-)--Dissolve 1.2877 g sodium bromide (NaBr) in water and dilute to 1.000 L.

6.6.4.7 Store stock standards in clean polyethylene bottles (cleaned without acid by using procedure in Appendix A) at 4°C. Prepare monthly.

6.6.5 Mixed Resolution Sample (1 mg/L F^-, 2 mg/L Cl^-, 2 mg/L NO_3^-, 2 mg/L P, 2 mg/L Br^-, 5 mg/L SO_4^{2-})

Prepare by appropriate mixing and dilution of the stock standard solutions.

6.7 Sample Collection, Preservation, and Storage

Samples are collected and filtered in the MPL. Store samples at 4°C when not in use.

6.8 Calibration and Standardization

Each day (or work shift) for each analyte, analyze a blank and a series of standards which bracket the expected analyte concentration range as described in section 6.10. Prepare the standards daily by quantitative dilution of the stock standard solutions. Suggested concentrations for the dilute standards are given in Table 6.1.

TABLE 6.1. SUGGESTED CONCENTRATION OF DILUTE CALIBRATION STANDARDS

	Concentration (mg/L)		
Standard	Cl^-	NO_3^-	SO_4^{2-}
1	0	0	0
2	0.020	0.020	0.20
3	0.10	0.10	0.50
4	0.50	0.50	2.00
5	1.00	1.00	5.00
6	3.00	3.00	10.00

Prepare a calibration curve for each analyte by plotting peak height versus standard concentration.

6.9 Quality Control

General QC procedures are described in section 3.4.

6.9.1 Resolution Test

After calibration, analyze the mixed standard containing fluoride, chloride, nitrate, phosphate, bromide, and sulfate. Resolution between adjacent peaks must equal or exceed 60 percent. If not, replace or clean the separator column and repeat calibration.

6.10 Procedure

6.10.1 Set up the IC for operation. Typical operating conditions for a Dionex 2010i IC are given in Table 6.2. Other conditions may be used depending upon the columns and system selected.

TABLE 6.2. TYPICAL IC OPERATING CONDITIONS

IC: Dionex 2010i — Sample Loop Size: 250 µL

Precolumn: AG-4A

Separator Column: AS-4A

Suppressor Column: AMMS

Eluant: 0.75mM $NaHCO_3$/2.0mM Na_2CO_3

Eluant Flow Rate: 2.0 mL/min

Regenerant: 0.025N H_2SO_4

Regenerant Flow Rate: 3 mL/min

Ion	Typical Retention Time (min)
Cl^-	1.8
NO_3^-	4.9
SO_4^{2-}	8.1

6.10.2 Adjust detector range to cover the concentration range of samples.

6.10.3 Load injection loop (manually or via an autosampler) with the sample (or standard) to be analyzed. Load five to ten times the volume required to thoroughly flush the sample loop. Inject the sample. Measure and record (manually or with a data system) the peak heights for each analyte.

6.10.4 Dilute and reanalyze samples with an analyte concentration exceeding the calibrated concentration range.

6.11 Calculations

Compute the sample concentration by comparing the sample peak height with the calibration curve.

Report results in mg/L.

6.12 Precision and Accuracy

Typical single operator results for surface water analyses are listed in Table 6.3 (O'Dell et al., 1984).

TABLE 6.3. SINGLE-OPERATOR ACCURACY AND PRECISION (O'Dell et al., 1984)[a]

Ion	Spike (mg/L)	Number of Replicates	Mean % Recovery	Standard Deviation (mg/L)
Cl^-	1.0	7	105	0.14
NO_3^-	0.5	7	100	0.0058
SO_4^{2-}	10.0	7	112	0.71

[a]The conditions used by O'Dell were slightly different than those listed in Table 6.2. However, the results are typical of what is expected.

6.13 References

American Society for Testing and Materials, 1984a. Annual Book of ASTM Standards, Vol. 11.01, Standard Test Method for Anions in Water by Ion Chromatography, D4327-84. ASTM, Philadelphia, Pennsylvania.

American Society for Testing and Materials, 1984b. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

O'Dell, J. W., J. D. Pfaff, M. E. Gales, and G. D. McKee, 1984. Technical Addition to Methods for the Chemical Analysis of Water and Wastes, Method 300.0, The Determination of Inorganic Anions in Water by Ion Chromatography. EPA-600/4-85-017. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Topol, L. E., and S. Ozdemir, 1981. Quality Assurance Handbook for Air Pollution Measurement Systems: Vol. V. Manual for Precipitation Measurement Systems, Part II. Operations and Maintenance Manual. EPA-600/4-82-042b. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

7.0 DETERMINATION OF DISSOLVED ORGANIC CARBON AND DISSOLVED INORGANIC CARBON

7.1 Scope and Application

This method is applicable to the determination of DIC and DOC in natural surface waters.

This method is applicable over the concentration range 0.1 to 30 mg/L DIC or DOC. The method detection limit is about 0.8 mg/L DOC and 0.1 mg/L DIC, as determined from replicate analyses of a blank sample.

The method is written with the assumption that a Dohrman-Xertex DC-80 Analyzer is used. However, any instrumentation having similar operating characteristics may also be used.

7.2 Summary of Method

Two samples, aliquots 4 and 5, are sent to the lab for analysis. Aliquot 4 is filtered and preserved in the field (acidified to pH <2 with H_2SO_4). It is analyzed for DOC. Aliquot 5 is an unfiltered sample. It is filtered and analyzed for DIC.

DOC is determined (after external sparging to remove DIC) by ultraviolet-promoted persulfate oxidation which is followed by IR detection. DIC is determined directly by acidifying to generate CO_2 which is followed by IR detection (U.S. EPA, 1983; Xertex-Dohrman, 1984).

7.3 Interferences

No interferences are known.

7.4 Safety

The sample types, standards, and most reagents pose no hazard to the analyst. Protective clothing (lab coat) and safety glasses should be worn when preparing reagents and operating the instrument.

7.5 Apparatus and Equipment

7.5.1 Disposable plastic Luer-Lok syringes (for DIC samples) equipped with Luer-Lok syringe valves.

7.5.2 Carbon Analyzer

This method is based on the Dohrman DC-80 Carbon Analyzer equipped with a high-sensitivity sampler. The essential components of the instrument are a sample injection valve, UV-reaction chamber, IR detector, and

integrator. The injection valve should have a 5- to 7-mL sample loop and should permit injection with a standard Luer-Lok syringe. Other instruments having similar performance characteristics may also be used.

7.5.3 Reagent Bottle for Standard Storage

Heavy-wall borosilicate glass bottle with three two-way valves in the cap. Possible sources are Rainin Instrument Co. (Catalog No. 45-3200) or Anspec Co. (Catalog No. H8332).

7.6 Reagents and Consumable Materials

7.6.1 DOC Calibration Stock Solution (2,000 mg/L DOC)

Dissolve 0.4250 g potassium hydrogen phthalate (KHP, primary standard grade, dried at 105°C for 2 hours) in water, add 0.10 mL phosphoric acid (ACS reagent grade), and dilute to 100.00 mL with water. Store in an amber bottle at 4°C. Prepare monthly.

7.6.2 Dilute Daily DOC Calibration Solutions

Using micropipets or volumetric pipets, prepare the following calibration standards daily.

a. 0.500 mg/L DOC - dilute 0.125 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
b. 1.000 mg/L DOC - dilute 0.250 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
c. 5.000 mg/L DOC - dilute 1.250 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
d. 10.00 mg/L DOC - dilute 2.500 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
e. 30.00 mg/L DOC - dilute 3.750 mL DOC stock solution plus 0.25 mL phosphoric acid to 250.00 mL with water.

Store in amber bottles at 4°C.

7.6.3 DOC QC Stock Solution (1,000 mg/L DOC)

Dissolve 0.5313 g KHP in water, add 0.25 mL phosphoric acid, then dilute to 250.00 mL with water. Store in an amber bottle at 4°C. The QC stock solution must be prepared by using an independent source of KHP. Prepare monthly.

7.6.4 Dilute Daily DOC QC Solutions

Prepare the following QC samples daily.

a. 0.500 mg/L DOC (Detection Limit QC Sample - DL QCCS) - dilute 0.250 mL QC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
b. 10.00 mg/L DOC - dilute 2.500 mL QC stock solution plus 0.25 mL phosphoric acid to 250.00 mL with water.
c. 30.00 mg/L DOC - dilute 3.000 mL QC stock solution plus 0.1 mL phosphoric acid to 100.00 mL with water.

Store in amber bottles at 4°C.

7.6.5 DIC Calibration Stock Solution (2,000 mg/L DIC)

Dissolve 4.4131 g sodium carbonate (Na_2CO_3, primary standard grade, freshly dried at 105°C for 2 hours) in water and dilute to 250.00 mL with water. Store in a tightly capped bottle under a CO_2-free atmosphere. Prepare weekly.

7.6.6 Dilute DIC Calibration Solutions

Prepare the following calibration standards daily.

a. 0.500 mg/L DIC - dilute 0.250 mL DIC stock solution to 1.000 L with water.
b. 1.000 mg/L DIC - dilute 0.250 mL DIC stock solution to 500.00 mL with water.
c. 5.000 mg/L DIC - dilute 1.250 mL DIC stock solution to 500.00 mL with water.
d. 10.00 mg/L DIC - dilute 2.500 mL DIC stock solution to 500.00 mL with water.
f. 30.00 mg/L DIC - dilute 3.750 mL DIC stock solution to 250.00 mL with water.

Store in tightly capped bottles under a CO_2-free atmosphere.

7.6.7 DIC QC Stock Solution (1,000 mg/L DIC)

Dissolve 2.2065 g Na_2CO_3 in water and dilute to 250.00 mL with water. Store in a tightly capped bottle under a CO_2-free atmosphere. The QC stock solution must be prepared with Na_2CO_3 from a source (bottle, lot, supplier) different from that used to prepare the calibration solution.

7.6.8 Dilute DIC QC Solutions

Prepare the following QC samples daily.

a. 0.500 mg/L DIC (Detection Limit QC Sample - DL QCCS) - dilute 0.250 mL QC stock solution to 500.00 mL with water.

b. 10.00 mg/L DIC - dilute 2.500 mL QC stock solution to 250.00 mL with water.
c. 30.00 mg/L DIC - dilute 3.000 mL QC stock solution to 100.00 mL with water.

7.6.9 Potassium Persulfate Reagent (2 percent w/v)

Dissolve 20 g potassium persulfate ($K_2S_2O_8$, ACS reagent grade or better) in water, add 2.0 mL phosphoric acid, then dilute to 1.0 L with water. This reagent is used for DOC analyses.

7.6.10 Phosphoric Acid Reagent (5 percent v/v)

Dilute 50.0 mL concentrated phosphoric acid (ACS reagent grade) to 1.0 L with water. This reagent is used for DIC analyses.

7.6.11 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

7.7 Sample Collection, Preservation, and Storage

The sample for DOC analysis (aliquot 4) is collected, filtered, and preserved in the field (pH adjusted to less than 2 with sulfuric acid). Store at 4°C when not in use.

The sample for DIC analysis (aliquot 5) is collected in the field and is not filtered or preserved. Store at 4°C and minimize atmospheric exposure.

7.8 Calibration and Standardization

7.8.1 DOC Calibration

7.8.1.1 Set-up--Set up the instrument according to the instructions provided by the manufacturer. Adjust all liquid and gas flow rates. Turn on UV lamp and allow the system to stabilize. The IR detector must warm up for at least 2 hours. For best results, leave the IR detector on at all times.

7.8.1.2 Routine Calibration--For the range of interest (0 to 30 mg/L DOC), the instrument is designed to be calibrated with a single 10.00 mg/L DOC standard. The linearity of the calibration is checked with the QC samples. If acceptable results are not obtained for the QC samples, the instrument must be calibrated by using the procedure in section 7.8.1.3.

Sparge the 10.00-mg/L calibration standard for 5 to 6 minutes with CO_2-free gas.

Following the instructions in the operating manual, calibrate the instrument by using three replicate analyses of the 10.00-mg/L standard.

Analyze a system blank and a reagent blank. Both must contain less than 0.1 mg/L DOC. If either contains more DOC, then the water is contaminated. In this case, all standards and reagents must be prepared again with DOC-free water, and the instrument must be recalibrated.

After sparging for 5 to 6 minutes, analyze the 0.500, 10.00, and 30.00 mg/L QC samples. Acceptable results are 0.50 ± 0.10, 10.0 ± 0.5, and 30.0 ± 1.5 mg/L, respectively. If acceptable results are not obtained for all QC samples, the instrument calibration is inadequate (nonlinear). In this case, recalibrate the instrument by using the procedure in section 7.8.1.3.

7.8.1.3 Nonroutine Calibration--If the inherent instrument calibration procedure is inadequate (nonlinear over the range of interest), then the instrument must be calibrated manually. This is done by analyzing a series of calibration standards and by generating a calibration curve by plotting instrument response versus standard concentration. Sample concentrations are then determined by inverse interpolation. The procedure is outlined in the following sections.

Sparge the 0.500, 1.000, 5.000, 10.00, and 30.00 mg/L DOC calibration standard for 5 to 6 minutes with CO_2-free gas.

Erase the instrument calibration (if present). Analyze each standard and record the uncalibrated response.

Plot the response versus standard concentration. Draw or calculate (using linear regression) the best calibration curve.

Analyze a system blank and a reagent blank. From their response and the calibration curve, determine their concentrations. Both must contain less than 0.1 mg/L DOC. If either contains more than 0.1 mg/L DOC, then the water is contaminated. In this case, the standards and reagents must be prepared again by using DOC-free water, and the instrument must be recalibrated.

After sparging for 5 to 6 minutes, analyze the 0.500 and 10.00 mg/L QC samples. From their response and the calibration curve, determine the concentration of each QC sample. Acceptable results are 0.5 ± 0.1 and 10.0 ± 0.5 mg/L, respectively. If unacceptable results are obtained,

the calibration standards must be prepared again and reanalyzed. Acceptable results must be obtained prior to sample analysis.

7.8.2 DIC Calibration

7.8.2.1 Set-up--Set up the instrument according to the instructions provided by the manufacturer. Adjust all liquid and gas flow rates, using 5 percent phosphoric acid as the reagent. Do not turn on the UV lamp. Allow the system to stabilize.

7.8.2.2 Routine Calibration--The calibration procedure is identical to that for DOC (section 7.8.1.2) with the exception that the DIC standards are not sparged prior to analysis.

7.8.2.3 Nonroutine Calibration--The nonroutine calibration procedure is identical to that for DOC (section 7.8.1.3) with the exception that the DIC standards are not sparged prior to analysis.

7.9 Quality Control

7.9.1 In addition to the QC inherent in the calibration procedures (section 7.8), the QC procedures described in section 3.4 must be performed.

7.10 Procedure

7.10.1 DOC Analysis

7.10.1.1 Calibrate the carbon analyzer for DOC.

7.10.1.2 Sparge samples with CO_2-free gas for 5 to 6 minutes (sparge gas should have a flow of 100 to 200 cc/min). Load and analyze the sample as directed by the instrument operating manual.

7.10.2 DIC Analysis

7.10.2.1 Calibrate the carbon analyzer for DIC.

7.10.2.2 Routine Determination

Rinse a clean syringe with sample. Withdraw a fresh sample portion into the syringe. Attach a syringe filter (0.45 µm) and simultaneously filter the sample and inject it into the carbon analyzer. Analyze as directed by the instrument operating manual.

For QA reasons, it is very important that the DIC is measured at the same time pH is measured (section 4).

7.10.2.3 Air-Equilibrated Determination

As described in section 4.10.3, equilibrate the sample with 300 ppm CO_2 in air. Rinse a clean syringe with the air-equilibrated sample. Withdraw a fresh portion of the air-equilibrated sample and attach a syringe filter (0.45 µm). Simultaneously filter and inject the sample into the carbon analyzer. Analyze as directed by the instrument operating manual.

For QA reasons, it is very important that the DIC be measured at the same time pH is measured.

7.11 Calculations

If the routine calibration procedure is satisfactory, the instrument outputs the sample results directly in mg/L. DOC or DIC calculations are not necessary.

If a calibration curve is necessary, determine the sample concentration by comparing the sample response to the calibration curve. Report results as mg/L DOC or DIC.

7.12 Precision and Accuracy

7.12.1 Precision - DOC

In a single laboratory (MERL-Cincinnati), using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from 10 replicates were 0.13, 0.03, 0.02, and 0.02 mg/L, respectively (U.S. EPA, 1983).

7.12.2 Bias - DOC

In a single laboratory (MERL-Cincinnati), using potassium hydrogen phthalate in distilled water at concentrations between 5.0 and 1.0 mg/L total organic carbon, recoveries were 80 percent and 91 percent, respectively (U.S. EPA, 1983).

7.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 415.2, Organic Carbon, Total (low level) (UV promoted, persulfate oxidation). EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

Xertex-Dohrman Corporation, 1984. DC-80 Automated Laboratory Total Organic Carbon Analyzer Systems Manual, 6th Ed. Xertex-Dohrman, Santa Clara, California.

8.0 DETERMINATION OF TOTAL DISSOLVED FLUORIDE BY ION-SELECTIVE ELECTRODE

8.1 Scope and Application

This method is applicable to the determination of total dissolved fluoride in natural surface waters, using a fluoride ion-selective electrode (ISE). The applicable concentration range is 0.005 to 2 mg/L fluoride (F^-).

8.2 Summary of Method

The total dissolved fluoride in a sample is determined electrometrically by using a fluoride ion-selective electrode after addition to the sample of a total ionic strength buffer solution (TISAB). The TISAB adjusts sample ionic strength and pH and breaks up fluoride complexes.

The potential of the fluoride ISE varies logarithmically as a function of the fluoride concentration. A calibration curve is prepared by measuring the potential of known fluoride standards (after TISAB addition) and by plotting the potential versus fluoride concentration (on a semi-log scale). Sample concentrations are determined by comparing the sample potential to the calibration curve.

This method is based on existing methods (U.S. EPA, 1983; Barnard and Nordstrom, 1982; Bauman, 1971; LaZerte, 1984; Kissa, 1983; Warner and Bressan, 1973).

8.3 Interferences

The electrode potential is partially a function of temperature. As a result, standards and samples must be equilibrated to the same temperature (±1°C).

The sample pH must be in the range 5 to 7 to avoid complexation of fluoride by hydronium (pH <5) and hydroxide (pH >7). The addition of TISAB to samples and standards ensures that the pH is maintained in the correct range.

Polyvalent cations may interfere by complexing fluoride, thereby preventing detection by the electrode. The TISAB solution contains a decomplexing agent to avoid potential interferences from polyvalent cations.

8.4 Safety

The sample types, calibration standards, and most reagents pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be worn when handling concentrated sodium hydroxide.

Fluoride is ubiquitous. Good laboratory practices and extra care must be used in order to minimize contamination of samples and standards.

8.5 Apparatus and Equipment

8.5.1 Digital electrometer (pH/mV meter) with expanded mV scale capable of reading 0.1 mV.

8.5.2 Combination Reference - Fluoride ion selective electrode.

8.5.3 Thermally isolated magnetic stirrer and Teflon-coated stir bar.

8.6 Reagents and Consumable Materials

Unless otherwise specified, all chemicals must be ACS reagent grade or better. Use only plasticware (cleaned as described in Appendix A) for reagent preparation.

