EPA/600/8-87/020
August 1987

Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey

by

K.A. Cappo, L.J. Blume, G.A. Raab, J.K. Bartz, and J.L. Engels

A Contribution to the
National Acid Precipitation Assessment Program

U.S. Environmental Protection Agency
Region 5, Library (5PL-16)
230 S. Dearborn Street, Room 1670
Chicago, IL 60604

U.S. Environmental Protection Agency
Office of Modeling, Monitoring Systems, and Quality Assurance
Office of Ecological Processes and Effects Research
Office of Research and Development
Washington, D.C. 20460

Environmental Monitoring Systems Laboratory, Las Vegas, Nevada 89193
Environmental Research Laboratory, Corvallis, Oregon 97333

Notice

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under Contract Number 68-03-3249 to Lockheed Engineering and Management Services Company, Inc. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an Agency document.

Mention of trade names or commercial products is for illustration purposes and does not constitute endorsement or recommendation for use.

This document is one volume of a set which fully describes the Direct/Delayed Response Project, Northeast and Southeast soil surveys. The complete document set includes the major data report, quality assurance plan, analytical methods manual, field operations reports, and quality assurance reports. Similar sets are being produced for each Aquatic Effects Research Program component project. Colored covers, artwork, and the use of the project name in the document title serve to identify each companion document. The proper citation of this document remains:

Cappo, K. A., L. J. Blume, G. A. Raab, J. K. Bartz, and J. L. Engels. 1987. *Analytical Methods Manual for Direct/Delayed Response Project Soil Survey.* EPA/600/8-87/020. U.S. Environmental Protection Agency, Office of Research and Development, Las Vegas, Nevada. 318 pp.

Abstract

The U.S. Environmental Protection Agency, in conjunction with the National Acid Precipitation Assessment Program, has designed and implemented a research program to predict the long-term response of watersheds and surface waters in the United States to acidic deposition. On the basis of this research, each watershed system studied will be classified according to the time scale in which it will reach an acidic steady state, assuming current levels of acidic deposition.

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 throughout the survey. For these reasons, the same detailed analytical methodology must be available to and must be used by all analysts participating in the study.

This manual specifies the analytical methods and internal quality control used to process and analyze samples for the Direct/Delayed Response Project Soil Survey. The determinations and methods described are the following:

1. Air-dry moisture content	Gravimetric
2. Particle size analysis	Sieve/pipet/gravimetric
3. pH (in deionized water) 0.01 M $CaCl_2$ 0.002 M $CaCl_2$	Combination electrode/millivoltmeter
4. Total C, Total N, Total S	Elemental analyzer
5. Inorganic C	Coulometric
6. Cation exchange capacity (using NH_4OAc and NH_4Cl saturating solutions)	Autotitration or flow injection analyzer
7. Exchangeable Ca, Mg, and Na in NH_4OAc, NH_4Cl, and $CaCl_2$	Flame atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy (or flame atomic emission spectroscopy for Na only)
8. Exchangeable K in NH_4OAc, NH_4Cl, and $CaCl_2$	Flame atomic absorption spectroscopy or flame atomic emission spectroscopy
9. Fe exchangeable in $CaCl_2$; extractable in pyrophosphate, acid-oxalate and citrate-dithionite	Flame atomic absorption spectroscopy or inductively coupled plasma atomic emission spectroscopy
10. Al extractable in pyrophosphate, acid-oxalate, and citrate-dithionite	Flame atomic absorption spectroscopy or inductively coupled plasma atomic emission spectroscopy
11. Al exchangeable in $CaCl_2$ and KCl	Inductively coupled plasma atomic emission spectroscopy
12. Nitrate (NO_3^-) water extractable	Ion chromatography

Abstract *(Continued)*

13. Sulfate (SO_4^{2-}) Water extractable, phosphate extractable, and sulfate adsorption 6-point isotherm	Ion chromatography
14. Exchangeable acidity in $BaCl_2$-Triethanolamine and KCl saturating solutions	Titrimetric
15. Specific surface	Gravimetric

This report was submitted in partial fulfillment of Contract Number 68-03-3249 by Lockheed Engineering and Management Services Company, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

Contents

Section		Page	Revision
1	Introduction	1 of 9	2
	1.1 Project Overview	1 of 9	2
	1.2 Field Activities	3 of 9	2
	1.3 Laboratory Activities	7 of 9	2
	1.4 Quality Assurance/Quality Control	9 of 9	2
	1.5 Data Handling	9 of 9	2
	1.6 References	9 of 9	2
2	Laboratory Operations	1 of 18	2
	2.1 Preparation Laboratory Procedures	1 of 18	2
	2.2 Sample Receipt and Handling at the Analytical Laboratory	1 of 18	2
	2.3 Cleaning Procedures for the Analytical Laboratory	2 of 18	2
	2.3.1 Plasticware to be used for pH, Acidity, Alkalinity, Cation Exchange Capacity (CEC) Titrations, and Anion Determinations	2 of 18	2
	2.3.2 Other Plasticware	2 of 18	2
	2.3.3 Glassware	2 of 18	2
	2.4 Procedure for Washing Filter Pulp	3 of 18	2
	2.5 Sample Analyses by the Analytical Laboratory	3 of 18	2
	2.6 Internal Quality Control Within Each Analytical Method	3 of 18	2
	2.6.1 Initial Calibration	3 of 18	2
	2.6.2 Calibration Blank	12 of 18	2
	2.6.3 Quality Control Calibration Samples (QCCS)	12 of 18	2
	2.6.4 Detection Limit QC Samples	13 of 18	2
	2.6.5 Reagent Blank	13 of 18	2
	2.6.6 Preliminary Sample Analysis	14 of 18	2
	2.6.7 Matrix Spike Analysis	14 of 18	2
	2.6.8 Duplicate Sample Analysis	14 of 18	2
	2.6.9 Ion Chromatography Resolution Test	15 of 18	2
	2.6.10 Continuing Sample Analysis	16 of 18	2
	2.7 Instrumental Detection Limits	16 of 18	2
	2.8 Reagent Blank Correction for Spectrometric and Ion Chromatographic Procedures	16 of 18	2
	2.9 Data Reporting	16 of 18	2
	2.10 Sample Handling for Mineralogical Analyses	16 of 18	2
	2.11 Laboratory Procedures for Mineralogical Analyses	17 of 18	2
	2.12 References	17 of 18	2
3	Moisture Content	1 of 2	2
	3.1 Scope and Application	1 of 2	2
	3.2 Summary of Method	1 of 2	2
	3.3 Interferences	1 of 2	2

Contents *(Continued)*

Section		Page	Revision
	3.4 Safety	1 of 2	2
	3.5 Apparatus and Equipment	1 of 2	2
	3.6 Reagents and Consumable Materials	1 of 2	2
	3.7 Sample Collection, Preservation, and Storage	1 of 2	2
	3.8 Calibration and Standardization	1 of 2	2
	3.9 Quality Control	1 of 2	2
	3.10 Procedure	1 of 2	2
	3.11 Calculations	2 of 2	2
	3.12 Precision and Accuracy	2 of 2	2
	3.13 References	2 of 2	2
4	Particle-Size Analysis	1 of 6	2
	4.1 Scope and Application	1 of 6	2
	4.2 Summary of Method	1 of 6	2
	4.3 Interferences	1 of 6	2
	4.4 Safety	1 of 6	2
	4.5 Apparatus and Equipment	1 of 6	2
	4.6 Reagents and Consumable Materials	2 of 6	2
	4.7 Sample Collection, Preservation, and Storage	2 of 6	2
	4.8 Calibration and Standardization	2 of 6	2
	4.9 Quality Control	2 of 6	2
	4.10 Procedure	2 of 6	2
	4.10.1 Removing Organic Matter	2 of 6	2
	4.10.2 Removing Dissolved Mineral and Organic Components	3 of 6	2
	4.10.3 Dispersing the Sample	3 of 6	2
	4.10.4 Separating Sand from Silt and Clay	3 of 6	2
	4.10.5 Pipetting	3 of 6	2
	4.10.6 Sieving and Weighing the Sand Fractions	5 of 6	2
	4.11 Calculations	6 of 6	2
	4.12 Precision and Accuracy	6 of 6	2
	4.13 References	6 of 6	2
5	Specific-Surface Determination	1 of 3	2
	5.1 Scope and Application	1 of 3	2
	5.2 Summary of Method	1 of 3	2
	5.3 Interference	1 of 3	2
	5.4 Safety	1 of 3	2
	5.5 Apparatus and Equipment	1 of 3	2
	5.6 Reagents and Consumable Materials	1 of 3	2
	5.7 Sample Collection, Preservation, and Storage	2 of 3	2
	5.8 Standardization and Calibration	2 of 3	2
	5.9 Quality Control	2 of 3	2
	5.10 Procedure	2 of 3	2
	5.11 Calculations	3 of 3	2

Contents *(Continued)*

Section		Page	Revision
	5.12 Precision and Accuracy	3 of 3	2
	5.13 References	3 of 3	2
6	pH Determination	1 of 4	2
	6.1 Scope and Application	1 of 4	2
	6.2 Summary of Method	1 of 4	2
	6.3 Interferences	1 of 4	2
	6.4 Safety	1 of 4	2
	6.5 Apparatus and Equipment	1 of 4	2
	6.6 Reagents and Consumable Materials	2 of 4	2
	6.7 Sample Collection, Preservation, and Storage	2 of 4	2
	6.8 Calibration and Standardization	2 of 4	2
	6.9 Quality Control	3 of 4	2
	6.9.1 Quality Control Calibration Sample	3 of 4	2
	6.9.2 Blank Samples	3 of 4	2
	6.9.3 Replicate Samples	3 of 4	2
	6.10 Procedure	3 of 4	2
	6.11 Calculations	5 of 4	2
	6.12 Precision and Accuracy	5 of 4	2
	6.13 References	5 of 4	2
7	Cation Exchange Capacity	1 of 10	2
	7.1 Scope and Application	1 of 10	2
	7.2 Summary of Method	1 of 10	2
	7.3 Interferences	1 of 10	2
	7.4 Safety	1 of 10	2
	7.5 Apparatus and Equipment	1 of 10	2
	7.5.1 Apparatus for Saturation Procedure	2 of 10	2
	7.5.2 Apparatus for Automated Distilled-Titration Analysis	2 of 10	2
	7.5.3 Apparatus for Manual Distillation/Automated Titration Analysis	2 of 10	2
	7.5.4 Apparatus for Ammonium Displacement-Flow Injection Analysis	2 of 10	2
	7.6 Reagents and Consumable Materials	2 of 10	2
	7.6.1 Reagents for Saturation Procedure	2 of 10	2
	7.6.2 Reagents and Consumable Materials for Automated Distillation-Titration Analysis	4 of 10	2
	7.6.3 Reagents and Consumable Materials for Manual Distillation-Automatic Titration Analysis	4 of 10	2
	7.6.4 Reagents and Consumable Materials for Ammonium Displacement-Flow Injection Analysis	5 of 10	2
	7.7 Sample Collection, Preservation, and Storage	5 of 10	2
	7.8 Calibration and Standardization	5 of 10	2
	7.9 Quality Control	6 of 10	2

Contents *(Continued)*

Section		Page	Revision
	7.10 Procedure	6 of 10	2
	7.10.1 Saturation Procedure	6 of 10	2
	7.10.2 Analytical Procedure using Automated Distillation-Titration	6 of 10	2
	7.10.3 Analytical Procedure using Manual Distillation-Automated Titration	6 of 10	2
	7.10.4 Analytical Procedure using Ammonium Displacement-Flow Injection Analysis	7 of 10	2
	7.10.5 NH_{4+} Cl Saturation Procedure	9 of 10	2
	7.11 Calculations	9 of 10	2
	7.11.1 Results for either Distillation-Titration Analytical Procedure (Section 7.10.2 or 7.10.3)	9 of 10	2
	7.11.2 Results from Ammonium Displacement-Flow Injection Analysis Procedure (Section 7.10.4)	9 of 10	2
	7.12 Precision and Accuracy	9 of 10	2
	7.13 References	9 of 10	2
8	Exchangeable Basic Cations	1 of 15	2
	8.1 Scope and Application	1 of 15	2
	8.2 Summary of Method	1 of 15	2
	8.2.1 Atomic Absorption (for Ca^{2+}, Mg^{2+}, K^+, and Na^+)	2 of 15	2
	8.2.2 Inductively Coupled Plasma (for Ca^{2+}, Mg^{2+}, and Na^+)	2 of 15	2
	8.2.3 Flame Photometry (for K^+ and Na^+)	3 of 15	2
	8.3 Interferences	3 of 15	2
	8.3.1 Spectral Interferences	3 of 15	2
	8.3.2 Chemical Interferences	4 of 15	2
	8.3.3 Physical Interferences	4 of 15	2
	8.3.4 Matrix Effects	5 of 15	2
	8.4 Safety	5 of 15	2
	8.5 Apparatus and Equipment	5 of 15	2
	8.5.1 Determinations by Atomic Absorption	5 of 15	2
	8.5.2 Determination by Inductively Coupled Plasma	5 of 15	2
	8.5.3 Determination by Flame Photometry	5 of 15	2
	8.6 Reagents and Consumable Materials	6 of 15	2
	8.6.1 Determination by Atomic Absorption	6 of 15	2
	8.6.2 Determination by Inductively Coupled Plasma	6 of 15	2
	8.6.3 Determination by Flame Photometry	7 of 15	2
	8.7 Sample Handling, Preservation, and Storage	7 of 15	2
	8.8 Calibration and Standardization	8 of 15	2
	8.9 Quality Control	9 of 15	2
	8.10 Procedure	9 of 15	2
	8.10.1 Procedure for Determination by Atomic Absorption	9 of 15	2
	8.10.2 Procedure for Determination by Inductively Coupled Plasma	12 of 15	2
	8.10.3 Procedure for Determination by Flame Photometry	12 of 15	2

Contents *(Continued)*

Section		Page	Revision
	8.11 Calculations	13 of 15	2
	8.11.1 Solution Concentrations	13 of 15	2
	8.11.2 Dilutions	13 of 15	2
	8.11.3 Flame Photometry	13 of 15	2
	8.11.4 Atomic Absorption or Inductively Coupled Plasma	13 of 15	2
	8.12 Precision and Accuracy	14 of 15	2
	8.12.1 Determination by Atomic Absorption	14 of 15	2
	8.12.2 Determination by Inductively Coupled Plasma	14 of 15	2
	8.12.3 Determination by Flame Photometry	14 of 15	2
	8.13 References	14 of 15	2
9	Exchangeable Acidity	1 of 7	2
	9.1 Scope and Application	1 of 7	2
	9.2 Summary of Method	1 of 7	2
	9.3 Interferences	1 of 7	2
	9.4 Safety	1 of 7	2
	9.5 Apparatus and Equipment	1 of 7	2
	9.5.1 General	2 of 7	2
	9.5.2 Instrumentation for Determination by ICP	2 of 7	2
	9.6 Reagents and Consumable Materials	2 of 7	2
	9.7 Sample Collection, Preservation, and Storage	3 of 7	2
	9.8 Calibration and Standardization	3 of 7	2
	9.8.1 Titration	3 of 7	2
	9.8.2 Determination of Aluminum	3 of 7	2
	9.8.3 Method of Standard Additions for Determination of Aluminum	3 of 7	2
	9.9 Quality Control	4 of 7	2
	9.10 Procedure	4 of 7	2
	9.10.1 Barium Chloride ($BaCl_2$-TEA) Method	4 of 7	2
	9.10.2 Potassium Chloride (KCL) Method	5 of 7	2
	9.10.3 Determination of Aluminum	6 of 7	2
	9.11 Calculations	7 of 7	2
	9.12 Precision and Accuracy	7 of 7	2
	9.13 References	7 of 7	2
10	Lime and Aluminum Potential	1 of 7	2
	10.1 Scope and Application	1 of 7	2
	10.2 Summary of Method	1 of 7	2
	10.3 Interferences	1 of 7	2
	10.4 Safety	1 of 7	2
	10.5 Apparatus	2 of 7	2
	10.5.1 General	2 of 7	2
	10.5.2 Instrumentation for Determination by AA	2 of 7	2
	10.5.3 Instrumentation for Determination by ICP	2 of 7	2

Contents *(Continued)*

Section		Page	Revision
	10.5.4 Instrumentation for Determination by Flame Photometery	2 of 7	2
	10.6 Reagents and Consumable Materials	2 of 7	2
	10.7 Sample Collection, Preservation, and Storage	3 of 7	2
	10.8 Calibration and Standardization	3 of 7	2
	10.9 Quality Control	4 of 7	2
	10.10 Procedure	4 of 7	2
	10.10.1 Preparation of Sample Tubes	4 of 7	2
	10.10.2 Sample Preparation	4 of 7	2
	10.10.3 Extraction	4 of 7	2
	10.10.4 Determination of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Fe^{3+}, and Al^{3+}	4 of 7	2
	10.11 Calculations	6 of 7	2
	10.12 Precision and Accuracy	6 of 7	2
	10.13 References	7 of 7	2
11	Extractable Iron and Aluminum	1 of 7	2
	11.1 Scope and Application	1 of 7	2
	11.2 Summary of Method	1 of 7	2
	11.3 Interferences	1 of 7	2
	11.4 Safety	1 of 7	2
	11.5 Apparatus and Equipment	2 of 7	2
	11.5.1 General	2 of 7	2
	11.5.2 Instrumentation for Detemination by AA	2 of 7	2
	11.5.3 Instrumentation for Determination by ICP	2 of 7	2
	11.6 Reagents and Consumable Materials	2 of 7	2
	11.6.1 Sodium Pyrophosphate Extraction	2 of 7	2
	11.6.2 Citrate-Dithionite Extraction	2 of 7	2
	11.6.3 Acid-Oxalate Extraction	3 of 7	2
	11.6.4 Determination of Fe and Al	3 of 7	2
	11.7 Sample Collection, Preservation, and Storage	3 of 7	2
	11.8 Calibration and Standardization	3 of 7	2
	11.8.1 General	3 of 7	2
	11.8.2 Method of Standard Additions for Detemination of Fe and Al	3 of 7	2
	11.9 Quality Control	4 of 7	2
	11.10 Procedures	4 of 7	2
	11.10.1 Sodium Pyrophosphate	4 of 7	2
	11.10.2 Citrate-Dithionite Extraction	4 of 7	2
	11.10.3 Acid-Oxalate Extraction	5 of 7	2
	11.10.4 Determination of Aluminum	6 of 7	2
	11.11 Calculations	7 of 7	2
	11.12 Precision and Accuracy	7 of 7	2
	11.13 References	7 of 7	2

Contents *(Continued)*

Section		Page	Revision
12	Extractable Sulfate and Nitrate	1 of 8	2
	12.1 Scope and Application	1 of 8	2
	12.2 Summary of Method	1 of 8	2
	12.3 Interferences	1 of 8	2
	12.4 Safety	2 of 8	2
	12.5 Apparatus and Equipment	2 of 8	2
	12.6 Reagents and Consumable Materials	2 of 8	2
	12.7 Sample Collection, Preservation, and Storage	3 of 8	2
	12.8 Calibration and Standardization	3 of 8	2
	12.9 Quality Control	3 of 8	2
	12.10 Procedure	4 of 8	2
	12.10.1 Extraction of Sulfate	4 of 8	2
	12.10.2 Extraction of Sulfate by Sodium Phosphate (NaH_2PO_4) Solution	4 of 8	2
	12.10.3 Determination of Sulfate (SO^{2+}_4) and Nitrate (NO^-_3) by Ion Chromatography	5 of 8	2
	12.11 Calculations	7 of 8	2
	12.12 Precision and Accuracy	7 of 8	2
	12.13 References	7 of 8	2
13	Sulfate-Adsorption Isotherms	1 of 3	2
	13.1 Scope and Application	1 of 3	2
	13.2 Summary of Method	1 of 3	2
	13.3 Interferences	1 of 3	2
	13.4 Safety	1 of 3	2
	13.5 Apparatus and Equipment	1 of 3	2
	13.6 Reagents and Consumable Materials	1 of 3	2
	13.7 Sample Collection, Preservation, and Storage	2 of 3	2
	13.8 Calibration and Standardization	2 of 3	2
	13.9 Quality Control	2 of 3	2
	13.10 Procedure	2 of 3	2
	13.11 Calculations	2 of 3	2
	13.12 Precision and Accuracy	3 of 3	2
	13.13 References	3 of 3	2
14	Total Carbon and Total Nitrogen	1 of 6	2
	14.1 Scope and Application	1 of 6	2
	14.2 Summary of Methods	1 of 6	2
	14.3 Interferences	1 of 6	2
	14.4 Safety	1 of 6	2
	14.5 Apparatus and Equipment	1 of 6	2
	14.6 Reagents and Consumable Materials	2 of 6	2
	14.7 Sample Collection, Preservation, and Storage	2 of 6	2

Contents *(Continued)*

Section		Page	Revision
	14.8 Calibration and Standardization	2 of 6	2
	14.8.1 Acetanilide Standards	2 of 6	2
	14.8.2 Blank Samples	3 of 6	2
	14.8.3 Calibration Sequence	3 of 6	2
	14.8.4 Quality Control Calibration Standard	3 of 6	2
	14.8.5 Linearity of Calibration Curve	4 of 6	2
	14.9 Quality Control	4 of 6	2
	14.10 Procedure	4 of 6	2
	14.10.1 Vial Preparation	4 of 6	2
	14.10.2 Sample Preparation	4 of 6	2
	14.10.3 Determination of Total Carbon and Total Nitrogen	4 of 6	2
	14.11 Calculations	5 of 6	2
	14.12 Precision and Accuracy	6 of 6	2
	14.13 References	6 of 6	2
15	Inorganic Carbon	1 of 5	2
	15.1 Scope and Application	1 of 5	2
	15.2 Summary of Method	1 of 5	2
	15.3 Interferences	1 of 5	2
	15.4 Safety	1 of 5	2
	15.5 Apparatus and Equipment	1 of 5	2
	15.6 Reagents and Consumable Materials	3 of 5	2
	15.7 Sample Collection, Preservation, and Storage	3 of 5	2
	15.8 Calibration and Standardization	4 of 5	2
	15.9 Quality Control	4 of 5	2
	15.10 Procedure	4 of 5	2
	15.11 Calculations	4 of 5	2
	15.12 Precision and Accuracy	4 of 5	2
	15.13 References	4 of 5	2
16	Total Sulfur	1 of 3	2
	16.1 Scope and Application	1 of 3	2
	16.2 Summary of Method	1 of 3	2
	16.3 Interferences	1 of 3	2
	16.4 Safety	1 of 3	2
	16.5 Apparatus and Equipment	1 of 3	2
	16.6 Reagents and Consumable Materials	1 of 3	2
	16.7 Sample Collection, Preservation, and Storage	2 of 3	2
	16.8 Calibration and Standardization	2 of 3	2
	16.9 Quality Control	2 of 3	2
	16.10 Procedure	2 of 3	2
	16.10.1 Sample Preparation	2 of 3	2
	16.10.2 Determination of Sulfur	3 of 3	2
	16.11 Calculations	3 of 3	2