8.6.1 TISAB Solution

To approximately 500 mL water in a 1-L beaker, add 57 mL glacial acetic acid (Baker Ultrex grade or equivalent), 4 g CDTA*, and 58 g sodium chloride (NaCl, ultrapure). Stir to dissolve, and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5N NaOH (about 150 mL will be required). Transfer the solution to a 1-L volumetric flask and dilute to the mark with water. Transfer to a clean polyethylene (LPE) bottle. (Note: Alternatively, commercially available TISAB solution may be used.)

8.6.2 Sodium Hydroxide Solution (5N NaOH)

Dissolve 200 g NaOH in water, cool, then dilute to 1 L. Store in a tightly sealed LPE bottle.

8.6.3 Fluoride Calibration Solutions

8.6.3.1 Concentrated Fluoride Calibration Stock Solution (1,000 mg/L F^-)-- Dissolve 0.2210 g of sodium fluoride (NaF, ultrapure, dried at 110°C for 2 hours and stored in a desiccator) in water and dilute to 100.00 mL. Store in a clean LPE bottle.

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*1,2-cyclohexylene dinitrilo tetraacetic acid.

8.6.3.2 Dilute Fluoride Calibration Stock Solution (10.00 mg/L F^-)--Dilute 1.000 mL of the concentrated fluoride calibration stock solution to 100.00 mL with water.

8.6.3.3 Dilute Fluoride Working Standards--Using micropipets or volumetric pipets, prepare daily a series of dilute working standards in the range 0.0-2 mg/L F^- by quantitatively diluting appropriate volumes of the 10.00 mg/L F^- solution and TISAB solution to 50.00 mL. The following series may be used:

mL of TISAB	mL of 10.00 mg/L F^- Solution	Resulting F^- Concentration When Diluted to 50.00 mL (mg/L)
5.00	0.000	0.0000
5.00	0.0500	0.0100
5.00	0.100	0.0200
5.00	0.250	0.0500
5.00	0.500	0.100
5.00	2.50	0.500
5.00	10.00	2.000

8.6.4 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

8.7 Sample Collection, Preservation, and Storage

Samples are collected and filtered and are shipped to the lab in LPE bottles. Store at 4°C when not in use.

8.8 Calibration and Standardization

8.8.1 Allow the electrometer to warm up, and ensure that the fluoride-ISE contains adequate internal filling solution.

8.8.2 With the electrometer set to measure mV, analyze the dilute fluoride working standards (in order of increasing concentration, beginning with the blank) by using the procedure described in sections 8.8.2.1 through 8.8.2.3.

8.8.2.1 Prior to use and between determinations, rinse the electrode with water until a potential of at least 200 mV is obtained. Blot dry to avoid carryover.

8.8.2.2 Place 20.00 mL of standard in a clean 30-mL plastic beaker. Add a clean Teflon-coated stir bar, place on a magnetic stirrer, and stir at medium speed.

8.8.2.3 Immerse the electrode in the solution to just above the stir bar and observe the potential. Record the potential when a stable reading is obtained (potential drift less than 0.1 mV/minute). Record the time required to obtain the reading. (It may take 15 to 30 minutes to obtain a stable reading for the low standards.)

8.8.3 Prepare a calibration curve on semi-logarithmic graph paper. Plot the concentration of F^- (in mg/L) on the log axis versus the electrode potential on the linear axis. Determine the slope of the line in the linear portion of the plot. The measured slope should be within ±10 percent of the theoretical slope (obtained from the electrode manual). If it is not, the electrode is not operating properly. Consult the electrode manual for guidance. (Note: The calibration curve may be nonlinear below 0.05 mg/L.)

8.9 Quality Control

The required QC procedures are described in section 3.4.

8.10 Procedure

8.10.1 Use only plasticware when performing fluoride determinations. Clean by using the acid-free washing procedure described in Appendix A.

8.10.2 Allow samples and standards to equilibrate at room temperature.

8.10.3 Analyze fluoride standards and prepare calibration curve as described in section 8.8.

8.10.4 Prior to use and between determinations, rinse the electrode with water until a potential of at least 200 mV is obtained. Blot dry to avoid carryover.

8.10.5 Place 10.00 mL of sample in a clean 30-mL plastic beaker. Add a clean Teflon-coated stir bar, place on a magnetic stirrer, and stir at a medium speed. Add 1.00 mL of TISAB to beaker. Record the reading when a stable potential is obtained (drift is less than 0.1 mV/minute). Also record the time required to reach the stable reading. (It may take as much as 15 to 30 minutes.) This assists the analyst in detecting electrode problems.

8.10.6 At the end of the day, thoroughly rinse the electrode and store it in deionized water.

8.11 Calculations

Compute the sample concentration by comparing the sample potential reading to the calibration curve.

Report results in mg/L.

8.12 Precision and Accuracy

A synthetic sample containing 0.85 mg/L fluoride and no interferences was analyzed by 111 analysts; the mean result was 0.84 mg/L and the standard deviation was 0.03 mg/L (U.S. EPA, 1983).

A synthetic sample containing 0.75 mg/L fluoride, 2.5 mg/L polyphosphate, and 300 mg/L ANC was analyzed by 111 analysts; the mean result was 0.75 mg/L fluoride and the standard deviation was 0.036 (U.S. EPA, 1983).

8.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Barnard, W. R., and D. K. Nordstrom, 1982. Fluoride in Precipitation - I. Methodology with the Fluoride-Selective Electrode. Atmos. Environ., v. 16, pp. 99-103.

Bauman, E. W., 1971. Sensitivity of the Fluoride-Selective Electrode Below the Micromolar Range. Anal. Chim. Acta, v. 54, pp. 189-197.

Kissa, E., 1983. Determination of Fluoride at Low Concentrations with the Ion-Selective Electrode. Anal. Chem., v. 55, pp. 1445-1448.

LaZerte, B. D., 1984. Forms of Aqueous Aluminum in BNC Catchments of Central Ontario: A Methodological Analysis. Can. J. Fish Aquat. Sci., v. 41, n. 5, pp. 766-776.

Warner, T. B., and D. J. Bressan, 1973. Direct Measurement of Less Than 1 Part-Per-Billion Fluoride in Rain, Fog, and Aerosols with an Ion-Selective Electrode. Anal. Chim. Acta, v. 63, pp. 165-173.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 340.2, Fluoride (Potentiometric, Ion Selective Electrode). EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

9.0 DETERMINATION OF TOTAL DISSOLVED PHOSPHORUS

9.1 Scope and Application

This method may be used to determine concentrations of total dissolved phosphorus in natural surface waters in the range from 0.001 to 0.200 mg/L P.

Samples preserved with $HgCl_2$ should not be analyzed with this method.

9.2 Summary of Method

All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Skougstad et al., 1979; Gales et al., 1966; Murphy and Riley, 1962).

9.3 Interferences

Barium, lead, and silver interfere by forming a precipitate. There is a positive interference from silica when the silica-to-total-phosphorus ratio exceeds about 400:1 (Table 9.1).

TABLE 9.1. PERCENT RECOVERY OF TOTAL P IN THE PRESENCE OF SiO_2 (Skougstad et al., 1979)

	SiO_2 (mg/L)				
Total P mg/L	20	15	10	5	1
0.200	98	100	100	102	101
0.100	103	---	---	---	103
0.050	104	104	102	102	102
0.010	144	133	122	111	100
0.005	160	140	120	120	100
0.002	550	350	250	250	100

$HgCl_2$-NaCl-preserved samples give inconsistent results and therefore should not be used.

9.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when handling concentrated sulfuric acid.

Use proper care when operating the autoclave. Follow the safety precautions provided by the manufacturer.

9.5 Apparatus and Equipment

9.5.1 Autoclave.

9.5.2 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

With this equipment the following operating conditions have been found satisfactory for the range from 0.001 to 0.200 mg/L P:

Absorption cell	50 mm
Wavelength	880 nm
Cam	30/h (1:1)
Heating bath temperature	37.5°C.

9.5.3 Glass tubes with plastic caps, disposable: 18 mm by 150 mm.

9.6 Reagents and Consumable Materials

All reagents must be ACS reagent grade or equivalent.

9.6.1 Ammonium Molybdate Solution (35.6 g/L)

Dissolve 40 g ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 800 mL water and dilute to 1 L.

9.6.2 Ascorbic Acid Solution (18 g/L)

Dissolve 18 g ascorbic acid ($C_6H_8O_4$) in 800 mL water and dilute to 1 L.

9.6.3 Antimony Potassium Tartrate Solution (3 g/L)

Dissolve 3.0 g antimony potassium tartrate [$K(SbO)C_4H_4O_6\cdot 1/2H_2O$] in 800 mL water and dilute to 1 L.

9.6.4 Combined Working Reagent

Combine reagents in the order listed below. (This reagent is stable for about 8 hours. The stability is increased if kept at 4°C):

50 mL	Sulfuric acid, 2.45M
15 mL	Ammonium molybdate solution
30 mL	Ascorbic acid solution
5 mL	Antimony potassium tartrate solution

9.6.5 Phosphate Stock Standard Solution (100 mg/L P)

Dissolve 0.4394 g potassium acid phosphate (KH_2PO_4, dried for 12 to 16 hours over concentrated H_2SO_4, sp gr 1.84) in water and dilute to 1,000 mL.

9.6.6 Phosphate Standard Solution I (10.00 mg/L P)

Quantitatively dilute 100.0 mL phosphate stock standard solution to 1,000 mL with water.

9.6.7 Phosphate Standard Solution II (1.000 mg/L P)

Quantitatively dilute 10.00 mL phosphate stock standard solution to 1,000 mL with water.

9.6.8 Dilute Phosphate Working Standards

Prepare a blank and 1,000 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solutions I and II. For example:

Phosphate standard solution II (mL)	Phosphate standard solution I (mL)	Total P concentration in working standard (mg/L)
0.0	0.0	0.000
1.00	-	0.001
5.00	-	0.005
10.00	-	0.010
-	5.0	0.050
-	10.0	0.100
-	20.0	0.200

9.6.9 Potassium Persulfate Solution (4 g/L)

Dissolve 4.0 g potassium persulfate ($K_2S_2O_8$) in water and dilute to 1 L.

9.6.10 Sulfuric Acid (2.45M)

Slowly and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL water. Cool and dilute to 1 L with water.

9.6.11 Sulfuric Acid (0.45M)

Slowly and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL water. Cool and dilute to 1 L with water.

9.6.12 Sulfuric Acid-Persulfate Reagent (1 + 1)

Mix equal volumes of 0.45M sulfuric acid and potassium persulfate solution.

9.6.13 Water Diluent

Add 1.0 mL Levor IV to 1 L water.

9.6.14 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

9.7 Sample Collection, Preservation, and Storage

Samples are collected and preserved (addition of H_2SO_4 until the pH <2). Store samples at 4°C when not in use.

9.8 Calibration and Standardization

Analyze the series of total P standards as described in section 9.10.

Prepare a calibration curve by plotting the peak height versus standard concentration.

9.9 Quality Control

The required QC is described in section 3.4.

9.10 Procedure

9.10.1 It is critical that the colorimeter is optically peaked prior to first analysis.

9.10.2 Mix each sample, pipet a volume of it containing less than 0.002 mg total P (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

9.10.3 Prepare blank solution and sufficient standards, and adjust the volume of each to 10.0 mL.

9.10.4 Add 4.0 mL acid-persulfate reagent to samples, blank, and standards.

9.10.5 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 minutes at 121°C and 15 psi pressure. After the samples have cooled, the caps may be pushed down.

9.10.6 Set up manifold (Figure 9.1).

9.10.7 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 minutes or until the temperature of the heating bath reaches 37.5°C. Zero the recorder baseline while pumping all reagents through the system.

9.10.8 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, with blank solution between each standard. Fill remainder of each tray alternately with unknown samples and blank solution.

9.10.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale. Using the baseline control, adjust each blank in the tray to read zero as it is analyzed.

9.10.10 Dilute and reanalyze samples with a total P concentration exceeding the calibrated range.

9.11 Calculations

9.11.1 Compute the concentration of total phosphorus in each sample by comparing its peak height to the calibration curve. Report results as mg/L P.

9.12 Precision and Accuracy

Data for the determination of the precision and accuracy of the method are given in Tables 9.1 through 9.4.

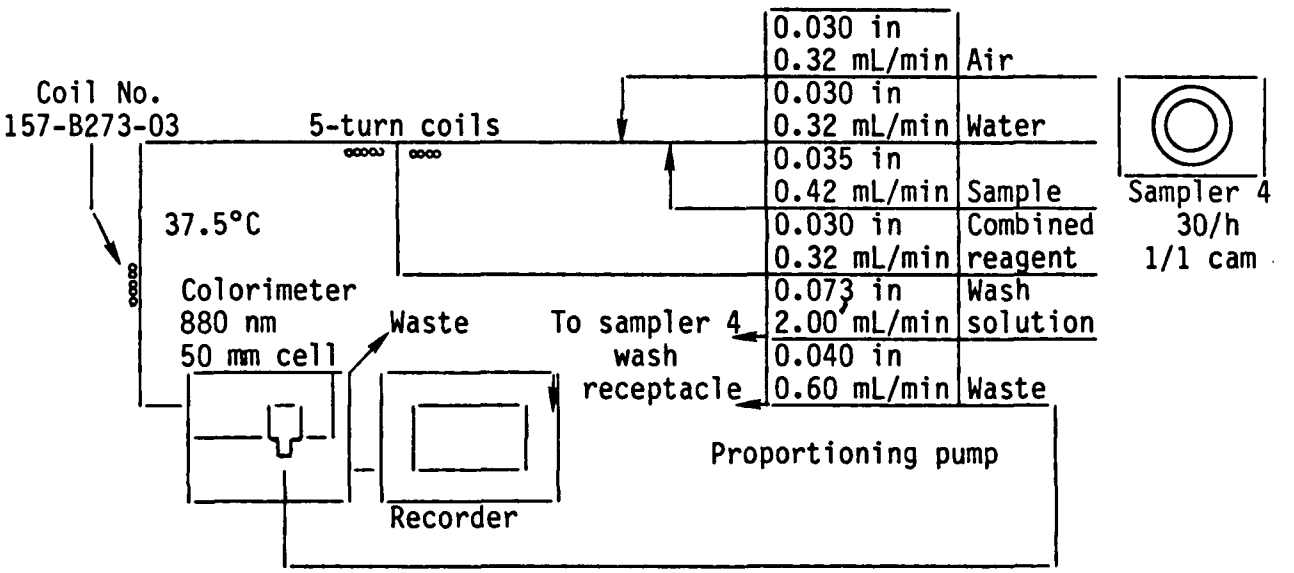

Figure 9.1. Total Dissolved Phosphorus Manifold.

TABLE 9.2. PRECISION AND ACCURACY OF THE METHOD FOR NATURAL WATER SAMPLES (Skougstad et al., 1979). (All data in mg/L P)

Sample	n	Mean	Std. Dev.	% Rel. Std. Dev.
4-065070	10	0.0347	0.0012	3.34
4-065080	10	0.1435	0.0031	2.16
4-066060	10	0.0902	0.0027	2.99

TABLE 9.3. PRECISION AND ACCURACY OF THE METHOD FOR ANALYST-PREPARED STANDARDS (Skougstad et al., 1979). (All data in mg/L P)

Sample	n	Mean	Std. Dev.	% Rel. Std. Dev.
0.040	9	0.0424	0.0007	1.71
0.030	10	0.0322	0.0006	1.96
0.020	10	0.0172	0.0004	2.45
0.004	9	0.0033	0.0007	21.21
0.001	9	0.0013	0.0005	37.5

It is estimated that the RSD (coefficient of variation) of this method is 38 percent at 0.001 mg/L, 2.5 percent at 0.020 mg/L, and 2.2 percent at 0.144 mg/L.

9.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Gales, M. E., Jr., E. C. Julian, and R. C. Kroner, 1966. Method for Quantitative Determination of Total Phosphorus in Water. J. Am. Water Works Assoc., v. 58, pp. 1363-1368.

Murphy, J., and J. P. Riley, 1962. A Modified Single-Solution Method for the Determination of Phosphate in Natural Waters. Anal. Chim. Acta, v. 27, pp. 31-36.

Skougstad, M. W., M. J. Fishman, L. C. Friedman, D. E. Erdman, and S. S. Duncan (eds.), 1979. Method I-4600-78, Automated Phosphomolybdate Colorimetric Method for Total Phosphorus. In: Methods for Determination of Inorganic Substances in Water and Fluvial Sediments: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1. U.S. Government Printing Office, Washington, D.C.

10.0 DETERMINATION OF DISSOLVED SILICA

10.1 Scope and Application

This method is applicable for the determination of dissolved silica in natural surface waters in the concentration range from 0.1 to 10 mg/L.

10.2 Summary of Method

Silica reacts with molybdate reagent in acid media to form a yellow silicomolybdate complex. This complex is reduced by ascorbic acid to form the molybdate blue color. The silicomolybdate complex may form either as an alpha or beta polymorph, or as a mixture of both. Because the two polymorphic forms have absorbance maxima at different wavelengths, the pH of the mixture is kept below 2.5, which favors formation of the beta polymorph (Govett, 1961; Mullen and Riley, 1955; Strickland, 1962).

A 1-hour digestion with 1.0M NaOH is required to ensure that all the silica is available for reaction with the molybdate reagent.

The procedure specified utilizes automated technology and is based on existing methodology (Skougstad et al., 1979).

10.3 Interferences

Interference from phosphate, which forms a phosphomolybdate complex, is suppressed by the addition of oxalic acid. Hydrogen sulfide must be removed by boiling the acidified sample prior to analysis. Large amounts of iron interfere. However, neither hydrogen sulfide nor iron is expected in appreciable quantities.

10.4 Safety

The calibration standards, samples, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when handling concentrated sulfuric acid and when performing sample digestions.

10.5 Apparatus and Equipment

10.5.1 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

10.5.2 With this equipment the following operating conditions are recommended:

Absorption cell	15 mm
Wavelength	660 nm
Cam	60/hour (6/1)

10.6 Reagents and Consumable Materials

10.6.1 Ammonium Molybdate Solution (9.4 g/L)

Dissolve 10 g ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 0.05M H_2SO_4 and dilute to 1 L with 0.05M H_2SO_4. Filter and store in an amber plastic container.

10.6.2 Ascorbic Acid Solution (17.6 g/L)

Dissolve 17.6 g ascorbic acid ($C_6H_8O_6$) in 500 mL water containing 50 mL acetone. Dilute to 1 L with water. Add 0.5 mL Levor IV solution. The solution is stable for 1 week if stored at 4°C.

10.6.3 Hydrochloric Acid (50 percent v/v)

Slowly add 500 mL concentrated HCl to 500 mL water.

10.6.4 Hydrochloric Acid (2 percent v/v)

Add 10 mL (concentrated) HCl to 490 mL water.

10.6.5 Hydrofluoric Acid (HF, ACS reagent grade)

10.6.6 Levor IV Solution

Technicon No. 21-0332 or equivalent.

10.6.7 Oxalic Acid Solution (50 g/L)

Dissolve 50 g oxalic acid ($C_2H_2O_4\cdot 2H_2O$) in water and dilute to 1 L.

10.6.8 Silica Standard Solution (500 mg/L SiO_2)

Dissolve 2.366 g sodium metasilicate ($Na_2SiO_3\cdot 9H_2O$) in water and dilute to 1.000 L. The concentration of this solution must be verified by standard gravimetric analysis (described in section 10.8.1). Store in a plastic bottle.

10.6.9 Silica Working Standards

Prepare a blank and 500 mL each of a series of silica working standards by appropriate quantitative dilution of the silica stock standard solution. The following series is suggested:

Silica stock standard solution (mL)	Silica concentration in working standard (mg/L)
0.0	0
0.200	0.200
0.500	0.500
1.00	1.00
5.00	5.00
10.0	10.0

10.6.10 Sodium Hydroxide Solution (1.0M NaOH)

Dissolve 4 g sodium hydroxide (NaOH) in water and dilute to 1 L.

10.6.11 Sulfuric Acid Solution (0.05M H_2SO_4) (50 percent v/v H_2SO_4)

Cautiously add 2.8 mL concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to water and dilute to 1 L for 0.05M H_2SO_4. Cautiously and slowly add 500 mL H_2SO_4 to 500 mL water. Beware of excessive heat buildup.

10.6.12 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

10.7 Sample Collection, Preservation, and Storage

Samples are collected and filtered in the field and then are shipped to the lab. Store at 4°C when not in use.

10.8 Calibration and Standardization

10.8.1 Verify the concentration of the silica stock standard solution by using the gravimetric procedure detailed in section 10.8.1.1 through 10.8.1.7 (APHA, 1980).

10.8.1.1 Sample Evaporation--Add 5 mL of 50 percent v/v HCl to 200.0 mL silica stock standard. Evaporate to dryness in a 200-mL platinum evaporating dish, in several portions if necessary, on a water bath or suspended on an asbestos ring over a hot plate. Protect against contamination by atmospheric dust. During evaporation, add a total of 15 mL 50 percent HCl in several portions. Evaporate sample to dryness and place dish with residue in a 110°C oven or over a hot plate to bake for 30 minutes.

10.8.1.2 First Filtration--Add 5 mL of 50 percent HCl, warm, and add 50 mL hot

water. While hot, filter sample through an ashless medium-texture filter paper, decanting as much liquid as possible. Wash dish and residue with hot 2 percent HCl and then with a minimum volume of water until washings are chloride-free. Save all washings. Set aside filter paper with its residue.

10.8.1.3 Second Filtration--Evaporate filtrate and washings from the above operations to dryness in the original platinum dish. Bake residue in a 110°C oven or over a hot plate for 30 minutes. Repeat steps in section 10.8.1.2. Use a separate filter paper and a rubber policeman to aid in transferring residue from dish to filter.

10.8.1.4 Ignition--Transfer the two filter papers and residues to a covered platinum crucible, dry at 110°C, and ignite at 1,200°C to constant weight. Avoid mechanical loss of residue when first charring and burning off the paper. Cool in desiccator, weigh, and repeat ignition and weighing until constant weight is attained. Record weight of crucible and contents.

10.8.1.5 Volatilization with HF--Thoroughly moisten weighed residue with water. Add 4 drops of 50 percent v/v H_2SO_4 followed by 10 mL concentrated HF, and measure the latter in a plastic graduated cylinder or by pouring an estimated 10 mL directly from the reagent bottle. Slowly evaporate to dryness over an air bath or hot plate in a hood, and avoid loss by splattering. Ignite crucible to constant weight at 1,200°C. Record weight of crucible and contents.

10.8.1.6 Blank--Repeat procedures in sections 10.8.1.1 through 10.8.1.5 with a blank sample.

10.8.1.7 Calculations

Perform the following calculations for both the standard and blank samples.

X = weight of crucible plus contents before HF treatment (mg)
Y = weight of crucible plus contents after HF treatment (mg)

Z = weight of silica in sample (mg) = X - Y

Calculate the silica concentration in the stock standard by:

$$\frac{\text{mg } SiO_2}{L} = \frac{Z \text{ (standard)} - Z \text{ (Blank) mg}}{0.200 \text{ L}}$$

10.8.2 Analyze the series of silica standards as described in section 10.10 (including digestion).

10.8.3 Prepare a calibration curve by plotting the peak height versus standard concentration.

10.9 Quality Control

The required QC is described in section 3.4.

10.10 Procedure

10.10.1 Set up the AutoAnalyzer manifold (Figure 10.1).

10.10.2 Allow colorimeter and recorder to warm up for at least 30 minutes. Zero the recorder baseline while pumping all reagents through the system.

10.10.3 Add 5.00 mL of 1.0M NaOH to 50.00 mL of sample. Digest for one hour.

10.10.4 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Fill remainder of each sample tray with unknown and QC samples.

10.10.5 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

10.10.6 Dilute and reanalyze any sample with a concentration exceeding the calibrated range.

10.11 Calculations

Compute the silica concentration of each sample by comparing its peak height to the calibration curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak. Report results as mg/L SiO_2.

10.12 References

American Public Health Association, American Water Works Association, and Water Pollution Control Foundation, 1980. Standard Methods for the Examination of Water and Wastewater, 15th Ed. Part 425-Silica. APHA, Washington, D.C.

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

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Skougstad, M. W., M. J. Fishman, L. C. Friedman, D. E. Erdman, and S. S. Duncan (eds.), 1979. Method I-2700-78, Automated Molybdate Blue Colorimetric Method for Dissolved Silica. In: Methods for Determination of Inorganic Substances in Water and Fluvial Sediments: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1. U.S. Government Printing Office, Washington, D.C.

Strickland, J.D.H., 1962. The Preparation and Properties of Silicomolybdic Acid; I. The Properties of Alpha Silicomolybdic Acid. J. Am. Chem. Soc., v. 74, pp. 852-857.

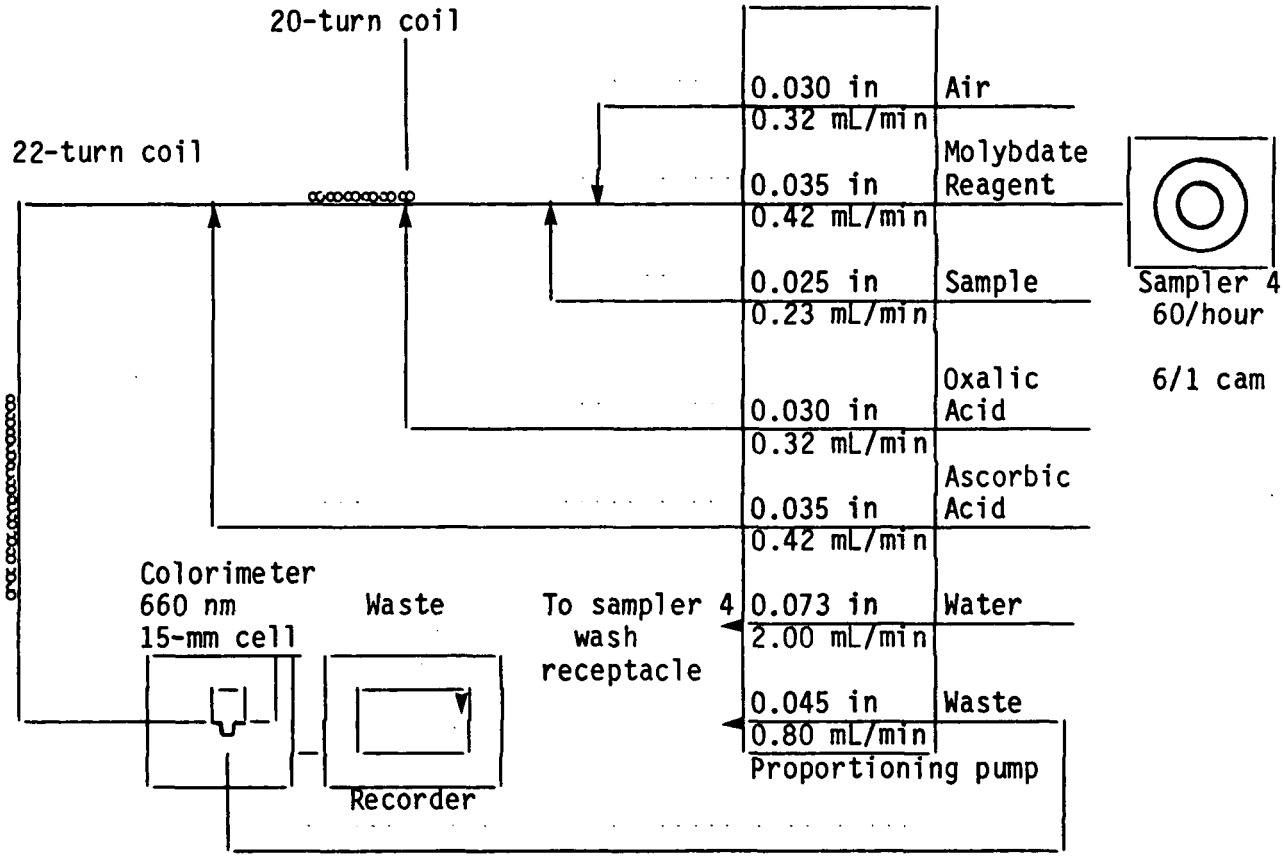

Figure 10.1. Silica manifold.

11.0 DETERMINATION OF SPECIFIC CONDUCTANCE

11.1 Scope and Application

This method is applicable to natural surface waters of low ionic strength.

The majority of streams sampled for the NSWS have a specific conductance in the range 10 to 100 µS/cm.

11.2 Summary of Method

The specific conductance in samples is measured by using a conductance meter and conductivity cell. The meter and cell are calibrated by using potassium chloride standards of known specific conductance (U.S. EPA, 1983).

Samples are preferably analyzed at 25°C. If they cannot be analyzed at 25°C, temperature corrections are made and results are reported at 25°C.

11.3 Interferences

Temperature variations represent the major source of potential error in specific conductance determinations. To minimize this error, calibration standards and samples must be measured at the same temperature.

Natural surface waters contain substances (humic and fulvic acids, suspended solids, etc.) which may build up on the conductivity cell. Such a buildup interferes with the operation of the cell and must be removed periodically by following the recommendations of the cell manufacturer.

11.4 Safety

The calibration standards and sample types pose no hazard to the analyst.

11.5 Apparatus and Equipment

11.5.1 Specific Conductance Meter

11.5.1.1 Digital meter with the following minimum specifications:

Range: 0.1 to 1,000 µS/cm
Readability: 0.1 µS/cm
Maximum Error: 1% of reading
Maximum Imprecision: 1% of reading

11.5.2 Conductivity Cell

High quality glass cell with a cell constant of 1.0 or 0.1. Cells containing platinized electrodes are recommended.

11.5.3 Thermometer

NBS-traceable thermometer with a range of 0 to 40°C and divisions of 0.1°C.

11.6 Reagents and Consumable Materials

11.6.1 Potassium Chloride Stock Calibration Solution (0.01000M KCl)

Dissolve 0.7456 g potassium chloride (KCl, ultrapure, freshly dried for two hours at 105°C and stored in a desiccator) in water and dilute to 1.000 L. Store in a tightly sealed LPE container.

11.6.2 Potassium Chloride Calibration Solution (0.001000M KCl)

Dilute 10.00 mL KCl stock calibration solution to 100.00 mL with water. This solution has a theoretical specific conductance of 147.0 µS/cm at 25°C.

11.6.3 Potassium Chloride QC Solution (0.000500M KCl)

Dilute 5.00 mL 0.0100M KCl solution (independent of the KCl stock calibration solution) to 100.00 mL with water. This solution has a theoretical specific conductance of 73.9 µS/cm at 25°C.

11.6.4 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

11.7 Sample Collection, Preservation, and Storage

The samples are collected in the field and are shipped to the lab in LPE bottles without treatment. Store at 4°C when not in use.

11.8 Calibration and Standardization

11.8.1 Measure and record the specific conductance of the KCl calibration solution as described in section 11.10.

11.8.2 Calculate the corrected cell constant, K_C, by using the following equation:

$$K_C = \frac{147.0\ \mu S/cm}{KCl_m}$$

KCl_m = measured specific conductance for the KCl calibration solution.

The corrected cell constant, K_C, includes the calculation for the cell constant and the temperature correction to 25°C.

11.9 Quality Control

The required QC procedures are described in section 3.4.

11.10 Procedure

11.10.1 Follow the instructions provided by the manufacturer for the operation of the meter and cell.

11.10.2 Allow the samples and calibration standard to equilibrate to room temperature.

11.10.3 Measure the sample temperature. If different from the standard temperature, allow more time for equilibration.

11.10.4 Rinse the cell thoroughly with water.

11.10.5 Rinse the cell with a portion of the sample to be measured. Immerse the electrode in a fresh portion of sample and measure its specific conductance.

11.10.6 Rinse the cell thoroughly with water after use. Store in water.

11.10.7 If the readings become erratic, the cell may be dirty or need replatinizing. Consult the operating manual which is provided by the manufacturer for guidance.

11.11 Calculations

Calculate the corrected specific conductance (S_C) for each sample using the following equation:

$$S_C = (K_C)\ (S_m)$$

K_C = corrected cell constant

S_m = measured specific conductance

Report the results as specific conductance, µS/cm at 25°C.

11.12 Precision and Accuracy

Forty-one analysts in 17 laboratories analyzed 6 synthetic samples containing increments of inorganic salts, with the following results (U.S. EPA, 1983):

Increment, as Specific Conductance (µS/cm)	Precision, as Standard Deviation (µS/cm)	Acccuracy as Bias (%)	Acccuracy as Bias (µS/cm)
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1,640	106	-5.36	-87.9
1,710	119	-5.08	-86.9

In a single laboratory (EMSL-Cincinnati) using surface-water samples with an average conductivity of 536 µS/cm at 25°C, the standard deviation was 6 µS/cm (U.S. EPA, 1983).

11.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 120.1, Conductance. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

12.0 DETERMINATION OF METALS (Al, Ca, Fe, K, Mg, Mn, Na) BY ATOMIC ABSORPTION SPECTROSCOPY

12.1 Scope and Application

Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to the determination of Al, Ca, Fe, K, Mg, Mn, and Na in natural surface waters.

Detection limits, sensitivity, and optimum ranges of the metals vary with the makes and models of atomic absorption spectrophotometers. The data listed in Table 12.1, however, provide some indication of the actual concentration ranges measurable by direct aspiration (flame) and furnace techniques. In the majority of instances, the concentration range shown in the table for analysis by direct aspiration may be extended much lower with scale expansion and, conversely, may be extended upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and through solvent extraction techniques. Lower concentrations may also be determined by using the furnace techniques. The concentration ranges given in Table 12.1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source, and the degree of electrical expansion of the output signal. When he is using furnace techniques, however, the analyst should be cautioned that chemical reactions may occur at elevated temperatures, which may result in either suppression or enhancement of the signal from the element being analyzed. To ensure valid data, the analyst must examine each matrix for interference effects (matrix spike analysis) and, if detected, must analyze the samples by the method of standard additions.

12.2 Summary of Method

In direct aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp, whose cathode is made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

When use is made of the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, is evaporated to dryness, is charred, and is atomized. As a greater percentage of available analyte

TABLE 12.1. ATOMIC ABSORPTION CONCENTRATION RANGES[a]

Metal	Flame			Furnace[b,c]	
	Detection Limit (mg/L)	Sensitivity (mg/L)	Optimum Concentration Range (mg/L)	Detection Limit (µg/L)	Optimum Concentration Range (µg/L)
Aluminum	0.1	1	5 - 50	3	20 - 200
Calcium	0.01	0.08	0.2 - 7	-	-
Iron	0.03	0.12	0.3 - 5	1	5 - 100
Magnesium	0.001	0.007	0.02 - 0.5	-	-
Manganese	0.01	0.05	0.1 - 3	0.2	1 - 30
Potassium	0.01	0.04	0.1 - 2	-	-
Sodium	0.002	0.015	0.03 - 1	-	-

[a]The concentrations shown are obtainable with any satisfactory atomic absorption spectrophotometer.
[b]For furnace sensitivity values, consult instrument operating manual.
[c]The listed furnace values are those expected when using a 20-µL injection and normal gas flow, except in the case of arsenic and selenium where gas interrupt is used.

atoms are vaporized and dissociated for absorption in the tube than in the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace and thereby cause the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp, and a photosensitive device measures the attenuated transmitted radiation.

Dissolved metals (Ca, Fe, K, Mg, Mn, and Na) are determined in a filtered sample (aliquot 1) by flame atomic absorption spectroscopy (U.S. EPA, 1983).

Total Al is determined in an unfiltered sample (aliquot 7) after digestion by graphite furnace atomic absorption spectroscopy (U.S. EPA, 1983).

Total extractable Al is determined in a sample that has been treated with 8-hydroxyquinoline and has been extracted into MIBK (aliquot 2) by graphite furnace atomic absorption spectroscopy (Barnes, 1975; May et al., 1979; Driscoll, 1984).

12.3 Definitions

Optimum Concentration Range

This is a range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and with the operating conditions employed.

Sensitivity

Sensitivity is the concentration in milligrams of metal per liter that produces an absorption of 1 percent.

Dissolved Metals

Dissolved metals are those constituents (metals) which can pass through a 0.45-μm membrane filter.

Total Metals

The concentration of metals is determined on an unfiltered sample following vigorous digestion.

12.4 Interferences

12.4.1 Direct Aspiration

12.4.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium and calcium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

12.4.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

12.4.1.3 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

12.4.1.4 Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high because of the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or when a metal impurity in the lamp cathode falls within the bandpass of the slit setting with that metal being present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

12.4.2 Flameless Atomization

12.4.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is this effect which must be determined and taken into consideration in the analysis of each different matrix encountered. To verify the absence of matrix or chemical interference, a matrix spike sample is analyzed by using the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots, add a known amount of analyte and dilute both aliquots to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1). The diluted aliquots should then be analyzed, and the unspiked results which are multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10 percent) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard helps confirm the finding from the dilution analysis. Those samples which indicate the presence of interference must be analyzed by the method of standard additions.

12.4.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Background correction can also compensate for nonspecific broad-band absorption interference.

12.4.2.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or by utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the element being analyzed.

12.4.2.4 The chemical environment of the furnace may cause certain elements to form carbides at high temperatures. This problem is greatly reduced, and the sensitivity is increased with the use of pyrolytically coated graphite.

12.5 Safety

The calibration standards, sample types, and most reagents pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated hydrochloric acid, ammonium hydroxide solutions, and MIBK should be restricted to a hood.

Follow the safety precautions provided by the manufacturer when operating the atomic absorption spectrophotometers.

Follow good laboratory practices when handling compressed gases.

12.6 Apparatus and Equipment

12.6.1 Atomic Absorption Spectrophotometer

The spectrophotometer used shall be a single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

12.6.2 Burner

The burner recommended by the particular instrument manufacturer should be used. For certain elements, the nitrous oxide burner is required.

12.6.3 Hollow Cathode Lamps

Single element lamps are preferred, but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.

12.6.4 Graphite Furnace

Any furnace device capable of reaching the specified temperatures is satisfactory.

12.6.5 Strip Chart Recorder

A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

12.7 Reagents and Consumable Materials

12.7.1 General reagents used in each metal determination are listed in this section. Reagents specific to particular metal determinations are listed in the particular procedure description for that metal.

12.7.2 Concentrated Hydrochloric Acid (12M HCl)

Ultrapure grade (Baker Instra-Analyzed or equivalent) is required.

12.7.3 HCl (1 percent v/v)

Add 5 mL concentrated HCl to 495 mL water.