Contents *(Continued)*

Section		Page	Revision
	16.12 Precision and Accuracy	3 of 3	2
	16.13 References	3 of 3	2
17	Semiquantitative Analysis by X-Ray Powder Diffraction of the <2-mm and <0.002-mm Fractions of Soil	1 of 12	2
	17.1 Scope and Application	1 of 12	2
	17.2 Summary of the Method	1 of 12	2
	17.3 Interferences	1 of 12	2
	17.4 Safety	1 of 12	2
	17.5 Apparatus and Equipment	1 of 12	2
	17.6 Reagents and Consumable Materials	2 of 12	2
	17.7 Sample Collection, Preservation, and Storage	3 of 12	2
	17.8 Calibration and Standardization	3 of 12	2
	17.9 Quality Control	4 of 12	2
	17.9.1 Sample Preparation	4 of 12	2
	17.9.2 Sample Analysis	4 of 12	2
	17.9.3 Indexing of Diffractograms	4 of 12	2
	17.10 Procedure	4 of 12	2
	17.10.1 Preparation and Analysis of the Multiphase Reference Standard	4 of 12	2
	17.10.2 Preparation of Randomly Oriented Powder Mounts from the <2-mm Fraction of Soil Samples	6 of 12	2
	17.10.3 Separation of the <0.002-mm Fraction from the <20mm Fraction of Soil Samples	6 of 12	2
	17.10.4 Preparation and Treatment of Oriented Slides from the <0.002-mm Fraction of Samples for Identification of Clay Minerals	7 of 12	2
	17.10.5 Preparation of Randomly Oriented Powder Mounts from the <0.002-mm Fraction of Soil Samples	9 of 12	2
	17.11 Calculations	9 of 12	2
	17.11.1 Mineral Identification and Quantification	9 of 12	2
	17.12 Precision and Accuracy	11 of 12	2
	17.13 References	11 of 12	2
18	Wavelength-Dispersive X-Ray Fluorescence Spectrometry	1 of 4	2
	18.1 Scope and Application	1 of 4	2
	18.2 Summary of Method	1 of 4	2
	18.3 Interferences	1 of 4	2
	18.4 Safety	1 of 4	2
	18.5 Apparatus and Equipment	2 of 4	2
	18.6 Reagents and Consumable Materials	2 of 4	2
	18.7 Sample Collection, Preservation, and Storage	2 of 4	2
	18.8 Calibration and Standardization	2 of 4	2
	18.9 Quality Control	3 of 4	2

Contents *(Continued)*

Section	*Page*	*Revision*
18.10 Procedure	3 of 4	2
18.10.1 Sample Preparation	3 of 4	2
18.10.2 Instrumental Requirements	3 of 4	2
18.11 Calculations	4 of 4	2
18.12 Precision and Accuracy	4 of 4	2
18.13 References	4 of 4	2
19 Scanning Electron Microscopy with Energy-Dispersive X-Ray Fluorescence Analysis	1 of 5	2
19.1 Scope and Application	1 of 5	2
19.2 Summary of Method	1 of 5	2
19.3 Interferences	1 of 5	2
19.4 Safety	1 of 5	2
19.5 Apparatus and Equipment	1 of 5	2
19.6 Reagents and Consumable Materials	2 of 5	2
19.7 Sample Collection, Preservation, and Storage	2 of 5	2
19.8 Calibration and Standardization	2 of 5	2
19.9 Quality Control	2 of 5	2
19.10 Procedure	3 of 5	2
19.11 Calculation	4 of 5	2
19.12 Precision and Accuracy	4 of 5	2
19.13 References	4 of 5	2
Appendices		
A Atomic Absorption Spectroscopy Methods	1 of 18	2
B Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes	1 of 16	2
C Forms for Reporting Analytical Laboratory Data	1 of 62	2
D Forms for Reporting Mineralogical Laboratory Data	1 of 8	2
E Glossary	1 of 2	2

Figures

Section		*Page*	*Revision*
1-1	Map of regions of concern for the Direct/Delayed Response Project	2 of 9	2
1-2	Sequence of major activities associated with the Direct/Delayed Response Project	4 of 9	2
1-3	Overall procedures for watershed classification as direct response, delayed response, or capacity protected	5 of 9	2
1-4	Decision chart showing the mechanisms hypothesized to be important in controlling surface water acidification	6 of 9	2
7-1	Mechanical extractor	3 of 10	2
8-1	Standard addition plot	8 of 15	2
12-1	Ion chromatography resolution test	6 of 8	2
15-1	Mineral carbon apparatus	2 of 5	2

Tables

Section		Page	Revision
2-1	List of Parameters and Corresponding Analytical Techniques	4 of 18	2
2-2	Summary of Internal Quality Control	5 of 18	2
2-3	Maximum Control Limits for QC Samples	13 of 18	2
2-4	Required Detection Limits, Expected Ranges, and Intralaboratory Relative Precision Goal	15 of 18	2
2-5	Index of Data Forms	17 of 18	2
2-6	Laboratory/Field Data Qualifiers	18 of 18	2
2-7	List of Decimal-Place Reporting Requirements	18 of 18	2
2-8	Mineralogical Parameters and Corresponding Analytical Techniques	18 of 18	2
4-1	Sedimentation Times for Particles of less than 0.002, less than 0.005, and less than 0.002 mm Diameter Settling through Water for a Depth of 10 cm	4 of 6	2
4-2	Sedimentation Times and Pipetting Depths for Particles of <0.002 mm	5 of 6	2
7-1	Typical Purpose and Size of Each Pump Tube	8 of 10	2
8-1	Expected Range of Analyte Concentrations in Soil Extracts	1 of 15	2
8-2	Atomic Absorption Performance Data for Determination of Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}	2 of 15	2
8-3	Recommended Wavelengths and Estimated Instrumental Detection Limits for Inductively Coupled Plasma Analysis	2 of 15	2
8-4	Precision and Accuracy Data for Inductively Coupled Plasma	14 of 15	2
10-1	Atomic Absorption Performance Data for Determination of Fe^{3+}	1 of 7	2
10-2	Recommended Wavelengths and Estimated Instrumental Detection Limits for Determination of Fe^{3+} and Al^{3+} by Inductively Coupled Plasma	1 of 7	2
10-3	Inductively Coupled Plasma Precision and Accuracy Data	6 of 7	2
11-1	Atomic Absorption Performance Data for Determination of Fe^{3+} and Al^{3+}	1 of 7	2

Tables (Continued)

Section	*Page*	*Revision*
12-1 Example of Concentration of Calibration Standards used for the Analysis of Water Samples by Ion Chromatography	3 of 8	2
12-2 Single-Operator Precision and Accuracy	7 of 8	2
14-1 Allowable Deviations in K-Factors	3 of 8	2
14-2 Allowable Blank Variations	3 of 6	2
17-1 Effect of Some Diagnostic Treatments on Spacing of First Low Angle Reflection of Clay Minerals	10 of 12	2
18-1 Optimum Combination of Operational Conditions	4 of 4	2
A-1 Atomic Absorption Concentration Ranges	2 of 18	2
B-1 Recommended Wavelengths and Estimated Instrumental Section Limits	2 of 16	2
B-2 Analyte Concentration Equivalents (mg/L) Arising from Interferents at the 100 mg/L Level	5 of 16	2
B-3 Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table B-2	5 of 16	2
B-4 ICP Precision and Accuracy Data	15 of 16	2

Acknowledgments

Critical reviews by the following individuals are gratefully acknowledged: S. A. Abboud, Alberta Research Council, Edmonton, Alberta, Canada; M. W. Findlay, Jr., Argonne National Laboratory, Argonne, Illinois; D. F. Grigal, University of Minnesota-Twin Cities, St. Paul, Minnesota; G. R. Holdren, Northrop Services, Inc., Corvallis, Oregon; R. Jenkins, JCPDS-International Centre for Diffraction Data, Swarthmore, Pennsylvania; M. J. Mitchell, State University of New York, Syracuse, New York; and G. Pierzynski, The Ohio State University, Columbus, Ohio.

The guidance of the following people was important in the documentation of the chemical and physical methods: D. C. Hillman and S. J. Simon, Lockheed Engineering and Management Services Company, Inc., Las Vegas, Nevada; I. Fernandez, University of Maine, Orono, Maine; F. M. Kaisaki, L. Juve (retired), L. Shields (retired), and others at the U. S. Department of Agriculture, Soil Conservation Service, National Soil Survey Laboratory, Lincoln, Nebraska; K. Doxsee, S. Vincent, and others at Weyerhaeuser Research and Technology Center, Federal Way, Washington; K. L. Weisgable and Colin Williams, The Perkin-Elmer Corporation, Norwalk, Connecticut; G. Ferguson, Cornell University, Ithaca, New York; E. W. D. Huffman, Jr., and R. G. Boyd, Coulometrics, Inc., Wheatridge, Colorado; R. N. Heistand, D. Raines, and others at Huffman Laboratories, Golden, Colorado; F. S. Latenser, D. Hartford, and K. Shields, Harris Laboratories, Inc., Lincoln, Nebraska; C. Trenton, Ford Forestry Center, Alberta, Michigan; P. Shaffer, Northrop Services, Inc., Corvallis, Oregon; D. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee; J. Reuss and M. Walthall, Colorado State University, Ft. Collins, Colorado; D. S. Coffey, formerly of Northrop Services, Inc., Corvallis, Oregon; J. J. Lee, U. S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon; and R. W. Arnold, U. S. Department of Agriculture, Washington, D. C.

Consultation with the following people was important in the documentation of the mineralogical methods: G. R. Holdren and M. E. Johnson, Northrop Services, Inc., Corvallis, Oregon; D. Bish, Los Alamos National Laboratory, Los Alamos, New Mexico; E. Smith, University of Nevada, Las Vegas, Nevada; J. Baham, G. Campi, and A. Soeldner, Oregon State University, Corvallis, Oregon; and M. Slaughter, Colorado School of Mines, Golden, Colorado.

The following people were instrumental in the completion of this manual: M. L. Faber and J. M. Nicholson of Lockheed Engineering and Management Services Company, Inc.; Computer Sciences Corporation word processing staff and Donald Clark Associates graphic arts staff at the U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Finally, recognition belongs to E. P. Meier and P. A. Arberg who have served as technical monitors of this project.

1 Introduction

1.1 Project Overview

The U.S. Environmental Protection Agency (EPA), in conjunction with the National Acid Precipitation Assessment Program (NAPAP), has designed and implemented a research program to predict the long-term response of watersheds and surface waters in the United States to acidic deposition. On the basis of this research, each watershed system studied will be classified according to the time scale in which it will reach an acidic steady state, assuming current levels of acidic deposition. The three classes of watersheds are defined as follows:

- *Direct response systems*--Watersheds in which surface waters are presently acidic (i.e., alkalinity < 0 μeq/L) or will become acidic within 3 to 4 mean water residence times (i.e., within 10 years). A mean water residence time is the average time period required to replenish totally the water contained in a lake.

- *Delayed response systems*--Watersheds in which surface waters will become acidic in the time frame of a few mean residence times to several decades (i.e., 10 to 100 years).

- *Capacity Protected Systems*--Watersheds in which surface waters will not become acidic for centuries to millennia.

As an element of NAPAP, the National Surface Water Survey (NSWS) was initiated to evaluate the water chemistry of lakes and streams, to determine the status of fisheries and other biotic resources, and to select regionally representative surface waters for a long-term monitoring program that will study future changes in aquatic resources. Subsequently, the Direct/Delayed Response Project (DDRP) was designed as the soil study complement to NSWS.

For DDRP, EPA is testing the hypothesis that atmospheric deposition of sulfur plays the *principal* role in controlling long-term acidification of surface waters (EPA, 1985a). Therefore, DDRP is "concerned with the effects on surface water chemistry related to deposition of sulfur only. If a 'direct' response exists between sulfur deposition and surface water alkalinity, then the extent of current effects on surface water probably would not change much at current levels of deposition, and conditions would improve as the levels of deposition decline. If surface water chemistry changes in a 'delayed' manner (e.g., due to chemical changes in the watershed), then future changes in surface water chemistry (even with level or declining rates of deposition) become difficult to predict. This range of potential effects has clear and significant implications to public policy decisions on possible additional emissions control [requirements for sulfur emission sources]" (EPA, 1985b).

DDRP, like NSWS, focuses on areas of the United States that have been identified as potentially sensitive to surface-water acidification. Two regions, the Northeast and the Southeast (see Figure 1-1), have been included in the DDRP soil survey. The Northeastern soil survey includes the New England states of Maine, New Hampshire, Vermont, Massachusetts, Connecticut, and Rhode Island, and portions of the states of New York and Pennsylvania. The Southeastern soil survey focuses on the area that is identified physiographically as the Southern Blue Ridge Province: bordering portions of Tennessee, North Carolina, South Carolina, and Georgia as well as portions of Virginia. Surface waters in these two regions were studied during the NSWS Eastern Lake Survey Phase I (1984) and the NSWS National Stream Survey - Pilot Study (1985).

Specific goals of the DDRP soil survey are (1) to define physical, chemical, and mineralogical characteristics of the soils and to

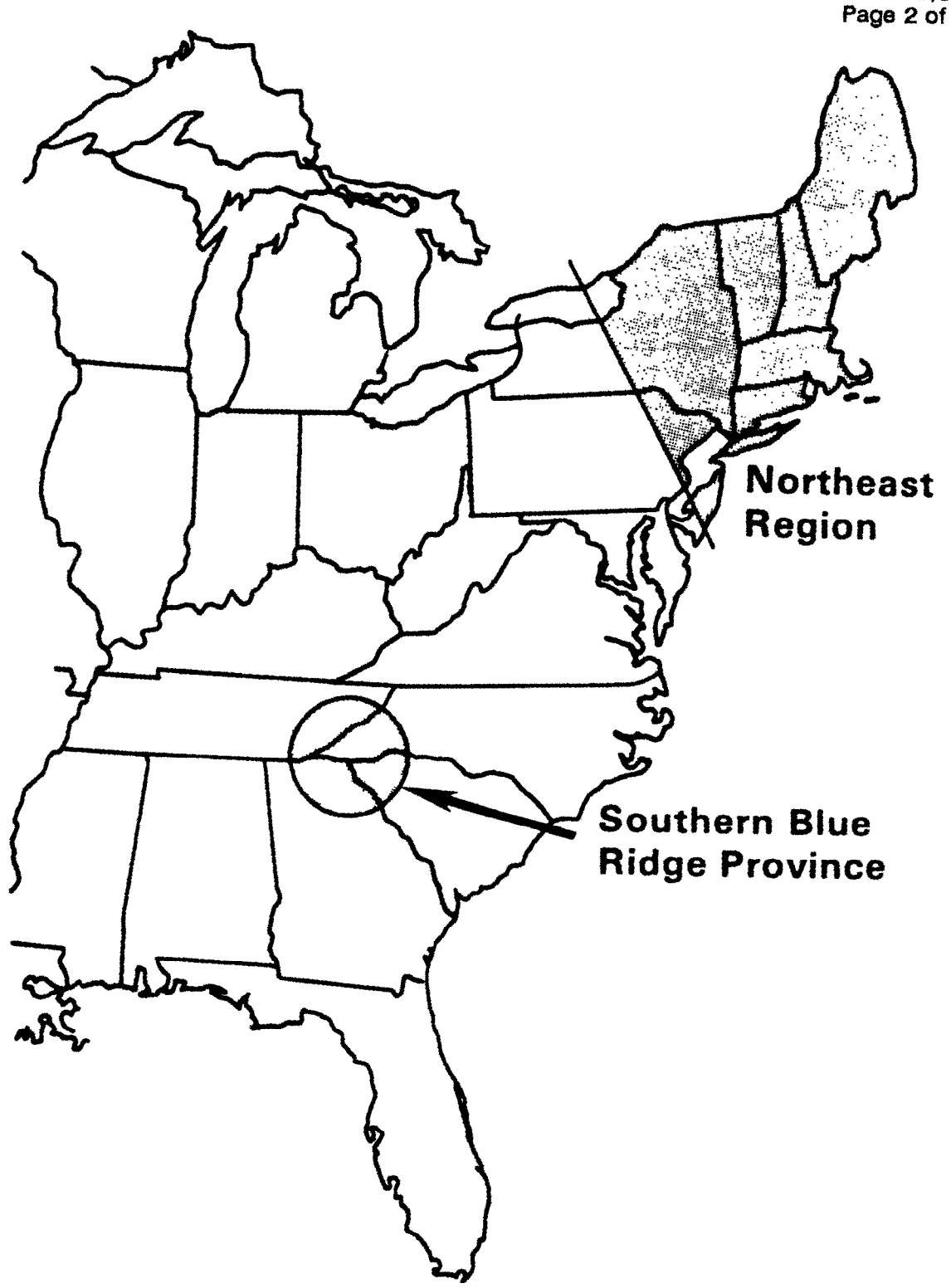


Figure 1-1. Map of regions of concern for the Direct/Delayed Response Project (modified from Radian Corporation, 1985).

define other watershed characteristics across these regions, (2) to assess the variability of these characteristics, and (3) to determine which of these characteristics are most strongly related to surface-water chemistry. Additional DDRP goals are (4) to estimate the relative importance of key watershed processes in controlling surface-water chemistry across the regions of concern, and (5) to classify the sample of watersheds as direct response, delayed response, or capacity protected (to the degree that is scientifically defensible) and to extrapolate the results from the sample of watershed to the regions of concern.

The general sequence of activities for DDRP is shown in Figure 1-2. A subset of watersheds was chosen from watersheds studied during NSWS. Following detailed mapping of the selected watersheds, the mapping units were aggregated into sampling units. Each sampling unit was composed of mapping units which were thought to have similar soil chemistry because of similarities in characteristics such as drainage and parent material. Representative sampling sites were chosen on several watersheds for each sampling unit, and samples were taken from each soil horizon at the selected sites. After preparation, the soil samples were analyzed for physical, chemical, and mineralogical characteristics.

A variety of data sources and methods of analysis will be used to address the objectives of DDRP. Figure 1-3 illustrates the strategy by which data will be integrated to achieve these objectives. In addition to the data collected during DDRP, data sources include other existing data, e.g., surface water data collected during NSWS, the Acid Deposition Data Network Data Base (ADDNET), GEOECOLOGY, the Soil Conservation Service (SCS) Soils-5 Data Base, and the Adirondack Watershed Data Base. The proposed methods of data analysis fall into three levels of complexity: (1) system description, (2) single-factor response time estimates, and (3) dynamic systems modeling. Each level of analysis involves decision criteria (see Figure 1-4) that are used to classify watersheds as direct response, delayed response, or capacity protected. After the representative watersheds are classified, the results will be extrapolated to classify the response time of each watershed in a given region.

1.2 Field Activities

The soils mapping of the watersheds was done by U.S. Department of Agriculture (USDA)/Soil Conservation Service (SCS) personnel using the standard National Cooperative Soil Survey procedures which are documented in *Soil Survey Manual* (USDA/SCS, 1951). After sampling sites were selected according to protocols developed by EPA (EPA, undated), each site was excavated, and the soil profile was described according to standard SCS protocol (USDA/SCS, 1975). Samples of these representative soils were taken by using modified SCS procedures (Blume et al., 1987).

The following watershed and soil profile characteristics were documented for each sampling site:

- Geology
  - type of bedrock
  - percent of bedrock exposed
  - degree of fractionation
  - type of parent material (e.g., till, outwash, alluvium, colluvium, residuum, lacustrine or marine sediments, eolian sands)
- Site description
  - site position (e.g., upland, flood plain, stream terrace, moraine, depression, kame terrace)
  - percent slope
  - average slope length and configuration
  - stream type and density
  - vegetation type (overstory and understory)

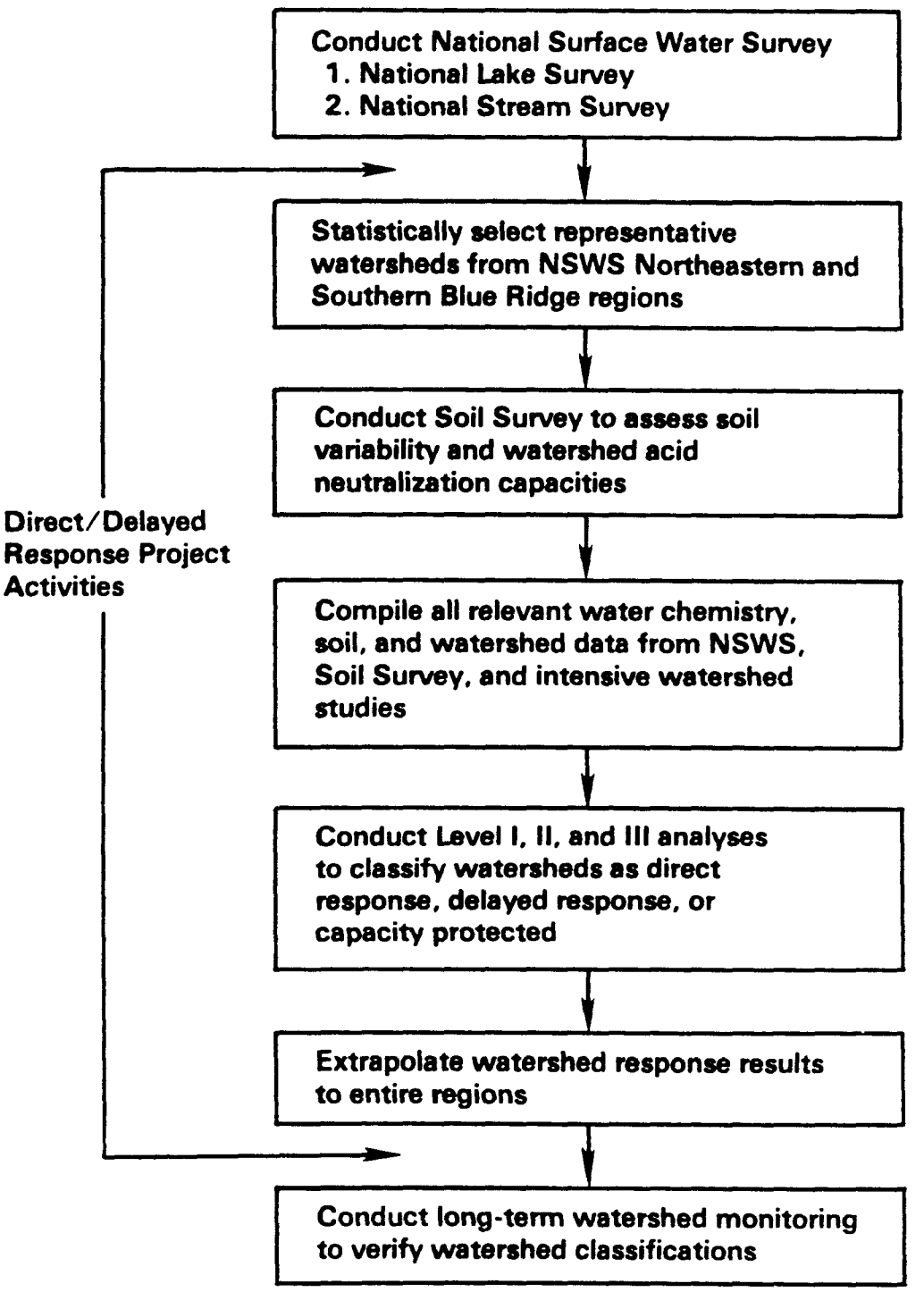


Figure 1-2. Sequence of major activities associated with the Direct/Delayed Response Project (modified from Radian Corporation, 1985).