12.7.4 Nitric Acid (0.5% v/v HNO_3 - Ultrapure grade, Baker Instra-Analyzed or equivalent).

Carefully dilute HNO_3 in water in the ratio of 0.5 to 100.

12.7.5 Stock Standard Metal Solutions

Prepare as directed in the individual metal procedures. Commercially available stock standard solutions may also be used.

12.7.6 Dilute Calibration Standards

Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

12.7.7 Fuel and Oxidant

Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

12.7.8 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

12.8 Sample Collection, Preservation, and Storage

Samples are collected and processed in the field. The sample for dissolved metals (aliquot 1) is filtered through a 0.45-μm membrane filter and is then preserved by acidifying to a pH <2 with nitric acid. The sample for total Al analysis (aliquot 7) is preserved by acidifying to a pH <2 with nitric acid. The sample for total extractable Al (aliquot 2) is prepared by mixing a portion of sample with 8-hydroxyquinoline followed by extraction with MIBK.

After processing, the samples are shipped to the analytical laboratory. For aliquot 2 samples, it is the MIBK layer from the extraction that is shipped.

12.9 Calibration and Standardization

12.9.1 The calibration procedure varies slightly with the various atomic absorption instruments.

12.9.2 For each analyte, calibrate the atomic absorption instrument by analyzing a calibration blank and a series of standards and by following the instructions in the instrument operating manual.

12.9.3 The concentration of standards should bracket the expected sample concentration. However, the linear range of the instrument should not be exceeded.

12.9.4 Method of Standard Additions

When indicated by the matrix spike analysis, the analytes must be quantified by the method of standard additions. In this method, equal volumes of sample are added to a deionized water blank and to three standards containing different known amounts of the test element. The volume of the blank and of each standard must be the same. The

absorbance of each solution is determined and is then plotted on the vertical axis of a graph with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 12.1. The method of standard additions can be very useful; however, for the results to be valid, the following limitations must be taken into consideration:

- The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20 percent), caution should be exercised.

- The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

- The determination must be free of spectral interference and must be corrected for nonspecific background interference.

12.10 Quality Control

The required QC procedures are described in section 3.4.

12.11 Procedure

12.11.1 General procedures for flame and furnace atomic absorption analysis are given in sections 12.11.2 and 12.11.3. Detailed procedures for determining Al, Ca, Fe, K, Mg, Mn, and Na are given in sections 12.11.4 through 12.11.11.

12.11.2 Flame Atomic Absorption Spectroscopy

Differences among the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the operating instructions of the manufacturer for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the recommendation provided by the manufacturer. Subsequently, light the flame and

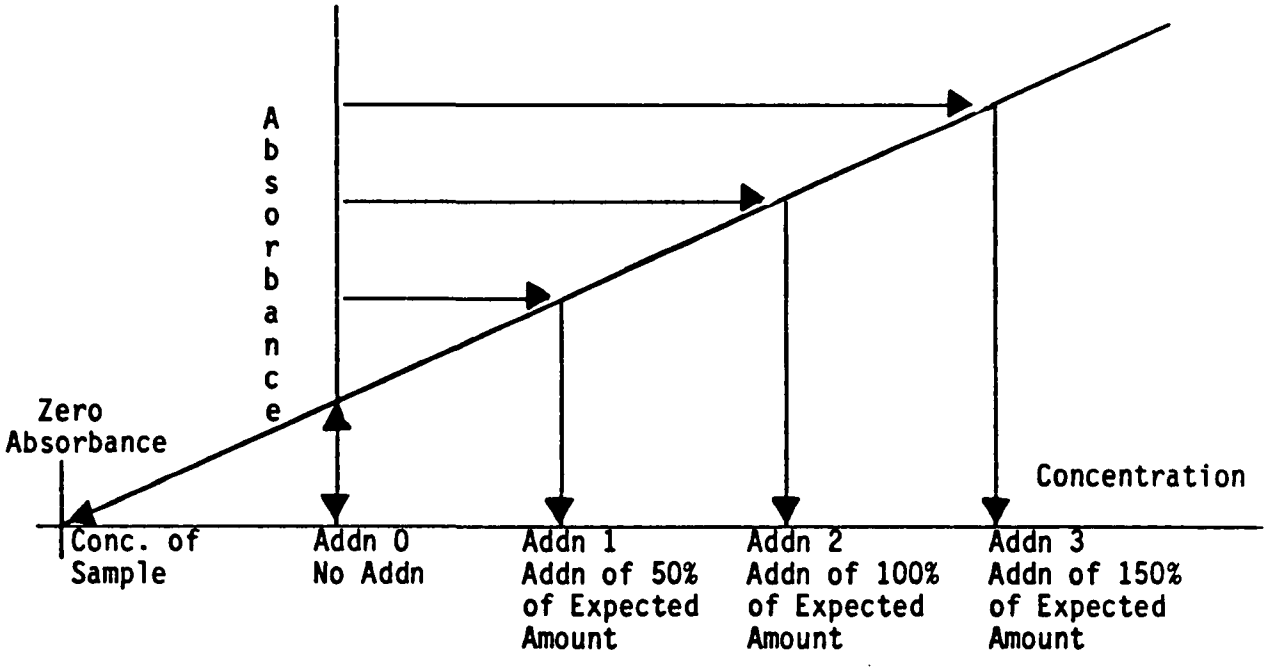

Figure 12.1. Standard Addition Plot.

regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and calibrate the instrument. Aspirate the samples and determine the concentrations either directly (if the instrument reads directly in concentration units) or from the calibration curve.

12.11.3 Furnace Atomic Absorption Spectroscopy

Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences among various makes and models of satisfactory instruments, no detailed operating instuctions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and should use as a guide the temperature settings and other instrument conditions listed in sections 12.11.4 through 12.11.11 (which are the recommended ones for the Perkin-Elmer HGA-2100). In addition, the following points may be helpful.

12.11.3.1 With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. These effects can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

12.11.3.2 If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period at regular intervals in the analytical scheme.

12.11.3.3 Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories MODEL 555, Perkin-Elmer MODELS HGA 2200 and HGA 76B, and Varian MODEL CRA-90) employing faster rates of atomization, can be operated when making use of lower atomization temperatures for shorter time periods than those listed in this manual.

12.11.3.4 Although prior digestion of the sample in many cases is not required provided that a representative aliquot of sample can be pipeted into the furnace, it provides for a more uniform matrix and possibly lessens matrix effects.

12.11.3.5 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and should be reanalyzed. The use of multiple injections can improve accuracy and can help detect furnace pipetting errors.

12.11.4 Procedure for Determination of Total Aluminum

12.11.4.1 Summary--A portion of sample is digested, and digestate is analyzed for Al by furnace atomic absorption spectroscopy (U.S. EPA, 1983).

12.11.4.2 Preparation of Aluminum Standard Solutions

Aluminum stock solution (1000 mg/L Al)--Carefully weigh 1.000 gram aluminum metal (analytical reagent grade). Add 15 mL concentrated HCl and 5 mL concentrated HNO_3 to the metal, cover the beaker, and warm gently. When metal is completely dissolved, transfer solution quantitatively to a 1-L volumetric flask and bring to volume with water. Alternatively, a commercially available, certified Al standard may be used.

Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

The calibration standard should be prepared in 0.5 percent (v/v) HNO_3.

12.11.4.3 Sample Preparation--The sample must be digested prior to analysis. Because of the low concentrations of analyte expected, contamination from atmospheric sources can be a major problem. To avoid contamination, all preparations must be performed in a laminar flow hood.

Quantitatively transfer a 50.00 mL aliquot of the well-mixed sample to a Griffin beaker. Add 3.0 mL of concentrated nitric acid. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Allow the beaker to cool, then again add 3.0 mL of concentrated nitric acid. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate until a gentle reflux action occurs. Continue refluxing, adding acid as necessary, until the digestion is complete (indicated by a light-colored residue or no change in appearance with continued refluxing). When complete, evaporate to near dryness. Allow to cool. Add 0.5 mL of 50 percent nitric acid and warm slightly to dissolve any precipitate or residue resulting from evaporation. Wash down the beaker walls and watch glass with water. Quantitatively filter the sample (to remove silicates and other insoluble materials) and adjust to 50.00 mL. The sample is now ready for analysis.

12.11.4.4 Suggested Instrument Conditions (General)

Drying time and temperature--30 seconds at 125°C.

Ashing time and temperature--30 seconds at 1,300°C.

Atomizing time and temperature--10 seconds at 2,700°C.

Purge gas atmosphere--Argon.

Wavelength--309.3 nm.

Other operating conditions should be set as specified by the particular instrument manufacturer.

12.11.4.5 Analysis Procedure

Calibrate the instrument as directed by the instrument manufacturer.

Analyze the samples (including required QC samples).

If a sample concentration exceeds the linear range, dilute (with acidic media) and reanalyze.

Report results as mg/L Al.

12.11.4.6 Notes

The above instrument conditions are for a Perkin-Elmer HGA-2100 and are based on the use of a 20 µL injection, continuous-flow purge gas, and nonpyrolytic graphite.

Background correction may be required if the sample contains a high level of dissolved solids.

It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore, the use of halide acids and nitrogen as a purge gas should be avoided.

The ashing temperature can be increased to 1,500 to 1,700°C by adding 30 µg magnesium nitrate ($Mg(NO_3)_2$) (Manning et al., 1982).

If blanks indicate that sample contamination is occuring, the use of Teflon labware is recommended.

12.11.5 Procedure for Determination of Total Extractable Aluminum

12.11.5.1 Summary--Samples for extractable aluminum are prepared in the field and are obtained as the 8-hydroxyquinoline complex in MIBK. The MIBK solution is analyzed for aluminum by graphite furnace atomic absorption (GFAA) (Barnes, 1975; May et al., 1979; Driscoll, 1984).

12.11.5.2 Preparation of Reagents

Glacial acetic acid (HOAc, 18M)--Baker Ultrex grade or equivalent.

Ammonium hydroxide (NH_4OH, 5M)--Baker Ultrex grade or equivalent.

Sodium acetate solution (NaOAc, 1.0M)--Dissolve 8.2 g NaOAc (Alfa Ultrapure grade or equivalent) in 100 mL water.

Methyl isobutyl ketone (MIBK)--HPLC grade or equivalent.

Phenol red indicator solution (0.04 percent w/v)--ACS reagent grade.

Hydrochloric acid (HCl, 12M)--Baker Ultrex grade or equivalent.

2.5 M HCl--Dilute 208 mL of 12 M HCl to 1.0 L.

NH_4^+/NH_3 buffer--Add 56 mL glacial acetic acid to 75 mL of 5M NH_4OH dilute to 250 mL. Adjust pH to 8.3 by using NH_4OH or HOAc.

8-hydroxyquinoline solution (10 g/L)--Dissolve 5 grams of 8-hydroxyquinoline (99 plus percent purity) in 12.5 mL HOAc, then dilute to 500 mL.

8-hydroxyquinoline sodium acetate reagent--Mix, in order, 10 mL 1.0M NaOAc, 50 mL water, and 10 mL hydroxyquinoline solution. This reagent must be prepared daily.

12.11.5.3 Preparation of Aluminum Standard Solutions

Aluminum stock solution--Prepare as described in section 12.11.4.2.1.

Dilute calibration standards--Daily, quantitatively dilute the Al stock solution to prepare a series of calibration standards over the range 0 to 0.1 mg/L Al. A blank must be prepared. Prior to analysis, the blank, standards (and any QC samples) must be extracted.

Pipet 25.00 mL of a calibration standard (or calibration blank or QC sample) into a clean 50-mL separatory funnel (or a clean 50-mL disposable centrifuge tube with cap).

Add 2 to 3 drops phenol red indicator and 5.00 mL 8-hydroxyquinoline NaOAc reagent. Swirl to mix.

Rapidly adjust the pH to 8 by dropwise additions of 5M NH_4OH until the solution turns red. Immediately add 2.0 mL NH_4^+/NH_3 buffer and 10 mL MIBK. Cap and shake vigorously for 7 to 10 seconds with a rapid, end-to-end motion. Be careful of pressure buildup.

Allow the phases to separate (10 to 15 seconds) and isolate the MIBK layer. If an emulsion forms, separation can be hastened by centrifugation. Keep the MIBK layer tightly capped to prevent evaporation.

12.11.5.4 Suggested Instrument Conditions (General)

Drying cycle--Ramp 10 seconds, hold 10 seconds.

Drying temperature--100°C.

Ashing cycle--Ramp 5 seconds, hold 20 seconds.

Ashing temperature--1,500°C.

Atomization cycle--Hold 5 seconds (no ramp, max. power heating).

Atomization temperature--2,500°C.

Purge gas--Argon at 20 cc/minute.

Lamp--Al HCl at 25 mA.

Wavelength--309.3.

Graphite tube--Nonpyrolytic.

Sample size--25 µL.

These operating conditions are for a Perkin-Elmer 5000 with a HGA-500 graphite furnace and AS-40 autosampler.

12.11.5.5 Analysis Procedure

Calibrate the instrument as directed by the instrument manufacturer.

Analyze the samples (including required QC samples).

If a sample concentration exceeds the linear range, dilute with MIBK and reanalyze.

Report results as mg/L Al.

12.11.5.6 Note - By using the same volumes for standards as for samples, concentration factors are taken into account.

12.11.6 Procedure for Determination of Dissolved Calcium

12.11.6.1 Summary--The samples (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for Ca (U.S. EPA, 1983).

12.11.6.2 Preparation of Reagents

Lanthanum chloride matrix modifier solution--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent) and dilute to 500 mL with water.

12.11.6.3 Preparation of Calcium Standard Solutions

Calcium stock solution (500 mg/L Ca)--Suspend 1.250 g $CaCO_3$ (analytical reagent grade, dried at 180°C for 1 hour before weighing) in water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with water.

Dilute calibration standards--Daily, quantitatively prepare a series of dilute Ca standards from the calcium stock solution to span the desired concentration range.

12.11.6.4 Suggested Instrumental Conditions (General)

Calcium hollow cathode lamp; wavelength, 422.7 nm; fuel, acetylene; oxidant, air; type of flame, reducing.

12.11.6.5 Analysis Procedure

To each 10.0 mL volume of dilute calibration standard, blank, and sample add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL sample).

Calibrate the instrument as directed by the manufacturer.

Analyze the samples.

Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

Report results as mg/L Ca.

12.11.6.6 Notes

Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium, and nitrate cause no interference.

Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame.

The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

12.11.6.7 Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), when use was made of distilled water spiked at concentrations of 9.0 and 36 mg Ca/L, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99 percent.

12.11.7 Procedure for Determination of Dissolved Iron

12.11.7.1 Summary--The samples (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy (U.S. EPA, 1983).

12.11.7.2 Preparation of Iron Standard Solutions

Fe stock solution (1,000 mg/L Fe)--Carefully weigh 1.000 g pure iron wire (analytical reagent grade) and dissolve in 5 mL concentrated HNO_3, warming if necessary. When iron is completely dissolved, bring volume of solution to 1 L with water.

Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

12.11.7.3 Suggested Instrumental Conditions (General)

Iron hollow cathode lamp; wavelength, 248.3 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

12.11.7.4 Analysis Procedure

Calibrate the instrument as directed by the instrument manufacturer.

Analyze the samples.

Dilute and reanalyze any samples with concentrations exceeding the calibrated range.

Report results in mg/L Fe.

12.11.7.5 Notes

The following lines may also be used: 248.8 nm, relative sensitivity 2; 271.9 nm, relative sensitivity 4; 302.1 nm, relative sensitivity 5; 252.7 nm, relative sensitivity 6; 372.0 nm, relative sensitivity 10.

12.11.7.6 Precision and Accuracy

An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL-Cincinnati. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead, and zinc were added to natural water samples. The statistical results for iron were as follows:

Number Of Labs	True Value (µg/L)	Mean Value (µg/L)	Standard Deviation (µg/L)	Accuracy as % Bias
82	840	855	173	1.8
85	700	680	178	-2.8
78	350	348	131	-0.5
79	438	435	183	-0.7
57	24	58	69	141
54	10	48	69	382

12.11.8 Procedure for Determination of Dissolved Magnesium

12.11.8.1 Summary--The samples (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for Mg.

12.11.8.2 Preparation of Reagents

Lanthanum chloride solution--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent) and dilute to 500 mL with water.

12.11.8.3 Preparation of Magnesium Standard Solutions

Stock solution (500 mg/L Mg)--Dissolve 0.829 g magnesium oxide, MgO (analytical reagent grade), in 10 mL of HNO_3 and dilute to 1 L with water.

Dilute calibration standards--Daily, quantitatively prepare from the Mg stock solution a series of Mg standards that spans the desired concentration range.

12.11.8.4 Suggested Instrumental Conditions (General)

Magnesium hollow cathode lamp; wavelength, 285.2 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

12.11.8.5 Analysis Procedure

To each 10.0 mL dilute calibration standard, blank, and sample, add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL sample).

Calibrate the instrument as directed by the manufacturer.

Analyze the samples.

Dilute and reanalyze any samples with a concentration exceeding the linear range.

Report results as mg/L Mg.

12.11.8.6 Notes

The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

The line at 202.5 nm may also be used. This line has a relative sensitivity of 25.

To cover the range of magnesium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that either the 202.5 nm

line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

12.11.8.7 Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), when use is made of distilled water spiked at concentrations of 2.1 and 8.2 mg/L Mg, the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100 percent.

12.11.9 Procedure for Determination of Dissolved Manganese

12.11.9.1 Summary--The samples (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for Mn (U.S. EPA, 1983).

12.11.9.2 Preparation of Manganese Standard Solutions

Mn stock solution (1,000 mg/L Mn)--Carefully weigh 1.000 g manganese metal (analytical reagent grade) and dissolve in 10 mL of HNO_3. When metal is completely dissolved, dilute solution to 1 liter with 1 percent (v/v) HCl.

Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

12.11.9.3 Instrumental Conditions (General)

Manganese hollow cathode lamp; wavelength, 279.5 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

12.11.9.4 Analysis Procedure

Calibrate the instrument as directed by the manufacturer.

Analyze the samples.

Dilute and reanalyze any samples with a concentration exeeding the calibrated range.

Report results as mg/L Mn.

12.11.9.5 Notes

The line at 403.1 nm may also be used. This line has a relative sensitivity of 10.

12.11.9.6 Precision and Accuracy

An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL-Cincinnati. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead, and zinc were added to natural water samples. The statistical results for manganese were as follows:

Number of Labs	True Value (µg/L)	Mean Value (µg/L)	Standard Deviation (µg/L)	Accuracy as % Bias
77	426	432	70	1.5
78	469	474	97	1.2
71	84	86	26	2.1
70	106	104	31	-2.1
55	11	21	27	93
55	17	21	20	22

12.11.10 Procedure for Determination of Dissolved Potassium

12.11.10.1 Summary--The samples (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for K (U.S. EPA, 1983).

12.11.10.2 Preparation of Potassium Standard Solutions

Potassium stock solution (100 mg/L K)--Dissolve 0.1907 g KCl (analytical reagent grade, dried at 110°C) in water and bring volume of solution to 1 L.

Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

12.11.10.3 Suggested Instrumental Conditions (General)

Potassium hollow cathode lamp; wavelength, 766.5 nm; fuel, acetylene; oxidant, air; type of flame, slightly oxidizing.

12.11.10.4 Analysis Procedure

Calibrate the instrument as directed by the manufacturer.

Analyze the samples.

Dilute and reanalyze any sample with a concentration exceeding the calibrated range.

Report results as mg/L K.

12.11.10.5 Notes

In air-acetylene or other high-temperature flames (>2,800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement which is due to sodium can be stabilized by adding excess sodium (1,000 µg/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

The 404.4-nm line may also be used. This line has a relative sensitivity of 500.

To cover the range of potassium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

12.11.10.6 Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), when use was made of distilled water samples spiked at concentrations of 1.6 and 6.3 mg/L K, the standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103 percent and 102 percent, respectively.

12.11.11 Procedure for Determination of Dissolved Sodium

12.11.11.1 Summary--The samples (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for Na (U.S. EPA, 1983).

12.11.11.2 Preparation of Sodium Standard Solutions

Sodium stock solution (1,000 mg/L Na)--Dissolve 2.542 g NaCl (analytical reagent grade, dried at 140°C) in water and bring the volume of the solution to 1 L.

Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

12.11.11.3 Suggested Instrumental Conditions (General)

Sodium hollow cathode lamp; wavelength, 589.6 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

12.11.11.4 Analysis Procedure

Calibrate the instrument as directed by the manufacturer.

Analyze the samples.

Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

Report results as mg/L Na.

12.11.11.5 Notes

The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1,000 mg/L) to both standards and samples.

12.11.11.6 Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), when use is made of distilled water samples spiked at levels of 8.2 and 52 mg/L Na, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102 percent and 100 percent.

12.12 Calculations

Generally, instruments are calibrated to output sample results directly in concentration units. If they do not, then a manual calibration curve must be prepared, and sample concentrations must be determined by comparing the sample signal to the calibrated curve.

If dilutions were performed, the appropriate factor must be applied to sample values.

Report results as mg/L for each analyte.

12.13 References

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13.0 DETERMINATION OF DISSOLVED METALS (Ca, Fe, Mg, and Mn) BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

13.1 Scope and Application

This method is applicable to the determination of dissolved Ca, Fe, Mg, and Mn in natural surface waters.

Table 13.1 lists the recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization for the specified elements. Actual working detection limits are sample-dependent, and as the sample matrix varies, these concentrations may also vary.

Because of the differences among makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

13.2 Summary of Method

The method describes a technique for the simultaneous or sequential determination of Ca, Fe, Mg, and Mn in samples collected for the NSWS. The method is based on the measurement of atomic emission by optical spectroscopy. Samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma (ICP) which is produced by a radio frequency (RF) generator. In the plasma (which is at a temperature of 6,000 to 10,000°K), the analytes in the aerosol are atomized, ionized, and excited. The excited ions and atoms emit light at their characteristic wavelengths. The spectra from all analytes are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. EPA, 1983; Fassel, 1982).

A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during sample analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Generally, each instrument has different background handling capabilities. The instrument operating manual should be consulted for guidance.

TABLE 13.1. RECOMMENDED WAVELENGTHS[a] AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength (nm)	Estimated detection limit (µg/L)[b]
Calcium	317.933	10
Iron	259.940	7
Magnesium	279.079	30
Manganese	257.610	2

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (EPA 1979).

[b]The estimated instrumental detection limits as shown are taken from Fassel, 1982. They are given as a guide for an instrumental limit. The actual method detection limits are sample-dependent and may vary as the sample matrix varies.

The possibility of additional interferences named in 13.3.1 should also be recognized, and appropriate corrections should be made.

13.3 Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They are summarized in sections 13.3.1 through 13.3.1.3.

13.3.1 Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high-concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, which would require the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in

Table 13.2 are some interference effects for the recommended wavelengths given in Table 13.1. The interference information is expressed as analyte concentration eqivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interfering element. The values in the table are only approximate and should be used as a guide for determining potential interferences. Actual values must be determined for each analytical system when necessary.

Only those interferents listed were investigated. The blank spaces in Table 13.2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 13.3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 to 5 percent of the peaks generated by the analyte concentrations (also listed in Table 13.3).

13.3.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample or utilization of standard addition techniques.

High dissolved solids may also cause salt buildup at the tip of the nebulizer. This affects aerosol flow rate and causes instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem.

It has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

13.3.3 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are negligible with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (i.e., incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and on the specific analyte element.

13.3.4 Whenever a new or unusual sample matrix is encountered, a series of tests should be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 13.3.4.1 through 13.3.4.4, will ensure that neither positive nor negative interference effects are operative on any of the analyte elements, which would distort the accuracy of the reported values.

TABLE 13.2. ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENTS AT THE 100 mg/L LEVEL

Analyte	Wavelength, (nm)	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--

TABLE 13.3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 13.2

Analytes	(mg/L)	Interferents	(mg/L)
Ca	1	Al	1,000
Fe	1	Ca	1,000
Mg	1	Cr	200
Mn	1	Cu	200
		Fe	1,000
		Mg	1,000
		Nn	200
		Ni	200
		Ti	200
		V	200

13.3.4.1 Serial Dilution--If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

13.3.4.2 Spiked Addition--The recovery of a spiked addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

CAUTION: The standard addition technique does not detect coincident spectral overlap. If overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

13.3.4.3 Comparison with Alternate Method of Analysis--When a new sample matrix is being investigated, a comparison test may be performed with other analytical techniques, such as atomic absorption spectrometry or other approved methodology.

13.3.4.4 Wavelength Scanning of Analyte Line Region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

13.4 Safety

Generally, the calibration standards, sample types, and most reagents pose no hazard to the analyst. Protective clothing (lab coats and gloves) and safety glasses should be worn when handling concentrated acids.

Follow the instrument safety recommendations provided by the manufacturer for the operation of the ICP.

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (NIOSH, 1977; OSHA, 1976; ACS, 1979) for the information of the analyst.

13.5 Apparatus and Equipment

Inductively Coupled Plasma-Atomic Emission Spectrometer

Computer-controlled ICP emission spectrometer with background correction capability shall be used.

13.6 Reagents and Consumable Materials

13.6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent (e.g., Baker Ultrex grade or SeaStar Ultrapure grade).

13.6.1.1 Hydrochloric Acid, concentrated (sp gr 1.19)

13.6.1.2 Hydrochloric Acid (50 percent v/v)--Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L.

13.6.1.3 Nitric Acid, concentrated (sp gr 1.41)

13.6.1.4 Nitric Acid (50 percent v/v)--Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 L.

13.6.2 Water

Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

13.6.3 Standard Stock Solutions

Solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

13.6.3.1 Calcium Stock Standard Solution (100 mg/L)--Suspend 0.2498 g $CaCO_3$ (dried at 180°C for 1 hour before weighing) in water and dissolve cautiously with a minimum amount of 50 percent HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

13.6.3.2 Iron Stock Standard Solution (100 mg/L)--Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL 50 percent HCl and 2 mL concentrated HNO_3. Cool, add an additional 5 mL concentrated HNO_3, and dilute to 1,000 mL with water.

13.6.3.3 Magnesium Stock Standard Solution (100 mg/L)--Dissolve 0.1658 g MgO in a minimum amount of 50 percent HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

13.6.3.4 Manganese Stock Standard Solution (100 mg/L)--Dissolve 0.1000 g of manganese metal in an acid mixture consisting of 10 mL concentrated HCl and 1 mL concentrated HNO_3, and dilute to 1,000 mL with water.

13.7 Sample Handling, Preservation, and Storage

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Labware should be thoroughly washed as described in Appendix A.

Samples are collected and processed in the field. A portion (aliquot 3) of each sample is filtered and acidified (0.1-mL increments) with nitric acid until the pH <2. The processed samples are then sent to the lab and are analyzed (as is) for dissolved metal (Ca, Fe, Mg, Mn) content.

13.8 Calibration and Standardization

Prepare a calibration blank and a series of dilute calibration standards from the stock solutions to span the expected sample concentration range. Match the acid content of the standards to that of the samples (written on the sample label, ca. 0.2 percent). A multi-element standard may be prepared.

The calibration procedure varies with the various ICPES instruments. Calibrate the ICPES for each analyte following the instrument operating conditions.

13.9 Quality Control

The required QC procedures are described in section 3.4.

13.10 Procedure

13.10.1 Set up instrument as recommended by the manufacturer or as experience dictates. The instrument must be allowed to become thermally stable before beginning (10 to 30 minutes).

13.10.2 Profile and calibrate instrument according to the recommended procedures provided by the instrument manufacturer. Flush the system with the calibration blank between each standard. (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

13.10.3 Begin sample analysis by flushing the system with the calibration blank solution between each sample. Remember to analyze required QC samples.

13.10.4 Dilute and reanalyze any samples with a concentration exceeding the calibration range.

13.11 Calculations

Generally, instruments are calibrated to output sample results directly in concentration units. If not, then a manual calibration curve must be prepared, and sample concentrations must be determined by comparing the sample signal to the calibrated curve.

If dilutions were performed, the appropriate factor must be applied to sample values.

Report results as mg/L for each analyte.

TABLE 13.4. INDUCTIVELY COUPLED PLASMA PRECISION AND ACCURACY DATA[a]

Element	Sample 1 True Value (µg/L)	Sample 1 Mean Reported Value (µg/L)	Sample 1 Mean %RSD	Sample 2 True Value (µg/L)	Sample 2 Mean Reported Value (µg/L)	Sample 2 Mean %RSD	Sample 3 True Value (µg/L)	Sample 3 Mean Reported Value (µg/L)	Sample 3 Mean %RSD
Mn	350	345	2.7	15	15	6.7	100	99	3.3
Fe	600	594	3.0	20	19	15	180	178	6.0

[a]Not all elements were analyzed by all laboratories.
Ca and Mg were not determined.

13.12 Precision and Accuracy

In an EPA round-robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 13.4 lists the true value, the mean reported value, and the mean %RSD (U.S. EPA, 1983).

13.13 References

American Chemical Society, 1979. Safety in Academic Laboratories, 3rd ed. Committee on Chemical Safety, ACS, Washington, D.C.

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Department of Health, Education, and Welfare, 1977. Carcinogens - Working with Carcinogens. No. 77-206. DHEW, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, Ohio.

Fassel, V. A., 1982. Analytical Spectroscopy with Inductively Coupled Plasmas - Present Status and Future Prospects. In: Recent Advances in Analytical Spectroscopy. Pergamon Press, Oxford and New York.

Occupational Safety and Health Administration, 1976. OSHA Safety and Health Standards, General Industry. OSHA 2206 (29 CFR 1910). OSHA.

U.S. Environmental Protection Agency, 1979. Inductively Coupled Plasma - Atomic Emission Spectroscopy - Prominent Lines. EPA-600/4-79-017. U.S. EPA, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometric Method for the Trace Element Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

APPENDIX A

CLEANING OF PLASTICWARE

A-1.0 SAMPLE CONTAINERS

A laboratory supplies clean plastic sample containers (cubitainers, Nalgene bottles, centrifuge tubes) to the field stations. The containers are composed of amber, high-density linear polyethylene, and are of the wide-mouth design. Each stream sample requires one 4-L cubitainer, one 500-mL capacity bottle, two 250-mL capacity bottles, three 125-mL capacity bottles, one 50-mL graduated centrifuge tube with cap, and one 10-mL polypropylene test tube with cap. An equipment list is given in Table 2.1

A-1.1 Cleaning of Plasticware

Plasticware, in keeping with its use, is cleaned by either an acid leaching procedure or water leaching procedure. Each is described below.

A-1.1.1 Cleaning Procedure 1 (Acid Leaching)

All plasticware (with the exceptions in the next paragraph) is rinsed three times with deionized water, three times with 3N HNO_3 (prepared from Baker Instra-Analyzed HNO_3 or equivalent), and six times with deionized water. It is then filled with deionized water and is allowed to stand for 48 hours. Next, it is emptied, is dried in a laminar-flow hood delivering Class 100 air (when dry containers are necessary), and is placed in clean plastic bags (bottles are capped first).

A-1.1.2 Cleaning Procedure 2 (DI Water Leaching)

Plasticware to be used for pH, BNC, ANC, and anion determinations is rinsed three times with deionized water, is filled with deionized water, is allowed to stand for 48 hours, and is then emptied and sealed in clean plastic bags.

A-1.1.3 Quality Control

After the initial cleaning, 5 percent of the containers are checked to ensure that rinsing has been adequate. The check is made by first adding 500 mL (or maximum amount) deionized water to a clean container, sealing the container with a cap or parafilm, and slowly rotating it so that the water touches all surfaces. The specific conductance of the water is then measured. It must be less than 1

µS/cm. If any of the containers fail the check, all of the containers are rerinsed, and 5 percent are retested.

NOTE: The deionized water used in cleaning the plasticware must meet or exceed specifications for ASTM Type I reagent grade Water.

NATIONAL SURFACE WATER SURVEY
FORM 11

SUMMARY OF SAMPLE RESULTS

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

SAMPLE ID:	ALIQUOT ID 1 Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	2 Extr. Al mg/L	3 Cl mg/L	SO_4 mg/L	NO_3 mg/L	SiO_2 mg/L	ISE Total F mg/L
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02												
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NOTE: Approved Data Qualifiers and instructions for their use are listed in Table 3.10.

NSWS Form 11

NATIONAL SURFACE WATER SURVEY
FORM 11

SUMMARY OF SAMPLE RESULTS

LAB NAME _____ · BATCH ID _____ LAB MANAGER'S SIGNATURE _____

SAMPLE ID:	ALIQUOT ID 4 DOC mg/L	4 NH_4 mg/L	5 Measured Eq. pH	5 Measured ANC Init. pH	5 Measured BNC Init. pH	5 BNC µeq/L	5 ANC µeq/L	5 COND. µS/cm	5 Eq. DIC mg/L	5 Init. DIC mg/L	6 Total P mg/L	7 Total Al mg/L
01												
02												
03												
04												
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06												
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NOTE: Approved Data Qualifiers and instructions for their use are listed in Table 3.10.

NSWS Form 11 (Continued)

NATIONAL SURFACE WATER SURVEY
Form 13

ANC AND BNC RESULTS

Lab Name____________________ Batch ID_______________ Sample ID____________
Lab Manager's Signature________________________ Analyst_____________________

RESULTS

[ANC] = ____________________ µeq/L

DATA

C_A = ______________________ eq/L DATE STANDARDIZED ___________________
C_B = ______________________ eq/L DATE STANDARDIZED ___________________

INITIAL SAMPLE VOLUME ____________________ mL
BLANK ANC ______________________

ACID TITRATION

VOLUME HCl (mL)	MEASURED pH'	CALCULATED pH
0.00		
0.00 (with KCl)		

BASE TITRATION

VOLUME NaOH (mL)	MEASURED pH'	CALCULATED pH
0.00		
0.00 (with KCl)		

NATIONAL SURFACE WATER SURVEY
Form 14*

QC DATA FOR ANC
AND BNC ANALYSES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

SAMPLE ID	ANC μeq/L	CO_2-BNC μeq/L	CALCULATED ANC		%D[b]
			RESULT	DIFFERENCE[a]	
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
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28					
29					
30					

*Form not required in data package but recommended for internal QC requirements.

[a]Difference = Calculated ANC-Measured ANC

[b]Refer to Section 4.0.

NATIONAL SURFACE WATER SURVEY
Form 15*

CONDUCTIVITY

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Sample ID	SPECIFIC CONDUCTANCE (µS/cm) Calculated	Measured	%D**	CALCULATED CONDUCTANCE FOR EACH ION µS/cm HCO_3^-	Ca^{+2}	CO_3^{-2}	Cl^-	Mg^{+2}	NO_3^-	K^+	Na^+	SO_4^{-2}	NH_4^+	H^+	OH^-
01															
02															
03															
04															
05															
06															
07															
08															
09															
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30															
Specific Conductance Factors of Ions [(µS/cm at 25°C) per mg/L]				0.715	2.60	2.82	2.14	3.82	1.15	1.84	2.13	1.54	4.13	3.5×10^3 (per mole/L)	1.92×10^5 (per mole/L)

* Form not required in data package but recommended for internal QC requirements

** % Conductance Difference = $\frac{\text{Calculated Cond.} - \text{Measured Cond.}}{\text{Measured Conductance}} \times 100$

NSWS Form 15

NATIONAL SURFACE WATER SURVEY
Form 16*

ANION-CATION BALANCE CALCULATION

LAB NAME _____ BATCH ID _____ LAB MANAGERS SIGNATURE _____

		Ions - (μeq/L)										
Sample ID	% Ion Difference **	Ca^{+2}	Cl^{-}	Mg^{+2}	NO_3^{-}	K^{+}	Na^{+}	SO_4^{-2}	F^{-}	NH_4^{+}	ANC	H^{+}***
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02												
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30												
Factor to Convert mg/L to μeq/L		49.9	28.2	82.3	16.1	25.6	43.5	20.8	52.6	55.4	----	----

* Form not required in data package but recommended for internal QC requirements

** % Ion Difference = $\dfrac{\text{ANC} + \Sigma \text{ Anions} - \Sigma \text{ Cations (except } H^{+})}{\Sigma \text{ Anions} + \Sigma \text{ Cation} + \text{ANC} + 2[H^{+}]} \times 100$

*** $[H^{+}] = (10^{-pH}) \times 10^{6}$

NATIONAL SURFACE WATER SURVEY
Form 17

IC RESOLUTION TEST

LAB NAME _____

BATCH ID _____

LAB MANAGER'S SIGNATURE _____

IC Resolution Test

IC Make and Model: _____

Date: _____

Concentration: SO_4^{2-} _____ µg/mL, NO_3^- _____ µg/mL

Column Back Pressure (at max. of stroke): _____ psi

Flow Rate: _____ mL/min

Column Model: _____ Date of Purchase: _____

Column Manufacturer: _____

Column Serial No: _____

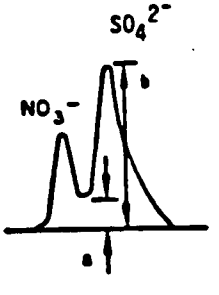
Is precolumn in system ____ Yes ____ No

(a) _____ cm (b) _____ cm

Percentage Resolution: 100 x (1-a/b) _____

The resolution must be greater than 60 percent

Test Chromatogram:



NSWS Form 17

NATIONAL SURFACE WATER SURVEY
Form 18

QUALITY ASSURANCE
(DETECTION LIMITS)

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Units	Contract Required Detection Limit	Instrumental Detection Limit	Date Determined (DD MMM YY)
Ca	mg/L	0.01		
Mg	mg/L	0.01		
K	mg/L	0.01		
Na	mg/L	0.01		
Mn	mg/L	0.01		
Fe	mg/L	0.01		
Total Extractable Al	mg/L	0.005		
Cl	mg/L	0.01		
SO_4	mg/L	0.05		
NO_3	mg/L	0.005		
SiO_2	mg/L	0.05		
Total dissolved F	mg/L	0.005 0.005		
NH_4	mg/L	0.01		
DOC	mg/L	0.1		
Specific Conductance	µS/cm	*		
DIC	mg/L	0.05		
Total dissolved P	mg/L	0.002		
Total Al	mg/L	0.005		

*Report the $\bar{X}$, which must not exceed 0.9 µS/cm, of six (6) nonconsecutive blanks.
Note 1: Indicate instrument for which IDL applies by using the following code letters - F (furnace AA), P (ICP), L (Flame AA). Place the code letter after the IDL value reported.