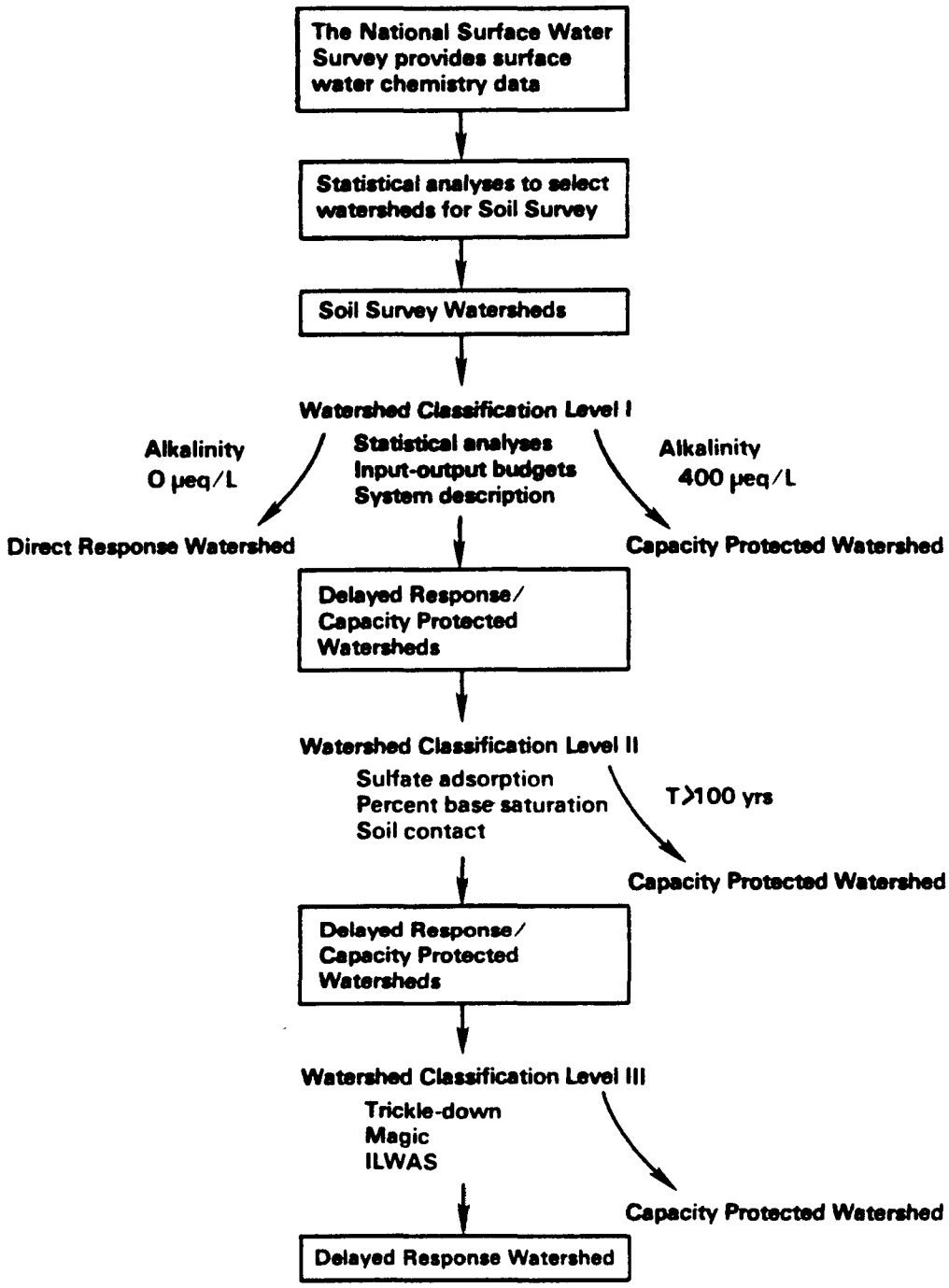
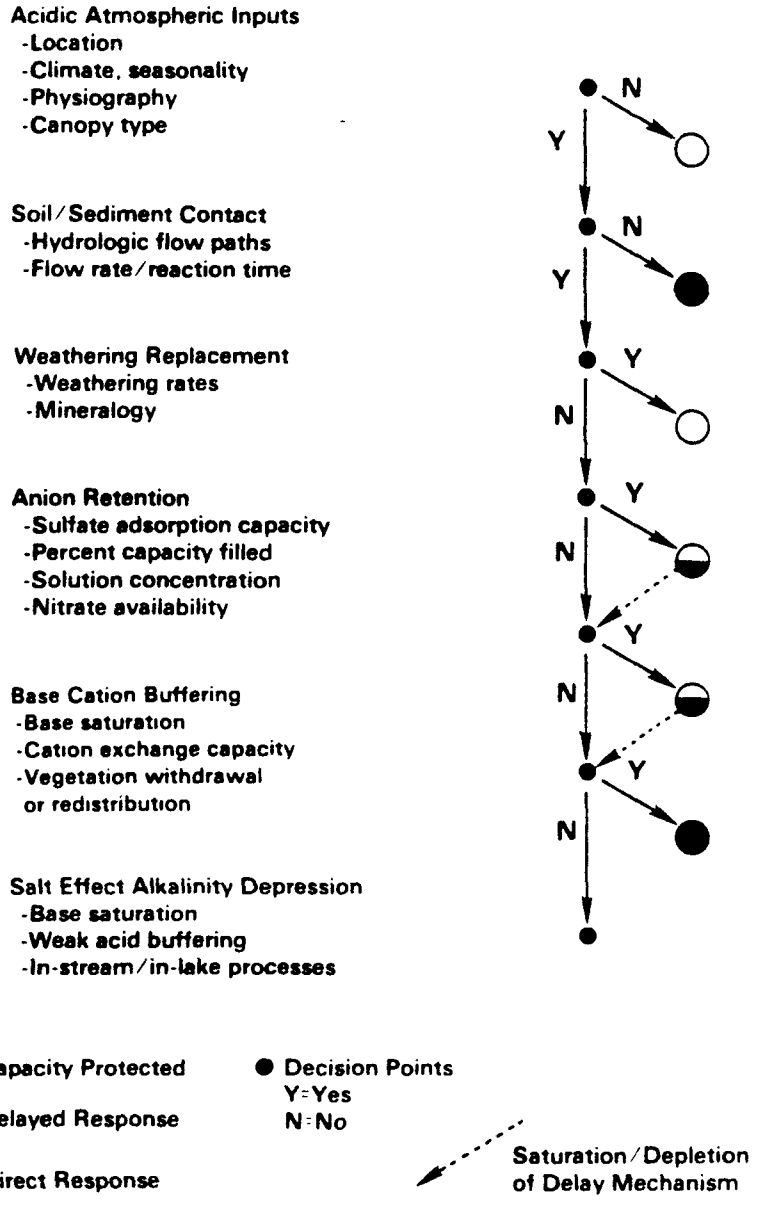


Figure 1-3. Overall procedures for watershed classification as direct response, delayed response, or capacity protected (modified from Radian Corporation, 1985).



NOTE: Each arrow points to the outcome that would be expected (direct/delayed/capacity protected). When a particular controlling mechanism is in effect for a given watershed. Subheadings indicate environmental factors thought to control each mechanism.

Figure 1-4. Decision chart showing the mechanisms hypothesized to be important in controlling surface water acidification (modified from Radian Corporation, 1985).

- Soil morphology by horizon
  - horizon designation
  - depth (upper and lower boundaries)
  - type of boundary
  - Munsell color
  - structure
  - consistence
  - drainage class
  - mottles (location, color, distinctness, frequency)
  - root distribution
  - presence of impermeable layers
  - texture (including rock fragments)

1.3 Laboratory Activities

The handling of soil samples at each preparation laboratory is summarized in Section 2.1. In addition to sample processing, air-dry moisture content, percent rock fragments in the 2-mm to 20-mm size fraction, and bulk density are determined at each preparation laboratory. The physical, chemical, and mineralogical procedures presented in detail in sections 3 through 19 are summarized below:

A. Physical Parameters

1. *Moisture Content*--A standard soil testing method is used to determine soil moisture content on a dry weight basis. Air-dry soil is weighed, dried in an oven, then reweighed. The moisture content is then used to place all measurements on an oven-dry basis.

2. *Particle Size*--Soil textural analysis is routinely determined for soil characterization and classification purposes. The standard pipet method is used. Rock fragments greater than 2 to 20 mm are determined by field sieving and weighing. Rock fragments 2 to 20 mm are determined at the soil preparation laboratory, and particles less than 2 mm are determined at the analytical laboratory.

3. *Specific Surface*--A gravimetric method that employs saturation with ethylene glycol monoethyl ether (EGME) is used to measure specific surface. Specific surface is highly correlated to cation exchange capacity, sulfate adsorption, analyte adsorption/desorption, and the type of clay mineral.

B. Physical/Chemical Parameters

1. *pH*--pH is an indication of free hydrogen ion activity. pH measurements are determined in three soil suspensions: one in deionized water, one in 0.01 M $CaCl_2$, and one in 0.002 M $CaCl_2$.

2. *Cation Exchange Capacity*--Cation exchange capacity (CEC) is a standard soil characterization parameter. CEC indicates the ability of a soil to adsorb cations, especially the exchangeable basic cations, Ca^{2+}, Mg^{2+}, K^+, and Na^+. CEC is highly correlated with the buffering capacity of the soil. Two saturating solutions are used: buffered ammonium acetate (NH_4OAc) solution to measure total CEC and neutral ammonium chloride (NH_4Cl) solution to measure effective CEC. Analysis is by titration or by flow injection analysis.

3. *Exchangeable Basic Cations*--The exchangeable basic cations, Ca^{2+}, Mg^{2+}, K^+, and Na^+ extracted during the CEC determinations, are determined by atomic absorption (AA) or by inductively coupled plasma (ICP). Measurement of the level of exchangeable basic cations indicates the base saturation of the soil.

4. *Exchangeable Acidity*--Exchangeable acidity is a measure of the exchangeable cations that are not part of the base saturation. Two methods of analysis are used. One employs a buffered $BaCl_2$-TEA extraction; the other, a neutral 1.0 N KCl extraction. The $BaCl_2$-TEA method is a back-titration method which indicates total exchangeable acidity. The KCl method is a direct titration method which estimates effective exchangeable acidity. KCl-extractable Al is determined by AA or by ICP.

C. Chemical Parameters

1. *Lime and Aluminum Potential*--Lime potential is used in place of base saturation as an input for certain models. Lime potential is defined as pH - 1/2 pCa. Another characteristic important to watershed modeling is the relationship of pH to solution Al^{3+} levels. This is defined as aluminum potential (K_A) which is equal to 3pH - pAl. This method involves extracting soil with 0.002 M $CaCl_2$ and determining Ca^{2+} and Al^{3+} in the extract. The cations, Na^+, K^+ and Mg^{2+}, and exchangeable Fe^{3+} are also determined in this extract for comparison to cation concentrations in other extracts.

2. *Extractable Iron and Aluminum*--Iron and aluminum oxides are highly correlated to sulfate adsorption and are important in standard soil characterization. Extractable Fe and Al are determined by AA or by ICP in three different extracts. Each extract yields an estimate of a specific Al or Fe fraction. The three fractions of extractable iron and aluminum include those extracted by: sodium pyrophosphate which estimates organic Fe and Al, ammonium oxalate which measures organic Fe and Al plus sequioxides, and citrate-dithionite which indicates non-silicate Fe and Al. Analysis is performed by AA or by ICP.

3. *Extractable Sulfate and Nitrate*--The amount of extractable sulfate and nitrate indicates the sulfate and nitrate saturation of the anion exchange sites. Sulfate is determined in two different extracts: deionized water and 500 mg P/L sodium phosphate. Nitrate is determined only in the deionized water extract. Analysis is by ion chromatography.

4. *Sulfate Adsorption Isotherms*--The ability of soil to adsorb sulfate is related to soil buffering capacity. Isotherms are developed by placing soil samples in six magnesium sulfate solutions of different concentrations: 0, 2, 4, 8, 16, and 32 mg S/L. Then the amount of sulfate remaining in solution after contact with the soil is determined. Subtraction yields the amount of sulfate adsorbed by the soil. These isotherms represent the maximum sulfate adsorption capacity of the soil under laboratory conditions.

5. *Total Carbon and Total Nitrogen*--These two parameters are closely related to soil organic matter type. The method of analysis is rapid oxidation followed by thermal conductivity detection using an automated CHN analyzer.

6. *Inorganic Carbon*--Inorganic carbon is quantified because of the inherent ability of carbonates to buffer acidic input. In soils with a water pH greater than or equal to 6.0, carbonates are determined by coulometric detection of evolved CO_2 after decomposition with a strong acid.

7. *Total Sulfur*--Total sulfur is measured to inventory existing sulfur levels in order to monitor future input of anthropogenic sulfur. An automated method involving sample combustion followed by infrared detection or titration of evolved sulfur dioxide is specified.

D. Mineralogical Parameters

1. *Semiquantitative X-Ray Diffraction*--The mineral content is quantified by X-raying the samples selected for mineralogical study. To determine the mineral content, the samples are X-rayed and are compared against mineral standards for quantification. Physical separations of the <0.002-mm fraction and the 2-mm to 0.002-mm fractions are required.

2. *X-Ray Fluorescence*--This method gives the general chemistry of the bulk sample and of the clay fraction. The samples are pulverized, pressed into pellets, and analyzed. These data combined with data from X-ray diffraction identify the distribution of the elements.

3. *Scanning Electron Microscopy/Energy Dispersive XRF*--With these two methods,

topographic features are examined, and local chemistry of discrete particles is analyzed. These results give information concerning type and degree of weathering.

1.4 Quality Assurance/Quality Control

Throughout the DDRP soil survey, rigorous quality assurance (QA)/quality control (QC) procedures were followed. The QA project plan (Bartz et al., 1987) documents the QA/QC requirements for soil sampling, preparation, and analysis. Internal QC requirements for analytical procedures also are summarized in Section 2.6 and are presented in sections 3 through 16 for each method.

1.5 Data Handling

A summary of the plan for data handling and data verification is given in Bartz et al. (1987). Data collected for DDRP will be maintained in a computerized data base by Oak Ridge National Laboratory. To facilitate interpretation of watershed and soils data, the data management system used for DDRP is compatible with the NSWS data base.

1.6 References

Bartz, J. K., S. K. Drousé, M. L. Papp, K. A. Cappo, G. A. Raab, L. J. Blume, M. A. Stapanian, F. C. Garner, and D. S. Coffey. 1987. *Direct/Delayed Response Project: Quality Assurance Plan for Soil Sampling, Preparation, and Analysis.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. Soil Sampling Manual for the *Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency.

Radian Corporation. 1985. *Overview of the Direct/Delayed Response Project* (First Draft). Prepared for R. Linthurst, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

U.S. Department of Agriculture/Soil Conservation Service. 1975. *Soil Taxonomy.* Handbook 436. U.S. Government Printing Office, Washington, D. C.

U.S. Department of Agriculture/Soil Conservation Service. 1951. *Soil Survey Manual.* Handbook 18, U.S. Government Printing Office, Washington, D. C.

U.S. Environmental Protection Agency. 1985a. *Direct/Delayed Response Project: Long-Term Response of Surface Waters to Acidic Deposition: Factors Affecting Response and a Plan for Classifying Response Characteristics on Regional Scales, Vol. II: Part A, State of Science.* U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon.

U.S. Environmental Protection Agency. 1985b. *Direct/Delayed Response Project: Long-Term Response of Surface Waters to Acidic Deposition: Factors Affecting Response and a Plan for Classifying Response Characteristics on Regional Scales, Vol. V:* Appendix B.2 Soil Survey--Action Plan/Implementation Protocol. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon.

U.S. Environmental Protection Agency. Undated. *Direct/Delayed Response Project: Definition of Soil Sampling Classes and Selection of Sampling Sites for the Northeast.* U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, Oregon.

2 Laboratory Operations

2.1 Preparation Laboratory Procedures

Soil samples are processed by a preparation laboratory before they are shipped to the analytical laboratory. When not undergoing preparation or subsequent analysis, soil samples are refrigerated at 4 °C. All samples are air-dried, crushed, and homogenized. Samples are tested for air-dried moisture content, percent rock fragments, and the presence of inorganic carbon. For each sample, a subsample of approximately 1 kg is split from the bulk sample by using a riffle splitter. The remaining bulk sample is archived.

Air-dry moisture content is determined as follows: An air-dry subsample is removed from the bulk sample, is weighed, and is placed in a convection oven for 24 hours at the prescribed temperature, 105 °C for mineral soils and 60 °C for organic soils. After it is oven-dried, the sample is reweighed, and the percent moisture lost is calculated.

The rock fragment determination is performed as follows: Each soil sample is weighed, then it is sieved to separate the rock fragments greater than 2 mm from the less than 2-mm, fine earth material. The rock fragments are separated by sieving into two size fractions: the 2-mm to 4.75-mm fraction and the 4.75-mm to 20-mm fraction. Each fraction is weighed, and the percent rock fragments in each size fraction is calculated.

For each sample, a qualitative test for inorganic carbon, i.e., carbonate, is performed as follows: Duplicate 1-g aliquots of the less than 2-mm material are placed on a porcelain spot-plate and are saturated with water. The soil is placed under a binocular microscope that has a reflected light source and is observed as a few drops of 4 N HCl are added. Effervescence indicates the presence of inorganic carbon. If the test for inorganic carbon is positive, rock fragments in the 2-mm to 20-mm fraction are crushed to pass a 2-mm sieve and are subsampled by using a riffle splitter. The subsample is ground to pass an 80-mesh sieve and is submitted to the analytical laboratory for inorganic carbon analysis.

Samples are combined into analytical batches. All samples in a set, i.e., the samples taken by a sampling crew within one day and including one field (or sampling) duplicate, are assigned to an analytical batch. Three to eight sets are combined to create one analytical batch of as many as 39 routine and field duplicate samples. One sample per batch is split to form a preparation duplicate. A minimum of two audit samples, supplied by the quality assurance (QA) staff, are included in each analytical batch. All samples within the batch are randomly assigned analytical sample numbers (Bartz et al., 1987b).

For further detail about the preparation laboratory and its operations, refer to Bartz et al. (1987a).

2.2 Sample Receipt and Handling at the Analytical Laboratory

All samples received by the analytical laboratory are checked in by a receiving clerk who (1) records on the shipping form the date samples are received, (2) checks the samples to identify discrepancies with the shipping form, and (3) mails a copy of the completed shipping form to the appropriate addresses. If there are any discrepancies or problems such as leakage or insufficient sample, these problems must be documented. The receiving clerk retains a copy of the completed shipping form for the laboratory records. The samples are refrigerated at 4 °C as soon as possible and must be refrigerated when not in use.

During shipping, the sample material within each container segregates both by particle size and by density; therefore, each

sample must be homogenized by thorough mixing prior to the removal of aliquots for analysis. One method is to place sample material on a 60-cm by 60-cm square of heavy white paper. Next, lift each corner of the paper alternately and roll the soil toward the opposite corner. Continue until the soil has been rolled toward each corner 20 times. Carefully return the sample to the sample container. Alternative methods of homogenizing the sample may be used.

Prior to the removal of an aliquot for analysis, the sample is thoroughly mixed within the sample container. After an aliquot is removed for analysis, the sample is returned to refrigerated storage as soon as possible.

After all analyses have been completed and the results have been checked, samples are stored in a refrigerator at 4 °C, in case reanalysis is necessary.

2.3 Cleaning Procedures for the Analytical Laboratory

Clean all materials that come into contact with the samples, e.g., AutoAnalyzer and autosampler tubes, cups, as described below. Whenever double-deionized (DDI) water is noted, the water must be double-distilled, double-deionized, or deionized and distilled to meet purity specifications for ASTM Type II Reagent Water given in ASTM D 1193 (ASTM, 1984).

2.3.1 Plasticware to be used for pH, Acidity, Alkalinity, Cation Exchange Capacity (CEC) Titrations, and Anion Determinations

For new plasticware, rinse each container with reagent grade methanol or ethanol. In cleaning plasticware for reuse, the alcohol rinse may be omitted. Also, repeat this step whenever an oily residue appears. Rinse each container three times with DDI water, empty the container, and invert it to dry. Protect each container from contamination prior to use.

After the initial cleaning, check 5 percent of the containers to ensure that rinsing has been adequate. Perform the check as follows:

Add 500 mL, or the maximum volume if the capacity of the container is less than 500 mL, of DDI water to each clean, dry container. Seal the container with a cap or with Parafilm, then rotate the container slowly until the water touches all surfaces.

Remove the cap, and measure the conductivity of the contained water. The conductivity must be less than 1 μmho/cm. If any of the containers fail the check, rerinse all the containers and perform the check again on 5 percent of the rerinsed containers.

When the plasticware containers pass the check, place the containers, capped or covered with Parafilm, in plastic bags which will remain sealed until the containers are used for sample analysis.

Syringes and centrifuge tubes may require the use of a brush and detergent to remove adhering soil particles. A detergent wash must be followed by at least three tapwater rinses followed by three DDI water rinses. Containers should be checked as described above.

2.3.2 Other Plasticware

Rinse plasticware with reagent grade methanol or ethanol, then continue cleaning as described for glassware (Section 2.3.3).

2.3.3 Glassware

Rinse each container three times with DDI water, then rinse the container three times with 3N HNO_3 or HCl (prepared from Baker Instra-analyzed acid or equivalent), then rinse the container six times with DDI water.

Allow the container filled with DDI water to stand overnight. Empty the container, invert it, and allow it to dry. All volumetric glassware should be air-dried. When dry, cap or cover containers with Parafilm. Place glassware in

a clean plastic bag until it is needed for analysis.

Kjeldahl flasks should be cleaned with H_2SO_4 acid because it is a better scavenger for ammonium ion. Sedimentation cylinders may be cleaned as follows: The acid rinse may be omitted. Brushing may be required to remove adhering soil particles and, in extreme cases, a detergent wash followed by at least three tap-water rinses and six deionized-water rinses may be used.

2.4 Procedure for Washing Filter Pulp

The filter pulp, used in conjunction with the mechanical extractor for procedures involving extraction by leaching, is a potential source of contamination. Acidity is produced as wood products age. The filter pulp also contains significant amounts of cations that are often greater than the soil sample concentrations. To alleviate the contamination problem, washing the filter pulp prior to sample analysis is recommended.

After the sample tube is prepared and is attached to the mechanical extractor as specified in the procedure, the reservoir syringe is filled with approximately 50 mL of the appropriate extracting solution. The solution is leached through the filter pulp and is collected in a waste recovery syringe. Excess solution retained in the pulp is removed by vacuum. The solution retained in the filter pulp will contribute to the dilution factor; therefore, it is important that excess solution be removed so that this effect may be considered negligible.

2.5 Sample Analyses by the Analytical Laboratory

A summary of physical and chemical parameters to be measured by the analytical laboratory and the corresponding analytical techniques is presented in Table 2-1. The detailed procedures for physical and chemical parameters are described in sections 3 through 16. Each section addresses the following:

1. Scope and Application
2. Summary of Method
3. Interferences
4. Safety
5. Apparatus and Equipment
6. Reagents and Consumable Materials
7. Sample Collection, Preservation, and Storage
8. Calibration and Standardization
9. Quality Control
10. Procedure
11. Calculations
12. Precision and Accuracy
13. References

2.6 Internal Quality Control Within Each Analytical Method

Internal quality control (QC) is an integral part of any measurement procedure in order to ensure that results are reliable. A summary of internal QC procedures for each method is given in Table 2-2. QC procedures are indicated in the appropriate method description. Details on internal QC procedures are described below.

2.6.1 Initial Calibration

Prepare all calibration standards in concentration units of mg/L or as specified in the procedure. Establish a calibration curve for each analytical method by using a minimum of three points within the linear range. The use of at least a three-point calibration curve is required in place of the manufacturer's recommendations for the instrumentation, unless those recommendations require more than three points within the linear range. The concentration of standards must bracket the expected sample concentration without exceeding the linear range of the instrument. Occasionally the standards suggested by a method must be adjusted to meet this requirement. The lowest standard should not be greater than 10 times the detection limit.

Next, determine the linear dynamic range (LDR) for the initial calibration. If during the analysis the concentration of a sample falls

Table 2-1. List of Parameters and Corresponding Analytical Techniques

Parameter	Method
Moisture	Gravimetric
Sand	Sieve/gravimetric
Silt	Pipet/gravimetric
Clay	Pipet/gravimetric
pH in deionized water pH in 0.01 M $CaCl_2$ pH in 0.002 M $CaCl_2$	Combination electrode/millivoltmeter
Total C	Elemental analyzer
Total N	Elemental analyzer
Total S	Elemental analyzer
Inorganic C	Coulometric
CEC (NH_4OAc saturating solution) CEC (NH_4Cl saturating solution)	Autotitration/flow injection analyzer
Ca Mg Exchangeable in NH_4OAc, NH_4Cl, and $CaCl_2$ Na	Flame atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy (or flame atomic emission spectroscopy for Na only)
K Exchangeable in NH_4OAc, NH_4Cl, and $CaCl_2$	Flame atomic absorption spectroscopy or flame atomic emission spectroscopy
Fe Exchangeable in $CaCl_2$; extractable in pyrophosphate, acid oxalate, and citrate-dithionite Al Extractable in pyrophosphate, acidoxalate, and citrate-dithionite	Flame atomic absorption spectroscopy or inductively coupled plasma atomic emission spectroscopy
Al Exchangeable in $CaCl_2$ and KCl	Inductively coupled plasma atomic emission spectroscopy
Nitrate (NO_3^-) Water extractable	Ion chromatography
Sulfate (SO_4^{2-}) Water extractable, phosphate extractable, and sulfate adsorption 6-point isotherm	Ion chromatography
Exchangeable acidity in $BaCl_2$-Triethanolamine and KCl saturating solutions	Titrimetric
Specific surface	Gravimetric

above the LDR, two options are available. The first option is to dilute and reanalyze the sample. In this case, the diluent should have the same matrix as the sample matrix. The second option is to calibrate two concentration ranges. Samples are first analyzed on the lower concentration range. Any samples whose concentrations exceed the upper end of the LDR are then reanalyzed on the higher concentration range. If this option is performed, separate QC calibration samples (QCCS) must be analyzed and reported for each range.

Spectroscopic-grade or high purity chemicals are required for primary standards when analysis is done by atomic absorption or emission methods. Also, calibration standards must have the same matrix as the solutions being analyzed. In order to meet the detection

Table 2-2. Summary of Internal Quality Control

Parameter	Procedure	Control Limits	Corrective Action
Moisture	Laboratory Triplicate Analysis		
	Analyze two additional portions of one sample in each batch.	Precision should be within 10% RSD.	Analyze a second sample in triplicate. If not within control limits, check temperature stability of the oven and repeat triplicate analyses.
Particle Size Analysis	QC Calibration Sample Analysis		
	Analyze a QCCS after every 10 or fewer samples.	Precision should be ±5% for sand, silt, and clay fractions ≥5% (wt/wt).	Recalibrate balance, volumetric pipet, and thermometer. Check water bath or room temperature. Then reanalyze QCCS and samples bracketed by the affected QCCS.
	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample in every batch.	Precision should be ±5% for sand, silt, and clay fractions ≥5% (wt/wt).	Analyze a second sample in duplicate. Determine the source of imprecision; homogenization of sample may have been inadequate. Recalibrate balance. Check sieves for broken wires. Reanalyze the batch.
Specific Surface	QC Calibration Sample Analysis		
	Analyze 1 QCCS per batch of 21 or fewer samples, and 2 QCCS per batch of 22 or more samples. Note: N_2 adsorption standards may be purchased from Duke Scientific Corp., Palo Alto, California.	Precision should be within 10% RSD.	Continue desorption of EGME with continuous vacuum. Check $CaCl_2$ in desiccator; if hydrated, replace. Recalibrate balance. Reanalyze QCCS and all affected samples.
	Laboratory Triplicate Analysis		
	Analyze two additional portions of one sample in every batch.	Precision should be within 10% RSD.	Analyze a second sample in triplicate. Check for vacuum in desiccator. Recalibrate balance. Reanalyze the batch.
	Reagent Blank Analysis		
	Analyze three reagent blanks per batch containing an amount of EGME equal to the greatest quantity required to saturate the soil samples.	Blanks show no EGME residual at end of equilibrium period.	No correction.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Specific Surface (continued)	Reagent Blank Analysis (continued)	Blanks show residual EGME at end of equilibrium peroid.	Determine if EGME reagent is old or otherwise contaminated. Purchase new reagent and reanalyze the batch.
pH	Calibration and Standardization Sample Analysis		
	Calibrate pH meter for the range of pH expected in the soil (usually pH = 4 and pH = 7 standards). Analyze a QCCS immediately after calibration and after analyzing every 10 or fewer samples.	The value of the QCCS must be 4.00 ± 0.05.	Recalibrate pH meter and reanalyze fresh QCCS. Check wiring, static electricity, and solution level in electrode, then reanalyze fresh QCCS. Replace electrode or pH meter, then reanalyze fresh QCCS.
	Reagent Blank Analysis		
	Analyze one blank of each suspension solution.	The value should be between pH = 4.5 and 7.5.	Determine source of contamination. Prepare new solutions for reanalysis of batch.
	Laboratory Triplicate Analysis		
	Analyze two additional portions of one sample in every batch.	Precision should be ±0.10 units.	Analyze a second sample in triplicate. Check for contamination in the suspension solution. Prepare new solutions for reanalysis of batch.
Cation Exchange Capacity (titration)	Calibration and Standardization For Distillation/Titration Method		
	Acid for titration must be restandardized weekly.	Normality of acid changes more than 5 percent.	Prepare new solution.
	Calibrate pH meter (titrator) for range of pH expected in the titration (end point pH = 4.60). Analyze QCCS immediately after calibration and after every 10 or fewer samples.	The value of the pH QCCS must be 4.00 ± 0.05.	Recalibrate pH meter and reanalyze fresh QCCS. Check wiring, static electricity, and solution level in electrode, then reanalyze fresh QCCS. Replace electrode or pH meter, then reanalyze fresh QCCS.
	Calculate instrumental detection limit based upon a minimum titration, i.e., smallest possible volume, and normality of acid.	Instrumental detection limit must not exceed the contract required detection limit (CRDL).	Use a more dilute titrant.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Cation Exchange Capacity (FIA)	Calibration and Standardization for Flow Injection Analysis		
	Determine instrumental detection limit.	Instrumental detection limit must not exceed the CRDL.	Check for possible contamination. Optimize instrumentation, e.g., wavelength.
	Analyze a detection limit QC sample.	Value must be within 20% of the theoretical concentration.	Identify and correct problem. Acceptable result must be obtained prior to sample analysis.
	One calibration blank ("0" mg/L standard) and three reagent blanks (reagents carried through the analytical procedure) per analytical batch.	Blank is less than the CRDL.	No correction.
		Blank exceeds the CRDL.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blanks.
	QCCS must be run every 10 or fewer samples if flow injection analysis is used.	Measure each CEC and plot the results on a control chart. Develop 99% and 95% confidence limits. Required precision is within 10%.	Recalibrate. Analyze a second QCCS and all samples bracketed by the affected QCCS.
Cation Exchange Capacity (both)	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample in each batch for each saturating solution.	Precision should be within 10% RSD.	Analyze a second sample in duplicate. Check for contamination, e.g., atmospheric NH_4^+ or CO_2. Recalibrate the balance, sample diluter (FIA), or titrator. Reanalyze the batch.
	Matrix Spike Sample Analysis		
	One spike is required for each analytical batch. Add standard solution of NH_4Cl or $(NH_4)_2SO_4$ at a level approximately equal to the endogenous level, or 10 times the instrumental detection limit, whichever is greater. Samples for flow injection analysis may be split and the spike added to one split. The distillation/titration method requires that a duplicate sample be extracted, then spiked for analysis.	Calculate the percent recovery. Acceptable range is 100 ± 15%.	Repeat on two additional samples. If either or both are outside the control limits, analyze the batch by the method of standard additions.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Metals - Na, K, Ca, Mg, Fe, and Al by AAS and ICPES.	Calibration and Standardization Sample Analysis		
	Calibrate the spectrometer as required in the analytical method. Analyze a QCCS immediately after calibration and after analysis of every 10 or fewer samples.	Calculate the QCCS value from calibration curve and plot result on a control chart. Develop the 99% and 95% confidence limit (warning and control). Acceptable range is ±10%.	Recalibrate instrument. Prepare new stock and calibration standards if necessary. Analyze a second QCCS and all samples bracketed by the affected QCCS.
	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least squares fit should not be less than 0.99.	Check calibration standards to see if properly prepared. Prepare new stock and calibration standards, if necessary, and recalibrate. Follow instrument manufacturer's troubleshooting procedures.
	Determine the instrumental detection limits.	Instrumental detection limits must not exceed the CRDL for each element.	Check for possible contamination. Optimize instrumentation, e.g., wavelength, burner or torch position, oxidant and fuel pressures, nebulizer flow rate, integrity of impact bead or spoiler, optical alignment.
	Analyze a detection limit QC sample.	Value must be within 20% of the theoretical concentration.	Identify and correct problem. Acceptable result must be obtained prior to sample analysis.
	One calibration blank ("0" mg/L standard) and one reagent blank (any necessary reagents carried through the analytical procedure) per analytical batch.	Blank is less than the CRDL.	No correction.
		Blank exceeds the CRDL.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blank.
	Matrix Spike Sample Analysis		
	To one solution in each batch, add standard solution of analyte at a level approximately equal to the endogenous level or 10 times the instrumental detection limits, whichever is greater. Check recovery in each matrix.	Calculate the percent recovery. Acceptable recovery is 100 ± 15%.	Repeat on two additional samples. If either or both are outside the control limits, analyze batch by the method of standard additions.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Metals - Na, K, Ca, Mg, Fe, and Al by AAS and ICPES. (continued)	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample in each batch for each analyte.	Precision should be within 10% RSD.	Analyze a second sample in duplicate. Recalibrate balance, repipet, and sample diluter. Check for source of contamination. Reanalyze the batch.
Exchangeable Acidity - $BaCl_2$-TEA, KCl	Standardization		
	The solutions used for titration must be restandardized weekly.	Normality of solution changes more than 5%.	Prepare new solution.
	Calculate instrumental detection limit, based upon a minimum titration, i.e., smallest possible volume, and normality of titrants.	Contract-required instrumental detection limits must not be exceeded.	Use more dilute titrants.
	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample in each batch for each method.	Precision should be within 10% RSD.	Analyze another sample in duplicate. Determine source of difficulty, e.g., reduce normality of titrant, replace electrode, or recalibrate titrator. Reanalyze the batch.
	Reagent Blank Analysis		
	Three reagent blanks per batch are required for each exchangeable acidity method.	Blanks for KCl method are equal to or less than twice the CRDL.	Determine source of contamination. Eliminate the problem then reanalyze samples associated with the high blank(s).
		Blanks for $BaCl_2$-TEA method should have a %RSD ≤5%.	Determine and eliminate source of variation, then reanalyze the batch.
Sulfate and Nitrate	Calibration and QA Calibration Sample Analysis		
	Calibrate as required in the analytical methods. Analyze a QCCS immediately after calibration and after analysis of every 10 or fewer samples.	Calculate the QCCS value from the calibration curve and plot result on a control chart. Develop the 99% and 95% confidence limits (warning and control). Acceptable range is ±5%.	Recalibrate instrument. Prepare new stock and calibration standards, if necessary. Analyze a second QCCS and all samples bracketed by the affected QCCS.
	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least squares fit should not be less than 0.99.	Check calibration standards to see if properly prepared. Prepare new stock and calibration standards, if necessary, and recalibrate. Follow instrument manufacturer's troubleshooting procedures.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Sulfate and Nitrate (continued)	Determine instrumental detection limits.	Instrumental detection limits must not exceed the CRDL.	Check for possible contamination. Optimize instrumentation.
	Resolution Check		
	Once per analytical run (day) check resolution of the anion separator column by analyzing a standard containing SO_4^{2-}, NO_4^{2-}, and NO_2^- in equal 1-mg/L concentrations. Set instrument for a nearly fullscale response on the most sensitive range used.	Resolution must exceed 60%.	Clean or replace anion separator column, then repeat calibration and resolution check.
	Calibration and Reagent Blank Analysis		
	One calibration blank ("0" mg/L standard) and one reagent blank (necessary reagents carried through the analytical procedure) per analytical batch.	Blank is equal to or less than the CRDL.	No correction.
		Blank exceeds the CRDL.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blank.
	Matrix Spike Sample Analysis		
	To one sample in each batch, add standard solution of analyte at a level approximately equal to the endogenous level or 10 times the instrumental detection limit, whichever is greater.	Calculate the percent recovery. Acceptable range is 100 ± 15%.	Repeat on two additional samples. If possible, determine and eliminate the source of the interference, then repeat analyses. If either or both are outside the control limits, analyze the batch by the method of standard additions.
	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample in each batch for each extraction procedure.	Precision should be within 5% RSD.	Analyze a second sample in duplicate. Recalibrate balance, repipet, and sample diluter. Check for source of contamination. Reanalyze the batch.
Total S, C, N	Calibration and QC Calibration Sample Analysis		
	Calibrate and standardize induction furnace and titrator as described in method and instrument manual. Analyze QCCS immediately after calibration and after analysis of every 10 or fewer samples.	Measure analyte and plot result on a control chart. Develop the 99% and 95% confidence limits (control and warning). Precision required is 10%.	Recalibrate and then analyze a second QCCS and all samples bracketed by the affected QCCS.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Total S, C, N (continued)	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least squares fit should not be less than 0.99.	Check calibration standards to see if properly prepared. Prepare new stock and calibration standards, if necessary, recalibrate. Follow instrument manufacturer's troubleshooting procedures.
	Determine instrumental detection limits.	Instrumental detection limits must not exceed the CRDL.	Check for possible contamination, e.g., purity of gas. Optimize instrumentation.
	Calibration Blank Analysis		
	Analyze one calibration blank per batch.	Blank is less than the CRDL.	No correction.
		Blank exceeds the CRDL.	Eliminate source of contamination, then reanalyze all samples associated with high blank.
	Matrix Spike Sample Analysis		
	To one sample per batch add a standard amount of analyte at the endogenous level or 10 times instrumental limit, whichever is greater.	Calculate the percent recovery. Acceptable range is 100 ± 15%.	Repeat on two additional samples. If possible, determine and eliminate the source of the interference, then repeat analyses. If either or both are outside the control limits, analyze the batch by the method of standard additions.
	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample in every batch for each procedure.	Precision should be within 10% RSD.	Analyze a second sample in duplicate. Increase sample size, e.g., use two combustion boats. Decrease particle size to pass a finer mesh. Sample may be inhomogeneous. Check for source of contamination. Recalibrate the instrument, then reanalyze the batch.
Inorganic Carbon	Calibration and QA Calibration Sample Analysis		
	Calibrate as required in analytical methods. Analyze a QCCS immediately after calibration and after analysis of every 10 or fewer samples.	Calculate the QCCS value from the calibration curve and plot result on a control chart. Develop the 99% and 95% confidence limits (control and warning). Acceptable range is 15% RSD.	Recalibrate instrument. Prepare new stock and calibration standards, if necessary. Analyze a second QCCS.

(continued)

Table 2-2. Continued

Parameter	Procedure	Control Limits	Corrective Action
Inorganic Carbon (continued)	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least squares fit should not be less than 0.99.	Check working standards to see if properly prepared. Prepare new stock and calibration standards, if necessary, and recalibrate.
	Determine instrumental detection limit.	Instrument detection limit must not exceed CRDL.	Check for possible contamination. Optimize instrumentation.
	Calibration Blank Analysis		
	Analyze one calibration blank per batch.	Blank is equal to or less than the CRDL.	No correction.
		Blank exceeds the CRDL.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blank.
	Laboratory Duplicate Analysis		
	Analyze a second portion of one sample per batch.	Precision should be within 15% RSD.	Analyze a second sample in duplicate. Recalibrate balance. Sample may be inhomogeneous. Check for source of contamination. Reanalyze the batch.
	Matrix Spike Sample Analysis		
	To one sample in each batch, add analyte at a level approximately equal to the endogenous level or 10 times the instrumental detection limit, whichever is greater.	Calculate the percent recovery. Acceptable range is 100 ± 15%.	Repeat on two additional samples. If possible, determine and eliminate the source of the interference, then repeat analyses. If either or both are outside the control limits, analyze the batch by the method of standard additions.

limits, some procedures require that the matrix, i.e., extracting or saturating solutions, be prepared from high purity chemicals.

2.6.2 Calibration Blank

Analyze one calibration blank per batch, immediately after the initial calibration, to check for baseline drift. The calibration blank is defined as a "0" mg/L standard and contains only the matrix of the calibration standards. The observed concentration of the calibration blank must be less than or equal to the detection limit. If it is not, rezero the instrument and recheck the calibration.

2.6.3 Quality Control Calibration Samples (QCCS)

Immediately after standardization of an instrument, analyze a QCCS containing the analyte of interest at a concentration in the midcalibration range. QCCS may be obtained commercially or may be prepared by the analyst from a source which is independent of the calibration standards.

The QCCS is analyzed to verify the calibration curve prior to any sample analysis, after every 10 samples, and after the last sample.

The observed value for the QCCS should be corrected for the calibration blank. Plot the observed concentration for the QCCS on a control chart and develop 99 percent and 95 percent confidence intervals. The 99 percent confidence interval must not differ from the theoretical value by more than the limits given in Table 2-3. A value outside the 99 percent confidence interval is unacceptable. When an unacceptable value for the QCCS is obtained, recalibrate the instrument and reanalyze all samples up to the last acceptable QCCS.

Table 2-3. Maximum Control Limits for QC Samples

Parameter	Maximum Control Limit for QC Sample (% Deviation from Theoretical Concentration of QC Sample)
Particle Size	*
pH	± 0.1 unit
Total C	±10%
Inorganic C	±15%
Total N	±10%
Total S	±10%
CEC	±10%
Na^+	±10%
K^+	±10%
Mg^{2+}	±10%
Ca^{2+}	±10%
Al^{3+}	±10%
Fe^{3+}	±10%
NO_3^-	± 5%
SO_4^{2-}	± 5%
SO_4^{2-} adsorption	± 5%
Specific Surface	±10%

*Refer to Section 4.12, Particle-Size Analysis.

After each day of analysis, update the control charts. Calculate cumulative means and new warning and control limits, i.e., 95 percent and 99 percent confidence intervals, respectively. Bias for a given analysis is indicated by at least seven successive points on one side of the cumulative mean. If bias is indicated, analysis must be stopped until an explanation is found.

The same QCCS must be used to establish all values on a given control chart to ensure continuity.

2.6.4 Detection Limit QC Samples

Analyze one detection limit QC sample per batch. This is a low-level QC sample that contains the analyte of interest at a concentration two to three times above the required detection limit. The purpose of the detection limit QC sample is to eliminate the necessity of formally determining the detection limit on a daily basis. The measured value must be within 20 percent of the theoretical concentration. If it is not, the problem must be identified and corrected, and an acceptable result must be obtained prior to sample analysis.

2.6.5 Reagent Blank

For methods that require sample preparation, prepare and analyze a reagent blank for each group of samples processed. A reagent blank is defined as a sample composed of all the reagents, in the same quantities, used in preparing an actual sample for analysis. The reagent blank undergoes the same digestion and extraction procedures as an actual sample. The concentration of the reagent blank must be less than or equal to the detection limit. If the concentration exceeds this limit, the source of contamination must be investigated and eliminated. A new reagent blank is then prepared and analyzed, and the same criteria are applied. All samples associated with the "high" blank must be reprocessed and reanalyzed after the contamination has been eliminated.

2.6.6 Preliminary Sample Analysis

Approximately seven samples and a reagent blank are analyzed prior to matrix spike and duplicate analyses so that approximate endogenous sample concentrations may be determined.

2.6.7 Matrix Spike Analysis

Prepare one matrix spike sample for each procedure, as specified.