NATIONAL SURFACE WATER SURVEY
FORM 19

SAMPLE HOLDING TIME SUMMARY

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

DATE* SAMPLED _____ DATE RECEIVED _____

Parameter	Ca	Mg	K	Na	Mn	Fe	Total Extr. Al	Cl	SO_4	NO	SiO_2	ISE Total F^-
Holding Time	28	28	28	28	28	28	7	28	28	7	28	28
Holding Time Plus Date Sampled												
Sample ID:	Date*						Analyzed**					
01												
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*Report these dates as Julian dates (i.e., March 26, 1984 = 4086).
**If parameter was reanalyzed because of QA problems, report the last date analyzed.

NSWS Form 19

NATIONAL SURFACE WATER SURVEY
FORM 19

SAMPLE HOLDING TIME SUMMARY

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

DATE* SAMPLED _____ DATE RECEIVED _____

Parameter	DOC	NH_4	Eq. pH	BNC	ANC	Specific Conductance	Eq. DIC	Init. DIC	Total P	Total Al
Holding Time	14	28	14	14	14	14	14	14	28	28
Holding Time Plus Date Sampled										
Sample ID:	Date*					Analyzed**				
01										
02										
03										
04										
05										
06										
07										
08										
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*Report these dates as Julian dates (i.e., March 26, 1984 = 4086).
**If parameter was reanalyzed because of QA problems, report the last date analyzed.

NSWS Form 19 (Continued)

NATIONAL SURFACE WATER SURVEY
FORM 20

BLANKS AND QCCS

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

Parameter	ALIQUOT ID 1 Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	2 Total Extr.Al mg/L	3 Cl mg/L	SO_4 mg/L	NO_3 mg/L	SiO_2 mg/L	ISE Total F mg/L
Calibration Blank												
Reagent Blank	N	N	N	N	N	N	N	N	N	N		N
DL Theoretical								N	N	N	N	N
QCCS Measured								N	N	N	N	N
Low QCCS True Value												
Low QCCS Upper Control Limit												
Low QCCS Lower Control Limit												
Initial												
Continuing												
Continuing												
Continuing												
Continuing												
Continuing												
Final												
High QCCS True Value												
High QCCS Upper Control Unit												
High QCCS Lower Control Limit												
Initial												
Continuing												
Continuing												
Continuing												
Continuing												
Continuing												
Final												

Note: Approved Data Qualifiers and instruction for their use are listed in Table 3.10.

NSWS Form 20

NATIONAL SURFACE WATER SURVEY
FORM 20

BLANKS AND QCCS

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

	ALIQUOT ID									
	4		5						6	7
			Measured							
Parameter	DOC mg/L	NH_4 mg/L	Eq pH	ANC pH	BNC pH	Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total P mg/L	Total Al mg/L
Calibration Blank			N	N	N					
Reagent Blank	N	N	N	N	N	N	N	N	N	
DL theoretical	N	N	N	N	N	N	N	N		
QCCS measured	N	N	N	N	N	N	N	N		
Low QCCS True Value										
Low QCCS Upper Control Limit										
Low QCCS Lower Control Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Continuing										
Final										
High QCCS True Value										
High QCCS Upper Control Limit										
High QCCS Lower Control Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Continuing										
Final										

Note: Approved Data Qualifiers and instruction for their use are listed in Table 3.10.

NSWS Form 20 (Continued)

NATIONAL SURFACE WATER SURVEY
FORM 21*

DILUTION FACTORS

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

SAMPLE ID:	ALIQUOT ID 1 Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	2 Total Extr. Al mg/L	3 Cl mg/L	SO_4 mg/L	NO_3 mg/L	SiO_2 mg/L	ISE Total F mg/L
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*Form not required in the data package but recommended for QA purposes.
NOTE: Indicate samples ran on higher concentration range by using a check mark for each parameter.

NSWS Form 21

NATIONAL SURFACE WATER SURVEY
FORM 21*

DILUTIONS FACTORS

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

SAMPLE ID:	ALIQUOT ID 4 DOC mg/L	4 NH_4 mg/L	5 Measured Eq. pH	5 Measured ANC Init. pH	5 Measured BNC Init. pH	5 CO_2 BNC µeq/L	5 ANC µeq/L	5 COND. µS/cm	5 Eq. DIC mg/L	5 Init. DIC mg/L	6 Total P mg/L	7 Total Al mg/L
01												
02												
03												
04												
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*Form not required in the data package but recommended for QA purposes.
NOTE: Indicate samples ran on higher concentration range by using a check mark for each parameter.

NSWS Form 21 (Continued)

NATIONAL SUFACE WATER SURVEY
Form 22

DUPLICATES

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

	ALIQUOT ID											
	1						2	3				
Parameter	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr.Al mg/L	Cl mg/L	SO_4 mg/L	NO_3 mg/L	SiO_2 mg/L	ISE Total F mg/L
Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												
Second Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												
Third Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												

Note: Approved Data Qualifiers and instructions for their use are listed in Table 3.10.

NSWS Form 22

NATIONAL SURFACE WATER SURVEY
Form 22

DUPLICATES

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

	ALIQUOT ID											
	4		Measured			5					6	7
Parameter	DOC mg/L	NH_4 mg/L	Eq. pH	ANC Initial pH	BNC Initial pH	CO_2 BNC µeq/L	ANC µeq/L	Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total P mg/L	Total Al mg/L
Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD*												
Second Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD*												
Third Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD*												

*Report absolute difference rather than RSD for pH determinations.
Note: Approved Data Qualifiers and instructions for their use are listed in 3.10.

APPENDIX C

EXAMPLES OF CALCULATIONS REQUIRED FOR ANC AND BNC DETERMINATIONS

C-1.0 HCl STANDARDIZATION (SECTION 4.8.1)

1.00 mL of a 0.01038N Na_2CO_3 plus 40.00 mL CO_2-free deionized water is titrated with HCl titrant. The titration data are given below.

mL HCl added	pH	mL HCl added	pH	mL HCl added	pH
0.00	10.23	0.800	6.37	1.700	3.84
0.100	9.83	0.900	6.03	1.900	3.72
0.200	9.70	1.000	5.59	2.100	3.63
0.300	9.54	1.100	4.91	2.300	3.56
0.400	9.28	1.200	4.48	2.500	3.49
0.500	8.65	1.300	4.26		
0.600	7.20	1.400	4.11		
0.700	6.71	1.500	4.00		

F_{1b} is calculated for the data sets (V, pH) with pH 4-7 by using the equation

$$F_{1b} = (V_s + V)\left[\frac{V_s C}{(V_s + V)}\left(\frac{[H^+]K_1 + 2\,K_1\,K_2}{[H^+]^2 + [H^+]K_1 + K_1\,K_2}\right) + \frac{K_w}{[H^+]} - [H^+]\right]$$

where

V_s = initial sample volume = 41.0 mL
V = volume of HCl added.
C = 1.266×10^{-4} = $(N\ Na_2CO_3)/(2 \times 41)$
$[H^+]$ = 10^{-pH}
K_1 = 4.4463×10^{-7}
K_2 = 4.6881×10^{-11}
K_w = 1.01×10^{-14}

The (V, F_{1b}) values are tabulated below.

V	F_{1b} (x 10^{-3})	V	F_{1b} (x 10^{-3})
0.700	3.57	1.100	-0.34
0.800	2.59	1.200	-1.33
0.900	1.60	1.300	-2.28
1.000	0.64	1.400	-3.26
		1.500	-4.23

The plot of F_{1b} versus V is shown in Figure C-1. The data lie on a straight line and are analyzed by linear regression to obtain the coefficients of the line:

$$F_{1b} = a + bV$$

from the regression,

r = 1.0000
a = 0.01038 ± 0.00001
b = -0.009747 ± 0.000012

Then $V_1 = -a/b = 1.065$ mL

and

$$N_{HCl} = \frac{N\ Na_2CO_3\ V_o}{V_1} = \frac{(0.01038)\ (1.00)}{1.065} = 0.009743\ \text{eq/L}$$

$$V_o = \text{Vol}\ N_{Na_2CO_3}$$

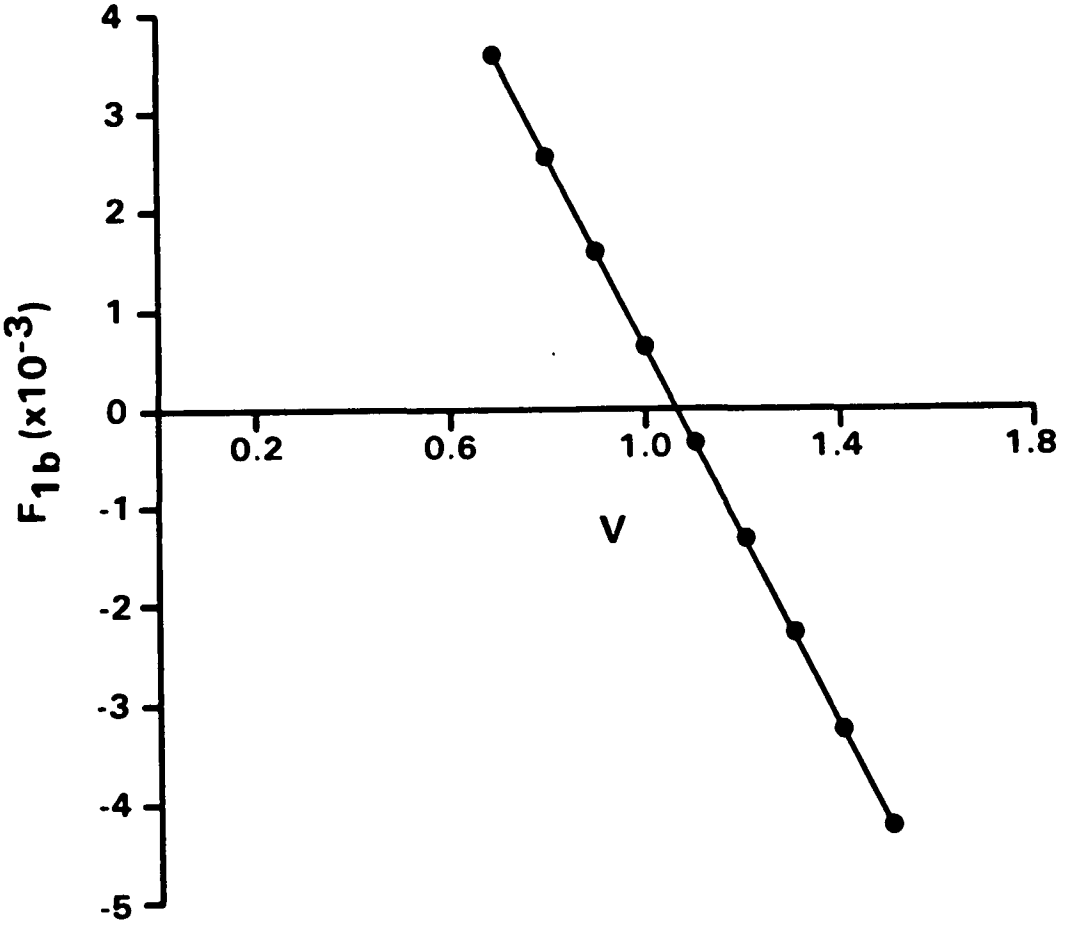

Figure C-1. Plot of F_{1b} versus V for HCl standardization.

C-2.0 NaOH STANDARDIZATION (SECTION 4.8.2)

C-2.1 Initial NaOH Standardization with KHP (Section 4.8.2.1)

5.00 mL of 9.793×10^{-4} N KHP plus 20.0 mL CO_2-free deionized water are titrated with approximately 0.01N NaOH. The titration data and appropriate Gran function values are given in the table below.

Volume NaOH (mL)	pH	$F_{3b}(\times 10^{-3})$
0.000	4.59	
0.050	4.78	
0.100	4.97	3.90
0.150	5.14	3.39
0.200	5.31	2.86
0.250	5.48	2.34
0.300	5.66	1.82
0.350	5.87	1.29
0.400	6.14	0.79
0.450	6.66	0.26
0.500	8.99	-0.25
0.700	9.95	-2.29
0.900	10.23	-4.40
1.100	10.39	
1.300	10.51	

The Gran function F_{3b} is calculated for data with pH 5-10. F_{3b} is calculated by

$$F_{3b} = (V + V_s)\left[\frac{V_s\, C}{(V_s + V)}\left(\frac{([H^+]K_1 + 2[H^+])}{([H^+]^2 + [H^+]K_1 + K_1K_2)}\right) + [H^+] - \frac{Kw}{[H^+]}\right]$$

V = Volume NaOH added
V_s = Initial sample volume = 25.00 mL
C = N KHP/5 = 1.9586×10^{-4}
$[H^+]$ = 10^{-pH}
K_1 = 1.3×10^{-3}
K_2 = 3.9×10^{-6}
K_w = 1.01×10^{-14}

F_{3b} versus V is plotted in Figure C-2. The data lie on a straight line with the equation $F_3 = a + bV$. The coefficients are calculated by using linear regression. From the regression,

r = 1.0000
a = 0.004931 ± 0.000008
b = -0.01036 ± 0.00002

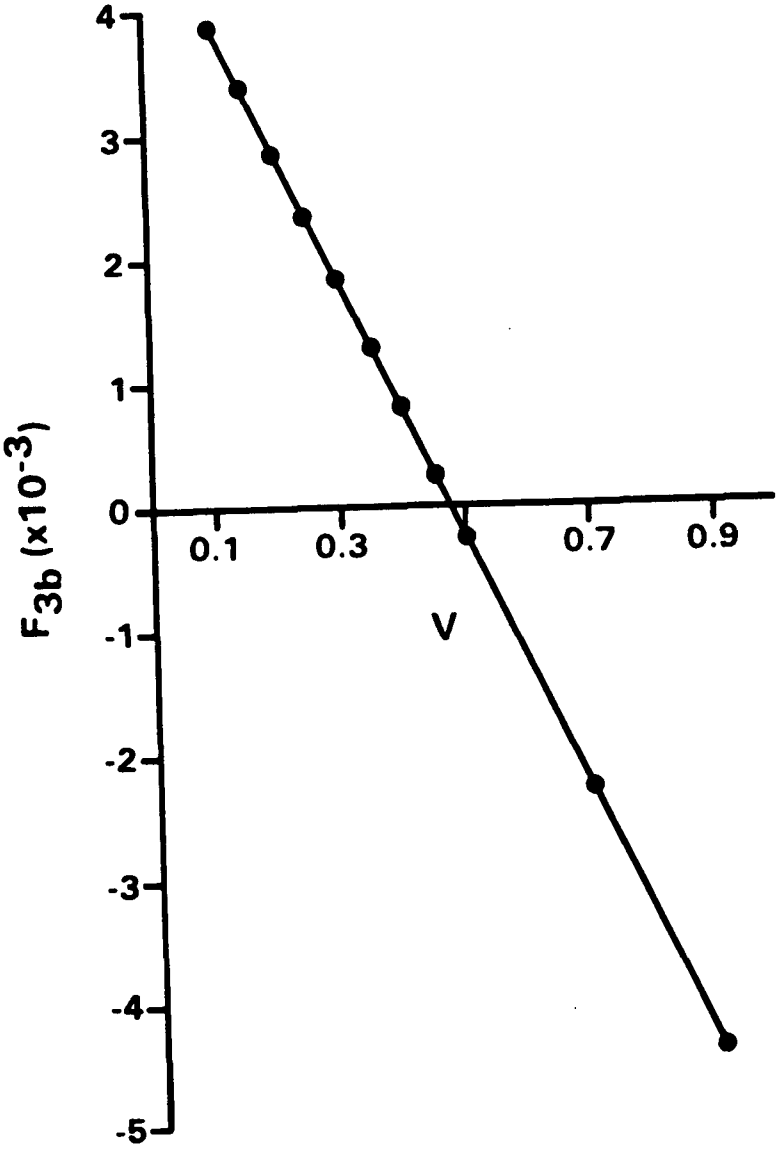

Figure C-2. Plot of F_{3b} versus V for initial NaOH standardization with KHP.

From this V_3 and N_{NaOH} are calculated by

$$V_3 = -a/b = 0.4761 \text{ mL}$$

$$N_{NaOH} = \frac{N_{KHP} \times V_{KHP}}{V_3} = 0.01028 \text{ eq/L}$$

C-2.2 Standardization Check (Section 4.8.2.2)

0.500 mL of 0.00921N NaOH plus 25.0 mL CO_2-free deionized water is titrated with 0.0101N HCl (standardized with Na_2CO_3). The titration data and appropriate Gran function values are given in the table below.

Volume HCl (mL)	pH	F_1 (x 10^{-3})
0.000	10.29	
0.100	10.15	
0.200	10.03	2.75
0.250	9.91	2.09
0.300	9.78	1.55
0.350	9.60	1.03
0.400	9.34	0.57
0.450	8.39	0.064
0.500	4.76	-0.45
0.550	4.44	-0.94
0.600	4.26	-1.43
0.650	4.12	-1.98
0.700	4.04	-2.39
0.800	3.88	

The Gran function F_1 is determined for data in the pH range 4-10. F_1 is calculated by:

$$F_1 = (V + V_s)\left(\frac{K_w}{[H^+]} - [H^+]\right)$$

V = volume of HCl added
V_s = initial sample volume = 25.5 mL
$[H^+]$ = 10^{-pH}
K_w = 1.0×10^{-14}

F_1 versus V is plotted in Figure C-3. The data are on a straight line with the equation $F_1 = a + bV$. The coefficients, determined by linear regression, are

r = 0.9994
a = 0.00465 ± 0.00005
b = -0.01016 ± 0.0001

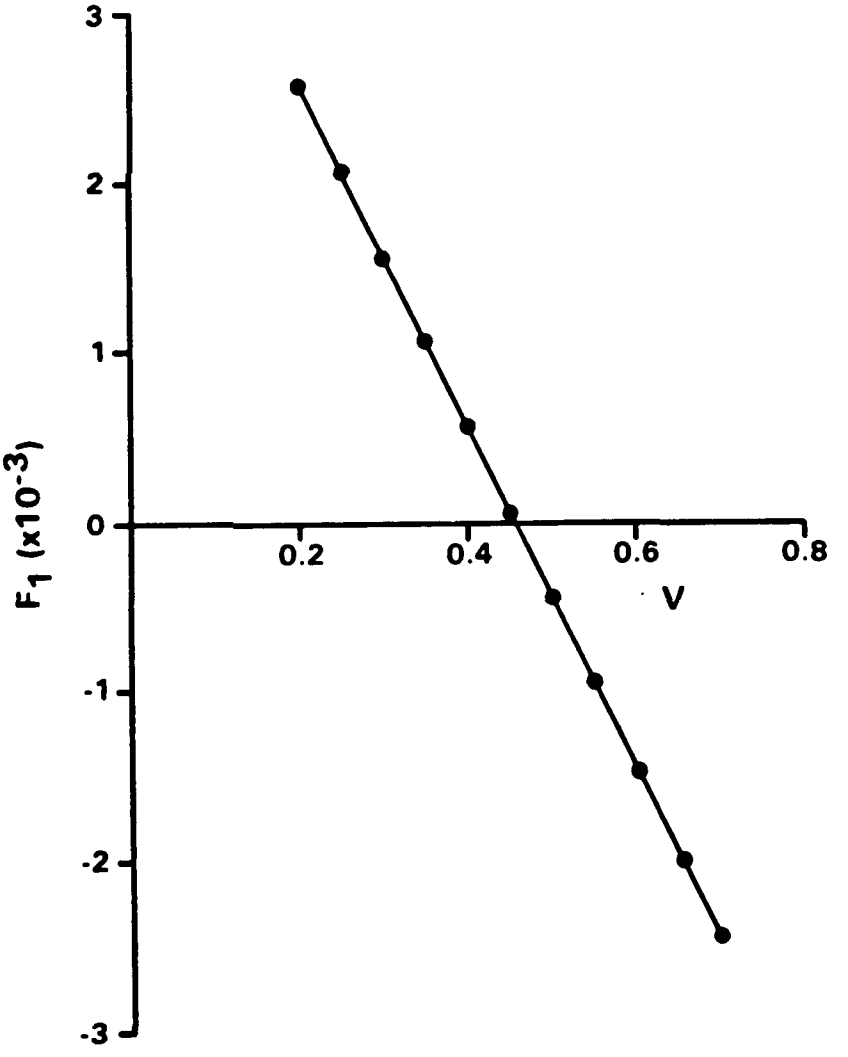

Figure C-3. Plot of F_1 versus V for standardization check-titration of NaOH with HCl.