2.6.7.1 Liquid Samples--

For liquid samples, a matrix spike sample is prepared by spiking an aliquot of a solution with a known quantity of analyte prior to analysis. The spike concentration must be approximately equal to the endogenous level or 10 times the detection limit, whichever is larger. Also, the volume of the added spike must be negligible, i.e., less than or equal to 0.01 of the sample aliquot volume. The spike recovery must be within 100 ± 15 percent to be acceptable.

If the recovery is not acceptable, two additional, different samples must be spiked with the analyte in question and must be analyzed. If the recovery for one or both samples is not within 100 ± 15 percent, the entire batch must be analyzed for the analyte in question by the method of standard additions. (Refer to Section 8.5 in Appendix A.) The method of standard additions is performed by analyzing the sample, analyzing the sample plus a spike at about the endogenous level, and analyzing the sample plus a spike at about twice the endogenous level. The concentration of the matrix spike sample must not exceed the linear range of the instrument. If it does, the spiked sample must be diluted before analysis. The % spike recovery is calculated as follows:

$$\%\text{ spike recovery} = \left(\frac{\text{value of sample plus spike} - \text{value of unspiked sample}}{\text{value of spike added}}\right)(100)$$

2.6.7.2 Solid Samples--

Matrix spikes for solid samples, e.g., for analysis of total carbon and total nitrogen, are prepared by adding a known weight of material containing the analyte of interest to a sample of known weight. The spike concentration should be twice the endogenous level or 10 times the detection limit, whichever is larger. The concentration of the matrix spike must not exceed the linear range of the instrument. Although it will not be negligible, the weight of the spike material should be considered negligible for the purposes of calculation.

The spike recovery must be within 100 ± 15 percent to be acceptable. If the recovery is not acceptable, two additional, different samples must be spiked with the analyte in question and must be analyzed. If the recovery for one or both samples is not within 100 ± 15 percent, the entire batch must be analyzed for that analyte by the method of standard additions.

2.6.8 Duplicate Sample Analysis

Prepare and analyze one sample per batch in duplicate for each parameter. (Some procedures require triplicate analysis. Refer to specific method.)

Calculate the percent relative standard deviation (%RSD) as follows:

$$\%RSD = \left(\frac{s}{\bar{X}}\right)100 \quad \text{where } s = \left(\frac{\Sigma(\bar{X} - X)^2}{n - 1}\right)^{1/2}$$

The relative standard deviation is plotted on a control chart, and 99 percent and 95 percent confidence intervals are established. These confidence intervals represent control and warning limits, respectively. Initial control limits are set at the precision levels given in Table 2-4. If duplicate values fall outside the control limits, an explanation must be sought, e.g., instrument malfunction or calibration drift. A second, different sample must then be analyzed in duplicate. No further samples

Table 2-4. Required Detection Limits, Expected Ranges, and Intralaboratory Relative Precision Goal

Parameter	Matrix	Calculated Reporting Units	Contract-Required Calculated Detection Limit	Contract-Required Instrumental Detection Limit	Expected Range	Intralaboratory Relative Precision Goal (%)[a]
Particle size	—	wt % [b]	-------	--------	0-100%	5%
pH	—	pH	-------	--------	2.5-7.0	0.05
Total C	—	wt %	0.010%	--------	0-50%	10%
Inorganic C	—	wt %	0.010%	--------	0	15%
Total N	—	wt %	0.010%	--------	0-20%	10%
Total S	—	wt %	0.010%	--------	0-0.25%	10%
CEC (FIA)	—	meq/100g	------	0.010 meq/L	0.2-200	10%
CEC (titration)	—	meq/100g	0.01 meq	--------	0.2-200	10%
Na^+	all	meq/100g	------	0.050 mg/L	0.00-0.50	10%
K^+	all	meq/100g	------	0.050 mg/L	0.00-1.00	10%
Mg^{2+}	all	meq/100g	------	0.050 mg/L	0.00-1.50	10%
Ca^{2+}	$CaCl_2$	meq/100g	------	2.000 mg/L	------	10%
Ca^{2+}	other	meq/100g	------	0.050 mg/L	0.00-8.00	10%
Al^{3+}	$CaCl_2$	meq/100g	------	0.050 mg/L	------	10%
Al^{3+}	KCl	meq/100g	------	0.10 mg/L	------	10%
Al^{3+}	other	wt %	------	0.50 mg/L	------	10%
Fe^{3+}	$CaCl_2$	meq/100g	------	0.050 mg/L	------	10%
Fe^{3+}	other	wt %	------	0.50 mg/L	------	10%
SO_4^{2-}	all	mg S/kg soil	0.32 mg/kg	0.10 mg S/L	0-200	5%
NO_3^-	water	mg N/kg soil	------	0.10 mg N/L	------	5%
SO_4^{2-} adsorption		mg S/L	0.32 mg/L	0.10 mg S/L	0-35	5%
Exchangeable acidity	KCl	meq/100g	0.40 meq	--------	0-100	10%
Exchangeable acidity	$BaCl_2$-TEA	meq/100g	0.25 meq	-------		
Specific surface		m^2/g	-------	--------	1.0-800	10%

[a] Unless otherwise noted, this is the relative precision at concentrations above 10 times instrumental detection limits.
[b] All values are determined on an oven-dried weight basis.

should be analyzed until duplicate sample results are within the control limits.

Because %RSD is affected by concentration, this criterion is applied only when the mean of duplicate analyses exceeds the detection limit by a factor of 10.

2.6.9 Ion Chromatography Resolution Test

Perform an ion chromatography resolution test once per analytical run by analyzing a standard that contains concentrations of approximately 1 mg/L for each of SO_4^{2-}, PO_4^{3-},

and NO_3^-. If the resolution does not exceed 60 percent, the column should be replaced, and the resolution test should be repeated.

2.6.10 Continuing Sample Analysis

The remaining samples are analyzed if the detection limit QC sample, QCCS, reagent blank, matrix spike, and duplicate samples are within the required limits. After every 10 or fewer samples and after the last sample, a QCCS is analyzed to periodically verify the calibration curve. If the measured value of the QCCS differs from the theoretical value by more than the limits given in Table 2-3, the instrument must be restandardized, and the previous 10 samples must be reanalyzed.

2.7 Instrumental Detection Limits

Instrumental detection limits (IDLs) are determined and recorded monthly for each parameter except pH. For this study, the detection limit is defined as three times the standard deviation of 10 nonconsecutive replicate calibration blank analyses run on separate days. In some analyses, such as ion chromatography, a signal may or may not be obtained for a blank analysis. If a signal is not obtained for a blank analysis, the instrumental detection limit is defined as three times the standard deviation of 10 nonconsecutive replicate analyses of a standard whose concentration is four times the lesser of the actual detection limit or the required detection limit.

2.8 Reagent Blank Correction for Spectrometric and Ion Chromatographic Procedures

For all spectrometric and ion chromatographic procedures presented in this manual, the equations presented in the calculations subsections assume that the concentration of the analyte in solution has been corrected for the reagent blank. The reagent blank, composed of all the reagents in the same quantities used for actual samples, undergoes the same manipulations as actual samples and therefore should reflect any analyte contamination from the sample matrix or analytical procedure. Specifically, the actual (corrected) solution concentration is equal to the analyte concentration in the sample solution minus the analyte concentration in the reagent blank.

2.9 Data Reporting

An index of the data forms used by the analytical laboratory is provided in Table 2-5. The data forms are in Appendix C. Record the raw data on forms 115, 116, 303b, 306, and 308. Summarize pH, moisture, and particle size analysis results on forms 103a and 103b. Summarize data that are corrected both for blanks and dilutions on the 200-series forms. Annotate the data by using the data qualifiers listed in Table 2-6, if applicable. Results should be reported to the same number of decimal places as listed in Table 2-7. However, no more than four significant figures should be reported. Forms 109 through 114 contain quality control data. After a form is completed, the laboratory manager must sign it to indicate that he or she has reviewed the data and that the samples were analyzed exactly as described in the procedure.

Document all deviations from the manual. All original raw data such as data system printouts, chromatograms, notebook, individual data sheets, QC charts, and standard preparation data should be retained.

2.10 Sample Handling For Mineralogical Analyses

The preparation laboratory splits a 500-g aliquot from each bulk soil sample chosen for analysis. This is stored in a 500-mL high-density polyethylene bottle. A mineralogical batch of 26 samples consists of 20 soil samples, 3 duplicates, and 3 audit samples.

Table 2-5. Index of Data Forms

Form Number	Title
102	Shipping Form
103 (a,b)	Summary of pH and Particle Size Results
109 (a,b,c)	Quality Control: Detection Limits
110 (a,b,c)	Quality Control: Matrix Spikes
111 (a through i)	Quality Control: Replicates
112 (a through h)	Quality Control: Blanks and QCCs
113	Quality Control: Ion Chromatograph Resolution Test
114 (a,b,c)	Quality Control: Standard Additions
115 (a through e)	Sample Weight in Grams
116 (a through h)	Dilution Factors and Dilution Blanks; Solution Concentration; Titer and Normality
204 (a,b,c,d)	Summary of Exchangeable Bases and CEC Results - Blank Corrected
205	Summary of Iron- and Aluminum-Extraction Data - Blank Corrected
206	Summary of Extractable Nitrate and Sulfate, Exchangeable Acidity, and Exchangeable Aluminum - Blank Corrected
207	Summary of Sulfate-Adsorption Isotherm Data - Blank Corrected
208	Summary of C, N, S, and Specific-Surface Results - Blank Corrected
303b	Summary of Particle Size Analysis Raw Data
306	Summary of BACL, Exchangeable Acidity Raw Data
308	Summary of C, N, S, and Specific Surface Raw Data

2.11 Laboratory Procedures For Mineralogical Analyses

Procedures for mineralogical analyses are detailed in sections 17, 18, and 19 of this manual. Table 2-8 summarizes the parameters determined and the corresponding analytical techniques. QC procedures are indicated in the appropriate method description.

2.12 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D1193-77* (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Bartz, J. K., D. S. Coffey, and L. J. Blume. 1987a. *Preparation Laboratory Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. II Sample Preparation.* U.S. Environmental Protection Agency.

Bartz, J. K., S. K. Drousé, M. L. Papp, K. A. Cappo, G. A. Raab, L. J. Blume, M. A. Stapanian, F. C. Garner, and D. S. Coffey. 1987b. *Direct/Delayed Response Project: Quality Assurance Plan for Soil Sampling, Preparation, and Analysis.* U. S. Environmental Protection Agency, Las Vegas, Nevada.

Table 2-6. Laboratory/Field Data Qualifiers

Data qualifiers	Indicates
A	Instrument unstable.
B	Redone, first reading not acceptable.
F	Result outside criteria with consent of QA manager.
G	Result obtained from method of standard additions.
J	Result not available; insufficient sample volume shipped to laboratory.
L	Result not available because of interference.
M	Result not available; sample lost or destroyed by laboratory.
N	Result outside QA criteria.
P	Result outside criteria, but insufficient volume for reanalysis.
R	Result from reanalysis.
S	Contamination suspected.
T	Container broken.
U	Result not required by procedure; unnecessary.
X	No sample.
Y	Available for miscellaneous comments.
Z	Result from approved alternative method.

Table 2-7. List of Decimal-Place Reporting Requirements

Parameter	Number of Decimal Places in Reported Results*
Moisture content	3
Particle size	1
pH	2
Total C	3
Inorganic C	3
Total N	3
Total S	2
CEC	3
Na^+	3
K^+	3
Mg^{2+}	3
Ca^{2+}	3
Al^{3+}	3
Fe^{3+}	3
NO_3^-	2
SO_3^{2-}	2
SO_4^{2-} adsorption	3
Exchangeable acidity	2
Specific surface	4

* Report to a maximum of four decimal places.

Table 2-8. Mineralogical Parameters and Corresponding Analytical Techniques

Parameter	Method
Mineralogy of <2-mm and <0.002-mm fractions	X-ray diffraction spectrometry
Elemental analysis of bulk sample and of clay fraction	Wavelength-dispersive X-ray spectrometry
Mineralogy of heavy mineral fraction	Scanning electron microscopy/energy dispersive X-ray spectrometry
Morphological features of samples	Scanning electron microscopy/energy dispersive X-ray spectrometry

3 Moisture Content

3.1 Scope and Application

Moisture will be determined in duplicate on all samples. The average percent moisture will be used to convert all results to an oven-dry basis and, if specified in a procedure, to calculate the weight of sample equivalent to a given weight of oven-dried soil.

3.2 Summary of Method

Replicates are weighed, are dried in an oven, and are reweighed. The drying is continued until the sample reaches a constant weight. By convention, the moisture content of soil is expressed as a weight percentage in terms of the water associated with the oven-dried soil weight. The weight of wet soil is undesirable as the basis for calculation because it varies as the moisture content changes (see Brady, 1974).

3.3 Interferences

Use forceps or finger cots to handle weighing containers to avoid adding deposits of salts and oil.

3.4 Safety

Use forceps or heat-resistant gloves to remove weighing containers from a hot oven.

3.5 Apparatus and Equipment

- Balance capable of weighing ±0.01 g.
- Ovens capable of being heated to 110 °C (two each).
- Thermometers, 0 °C to 200 °C range (two each).
- Weighing containers capable of withstanding intermittent heating to 110 °C and cooling to room temperature.
- Desiccator and desiccant.

3.6 Reagents and Consumable Materials

No reagents or consumable materials are required for this determination.

3.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not being used.

3.8 Calibration and Standardization

Check thermometers periodically to ensure that they are measuring temperature accurately. The ovens should be monitored to ensure that temperature fluctuation does not exceed ±5 °C.

3.9 Quality Control

QC procedures are specified in Section 2.6. Run at least one sample from each batch in triplicate. In addition to the sample that is run in triplicate, a hydrated laboratory chemical that loses a known amount of water at a temperature slightly below the oven temperature may be run as a QCCS.

3.10 Procedure

1. Allow each oven to equilibrate at the required temperature ±5 °C for at

least 24 hours. Heat the ovens used to dry mineral soils to 105 °C; heat the oven used to dry organic soils to 60 °C.

2. Weigh two 10-g replicates of each sample accurately to ±0.01 g and record the air-dry weight.

3. Dry mineral soils for 24 hours at 105 °C. Dry organic soils for 24 hours at 60 °C.

4. Allow soil to cool in a desiccator. Weigh each replicate and record initial oven-dry weight.

5. Dry each replicate for an additional 2 hours at the appropriate temperature: 105 °C for mineral soils or 60 °C for organic soils.

6. Cool the soil in a desiccator. Weigh each replicate and record the oven-dry weight. The second value for weight should be within 1 percent of the initial oven-dry weight. If it is not, repeat drying for 2-hour intervals until oven-dry weights are within 1 percent.

NOTE: It is possible that some of the fine silt and clay fractions may be lost because of excessive movement of sample to and from the oven.

3.11 Calculations

$$\% \text{ Moisture} = \left(\frac{\text{wt air-dried soil} - \text{wt oven-dried soil}}{\text{wt oven-dried soil}}\right)(100) \qquad (3\text{-}1)$$

air-dried soil equivalent to oven-dried weight of soil =

$$\frac{\text{(grams oven-dried soil desired)}}{1.000 - \left(\frac{\%\ \text{moisture}}{100}\right)} \qquad (3\text{-}2)$$

Example: If % moisture equals 3.5%, then:

$$\frac{\text{10 g oven-dried soil}}{1.000 - 0.035} = \text{10.36 g air-dried equivalent to 10.00 g oven-dried soil}$$

3.12 Precision and Accuracy

The %RSD of triplicate samples should be ±5 percent. All weights should be recorded in grams to two decimal places, ±0.01 g.

3.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency.

Brady, N. C. 1974. *The Nature and Property of Soils.* Eighth Edition. Macmillan Publishing Co., Inc., New York, New York.

4 Particle-Size Analysis

4.1 Scope and Application

Particle-size analysis or soil texture is determined on the less than 2-mm fraction from mineral horizons only. The mineral horizons constitute about 88 percent of the samples. The sieve/pipet/gravimetric method described in Soil Survey Investigations Report No. 1 (USDA/SCS, 1984) is used. Most pre-existing data have been determined by using this method.

4.2 Summary of Method

Organic matter and dissolved minerals are removed from the sample. The sand fractions are separated from the silt and clay fractions by a washing process. The silt and clay are put in suspension, and then aliquots taken from the suspension are dried. The dried residues are then weighed. The sand fractions are sieved, and each fraction is weighed. The resulting gravimetric data allow for calculation of the percentage of each particle size.

4.3 Interferences

While the soil in suspension is settling, the graduated cylinders containing the suspension cannot be disturbed, nor can the temperature vary. When handling weighing bottles, use forceps, finger cots, cotton gloves, or vinyl gloves to avoid adding weight from moisture and from body salts and oils.

4.4 Safety

Use forceps or heat-resistant gloves to remove weighing bottles from hot ovens. Use waterproof gloves while handling hydrogen peroxide. Follow standard laboratory safety practices when handling reagents and equipment.

4.5 Apparatus and Equipment

- Erlenmeyer flask, or other suitable container, 250 mL or equivalent (tare to ±0.1 mg).
- Pasteur-Chamberlain filter candles (or equivalent), fineness "F"; store in double-deionized (DDI) water.
- Reciprocating shaker, 120 oscillations per minute.
- Sedimentation cylinders (1-L graduated cylinders, optional).
- Stirrer, motor-driven.
- Stirrer, hand. Fasten a circular piece of perforated plastic to one end of a brass rod.
- Shaw pipet rack, or equivalent.
- Pipets, 25 mL automatic (Lowy with overflow bulb, or equivalent).
- Polyurethane foam, pipe-insulation; constant temperature bath (±1 °C) or temperature-controlled room (±1 °C).
- Shaker, 1.25-cm vertical and lateral movement, and 500 oscillations per minute, or equivalent. Unit must accommodate a nest of sieves.
- Glass weighing bottles, 90 mL, wide-mouth with screw caps, or equivalent, (tare to ±0.1 mg), capable of withstanding intermittent heating to 110 °C and cooling to room temperature.
- Electronic analytical balance (0.1 mg sensitivity).

- Set of sieves, square-mesh, woven phosphor-bronze or stainless steel wire cloth; U.S. Series and Tyler Screen Scale equivalent designations as follows:

Nominal Opening (mm)	U.S. No.	Tyler Mesh Size
1.0	18	16
0.5	35	32
0.25	60	60
0.105	140	150
0.046	300	300

- Receiving pan, used with sieves.
- Hot plate (block digestor, optional).
- Thermometer, range 10 to 50 °C.
- Evaporating dishes, or equivalent, 125 or 250 mL.
- Desiccator and desiccant.

4.6 Reagents and Consumable Materials

- Hydrogen peroxide (H_2O_2), 30 to 35 percent.
- Sodium carbonate (Na_2CO_3).
- Sodium hexametaphosphate $(NaPO_3)_6$, dispersing agent -- Dissolve 35.7 grams of $(NaPO_3)_6$ and 7.94 grams of Na_2CO_3 per liter of water.
- Double-deionized (DDI) water.

4.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected.

4.8 Calibration and Standardization

Calibrate thermometers periodically to ensure that they are measuring temperature accurately. Temperatures of the suspensions should vary no more than ±1 °C.

4.9 Quality Control

QC procedures are specified in Section 2.6. At least one well-characterized soil must be used as a QCCS for each set of soils fractionated. If the QCCS does not cover the entire range of particle sizes (including a minimum of 5 percent each of the sand, silt, and clay fractions), a second well-characterized soil must be used to cover the missing range. The temperature of the water in the sedimentation cylinders must remain within 1 °C of the initial temperature.

4.10 Procedure

4.10.1 Removing Organic Matter

1. Weigh 10.00 g air-dried soil into a tared Fleaker. For soils low in clay, it may be necessary to double the amount of soil in order to meet the required precision. Doubling the amount of soil does not require any adjustments to the remaining steps in this procedure.

2. Add 50 mL of DDI water followed by 5 mL of H_2O_2. Cover the Fleaker with a watch glass. If a violent reaction occurs, repeat the H_2O_2 treatment periodically until no more foaming occurs.

3. Heat the Fleaker to about 90 °C on an electric hot plate. Add H_2O_2 in 5-mL quantities at 45-minute intervals until the organic matter is destroyed, as determined visually. Continue heating for about 30 minutes to remove excess H_2O_2.

NOTE: For simplicity, use block digestion apparatus, if available, and replace Fleakers with block digestor tubes. The removal of the organic matter may require 24 to 36 hours.

4.10.2 Removing Dissolved Mineral and Organic Components

1. Place the Fleaker in a rack and add about 150 mL of DDI water in a jet strong enough to stir the sample well. Remove solution from the suspension with a filter-candle system. Five such washings and filterings are usually sufficient, except for soils that contain much coarse gypsum; these soils require additional treatments.

2. Remove soil that adheres to the filter by applying gentle air pressure.

3. Dry the sample overnight in an oven at 105 °C, cool the sample in a desiccator, and weigh the sample to the nearest milligram. Use the weight of the oven-dried, H_2O_2-treated sample as the weight for calculating percentages of the particle-size fractions.

4.10.3 Dispersing the Sample

Add 10 mL of sodium hexametaphosphate dispersing agent to the Fleaker that contains the oven-dried, treated sample. Bring the volume to approximately 200 mL. Stopper the Fleaker and shake overnight on a horizontal reciprocating shaker at 120 oscillations per minute.

4.10.4 Separating Sand from Silt and Clay

1. Place the 300-mesh sieve on top of the sedimentation cylinder. A clamp and ring stand may be used to hold the sieve in place. Wash the dispersed sample onto the sieve with DDI water. Avoid using jets of water because they may break the fine mesh of the sieve. Silt and clay will pass through the sieve into the cylinder. The sand and some coarse silt will remain on the sieve. It is important to wash all particles of less than 0.02-mm diameter through the sieve. Gently tapping the sieve clamp with the side of the hand will facilitate sieving.

2. Continue washing the sand until the suspension volume in the cylinder is about 800 mL.

3. Remove the sieve from the cylinder. Wash the sand into an evaporating dish with DDI water. Dry the sand overnight at 105 °C. Continue at 4.10.6 for fractionation of the sand.

4. Dilute the silt and clay suspension in the cylinder to 1.00 L with DDI water. Cover the cylinder with a watch glass.

4.10.5 Pipetting

All pipetting is performed in a location free from drafts and temperature fluctuations. A temperature-controlled room, constant-temperature water bath, or foam insulation may be used.

1. Allow 12 to 24 hours for the temperature of suspension to equilibrate.

2. Stir the material in the sedimentation cylinder for 6 minutes with the motor-driven stirrer. Stir 8 minutes if suspension has been standing for more than 16 hours.

   If stoppers of adequate size are available, it is preferable to stopper the cylinder, invert, and swirl. Repeat this procedure at least six times. Inspect the bottom and sides of the cylinder to ensure that fine particles are not adhering to the glass walls of the cylinder.