From these values, V_1 and N_{HCl} are calculated by

$$V_1 = -a/b = 0.4577$$

$$N_{HCl} = \frac{N_{NaOH} \times V_{NaOH}}{V_1} = 0.01006$$

Comparing this value for N_{HCl} with the previously determined value of N_{HCl}, the % difference is

$$\% \text{ difference in } N_{HCl} \text{ values} = \left| \frac{0.01006 - 0.0101}{0.0101} \right| \times 100 = 0.4\%$$

This % difference is acceptable since it is less than 5%.

C-2.3 Routine NaOH Standardization with Standardized HCl (Section 4.8.2.3)

1.000 mL of an approximately 0.01N NaOH solution plus 25.00 mL of CO_2-free deionized water is titrated with 0.009830N HCl. The titration data are given below.

mL HCl added	pH	mL HCl added	pH	mL HCl added	pH
0.00	10.44	0.750	5.35	1.200	3.78
0.200	10.30	0.800	4.65	1.400	3.62
0.400	10.13	0.850	4.37		
0.600	9.71	0.900	4.22		
0.650	9.51	1.000	4.02		
0.700	9.19	1.100	3.88		

F_1 is calculated for each data pair (V, pH) with a pH 4-10 by using the equation

$$F_1 = (V_s + V)\left(\frac{K_w}{[H^+]} - [H^+]\right)$$

where

V_s = initial sample volume = 26.00 mL
V = volume of HCl added.
$[H^+] = 10^{-pH}$
$K_w = 1.0 \times 10^{-14}$

The new data pairs (V, F_1) are tabulated below.

V	F_1 (x 10^{-3})	V	F_1 (x 10^{-3})
0.400	3.56	0.850	-1.14
0.600	1.36	0.900	-1.62
0.650	0.86	1.000	-2.58
0.700	0.41	1.100	-3.57
0.750	-0.12		
0.800	-0.60		

A plot of F_1 versus V is shown in Figure C-4. The data sets corresponding to volumes from V = 0.40 to V = 1.10 lie on a straight line with the equation

$$F_1 = a + bV$$

The coefficients are obtained by linear regression. The results are

r = 0.9996
a = 0.007488 ± 0.00008
b = -0.0101 ± 0.0001

From these results,

$V_1 = -a/b = 0.741$

$$N_{NaOH} = \frac{N_{HCl} \times V_1}{V_{NaOH}} = \frac{(0.009830)\ (0.741)}{1.000} = 0.00728$$

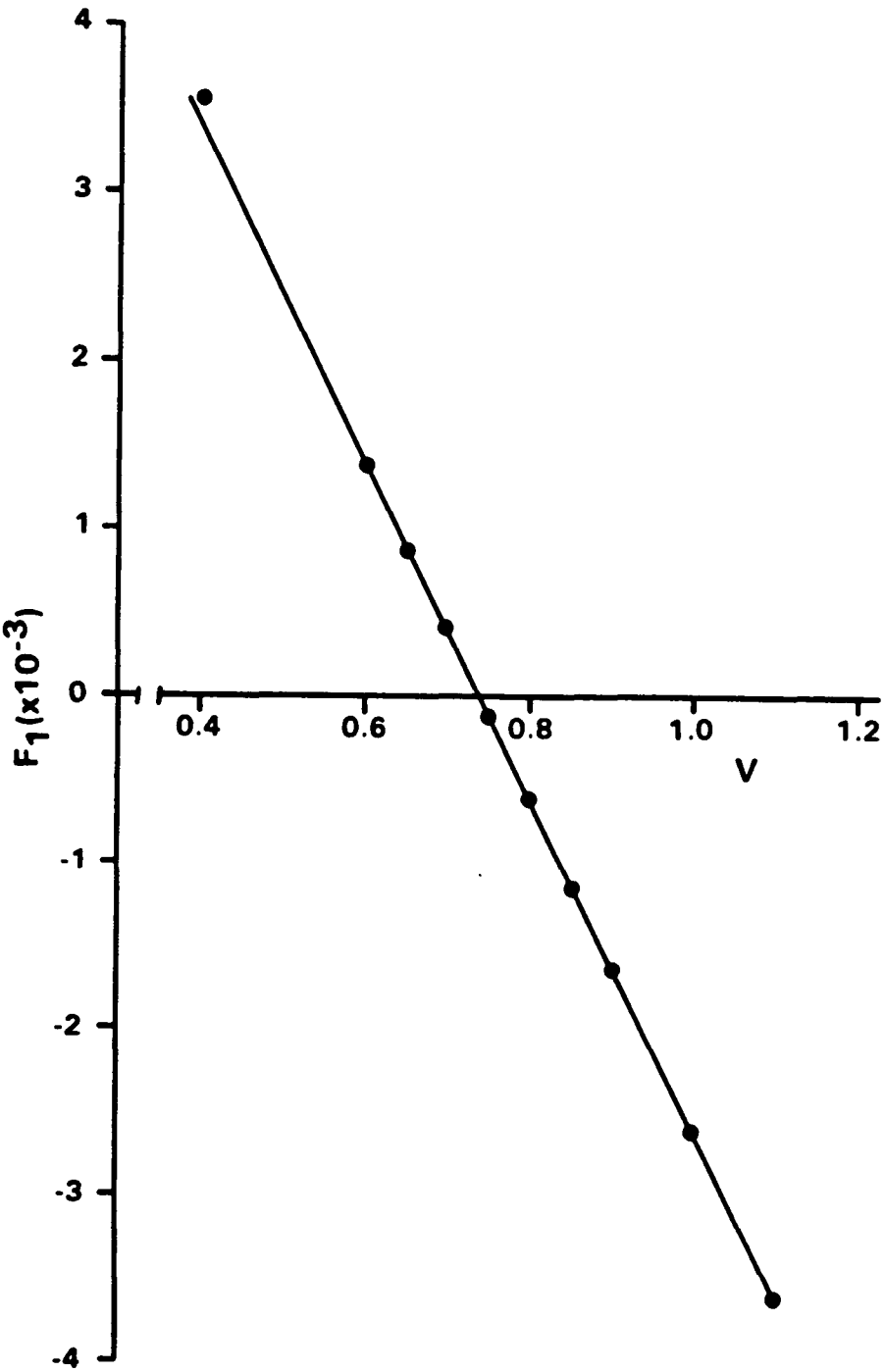

Figure C-4. Plot of F_1 versus V for routine NaOH standardization.

C-3.0 ELECTRODE CALIBRATION (SECTION 4.8.3)

This section describes the electrode calibration procedure. The tables below (A and B) tabulate both the titration data (V and pH), the calculated pH values (pH*), and the coefficients for the line pH = a + b pH*.

TABLE A. ACID TITRATION

V_s = 50.50 mL N_{HCl} = 0.00983

Volume HCl (mL)	pH	pH*	Volume HCl (mL)	pH	pH*
0.000	5.87	---	0.450	4.05	4.06
0.025	5.25	5.31	0.500	4.00	4.02
0.050	4.97	5.01	0.600	3.92	3.94
0.100	4.68	4.71	0.800	3.80	3.81
0.150	4.51	4.54	1.000	3.71	3.72
0.200	4.38	4.41	1.200	3.64	3.64
0.250	4.29	4.31	1.500	3.55	3.55
0.300	4.22	4.24	1.700	3.50	3.50
0.350	4.15	4.17	2.000	3.43	3.43
0.400	4.10	4.11			

r = 1.00 a = 0.10 ± 0.01 b = 0.971 ± 0.002

TABLE B. BASE TITRATION

V_s = 40.4 mL N_{NaOH} = 0.00804

Volume HCl (mL)	pH	pH*	Volume HCl (mL)	pH	pH*
0.000	6.66	---	0.820	10.18	10.20
0.050	9.03	9.00	0.940	10.25	10.26
0.200	9.55	9.60	1.080	10.31	10.32
0.300	9.66	9.77	1.200	10.36	10.37
0.400	9.75	9.90	1.300	10.40	10.40
0.500	9.90	9.99	1.400	10.43	10.43
0.600	10.00	10.07	1.500	10.47	10.46

r = 0.99 a = 0.08 ± 0.27 b = 0.99 ± 0.03

The data in Tables A and B are plotted in Figure C-5. Except for two points in the base titration (at V = 0.3 and 0.4), the data lie on a straight line. (The lines calculated for each titration are essentially coincident as indicated by their coefficients.) Excluding these two points, the data are fit to the line with the equation pH = a + b pH*. The coefficients of the line (obtained by linear regression) are

r = 1.0000
a = -0.014 ± 0.0011
b = 0.999 ± 0.002

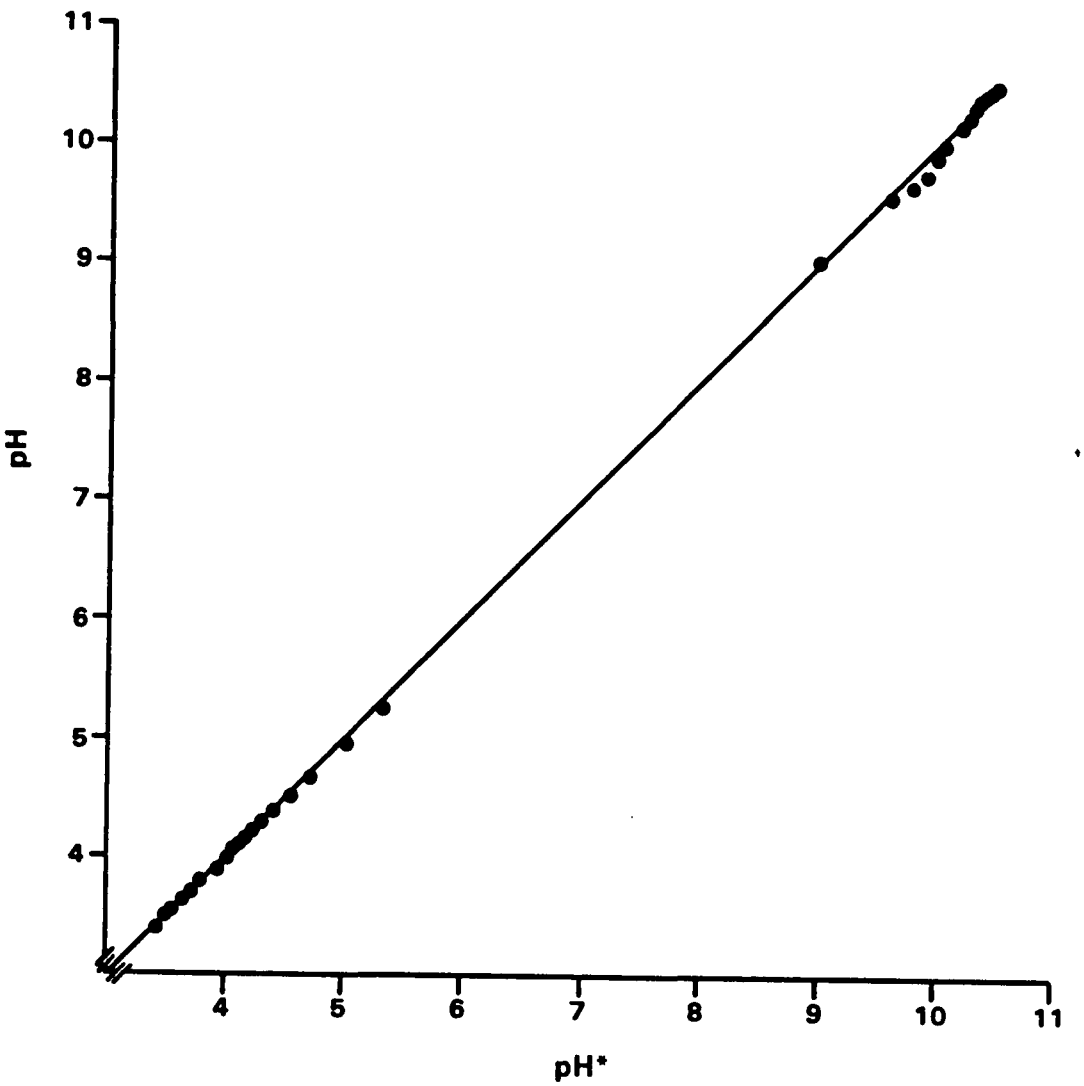

Figure C-5. Plot of pH versus pH* for electrode calibration.

C-4.0 BLANK ANALYSIS - ANC DETERMINATION (SECTION 4.9.2)

This section describes the determination of ANC in a blank solution. The blank is prepared by adding 0.40 mL of 0.10M NaCl to 40.00 mL deionized water. It is titrated with 0.00983N HCl. The titration data are given below (both measured and calculated pH* values are included).

Volume HCl (mL)	pH	pH*	F_1	Volume HCl (mL)	pH	pH*	F_1
0.000	5.84	5.85		0.500	3.91	3.91	0.00503
0.080	4.69	4.70		0.600	3.84	3.84	0.00593
0.120	4.52	4.53		1.700	3.77	3.77	0.00698
0.200	4.31	4.32	0.00194	1.000	3.62	3.62	0.00993
0.300	4.14	4.14	0.00295	1.200	3.55	3.55	0.0117
0.400	4.01	4.02	0.00390	1.500	3.45	3.45	0.0149

The Gran function F_1 ($F_1 = (V_s + V)\,[H^+]$) is calculated for pH* value less than 4.5, and the values are included in the table.

F_1 versus V is plotted in Figure C-6. The data are linear and fit the line $F_1 = a + bV$ by using linear regression. The resulting coefficients are:

$r = 0.9998$
$a = (-0.70 \pm 5.6) \times 10^{-5}$
$b = 0.00989 \pm 0.00007$

From this,

$$V_1 = -a/b = 7.05 \times 10^{-4} \text{ mL}$$

$$[\text{ANC}] = \frac{V_1 C_{HCl}}{V_o} = 1.7 \times 10^{-7} \frac{\text{eq}}{\text{L}} = 0.17 \text{ µeq/L}$$

V_o = blank volume = 40.4 mL

This value for [ANC] is acceptable.

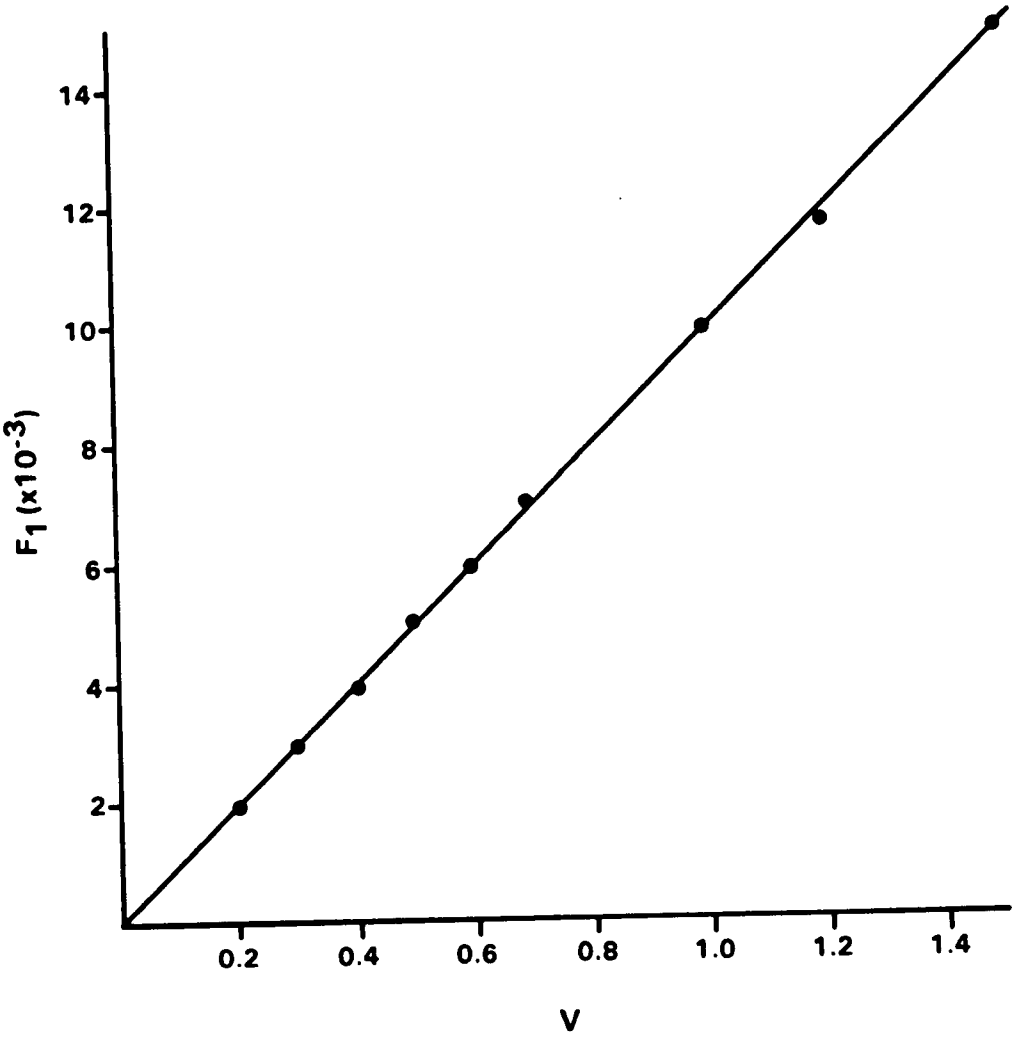

Figure C-6. Plot of F_1 versus V for ANC determination of blank.

C-5.0 SAMPLE ANALYSIS

C-5.1 Titration Data

A sample was titrated as described in section 4.10. The titration data are given below. Also included are values for the calculated pH (pH*).