3. Remove the stirrer and either (1) cover the cylinder with a length of polyuret-

hane foam pipe-insulation, (2) immerse the cylinder in a constant-temperature water bath, or (3) place the cylinder in a temperature-controlled room.

4. Stir the suspension for 30 seconds with a hand stirrer; use an up-and-down motion. Record the time when the stirring is complete. Do not move, stir, or otherwise disturb the cylinder from this point until all pipetting has been completed.

   (Alternative Procedure: At time zero, a 25-mL aliquot may be taken as described in steps 7 through 10 of this section. This aliquot represents all silts and clays. By subtracting the values obtained in Section 4.11 for fine silt and clay, the result is a more direct quantitation of the coarse silt fraction. If this alternative procedure is used, the resulting data *must* be tagged with a "Z" when reported on the data summary forms.)

5. Take the temperature of the solution in the cylinder by gently lowering a thermometer 5 cm into the suspension. Support the thermometer with a clamp to reduce disturbance to the suspension.

6. Use the temperature and Table 4-1 to determine the settling time required for the <0.02-mm fraction, e.g., at 27 °C allow 4 minutes, 4 seconds.

7. About 60 seconds before the sedimentation time has elapsed, slowly lower the Lowy automatic pipet 10 cm into the suspension. (A 25-mL volumetric pipet premarked for a 10-cm depth and clamped firmly in place on a stand may be used.)

8. At the appropriate time, slowly (allow about 12 seconds) fill the pipet. Carefully remove it from the suspension.

9. Wipe clean the outside of the pipet and empty the contents into a tared, drying container such as a 90-mL widemouth bottle. Rinse the pipet into the bottle once with DDI water (add the rinse water to the contents of the bottle.

Table 4-1. Sedimentation times* for Particles of less than 0.002, less than 0.005, and less than 0.002 mm Diameter Settling Through Water for a Depth of 10 cm

Temperature °C	Settling time with indicated particle diameter <0.002 mm hr.:min	<0.005 mm hr.:min	<0.02 mm min.:sec.
20	8 : 0	1 : 17	4 : 48
21	7 : 49	1 : 15	4 : 41
22	7 : 38	1 : 13	4 : 35
23	7 : 27	1 : 11	4 : 28
24	7 : 17	1 : 10	4 : 22
25	7 : 7	1 : 8	4 : 16
26	6 : 57	1 : 7	4 : 10
27	6 : 48	1 : 5	4 : 4
28	6 : 39	1 : 4	4 : 0
29	6 : 31	1 : 3	3 : 55
30	6 : 22	1 : 1	3 : 49
31	6 : 14	1 : 0	3 : 44

* Values calculated from Stokes' equations, assuming a particle density of 2.60 g/cm^3. This figure for particle density is arbitrary and has been chosen to satisfy simultaneously the two definitions of the clay fraction, i.e., particles that have an effective diameter of 0.002 mm and particles that have a settling velocity of 10 cm in 8 hours at 20 °C.

10. Dry the bottle and contents in an oven overnight at 105 °C. Cool in a desiccator over phosphorus pentoxide (P_2O_5). Weigh.

11. Repeat steps 5 through 10 for the <0.002-mm fraction. The <0.002-mm fraction may be pipetted at a time between 4.5 and 8 hours depending on the temperature and the table (4-1 or 4-2) used. Using Table 4-1 and a depth of 10 cm is the most desirable and easiest method.

Table 4-2.[a] Sedimentation Times and Pipetting Depths for Particles of <0.002 mm[b]

Temperature C°	Sedimentation time			
	4 hr. 30 min.	5 hr.	5 hr. 30 min.	6 hr. 30 min.
20.0	5.79 cm	6.44 cm	7.08 cm	8.37 cm
20.3	5.81	6.48	7.13	8.43
20.5	5.86	6.52	7.17	8.47
20.7	5.89	6.55	7.20	8.51
21.0	5.93	6.59	7.25	8.57
21.3	5.97	6.64	7.30	8.63
21.5	6.01	6.68	7.34	8.68
21.7	6.04	6.72	7.39	8.73
22.0	6.09	6.75	7.43	8.78
22.3	6.13	6.80	7.49	8.85
22.5	6.15	6.83	7.51	8.88
22.7	6.18	6.86	7.55	8.92
23.0	6.22	6.91	7.60	8.98
23.3	6.27	6.96	7.66	8.98
23.5	6.29	6.98	7.68	9.08
23.7	6.33	7.04	7.74	9.15
24.0	6.37	7.08	7.78	9.20
24.3	6.40	7.12	7.83	9.25
24.5	6.43	7.15	7.86	9.29
24.7	6.45	7.18	7.89	9.33
25.0	6.51	7.24	7.96	9.41
25.3	6.56	7.28	8.01	9.47
25.5	6.58	7.31	8.04	9.50
25.7	6.61	7.35	8.08	9.55
26.0	6.66	7.40	8.14	9.62
26.3	6.69	7.44	8.18	9.67
26.5	6.72	7.47	8.22	9.72
26.7	6.76	7.51	8.26	9.76
27.0	6.81	7.56	8.32	9.83
27.3	6.85	7.61	8.37	9.89
27.5	6.87	7.64	8.40	9.93
27.7	6.91	7.68	8.44	9.98
28.0	6.97	7.74	8.51	10.06
28.3	7.01	7.79	8.57	10.13
28.5	7.04	7.82	8.61	10.17
28.7	7.07	7.86	8.65	10.22
29.0	7.12	7.91	8.70	10.28
29.3	7.16	7.95	8.75	10.34
29.5	7.19	7.99	8.79	10.39
29.7	7.22	8.02	8.82	10.43
30.0	7.27	8.08	8.88	10.50

[a] Table and calculations provided by Duane Mays, USDA-SCS National Soil Survey Laboratory, Lincoln, Nebraska (May, 1985).
[b] Assuming a particle density of 2.65 g/cm^3.

4.10.6 Sieving and Weighing the Sand Fractions

Stack sieves from largest (1.0 mm) to smallest (0.046 mm) nominal opening with the 1.0-mm sieve at the top and the receiving panat the bottom. Transfer the dried sand to the nest of sieves. Place sieves on a shaker that has 1.25-cm vertical and lateral movements and oscillates at 500 strokes per minute, or an equivalent shaker. Shake for 3 minutes. Weigh the sand fraction that is retained by each sieve and by the receiving pan. Theoretically no soil should pass through the lowest sieve (0.046 mm) into the receiving pan. Soil that does pass the sieve is either silt or clay, and should not be included in the very fine sand fraction.

4.11 Calculations

Pipetted fractions:

Percentage of pipetted fractions = (A - B)KD

where

A = oven-dry weight (g) of pipetted fraction
B = weight correction for dispersing agent (g) = oven-dry weight (g) of aliquot of dispersing solution as diluted for analysis

$$K = \frac{1{,}000}{\text{mL in pipet}}$$

$$D = \frac{100}{\text{g of } H_2O_2\text{-treated oven-dried total sample}}$$

The fraction remaining when the <0.002-mm fraction is subtracted from the <0.02-mm fraction is the fine silt. The sum of the sand and clay fractions (in percentage) subtracted from 100 will equal the silt fraction as defined by the USDA/SCS (1984). The coarse silt is equal to the USDA silt fraction minus the fine silt fraction.

% silt = 100 - (% clay + % sand) (4-1)

% clay = (A - B)KD (4-2)

% sand = (summation of percentages for individual sand fractions) (4-3)

% of sieved sand fractions = weight [g] of fraction on sieve (D) (4-4)

Calculate percent sand, silt, and clay. Also calculate sand fraction percentages (very fine sand [0.05 to 0.10 mm], fine sand [0.10 to 0.25 mm], medium sand [0.25 to 0.50 mm], coarse sand [0.50 to 1.0 mm], very coarse sand [1.0 to 2.0 mm]), and silt fraction percentages (fine silt [0.002 to 0.02 mm] and coarse silt [0.02 to 0.05 mm]).

4.12 Precision and Accuracy

The required precision for values less than 10 percent absolute is 1 percent absolute. From 10 percent to 100 percent absolute, the required precision starts at 10 percent relative and tapers to 5 percent relative at 100 percent absolute. The %RSD for replicates is 10 percent or less.

4.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

5 Specific-Surface Determination

5.1 Scope and Application

Specific surface is determined on the less than 2-mm material of mineral horizons only. The mineral horizons constitute about 88 percent of the samples. Specific surface is defined as the total surface area per unit mass. It is usually expressed as square meters or square centimeters per gram of soil. Specific surface is important in evaluating soil characteristics because it is highly correlated with cation-exchange capacity (CEC) and with the adsorption and desorption of numerous chemicals such as nutrients and pollutants (Hillel, 1980). For example, two soils with the same percentages of sand, silt, and clay might have extremely different measurements of CEC and sulfate adsorption due to differences in surface area of different clay minerals. The differences in surface area can be determined by comparing specific surface measurements.

5.2 Summary of Method

Many procedures are available for determination of specific surface. These methods each involve coating the surface of the entire sample with a monomolecular layer of a polar liquid, such as glycerol, or an inert gas, such as nitrogen. The method used here employs a glycerol, ethylene glycol monoethyl ether (EGME), to establish the monomolecular layer, as described in Soil Survey Investigations Report No. 1 (USDA/SCS, 1984). The amount of EGME used for each sample varies with soil texture and is measured gravimetrically.

5.3 Interferences

No specific interferences are expected if normal laboratory technique is practiced. The soil in the vacuum desiccators is highly hygroscopic and will pick up moisture within minutes of exposure to atmospheric conditions. Minimum exposure time to the atmosphere while weighing is essential. The desiccators should be as close to the balances as possible. Small but significant amounts of soil may be lost from each sample any time the sample is transported from the desiccator to the balance and back again.

5.4 Safety

Normal laboratory safety practices should be observed when handling reagents. P_2O_5 is corrosive and reacts violently with water; EGME is combustible. Both reagents are fire hazards. Standard protective clothing and equipment should be used when handling these reagents.

5.5 Apparatus and Equipment

- Analytical balance, capable of measuring to ±0.1 mg.
- Vacuum desiccator.
- Rubber ring, cushion for glass surfaces of desiccator.
- Vacuum pump, capable of reducing pressure within the desiccator to between 0.65 and 0.75 bar.
- Drying tube--Fill with anhydrous $CaCl_2$ to form EGME trap; place between vacuum desiccator and vacuum source.
- Syringe, 1 mL.

5.6 Reagents and Consumable Materials

- Ethylene glycol monoethyl ether (EGME), reagent grade.
- Phosphorus pentoxide (P_2O_5), anhydrous.

- $CaCl_2$, 4- to 8-mesh, anhydrous reagent grade.

- N_2 adsorption standards, may be purchased from Duke Scientific Corp., Palo Alto, California.

5.7 Sample Collection, Preservation, and Storage

Sample collection and preservation are discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not being used.

5.8 Standardization and Calibration

The analytical balance should be regularly serviced by a qualified technician. The vacuum desiccator must be checked on a regular basis for ability to maintain a vacuum.

5.9 Quality Control

QC procedures are specified in Section 2.6. Analyze three replicates per batch. If multiple desiccators are used, place one replicate in each desiccator. Run three blanks containing an amount of EGME equal to the greatest quantity required to saturate the soil samples. Measure and record the weight of each blank every two to three days until the last sample has equilibrated. These blank values are reported on Form 112h (Appendix C). New EGME will not produce a measurable residue. Therefore, if the blanks are greater than or equal to 0.001 g, obtain new EGME and rerun all affected samples. Use the N_2 adsorption standard or at least one well-characterized soil sample as a QCCS. Analyze one QCCS per batch of 21 or fewer samples, and two QCCS per batch of 22 or more samples. It may be desirable to use well-characterized soils in the low, medium, and high range as QCCS if repeatability is difficult to attain.

5.10 Procedure

1. Dry about 4 g of <2-mm oven-dried equivalent-weight soil in a weighing dish for 2 days over P_2O_5 in a vacuum desiccator. Weight the P_2O_5-dried sample to ±0.1 mg.

2. Using a 1-mL syringe, thoroughly saturate the soil with EGME and add 5 drops EGME in excess. Record weight of sample plus EGME. Place the soil-EGME mixture over anhydrous 4- to 8-mesh $CaCl_2$ in a vacuum desiccator. Connect the desiccator to a vacuum source, and slowly apply vacuum until a pressure of 0.65 to 0.75 bar is reached within the desiccator.

3. After 24 hours of continuous vacuum, weigh the soil-EGME mixture. Compare the soil-EGME weight to the initial weight of soil dried over P_2O_5. If the difference between the two weights is greater than 10 mg of EGME per gram of P_2O_5-dried soil, continue the desorption of EGME with continuous vacuum and weigh the mixture daily.

4. When the difference between the two weights is less than 10 mg of EGME per gram of P_2O_5-dried soil, reduce the time of desorption under vacuum to 1 hour per day. Continue weighing the soil-EGME mixture every 24 hours. It is not always necessary to weigh daily for the first few days because only very sandy soils equilibrate that rapidly. Additionally, small but significant amounts of soil can be lost each time the sample is moved. Repeat this procedure of desorption of EGME and daily weighings until constant weight is attained. Constant weight is indicated when three successive weighings are within 0.20 mg of EGME

per gram of P_2O_5-dried soil or about 0.80 mg per 4-g sample. Average the three values for use in calculating the retention of EGME (in Equation 5-1).

NOTE: Equilibration generally requires 5 to 25 days.

5.11 Calculations

Data uncorrected for blanks are calculated according to the following equations:

Retention of EGME, (mg/g) =

$$\frac{\bar{X}\ \text{soil wt (g)}_{EGME} - \text{soil wt (g) } P_2O_5\ (1000)}{\text{soil wt (g) } P_2O_5} \qquad (5\text{-}1)$$

$$\text{Specific surface } (m^2/g) = \frac{\text{Retention of EGME (mg/g)}}{0.286\ mg/m^2} \qquad (5\text{-}2)$$

NOTE: The constant 0.286 is the calculated amount of EGME (in milligrams) needed to cover 1 m^2 of clay surface with a molecular coverage of 5.2×10^{-15} cm^2/molecule. This assumes that 810 m^2/g is the theoretical specific surface for montmorillonite and that a measured value of 23.7 mg EGME is retained per gram of clay (Phyal and Hendricks, 1950).

5.12 Precision and Accuracy

Results should be reported in milligrams per gram (mg/g) and should be carried out to four decimal places. A minimum of three replicates of one sample should be run with each batch and should yield a %RSD of no more than 10 percent. All weighings should be made to ±0.1 mg on an analytical balance.

5.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency.

Hillel, D. 1980. *Fundamentals of Soil Physics.* Academic Press, New York.

Phyal, R. S., and S. B. Hendricks. 1950. *Total Surface of Clays in Polar Liquids* as a Characteristic Index. *Soil Sci.*, Vol. 69, pp. 421-432.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

6 pH Determination

6.1 Scope and Application

The following procedure was developed to standardize the measurement of pH in soils. Factors that normally affect the measurement of pH are (1) electrolyte content of the extractant; (2) soil-to-solution ratio; (3) temperature and CO_2 content of the extractant; (4) errors that occur with instrument calibration, standard preparation, and liquid junction potential; (5) organic and inorganic constituents; and (6) length of time the soil and solution stand before they are measured. These factors were considered in the preparation of the methodology.

6.2 Summary of Method

Three suspensions of each soil sample are prepared, one in DDI water, one in 0.01 M $CaCl_2$, and one in 0.002 M $CaCl_2$. The pH of each suspension is measured with a pH meter and a combination electrode. This method is modified from USDA/SCS (1984).

6.3 Interferences

Soils high in salts, especially sodium (Na^+) salts, may interfere with the pH reading and the electrode response time.

Clays may clog the KCl junction and may slow the electrode response time. Thoroughly clean the electrode between samples to avoid this problem.

Wiping the electrode dry with cloth, laboratory tissue, or similiar materials or removing the electrode from solution when the meter is not on standby may cause electrode polarization.

The initial pH of a nonalkaline soil will usually be as much as 0.5 pH unit greater than the pH taken after the sample has set for 30 minutes or longer.

The pH will vary as much as 1.0 pH unit between the supernatant and soil sediment. Always place the electrode junction at the same distance above the surface of the soil to maintain uniformity in pH readings.

6.4 Safety

No specific hazards are associated with this procedure or with the required reagents. Normal laboratory safety practices are to be observed. Protective clothing and safety glasses should be worn, especially when handling concentrated HCl and dry $Ca(OH)_2$ to prepare reagents.

6.5 Apparatus and Equipment

- Digital pH/mV meter, capable of measuring pH to ±0.01 pH unit and potential to ±1 mV and temperature to ±0.5 °C. The meter must also have automatic temperature compensation capability.

- pH and reference electrodes, high quality, low-sodium glass. Geltype reference electrodes must not be used. A combination electrode is strongly recommended, and the procedure is written assuming that one is used. The Orion Ross combination pH electrode or equivalent with a retractable sleeve junction is recommended. At least two electrodes, one a backup, should be available to the analytical laboratory.

- Beakers, plastic or paper containers, 50 mL.

- Glass stirring rods or disposable stirrers, one per sample.

6.6 Reagents and Consumable Materials

- NBS-traceable pH buffers of pH = 4, pH = 7 and pH = 10, for electrode calibration.

- Buffer of pH 4.0 for QCCS--The QCCS can be purchased, or it can be prepared from 0.05 M potassium hydrogen phthalate ($KHC_8H_4O_4$ or KHP). This buffer must be from a different container or lot than the NBS standards used for electrode calibration.

  Dry KHP for 2 hours at 110 °C, cool to room temperature in a desiccator. Weigh 10.21 g of KHP, dissolve it in DDI water, and dilute the solution to 1.000 L. To preserve the KHP solution, add 1.0 mL of chloroform or one crystal (about 10 mm in diameter) of thymol per liter of the buffer solution. This solution has the following pH values at the temperatures given:

T °C	pH
15	3.999
20	4.002
25	4.008
30	4.015

- Double-deionized water (DDI).

- Stock calcium chloride solution ($CaCl_2$, 1.0 M)--Dissolve 55.493 g of anhydrous $CaCl_2$ in DDI water and dilute to 500 mL.

- Calcium chloride 0.01 M $CaCl_2$--Dilute 20 mL of stock 1.0 M $CaCl_2$ to 2.000 L with DDI water. If the pH of this solution is not between 5 and 6.5, adjust the pH by addition of dilute $Ca(OH)_2$ or HCl, as needed. Verify the concentration of the $CaCl_2$ solution by measuring the electrical conductivity. The specific conductivity should be 2.32 ± 0.08 mmho/cm at 25 °C. If it is not, prepare fresh solution.

- Calcium chloride ($CaCl_2$) 0.002 M--Dilute 4 mL of stock 1.0 M $CaCl_2$ solution to 2.000 L with DDI water. If the pH of this solution is not between 5 and 6.5, adjust the pH by addition of dilute $Ca(OH)_2$ or HCl.

- Calcium hydroxide ($Ca(OH)_2$)--Dissolve 0.185 g $Ca(OH)_2$ in 1 L of DDI water.

- Hydrochloric acid (HCl)--Dilute 1 mL concentrated HCl to 1 L with DDI water.

6.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not being used.

6.8 Calibration and Standardization

For storage and readings, the electrode need only be immersed to cover the liquid junction of the reference electrode (typically about 2.5 cm).

Rinse electrode with DDI water between each sample and each buffer to prevent solution carryover. Do not rub or blot electrode dry because this may produce a static electric charge and thereby polarize the electrode.

To prepare the pH electrode for use, move the band covering the fill hole and fill the reference reservoir to the hole with 4.0 M KCl filling solution. Allow 5 minutes for the ceramic frit to become wet with filling solution before immersing the electrode in sample or

buffer. The retractable sleeve junction allows easy cleaning of clay particles and insolubles that clog the junction and thereby produce drift and slow response.

Each analyst must be thoroughly acquainted with the procedure and familiar with all instrument functions. Read and follow all operating and start-up procedures for the pH meter. Leave the instrument on standby and verify that the combination electrode is connected and that the level of reference filling solution is at least 3 cm above the sample surface. Check the temperature calibration by measuring room temperature of a solution with the electrode and meter and with a thermometer.

Calibrate the electrode at a minimum of two points that bracket the expected pH and that are three pH units or more apart. Use NBS buffers of pH 4, 7, and 10 for samples in the expected pH range.

Stir pH 4.0 buffer solution for 30 seconds, then stop stirring, read the pH after equilibration, and adjust the meter if necessary. Perform the step again, using the pH 7.0 buffer. Repeat measurements and adjustments until readings for both buffer solutions are within 0.1 pH units of the respective true buffer values. Repeat the process substituting a pH 10.0 buffer in place of the pH 4.0 buffer for soils of pH greater than 7.0.

6.9 Quality Control

QC procedures are specified in Section 2.6.

6.9.1 Quality Control Calibration Sample

Analyze a QCCS, pH 4.0: (1) before beginning analysis of routine samples, (2) after every ten samples, and (3) after completion of routine sample analysis for the day. The value of the QCCS must be 4.00 ± 0.05. If the QCCS does not meet this criterion, recalibrate the electrode according to the procedure in Section 6.8. Repeat the QCCS measurement using a fresh QCCS sample. If acceptable results still cannot be obtained: (1) check electrode for clean reference junction, (2) check wiring straps into meter, (3) check for static electricity from another instrument or from yourself, and (4) check to see if enough filling solution is contained within the electrode. If a problem still persists, replace electrode, meter, or both.

6.9.2 Blank Samples

Analyze one blank of each suspension solution. The blank used for each pH method is the reagent used: DDI water, 0.01 M $CaCl_2$, or 0.002 M $CaCl_2$.

6.9.3 Replicate Samples

Analyze one sample in triplicate for each of the following solutions: DDI water, 0.01 M $CaCl_2$, and 0.002 M $CaCl_2$. Report individual pH values and the mean and standard deviation on Form 103a (Appendix C).

6.10 Procedure

1. Prepare two suspensions of each soil sample, one in DDI water and one in 0.01 M $CaCl_2$, using soil-to-solution ratios of 1:1 for mineral horizons and 1:5 for organic horizons. For mineral horizons, add 20 mL of the appropriate solution to 20.00 g soil. For organic horizons, add 25 mL solution to 5.00 g soil.

   Prepare one suspension of each soil sample for determination of pH in 0.002 M $CaCl_2$ solution. Use a ratio of 1:2 for mineral horizons (20 mL 0.002 M $CaCl_2$ to 10 g soil). For most organic soils, use a ratio of 1:10 (50 mL 0.002 M $CaCl_2$ to 5 g soil); however, for highly absorbent organic soils, use a ratio of 1:25 (50 mL 0.002 M $CaCl_2$ to 2 g soil). The ratio used here for each sample must correspond with the ratio used for Lime and Aluminum Potential (Section 10).