Acid Titration

V_{sa} = 40.00 mL V_{salt} = 0.40 mL
C_a = 0.00983 eq/L

V_a	pH	pH*	V_a	pH	pH*
0.000	5.10	5.11	0.460	3.99	3.99
0.040	4.89	4.90	0.550	3.91	3.91
0.080	4.71	4.72	0.650	3.84	3.84
0.120	4.56	4.57	0.750	3.77	3.77
0.140	4.50	4.51	0.900	3.69	3.69
0.160	4.44	4.44	1.100	3.61	3.61
0.260	4.24	4.24	1.400	3.50	3.50
0.280	4.21	4.21	1.700	3.42	3.42
0.380	4.08	4.08			

Base Titration

V_{sb} = 40.00 mL V_{salt} = 0.40 mL
C_b = 0.00702 eq/L

V_b	pH	pH*	V_b	pH	pH*
0.00	5.08	5.09	0.425	8.30	8.32
0.015	5.13	5.14	0.470	8.66	8.68
0.030	5.26	5.27	0.500	8.85	8.87
0.050	5.35	5.36	0.540	9.01	9.03
0.080	5.57	5.58	0.560	9.10	9.12
0.120	5.78	5.79	0.600	9.21	9.23
0.160	6.06	6.07	0.660	9.35	9.37
0.200	6.30	6.31	0.700	9.44	9.47
0.240	6.65	6.66	0.780	9.57	9.60
0.280	6.98	7.00	0.900	9.72	9.75
0.320	7.29	7.31	1.000	9.83	9.86
0.340	7.46	7.48	1.100	9.92	9.95
0.360	7.62	7.64	1.405	10.12	10.15

V_b	pH	pH*	V_b	pH	pH*
0.380	7.83	7.85	1.700	10.26	10.29
0.400	8.03	8.05	2.200	10.43	10.43
			2.500	10.51	10.54

C-5.2 Initial Estimate of V_1 (Section 4.11.1)

The Gran function F_{1a} is calculated for each data pair from the acid titration with a pH* <4. The values are given in the table below.

V_a	$F_{1a}(\times 10^{-3})^*$	V_a	$F_{1a}(\times 10^{-3})^*$
0.460	4.18	0.900	8.43
0.550	5.04	1.100	10.2
0.650	5.93	1.400	13.2
0.750	6.99	1.700	16.0

*$F_{1a} = (V_a + V_s)\,[H^+]$

F_{1a} versus V_a is plotted in Figure C-7. A regression of F_{1a} on V_a is performed to fit the data to the line $F_{1a} = a + bV$. The resulting coefficients are:

$r = 0.9999$
$a = -0.00014 \pm 0.000031$
$b = 0.00948 \pm 0.000038$

From this, the initial estimate of V_1 is calculated by

$$V_1 = -a/b = 0.0148 \text{ mL}$$

Since V_1 >0 and the initial sample pH* <7.6, calculation procedure B (Section 4.11.3) is used to determine the ANC and BNC of the sample.

C-5.3 Initial Estimates of V_2, ANC, BNC, and C (Section 4.11.3.1)

From the base titration data, V_2 is estimated to be 0.40 mL (the first point with a pH* <8.2). Now that initial estimates of V_1 and V_2 have been obtained, estimates of ANC, BNC, and C can be calculated.

$$ANC = \frac{V_1\, C_a}{V_{sa}} = 3.6 \times 10^{-6} \text{ eq/L}$$

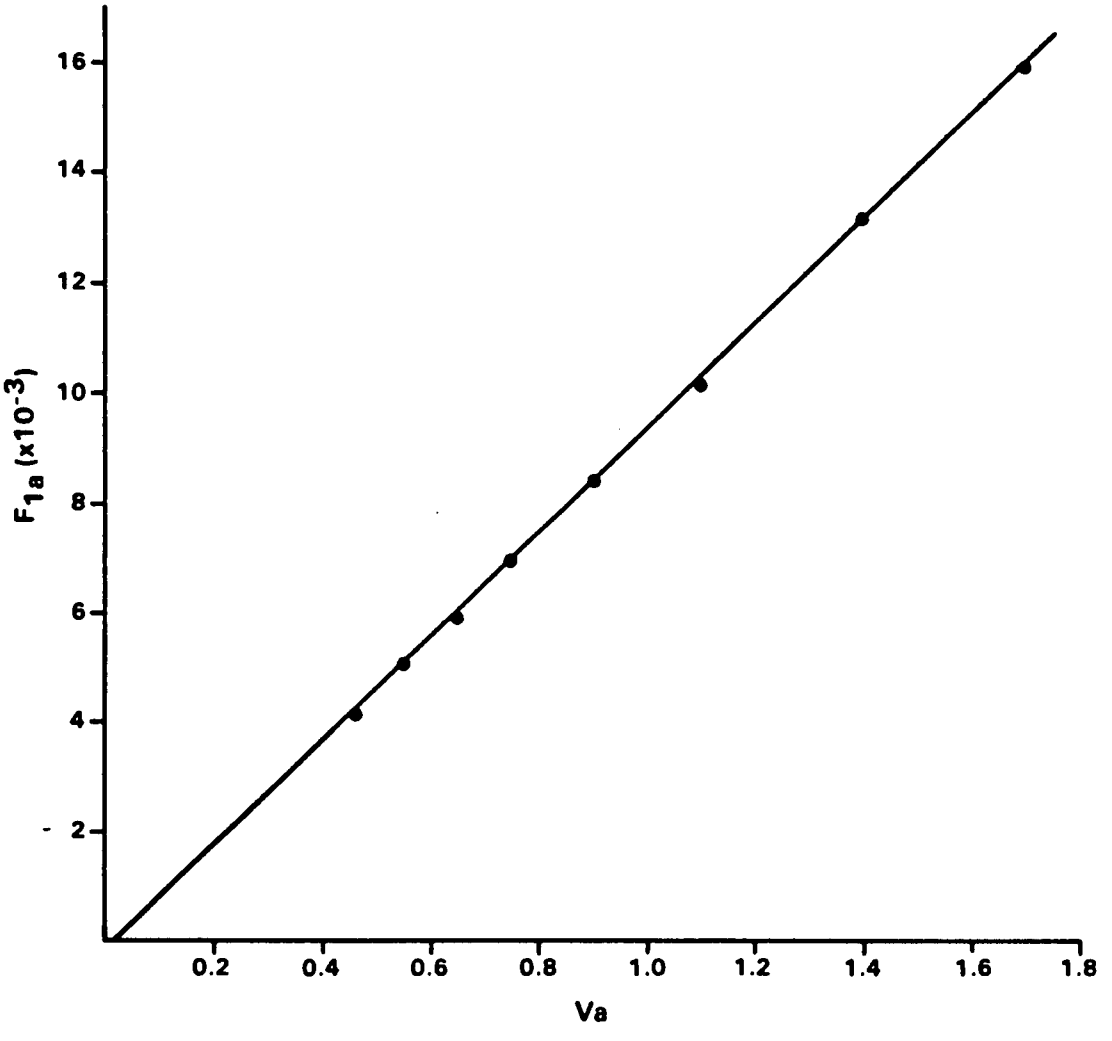

Figure C-7. Plot of F_{1a} versus V_a for initial determination of V_1.

$$BNC = \frac{V_2\ C_b}{V_{sb}} = 7.02 \times 10^{-5}\ eq/L$$

$$C = ANC + BNC = 7.38 \times 10^{-5}\ eq/L$$

C-5.4 Refined Estimates of V_1 and V_2

The Gran function F_{1c} (Equation 1 in 4.11.1.3) is calculated for acid titration data with volumes across the current estimate of V_1. The values are given below.

V_a	$F_{1c}(x10^{-4})$	V_a	$F_{1c}(x10^{-4})$
0.000	-1.68	0.160	-14.4
0.040	-4.10	0.260	-23.2
0.080	-7.05	0.280	-24.9
0.120	-10.4	0.380	-33.8
0.140	-12.1		

F_{1c} versus V_a is plotted in Figure C-8. A regression of F_{1b} on V_a is performed. The regression results are

r = 0.999
a = -0.00006 ± 0.00003
b = -0.00864 ± 0.00016

A new estimate of V_1 is

$$V_1 = -a/b = -0.007\ mL$$

Next the Gran function F_{2c} (Equation 2, section 4.11.1.3) is calculated from data sets from the base titration with volumes across the current estimate of V_2. The values are given below.

V_b	$F_{2c}(x\ 10^{-4})$	V_b	$F_{2c}(x\ 10^{-4})$
0.340	1.99	0.470	-2.60
0.360	1.28	0.500	-4.14
0.380	.555	0.540	-6.03
0.400	-0.031	0.560	-7.43
0.425	-.868	0.600	-9.55

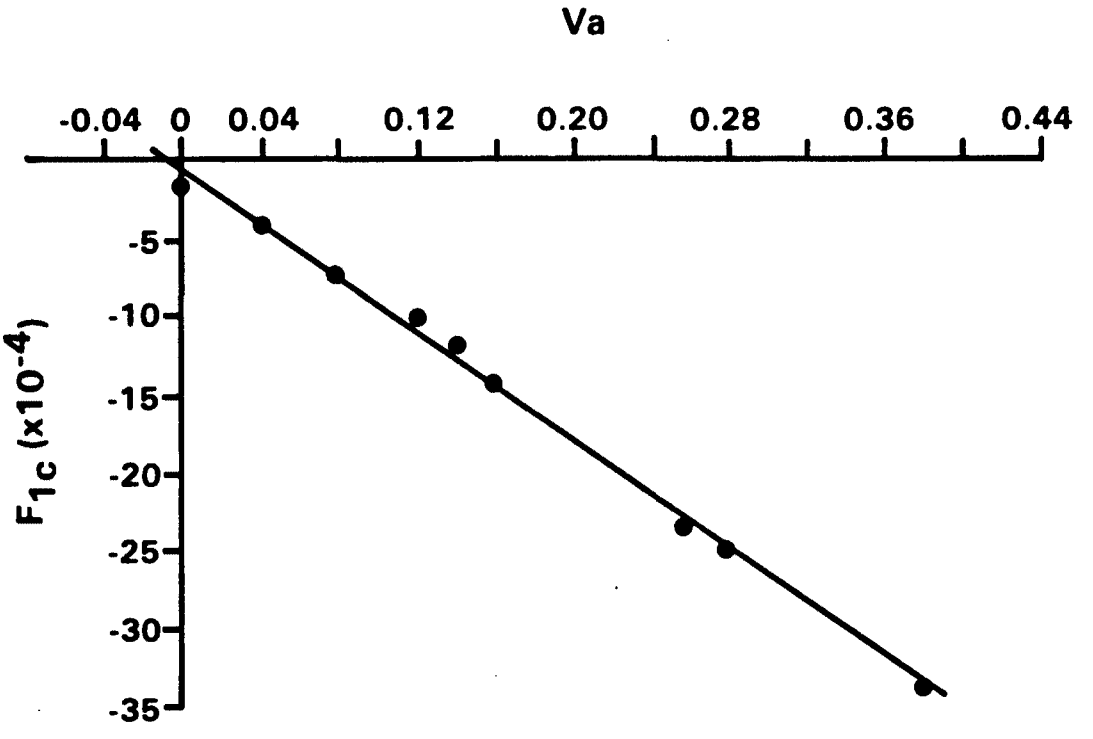

Figure C-8. Plot of F_{1c} versus V_a for V_1 determination.

F_{2c} versus V_b is plotted in Figure C-9. A regression of F_{2c} on V_b is performed. (Data with V_b >0.5 are not used in the regression.) The regression results are

$$r = 0.999$$
$$a = 0.00138 \pm 0.00003$$
$$b = -0.00348 \pm 0.00007$$

A new estimate of V_2 is

$$V_2 = -a/b = 0.397 \text{ mL}$$

C-5.5 New Estimates of ANC, BNC, and C

From the new estimates of V_1 and V_2, new estimates of ANC, BNC, and C are calculated.

$$ANC^* = \frac{V_1 C_a}{V_{sa}} = -1.7 \times 10^{-6} \text{ eq/L}$$

$$BNC^* = \frac{V_2 C_b}{V_{sb}} = 6.97 \times 10^{-5} \text{ eq/L}$$

$$C^* = ANC + BNC = 6.80 \times 10^{-5} \text{ eq/L}$$

C-5.6 Comparison of Latest Two Estimates of Total Carbonate

$$\left|\frac{C - C^*}{C + C^*}\right| = 0.041 > 0.001$$

Since C and C* do not agree, a new C is calculated from their average:

$$C(new) = (C + C^*)/2 = 7.09 \times 10^{-5} \text{ eq/L}$$

The calculations in 5.4 and 5.6 are repeated until successive iterations yield total carbonate values which meet the above criteria. The results from each iteration (including those already given) are given below.

Iteration	V_1(mL)	V_2(mL)	ANC (μeq/L)	BNC (μeq/L)	C (μeq/L)	$\left\|\frac{C - C^*}{C + C^*}\right\|$	New C (μeq/L)
1	0.0148	0.400	3.6	70.2	73.8	-	-
2	-0.007	0.397	-1.7	69.7	68.0	0.042	70.9
3	-0.0070	0.397	-1.7	69.7	68.0	0.021	69.4
4	-0.0076	0.397	-1.9	69.7	67.8	0.012	68.6
5	-0.0077	0.396	-1.9	69.5	67.6	0.007	-

The final values for ANC and BNC are reported on Form 11.

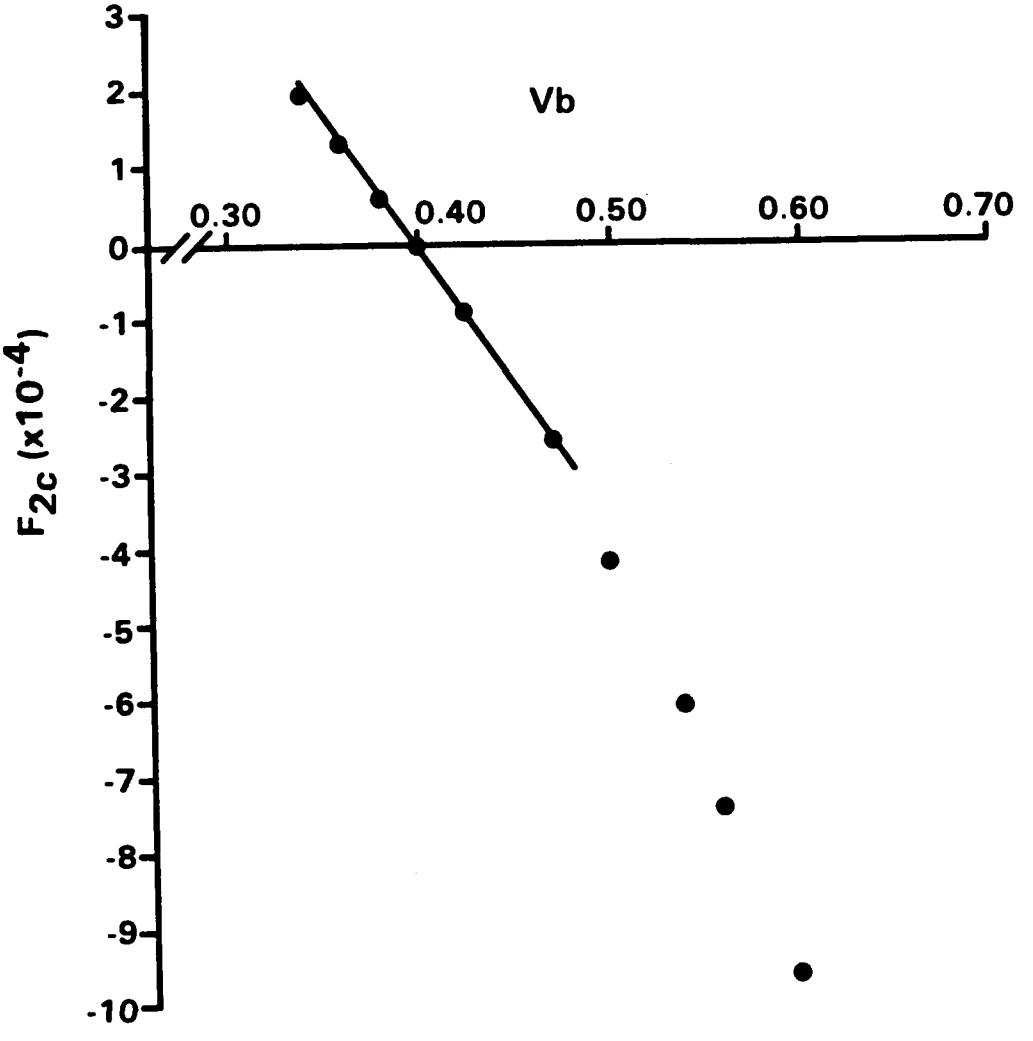

Figure C-9. Plot of F_{2c} versus V_b for V_2 determination.

C-6.0 QUALITY CONTROL CALCULATIONS

Examples of the QC calculations are described in this section.

C-6.1 Comparison of Calculated ANC and Measured ANC (Section 4.9.6)

For the sample analyzed in section C-5, the following data were obtained.

initial pH = 5.09 air-equilibrated pH = 5.06
DIC = 0.59 mg/L air-equilibrated DIC = 0.36

From these data, the calculated ANC values are computed by using the equation:

$$[ANC]_c = \left[\frac{DIC}{12011}\left(\frac{[H^+]K_1 + 2K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}\right) + \frac{Kw}{[H^+]}\right] - [H^+] \times 10^6$$

The results are:

$$[ANC]_{C1} = -5.7\ \mu eq/L \qquad [ANC]_{C2} = -7.3\ \mu eq/L$$

Then:

$$|[ANC]_{C1} - [ANC]_{C2}| = 1.6\ \mu eq/L < 15\ \mu eq/L$$

Since $[ANC]_{C1}$ and $[ANC]_{C2}$ are in agreement, their average value is used for comparison to the measured value.

$$[ANC]_{C\text{-}avg} = -6.5\ \mu eq/L \qquad ANC = -1.9\ \mu eq/L$$

$$D = |ANC_C - ANC| = 4.6\ \mu eq/L < 15\ \mu eq/L$$

The calculated and measured ANC values agree, and this backs up the assumption of a carbonate system.

C-6.2 Comparison of Calculated and Measured BNC (Section 4.9.7)

For the sample analyzed in section C-5, the following data were obtained.

initial pH = 5.09

DIC = 0.59 mg/L

BNC = 69.0 μeq/L

From these data, the BNC is computed by using the equation:

$$[BNC]_c = \left[\frac{DIC}{12011}\left(\frac{[H^+]^2 - K_1 K_2}{[H^+]^2 + [H^+]K_1 + K_1 K_2}\right) + [H^+] - \frac{K_w}{[H^+]}\right] \times 10^6$$

The result is:

$$[BNC]_c = 54.8 \text{ μeq/L}$$

This value is compared to the measured value.

$$D = [BNC]_c - BNC = -14.2 \text{ μeq/L} < -10 \text{ μeq/L}$$

Although borderline, this value of D is indicative of other protolytes in the system which are contributing to the measured BNC. This might be expected since the sample also contains 3.2 mg/L DOC.

C-6.3 *Comparison of Calculated Total Carbonate and Measured Total Carbonate (Section 4.9.8)*

For the sample analyzed in section C-5, the following data were obtained.

initial pH = 5.09 BNC = 69.0 μeq/L = 69.0 μmole/L
DIC = 0.59 mg/L ANC = -1.9 μeq/L = -1.9 μmole/L

From the DIC value, the total carbonate is calculated.

$$C_c = 83.26 \times DIC = 49.1 \text{ μmole/L}$$

This calculated value is then compared to the measured value.

$$D = C_c - (ANC + BNC) = -18.0 \text{ μmole/L} < -10 \text{ μmole/L}$$

Although borderline, this value of D is indicative of other protolytes in the system. This might be expected since the sample also contains 3.2 mg/L DOC. Notice that the same conclusion was reached in the BNC comparison.

In general, noncarbonate protolytes are significant (i.e., contribute significantly to the total protolyte concentration) when they are indicated by one (or both) of the individual comparisons (ANC and BNC comparisons) and the total carbonate comparison.