2. Allow soil to absorb solution without stirring, then thoroughly stir the soil-solution mixture for 10 seconds with a glass stirring rod or disposable stirrer. Stir again for 10 seconds after 15, 30, 45, and 60 minutes.

3. After the final stirring, allow the suspension to settle for 1 minute. Place the pH electrode in the supernatant of the soil suspension.

   For mineral soils, the electrode junction should be below the solution surface and above the soil-solution interface.

   Some organic soils swell, so there is no free water available. As long as the electrode junction is below the surface of the organic material, an acceptable, repeatable reading generally is attained. If the reading is not stable, add enough solution to cover the electrode junction. When the reading is stable, record pH to the nearest 0.01 pH unit.

4. Report the pH of the soil:DDI water suspension, the soil:0.01 M $CaCl_2$ suspension, and the soil:0.002 M $CaCl_2$ suspension for each sample.

5. Analyze three replicates of at least one sample for each pH solution from each batch of samples.

6. After measurements are completed, store the electrode in 0.1 M KCl manufactured storage solution. Do not let the sensing element and reference junction dry out. The level of the storage solution should be 1 inch below the filling solution level to prevent influx of the storage solution. Check periodically that the electrode reservoir is full of filling solution.

6.11 Calculations

No calculations are required to obtain pH values. The mean and standard deviation must be determined for the triplicate samples for each pH solution.

6.12 Precision and Accuracy

The standard deviation of the blanks is a measure of the precision of the method.

6.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

7 Cation Exchange Capacity

7.1 Scope and Application

Cation exchange capacity (CEC) is a measure of the negative charge that exists on organic and mineral colloids allowing the particle surfaces to exchangeably bind cations. The quantity of cations needed to neutralize the charge is measured in milliequivalents per 100 g of oven-dried soil. A close approximation of CEC is the summation of exchangeable acidity and exchangeable bases. CEC consists of permanent charge CEC and pH-dependent CEC. Permanent charge CEC is a result of isomorphic substitution of the central cation within the clay structure. The pH-dependent CEC, a result of interrupted lattice structure at the clay particle surface and of the dissociation of functional groups, varies with H^+ ion concentrations. Two saturating solutions are used for CEC determination. Ammonium acetate (1.0 N NH_4OAc) buffered at pH 7 yields a theoretical estimate of the maximum CEC potential for a specific soil. For this reason, it is termed total CEC. In acid soils, this estimate results in a high CEC value because of adsorption of NH_4^+ ions to the pH-dependent exchange sites that exist at a neutral pH level. This overestimation will not occur when a neutral unbuffered saturating solution (1.0 N NH_4Cl) is used. For this study, ammonium chloride (1.0 N NH_4Cl) and ammonium acetate (1.0 N NH_4OAc) will be used. This NH_4Cl CEC has been termed effective CEC or that which occurs at field pH. This parameter will be of greater importance because it is a more realistic estimate of CEC than is the the total CEC (NH_4OAc).

Micaceous clay minerals such as biotite, vermiculite, and muscovite contain K^+ and NH_4^+ as interlayer cations. These cations are not readily exchangeable, and soils containing large quantities of these silicate minerals will produce erroneous results when NH_4^+ is used to replace cations. These minerals generally occur only in soils found in the Western United States.

7.2 Summary of Method

The soil sample is saturated with NH_4^+ from a solution of NH_4OAc; excess NH_4^+ is removed by ethanol rinses. The sample is then analyzed for NH_4^+ content by one of three methods: automated distillation-titration; manual distillation-automated titration; or ammonium displacement - flow injection analysis. The entire procedure is repeated with a fresh aliquot of sample and a solution of NH_4Cl as the NH_4^+ source. This method is based on Doxsee (1985), Rhodes (1982), and USDA/SCS (1984).

7.3 Interferences

Inconsistency in the NH_4^+ saturating and rinsing steps is the greatest source of error. Soils containing minerals such as biotite, vermiculite, and muscovite (which contain K^+ or NH_4^+) will produce artificially low results. The use of a mechanical extractor minimizes inconsistency.

7.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a hood.

7.5 Apparatus and Equipment

Apparatus and equipment required are for the saturation procedure and for the analytical procedure that is selected for use. It is not necessary to have equipment for all three analytical procedures.

7.5.1 Apparatus for Saturation Procedure

- Mechanical extractor, 24 place (see Figure 7-1).
- Syringes, disposable, 60 mL polypropylene (Use one sample tube, one reservoir tube, and one tared extraction syringe for each sample).
- Rubber tubing, 1/8 x 1/4 inch (for connecting syringe barrels).
- Analytical filter pulp, Schleicher and Schuell, No. 289, washed according to the procedure given in Section 2.4.
- Bottles, polyethylene (LPE), 25 mL.
- Reciprocating shaker.
- Tubes, glass, centrifuge or culture, with caps, 25 mL.

7.5.2 Apparatus for Automated Distillation-Titration Analysis

- Steam distillation-titration apparatus, Kjeltec auto 1030 analyzer, or comparable unit.
- Printer, Alphacom 40, or equivalent.
- Digestion tubes, 250 mL, straight neck.

7.5.3 Apparatus for Manual Distillation-Automated Titration Analysis

- Automatic titrator with autosampler, Metrohm or equivalent.
- Kjeldahl flasks, 800 mL.

7.5.4 Apparatus for Ammonium Displacement-Flow Injection Analysis

- Flow injection analyzer (FIA), Lachat or equivalent, modified for ammonia chemistry with 630 nm interference filter.

7.6 Reagents and Consumable Materials

Reagents and consumable materials required are for the saturation procedure and for the analytical procedure that is selected for use. It is not necessary to have the reagents for all three analytical procedures.

7.6.1 Reagents for Saturation Procedure

- Glacial acetic acid ($HC_2H_3O_2$).
- Ammonium hydroxide (NH_4OH), concentrated.
- Ammonium acetate ($NH_4C_2H_3O_2$ or NH_4OAc), 1 N, pH 7.0--Purchased or made according to one of the following procedures:

  1. To 15 L DDI water in a 20-L bottle, add 1,026 mL glacial acetic acid, mix, then add 1,224 mL concentrated ammonium hydroxide. Mix, cool, dilute to 18 L with DDI water, and adjust pH to 7.0 with acetic acid or with ammonium hydroxide.

  2. To 15 L DDI water in a 20 L bottle, add 1,388 g crystalline ammonium acetate (reagent grade). Mix, allow to come to ambient temperature, then dilute to 18 L with DDI water. Adjust to pH 7.0 with acetic acid or with ammonium hydroxide.

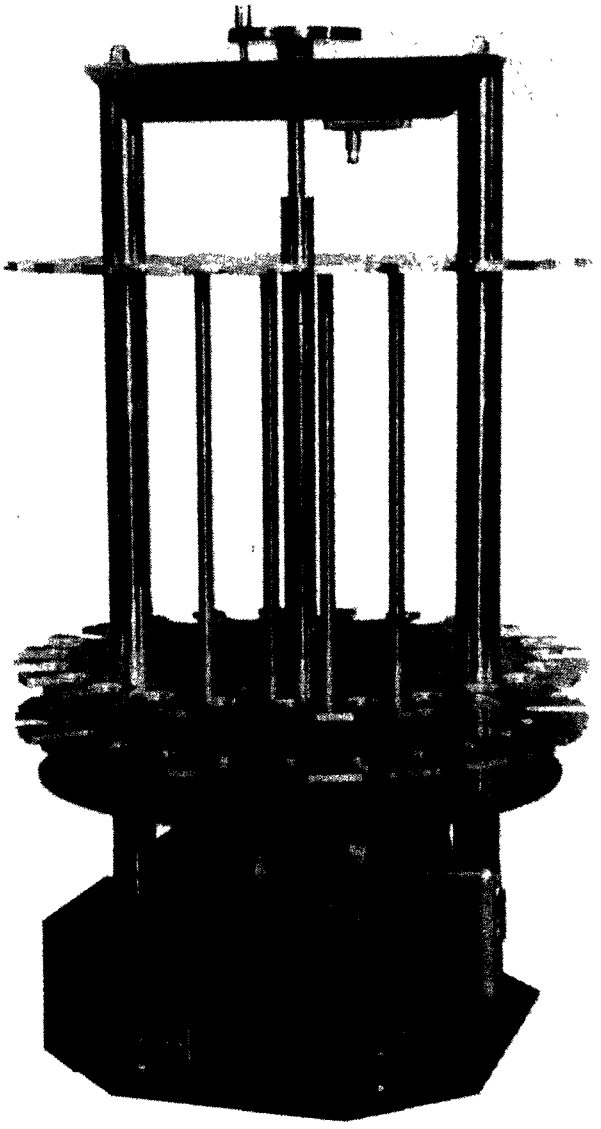


Figure 7-1. Mechanical extractor. This extractor is a mechanical device that can be used to perform an extraction by leaching technique. (Manufactured by Centurion International, Inc., P.O. Box 82846, 4555 North 48th Street, Lincoln, Nebraska 68501.).

- Ammonium chloride (NH_4Cl), spectroscopic grade, 1 N--Dissolve 535 g NH_4Cl in DDI water and dilute to 10 L. Two sources of spectroscopic grade NH_4Cl are (1) Aldrich Chemical Company, Inc., 940 West Saint Paul Avenue, Milwaukee, Wisconsin 53233; telephone (800) 558-9160, No. 25,413-4, and (2) Aesar - Johnson Matthey, Inc., Eagles Landing, P.O. Box 1087, Seabrook, New Hampshire 03874; telephone (800) 343-1990, No. 10632.

- Ethanol (CH_3CH_2OH), 95 percent, U.S.P.

- Nessler's reagent.

  1. Add 4.56 g potassium iodide (KI) to 30 mL DDI water in a beaker. Then add 5.68 g mercuric iodide (HgI_2). Stir until dissolved.

  2. Dissolve 10 g NaOH in 200 mL DDI water.

  3. Transfer NaOH solution to 250-mL volumetric flask. Add Hg solution slowly, then dilute to volume and mix thoroughly. Solution should not contain a precipitate. It can be used immediately.

7.6.2 Reagents and Consumable Materials for Automated Distillation-Titration Analysis

- Sodium chloride (NaCl).

- Antifoam, silicone spray bottle.

- Hydrochloric acid (HCl), 0.10 N, standardized--Purchased or prepared by the following procedure: Add 150 mL concentrated HCl to approximately 15 L DDI water, dilute to 18 L. Standardize against sodium carbonate.

  Standardize 0.1 N HCl with the following equipment and method:

  1. Apparatus
     (a) Automatic titrator (buret, optional).
     (b) Erlenmeyer flasks, 250 mL.

  2. Reagents
     (a) Hydrochloric acid (HCl), 0.1 N.
     (b) Sodium carbonate (Na_2CO_3), primary standard grade.
     (c) Methyl orange indicator solution, 0.1 percent aqueous solution.

  3. Procedure

     Dry Na_2CO_3 for 2 hours at 110 °C. Cool in a desiccator. Weigh 0.25 g ± 0.1 mg Na_2CO_3 into 250-mL Erlenmeyer flasks. Dissolve in about 50 mL DDI water. Add 3 drops methyl orange indicator and titrate with HCl until the first permanent pink end-point (pH = 4.0).

- Boric acid (H_3BO_3), 4 percent (w/v) aqueous solution--Add 720 g boric acid to about 4 L DDI water in a large stainless steel beaker. Heat to near boiling and stir until crystals dissolve. Fill a 5-gallon Pyrex solution bottle with about 12 L DDI water. Transfer hot solution through a large polyethylene funnel into the bottle. Dilute to 18 L with DDI water and mix well.

7.6.3 Reagents and Consumable Materials for Manual Distillation-Automatic Titration Analysis

- Sodium chloride (NaCl).

- Antifoam mixture--Mix equal parts of mineral oil and octanol.

- Boric acid (H_3BO_3), 4 percent--(See Section 7.6.2).

- Hydrochloric acid (HCl), 0.10 N, standardized--Purchased or prepared

by the following procedure: Add 150 mL concentrated HCl to approximately 15 L DDI water. Dilute to 18 L. Standardize against sodium carbonate as described in Section 7.6.2.

- Sodium hydroxide (NaOH), 1 N--Add 500 mL 50 percent NaOH solution to 8 L of DDI water in a 9.5-L Pyrex solution bottle. Dilute to 9 L with DDI water and mix well.

- Zinc, granular.

7.6.4 Reagents and Consumable Materials for Ammonium Displacement-Flow Injection Analysis

The reagents and consumable materials used depend on recommendations of the manufacturer of the FIA and may vary by make and model.

- Hydrochloric acid 0.1 N (HCl)--(see Section 7.6.2).

- Nitroferricyanide reagent--Dissolve 40 g potassium sodium tartrate ($KNaC_4H_4O_6$) and 30 g sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 500 mL DDI water. Add 10 g sodium hydroxide pellets (NaOH). Add 1.5 g sodium nitroferricyanide ($Na_2Fe(CN)_5$-$NO \cdot 2H_2O$), dilute to 1.00 L, and mix well. Store in a dark bottle. Prepare fresh solution monthly.

- Sodium hypochlorite reagent--Dissolve 20 g sodium hydroxide and 20 g boric acid in 150 mL of DDI water. Add 800 mL 5 percent solution NaOCl (household bleach). Dilute to 1.00 L with DDI water. Store in a dark bottle. Prepare fresh solution monthly.

- Sodium phenate reagent--Dissolve 95 mL 88 percent liquified phenol in 600 mL DDI water. While stirring, slowly add 120 g NaOH. Cool. Add 100 mL ethanol and dilute to 1.00 L. Store in a dark bottle.

- Nitrogen standard solution, 1,000 mg N/L--Dissolve 3.819 g ammonium chloride (NH_4Cl), dried at 105 °C, in DDI water and dilute to 1.00 L. Pipet 15.0, 10.0, 6.0, and 2.0 mL of this solution into 100-mL volumetric flasks. Take to volume with 0.1 N HCl. This will yield 150, 100, 60, and 20 mg N/L working standards. Pipet 5 mL of the 100 mg N/L working standard into a 100-mL volumetric flask and dilute to volume with 0.1 N HCl. This provides a 5 mg N/L working standard. Prepare fresh working standards weekly.

7.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not being used.

7.8 Calibration and Standardization

Use standards containing 0, 5, 20, 60, 100, and 150 mg N/L as NH_4 to develop a calibration curve. A regression of the standard curve should have an intercept close to zero. A QCCS is run immediately after the calibration standards and is run again after every tenth sample. Air bubbles produce sharp sudden peaks which destroy the calibration curve. In the event of air bubbles, the calibration curve and all samples between QCCSs (as many as 10 samples) must be reanalyzed. Standard values should not vary by more than 5 %RSD. Standardization is accomplished through use of the mechanical extractor, volumetric glassware, and repipets (automatic pipettors).

7.9 Quality Control

QC procedures are specified in Section 2.6. One sample is run in duplicate for each saturating solution with each batch of samples. Three reagent blanks are processed for each saturating solution with each batch of samples, and the mean and standard deviation of the results for each are recorded.

If CEC is determined by FIA, the QCCS is a solution; QCCSs are run immediately after the calibration curve is established and after every tenth sample. There is no QCCS for the distillation-titration method; however, the acid used for titration must be restandardized weekly.

Matrix spikes are required for both methods. Use a solution of NH_4Cl or $(NH_4)_2SO_4$ as the spiking solution. For FIA, the final displaced solution (Section 7.10.4.1, step 1) may be split, and the matrix spike may be added to one split. For distillation-titration, a second sample must be processed, and the matrix spike must be added to the sample just prior to distillation.

7.10 Procedure

The following procedure is performed twice for each sample; once with an NH_4OAc solution as the NH_4 source for the saturating procedure, and once with an NH_4Cl solution as the NH_4^+ source. The NH_4 adsorbed by the soil is measured by one of the three analytical procedures given in sections 7.10.2, 7.10.3, and 7.10.4.

7.10.1 Saturation Procedure

1. Prepare sample tubes by tightly compressing a 1-g ball of filter pulp into bottom of syringe barrel with a modified plunger. Modify the plunger by removing the rubber portion of the plunger, and cut off the plastic protrusion.

2. For mineral soils, weigh 2.50 ± 0.01 g air-dried soil and place in sample tube. Place sample tube in upper disc of extractor and connect to inverted tared extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor. Fill syringe to 20-mL mark with NH_4OAc. Stir sample and NH_4OAc with glass stirring rod for 15 seconds, rinse rod with NH_4OAc, and fill syringe to 25-mL mark. Let stand for 20 minutes. Continue at step 3.

   For organic soils, weigh 2.50 ± 0.01 g of air-dried soil into a small glass tube. Add 2 mL of ethanol as a wetting agent. (If the organic soil wets easily, it is not necessary to add the ethanol.) When the soil is moistened, add 15 mL NH_4OAc, cap, and shake for 1 hour on a reciprocating shaker. Place sample tube in upper disc of extractor and connect to inverted, *tared* extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor. Then quantitatively transfer the sample and NH_4OAc to the sample tube and fill to the 30-mL mark with NH_4OAc. Let stand for 20 minutes. Continue at step 3.

3. Put reservoir tube on top of sample tube. Extract rapidly until NH_4OAc is at a depth of 0.5 to 1.0 cm above sample. Turn off extractor. Add about 45 mL NH_4OAc to reservoir tube, turn on extractor, and extract overnight or for approximately 17 hours.

4. The next morning, switch off extractor and pull plungers down as far as extractor will allow. Disconnect syringes from sample tubes, leaving rubber connectors on sample tubes. Weigh each syringe containing the NH_4OAc extract to the nearest 0.01 g. Use the following density factor of the solutions to convert solution weight to volume: 1.0124 g/cm^3 for NH_4OAc, 1.0106 g/cm^3 for NH_4Cl.

(As an alternative, quantitatively transfer the solution recovered in the syringe to a volumetric flask and dilute to volume. This solution is reserved for analysis of exchangeable basic cations as described in Section 8.)

5. Mix the extract in each syringe by shaking manually. Rinse the polyethylene bottle twice with small volumes of the extract solution, then fill the container with extract solution, and discard the excess. This solution is reserved for analysis of exchangeable cations as described in Section 8.

6. Return upper 2-disc unit to starting position. Attach the syringes to the sample tubes, and rinse the sides of sample tubes with ethanol from a wash bottle. Fill sample tubes to the 20-mL mark, stir, and let stand for 15 to 20 minutes. Place reservoir tube in sample tube. Extract rapidly until the level of ethanol is 0.5 to 1.0 cm above sample. Turn off extractor and add enough ethanol to the reservoir to ensure an excess over the capacity of the syringe. Extract for 45 minutes.

7. After the extractor has stopped, turn off the switch, pull the plungers down, remove syringes, and discard the ethanol wash. Return the upper unit of the extractor to starting position, reattach syringes to the sample tube, fill reservoir tubes with about 45 mL ethanol, and extract a second time for approximately 45 minutes.

   When extractor has stopped, remove syringes and discard ethanol. After the second ethanol extraction, collect a few drops of ethanol extract on a spot plate. Test for residual NH_4^+ in each sample by using Nessler's reagent. If the test is positive, repeat another ethanol extraction of the affected samples and test by using Nessler's reagent until a negative test is obtained. If analyzing by FIA, go to Section 7.10.4.

8. Remove sample tubes and quantitatively transfer each sample to a 800-mL Kjeldahl flask, if direct distillation is used, or to a 250-mL digestion tube, if steam distillation is used. To remove the sample, blow the filter pulp and soil out of the syringe by using a gentle flow of compressed air. Wash with a minimum of CO_2-free, DDI water. Use a rubber policeman to complete the transfer. The solution is reserved for analysis as described in sections 7.10.2, 7.10.3, or 7.10.4.

7.10.2 Analytical Procedure using Automated Distillation-Titration

To soil and filter pulp in a 250-mL digestion tube (from Section 7.10.1, step 7), add 6 to 7 g sodium chloride. Refer to the instructional manual for operation of the Kjeltec auto 1030 analyzer or other similar unit. Spray silicone antifoam solution into the digestion tube and connect it to the distillation unit. Close the safety door. The distillation, titration, and calculation are performed automatically in about 4 minutes. The result is printed in milliliters of titrant.

7.10.3 Analytical Procedure using Manual Distillation-Automated Titration

To soil and filter pulp in 800-mL Kjeldahl flask (from Section 7.10.1, step 7), add 400 mL DDI water and 10 g NaCl, 5 drops antifoam mixture, 1 to 2 g granular zinc, and 40 mL 1 N NaOH. Connect the flask with the condenser of the Kjeldahl unit. Turn on cooling water of condenser and heat sample, being careful not to allow sample to boil over into condenser. If excessive foaming occurs or solution appears about to boil over, reduce the heat source. Should the sample boil over into the trap or beyond the trap into the condenser, the system should be thoroughly steamed and back-flushed before using again.

Collect 175 to 180 mL distillate in a 250-mL plastic titrator beaker containing 50 mL 4 percent boric acid solution. Transfer beakers to titrator magazines and load onto sample changer of automatic titrator. Titrate with 0.10 N HCl to a pH 4.60 end point. Follow instructions for operation of Metrohm automatic titrator or other comparable instrument in setting up instrument for titration for cation exchange capacity.

7.10.4 Analytical Procedure using Ammonium Displacement-Flow Injection Analysis

- This procedure is modified from Doxsee (1985). Continue from Section 7.10.1, step 7, after the second extraction of 45 mL ethanol. Add 50 mL 0.1 M HCl and extract at a setting of 10 (approximately 1 hour) until all the leachate has passed through the soil. Switch off extractor and pull plungers down as far as extractor will allow. Disconnect syringes from sample tube and leave the rubber connector on the sample tube. Save filtrate for analysis on the flow injection analyzer.

- The following procedure is specific for a Lachat FIA. If another FIA is used, the laboratory must follow the operating procedures for that instrument.

  1. Turn on the instrument and related peripheral equipment.

  2. Adjust the instrument and peripherals according to the manufacturer's specifications necessary for the method.

  3. Check all connections on chemistry manifolds to be sure none are loose. Also check pump lines for wear. Remove dilution line from ammonia manifold and put CEC sample loop in place on valve.

  4. With pump on regular speed, apply tension on pump tube and immerse pump lines into appropriate reagent bottles (see Table 7-1). Color and purpose of each tube will vary with the instrument and method used.

Table 7-1. Typical Purpose and Size of Each Pump Tube

Pump Line	Tubing Size (Color Code)
Distilled water for sampler	Green/green
Cyanide reagent	Orange/orange
Phenate reagent	Orange/orange
Hypochlorite reagent	White/white
Distilled water for ammonium reaction	Blue/blue
Degas line for ammonia reaction	Orange/white
Valve pump	Green/green

  5. Insert the pens into the chart recorder. After the baselines have stabilized, use the zero potentiometer on the colorimeter to zero each of the channels. The reading on the colorimeter should be within the manufacturer's specified range for each channel.

  6. Activate the computer which is used to operate the FIA system.

  7. Prepare standards containing 150-100-, 50-, 20-, and 0-mg N/L as NH_4^+ for use in developing a calibration curve and for standard checks every tenth sample.

  8. Adjust peak height on a chart recorder to full scale for the 150-mg N/L as NH_4^+ standard.

  9. Analyze the solutions, blanks, and standards following the manufacturer's procedure.

  10. After the samples have been analyzed, follow the manufacturer's instructions for cleaning and shutting down the instrument.

7.10.5 NH_4Cl Saturation Procedure

After completion of analysis by the steps given in Sections 7.10.2, 7.10.3, or 7.10.4, repeat the entire process with fresh samples (starting with Section 7.10.1), except use NH_4Cl instead of NH_4OAc throughout the saturation procedure.

7.11 Calculations

All CEC results are reported to the nearest 0.01 meq/100g oven-dry equivalent-weight soil.

7.11.1 Results from Either Distillation-Titration Analytical Procedure (Section 7.10.2 or 7.10.3)

Results are provided by the analysis or titration unit in milliliters of titrant (0.1 N HCl). To determine CEC, use the following equation:

$$\text{CEC (meq/100 g)} = (\text{mL HCl})\ \frac{\text{Normality of acid}}{\text{oven-dry sample wt (g)}}\ (100) \qquad (7\text{-}1)$$

where

$$\text{Oven-dry sample wt (g)} = \frac{100 - \%\ \text{moisture}}{100}\ \text{air-dry sample wt (g)} \qquad (7\text{-}2)$$

7.11.2 Results from Ammonium Displacement-Flow Injection Analysis Procedure (Section 7.10.4.)

Results are provided by computer as milligrams nitrogen per liter or milliequivalents NH_4^+ per liter depending upon how the standards are set up. To determine CEC, one of the following equations is used:

7.11.2.1 Using mg N/L

$$\text{CEC (meq/100 g)} = \frac{\text{mg N}}{\text{L}}\ \frac{\frac{\text{L}}{1000\ \text{mL}} \cdot 50\ \text{mL extract}}{\text{oven-dry soil sample wt (g)}\ \frac{14.0067\ \text{mg N}}{\text{meq}}}\ (100\ \text{g Soil}) \qquad (7\text{-}3)$$

7.11.2.2 Using meq NH_4^+/L--

$$\text{CEC (meq/100 g)} = \frac{\text{meq}\ NH_4^+}{\text{L}}\ \frac{\frac{\text{L}}{1000\ \text{mL}} \cdot 50\ \text{mL extract}}{\text{Oven-dry soil sample wt (g)}}\ (100\ \text{g Soil}) \qquad (7\text{-}4)$$

where: Oven-dry soil sample wt (g) = $\frac{100 - \%\ \text{moisture}}{100}$ air-dry soil sample wt (g)

and meq NH_4^+ = 18.0383 mg

7.12 Precision and Accuracy

Relative intralaboratory precision is within 10 percent. For most soils, the NH_4OAc CEC should be greater than the NH_4Cl CEC.

7.13 References

Blume, L. J., M. A. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

Doxsee, Kari. 1985. *Cation Exchange Capacity in Nursery Soils Using FIA (Flow Injection Analysis).* Am. No. 1503-15. Weyerhaeuser Technology Center, Research Division, Tacoma, Washington.

Rhodes, J. D. 1982. Cation Exchange Capacity, pp. 149-158. In: *Methods of Soil Analysis: Part 2 - Chemical and Microbiological Properties,* Second Edition, A. L. Page, R. H. Miller, and D. R. Keeney (eds.). American Society of Agronomy, Inc./Soil Science Society of America, Inc., Madison, Wisconsin.

United States Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

8 Exchangeable Basic Cations

8.1 Scope and Application

The exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) in the soil can be used to estimate the fertility of a soil and its ability to buffer against acidic deposition. Ammonium chloride and buffered ammonium acetate are used to estimate exchangeable basic cations at the soil pH and at the buffered pH.

Base saturation is given as the total amount of exchangeable basic cations divided by the CEC. Cation exchange sites not occupied by basic cations are assumed to be occupied by acidic cations such as hydrogen and aluminum.

Cation exchange capacity relates to the buffering capacity of the soil. Base saturation is a measure of how much buffering capacity remains in the soil. Exchangeable acidity is a measure of the amount of exchangeable basic cations which have been displaced by acidic cations (H^+, Al^{3+}) through weathering and acid deposition.

Inductively coupled plasma emission spectroscopy (ICP) may be used to analyze the extracts for sodium, calcium, and magnesium. Flame atomic emission spectroscopy (flame photometry) may be used for potassium and sodium determinations. The AA and ICP methods described here are taken from *Methods for Chemical Analysis of Water and Wastes* (U.S. EPA, 1983). The flame photometric method is taken from *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 1985).

The following concentration ranges of analytes may be expected in the soil extracts (Table 8-1).

Typical performance data for concentration range, sensitivity, and detection limit may be obtained from Table 8-2.

Table 8-1. Expected Range of Analyte Concentrations in Soil Extracts

Analyte	meq/L	mg/L
Ca^{2+}	0-30	0-600
Mg^{2+}	0-10	0-122
K^+	0-05	0-196
Na^+	0-20	0-460

Recommended wavelengths and estimated detection limits for ICP analysis are given in Table 8-3.

When analyzing by flame photometry, the better instruments can be used to determine sodium levels approximating 100 µg/L. With proper modifications in technique, the range of sodium measurement can be extended to 10 µg/L or lower. Potassium levels of approximately 0.1 mg/L can be determined.

8.2 Summary of Method

Previously prepared extracts from the CEC procedure (Section 7) are analyzed for calcium, magnesium, potassium, and sodium by one or by a combination of the following methods.

Once the concentration of each cation in the soil extract is determined, the cation concentrations in the original soil sample may be calculated.

8.2.1 Atomic Absorption (for Ca^{2+}, Mg^{2+}, K^+, and Na^+)

A portion of the extract is aspirated into the AA unit and is 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

Table 8-2. Atomic Absorption Performance Data for Determination of Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} (U.S. EPA, 1983)

	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}
Optimum concentration range	0.2-7 mg/L	0.02-0.05 mg/L	0.1-2 mg/L	0.3-1 mg/L
Wavelength	422.7 nm	285.2 nm	766.5 nm	589.6 nm
Sensitivity	0.08 mg/L	0.007 mg/L	0.04 mg/L	0.15 mg/L
Detection limit	0.001 mg/L	0.001 mg/L	0.01 mg/L	0.002 mg/L

Table 8-3. Recommended Wavelengths and Estimated Instrumental Detection Limits for Inductively Coupled Plasma Analysis

Element	Wavelength[a] (nm)	Estimated detection limit (μ/L)[b]
Calcium	317.933	10
Magnesium	279.079	30
Sodium	588.995	29

[a] The wavelengths are listed because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and if they are treated with the same corrective techniques for spectral interference.

[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.

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 cation in the extract.

8.2.2 Inductively Coupled Plasma (for Ca^{2+}, Mg^{2+}, and Na^{+})

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 side 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.

8.2.3 Flame Photometry (for K^{+} and Na^{+})

Trace amounts of sodium and potassium are determined by flame emission photometry at wavelengths of 589 and 766.5 nm, respectively. The sample is sprayed into a gas

flame, and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light-dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at the appropriate wavelength, e.g., 589 nm for Na^+, is approximately proportional to the concentration of the element. If alignment of the wavelength dial with the prism is not precise in the available photometer, the exact wavelength setting can be determined from the maximum needle deflection and then can be used for the emission measurements. The calibration curve may be linear but has a tendency to level off at higher concentrations.

8.3 Interferences

Three types of interferences, spectral, chemical, and physical, can be identified for the analytical portion of the method. These vary in importance depending on the particular analytical procedure chosen.

8.3.1 Spectral Interferences

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 for by utilizing a computer correction of the raw data. This correction requires 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 multielement 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.

Spectral interference in AA determinations is rare but can occur when an absorbing wavelength of an element present in the sample, but which is not being determined, falls within the width of the absorption line of the analyte. 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 multielement lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and when that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

8.3.2 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. For all determinations, chemical interference is the most troublesome type of interference 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. Chemical interferences may also be eliminated by separating the cation from the interfering materials. While they are primarily employed to increase the sensitivity of the analysis, complexing agents may also be used to eliminate or reduce interferences.

Ionization interferences occur when the flame temperature is sufficiently high to remove an electron from a neutral atom, thereby giving a positively charged ion. This type of interference generally can be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

Normally, chemical interference is negligible with the ICP technique. If observed, chemical interference can be minimized by careful selection of operating conditions, e.g., incident power or observation position, by buffering the sample, by matrix matching, and by standard addition procedures. Chemical interference can be highly dependent on the matrix type and the specific analyte.

Flame photometers operating on the internal standard principle may require adding a standard lithium solution to each working standard and sample in order to control chemical interference. The optimum lithium concentration may vary among individual instruments.

To suppress ionization and anion interference, radiation buffers should be added to sample and standard solutions. Among common anions capable of causing radiation interference are Cl^-, SO_4^{2-}, and HCO_3^- in relatively large amounts.

In the same manner as for AA analysis, chemical interference may be removed by separating the cation from the interfering material. When using the internal standard method for sodium determinations, potassium and calcium may interfere if the potassium-to-sodium ratio is greater than or equal to 5:1 and when the calcium-to-sodium ratio is greater than or equal to 10:1. When these ratios are exceeded, measure calcium and potassium first so that the approximate concentration of interfering ions may be added to the sodium calibration standards. Magnesium interference does not appear until the magnesium-to-sodium ratio exceeds 100:1, a rare occurrence.

For potassium determinations by the internal standard method, interference may occur at sodium-to-potassium ratios of 5:1 or greater. Calcium may interfere if the calcium-to-potassium ratio is 10:1 or more. Magnesium begins to interfere when the magnesium-to-potassium ratio exceeds 100:1.

8.3.3 Physical Interferences

For ICP determinations, physical interferences are generally considered to be associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high amounts of dissolved solids or high acid concentrations. The use of a peristaltic pump may lessen these interferences. If they are occurring, these types of interferences must be reduced by either dilution of the sample or by 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, and 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.

For flame photometric determinations, burner-clogging particulate matter may be removed from the sample solution by filtering the solution through a quantitative filter paper of medium retentiveness. A nonionic detergent may be incorporated in the standard lithium solution to ensure proper aspirator function.

8.3.4 Matrix Effects

Whenever a new or unusual sample matrix is encountered, a series of tests should be performed prior to reporting concentration data for the analyte. Such tests ensure that neither positive nor negative interferences are affecting any of the analytes, thereby distorting the accuracy of the reported values. These tests are the following:

8.3.4.1 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.

8.3.4.2 Spiked Addition--

The recovery of a spike added to the original sample at a minimum level of 10 times the instrumental detection limit (maximum 100 times) should be within 85 to 115 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 additions technique does not detect coincident spectral overlap (usually only a factor in ICP determinations). If overlap is suspected, the use of computerized compensation, an alternative wavelength, or comparison with an alternative method is recommended.

8.3.4.3 Comparison with Alternative Method of Analysis--

When investigating a new sample matrix, a comparison test may be performed with other analytical techniques such as atomic absorption spectrometry or other approved methodology.

8.3.4.4 Wavelength Scanning of Analyte Line Region--

If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

8.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses. When preparing reagents, especially when concentrated acids and bases are used, special care should be exercised. The use of concentrated hydrochloric acid and nitric acid should be restricted to a hood. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Follow the safety precautions of the manufacturer when operating instruments.

Follow good laboratory practices when handling compressed gases. Cylinders should be chained or bolted in an upright position.

8.5 Apparatus and Equipment

8.5.1 Determinations by Atomic Absorption

- Spectrophotometer, single- or dual-channel, single- or double-beam instrument with grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, provisions for interfacing with a strip chart recorder.
- Burner, as recommended by the instrument manufacturer. When nitrous oxide is used as the oxidant, a nitrous oxide burner is required.
- Hollow cathode lamps, single element lamps preferred; multielement lamps may be used. Electrodeless discharge lamps may be used when available.
- Strip chart recorder.

8.5.2 Determination by Inductively Coupled Plasma

- Inductively Coupled Plasma-Atomic Emission Spectrometer.

8.5.3 Determination by Flame Photometry

- Flame photometer, direct-reading or internal-standard type; or an atomic

absorption spectrometer operated in the flame emission mode.

8.6 Reagents and Consumable Materials

Water used for preparing or diluting reagents, standards, or samples must meet purity specifications for Type II Reagent Water given in ASTM D 1193 (ASTM, 1984). Acids used in the preparation of standards and for sample processing must be ultra-high purity grade, e.g., Baker Ultrex grade or SeaStart Ultrapure grade. To minimize pickup of cations in standard solutions, store solutions in linear or high density polyethylene bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake each container thoroughly to wash accumulated salts from walls before pouring solution.

8.6.1 Determination by Atomic Absorption

- Hydrochloric acid, concentrated (12M HCl)--Ultrapure grade (Baker Instra-Analyzed or equivalent).
- HCl (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL water.
- Nitric acid, concentrated--Ultrapure grade, Baker Instra-Analyzed or equivalent.
- Nitric Acid (0.5 percent v/v HNO_3)--Add 0.50 mL HNO_3 to 50 mL DDI water and dilute to 100 mL.
- Primary standard solutions--Prepare from ultra-high purity grade chemicals as directed in the individual procedures. Commercially available stock standard solutions may also be used.
- Dilute calibration standards--Prepare a series of standards of the cation by dilution of the appropriate stock metal solution in the specific matrix to cover the concentration range desired. Prepare all calibration standards in concentration units of mg/L.
- Fuel--Commercial grade acetylene is generally acceptable.
- Oxidant--Air may be supplied from a compressed-air line, a laboratory compressor, or from a cylinder of compressed air. Nitrous oxide is supplied from a cylinder of compressed gas.

8.6.2 Determination by Inductively Coupled Plasma

- Hydrochloric acid, concentrated (12 M, specific gravity 1.19) Ultrapure grade.
- Hydrochloric acid (50 percent v/v)--Add 500 mL concentrated HCl to 400 mL DDI water and dilute to 1.00 L.
- Nitric acid, concentrated (specific gravity 1.41)--Ultrapure grade.
- Nitric acid (50 percent v/v)--Add 500 mL concentrated HNO_3 to 400 mL DDI water and dilute to 1 L.
- Primary standard solutions--May be purchased or prepared from ultrahigh 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.

(1) Calcium stock standard solution (100 mg/L)--Suspend 0.2498 g $CaCO_3$ (dried at 180 °C for 1 hour before weighing) in DDI 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 DDI water.

(2) 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 DDI water.

(3) Sodium stock standard solution (100 mg/L)--Dissolve 0.2542 g NaCl dried at 140 °C in 0.1N NH_4Cl or 0.1N NH_4OAc, add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with DDI water.

8.6.3 Determination by Flame Photometry

- Sodium stock standard solution (1,000 mg/L)--Dissolve 2.542 g NaCl dried at 140 °C and dilute to 1,000 mL with DDI water.

- Intermediate sodium solution (100 mg/L)--Dilute 10.00 mL stock sodium solution with 1.0 N NH_4Cl or 1.O N NH_4OAc, as needed to match sample extract matrix, to 100.0 mL. Use this intermediate solution to prepare calibration curve in sodium range 1 to 10 mg/L.

- Standard sodium solution (10 mg/L)--Dilute 10.00 mL intermediate sodium solution with 1.0 N NH_4Cl or 1.0 N NH_4OAc, as needed to match sample extract matrix, to 100 mL. Use this solution to prepare calibration curve in sodium range of 0.1 to 1.0 mg/L.

- Potassium stock standard solution (1,000 mg/L)--Dissolve 1.907 g KCl dried at 110 °C and dilute to 1,000 mL with DDI water.

- Intermediate potassium solution (100 mg/L)--Dilute 10.0 mL stock potassium solution with 1.0 N NH_4Cl or 1.0 N NH_4OAc, as needed to match sample extract matrix, to 100 mL. Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L.

- Standard potassium solution (10 mg/L)--Dilute 10.0 mL intermediate potassium solution with 1.0 N NH_4Cl or 1.0 N NH_4OAc, as needed to match the sample extract matrix, to 100 mL. Use this solution to prepare calibration curve in potassium range of 0.1 to 1.0 mg/L.

- Standard Lithium Solution--Use either lithium chloride (LiCl) or lithium nitrate ($LiNO_3$) to prepare standard lithium solution containing 1,000 mg Li/L.

  Dry LiCl overnight in an oven at 105 °C. Rapidly weigh 6.109 g LiCl and dissolve in 1.0 N NH_4Cl or 1.O N NH_4OAc, as needed to match the sample extract matrix. Dilute to 1,000 mL with the same 1.0 N NH_4^+ solution.

  Dry $LiNO_3$ overnight in an oven at 105 °C. Rapidly weigh 9.935 g $LiNO_3$ and dissolve in 1.0 N NH_4Cl or 1.O N NH_4OAc, as needed to match the sample extract matrix. Dilute to 1,000 mL with the same 1.0 N NH_4^+ solution.

  Prepare a new calibration curve whenever the standard lithium solution is changed. Where circumstances warrant, alternatively prepare a standard lithium solution containing 2,000 mg or even 5,000 mg Li/L.

8.7 Sample Handling, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not being used.

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 Section 2.3. All sample solutions should be kept sealed and refrigerated at 4 °C when not being used.

8.8 Calibration and Standardization

Within each class of instruments (AA, ICP, and flame photometer), the calibration procedure varies slightly. Calibrate by analyzing a calibration blank and a series of at least three standards within the linear range. If an ICP is used, a multielement standard may be prepared and analyzed. For AA and flame photometric determinations, the instrument must be calibrated for each analyte by using a separate standard.

The concentration of standards should bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded. An alternative less sensitive resonance line may be used, but the standards still must bracket the samples.

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 that contain different known amounts of the test element. The volume of the blank and of each standard must be the same. The absorbence or emission 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 absorbence or emission, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left side 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 8-1. The method of standard additions can be very useful; however, for the results to be valid, the following limitations must be taken into consideration:

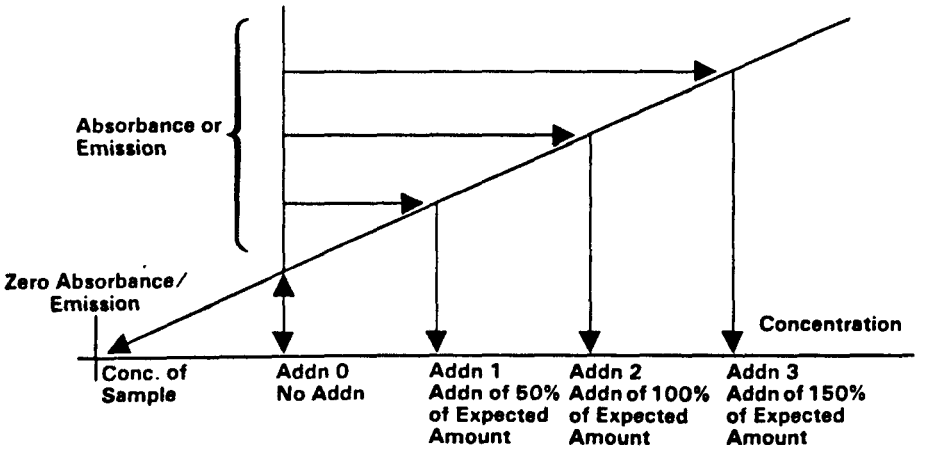


Figure 8-1. Standard addition plot.

- The absorbance plot of sample and standard 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 on 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.

8.9 Quality Control

In addition to the QC inherent in the calibration procedures, the QC procedures described in Section 2.6 must be followed.

8.10 Procedure

General procedures for flame atomic absorption, inductively coupled plasma, and flame emission are given in Sections 8.10.1, 8.10.2, and 8.10.3, respectively.

8.10.1 Procedure for Determination by Atomic Absorption

Differences among atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the operating instructions for the particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes unless the instrument is 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 of the manufacturer. Subsequently, light the flame and 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 analyte and calibrate the instrument. Aspirate the samples and determine the concentrations either directly (if the instrument reads directly in concentration units) or from a calibration curve.

8.10.1.1 Determination of Dissolved Calcium--

NOTE: Standards are made in 1.0 N NH_4OAc, 1.0 N NH_4Cl, and 0.002 M $CaCl_2$.

8.10.1.1.1 Preparation of Reagents--

- Lanthanum chloride ($LaCl_3$) matrix modifier solution--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl. CAUTION: Reaction is violent. Dilute to 500 mL with DDI water.

8.10.1.1.2 Preparation of Calcium Standard Solutions--

- Calcium stock solution (500 mg/L Ca) --Suspend 1.250 g $CaCO_3$ (spectroscopic grade, dried at 180 °C for 1 hour before weighing) in DDI 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^{2+} standards from the calcium stock solution in the correct matrix to span the desired concentration range. Prepare all calibration standards in concentration units of milligrams per liter (mg/L).

8.10.1.1.3 Suggested Instrumental Conditions (General)--Calcium hollow cathode lamp; wavelength, 422.7 nm; fuel, acetylene; oxidant, air; type of flame, reducing.

8.10.1.1.4 Analytical Procedure--

1. To each 10.0-mL volume of dilute calibration standard, blank, and sample (the soil extract), add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0-mL sample).

2. Calibrate the instrument. Analyze the samples. Dilute and reanalyze any samples for which the concentration exceeds the calibrated range. Record results as mg Ca^{2+}/L in the soil extract. (See Section 8.11.)

8.10.1.1.5 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, standards and samples are prepared in dilute acid solution. (NH_4Cl extract is somewhat acidic. NH_4OAc is pH 7.0.) Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values. Concentrations of as much as 500 mg/L of sodium, potassium, and nitrate cause no interference.

Anionic chemical interferences can be expected if lanthanum is not added to samples and standards.

A nitrous oxide-acetylene flame will provide two to five times greater sensitivity than an air-acetylene flame and will provide freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali, e.g., K^+ or Cs^+, 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.

8.10.1.1.6 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati) evaluation using distilled water spiked at concentrations of 9.0 and 36 mg Ca^{2+}/L, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99 percent.

8.10.1.2 Determination of Dissolved Magnesium--

8.10.1.2.1 Preparation of Reagents--

- Lanthanum chloride ($LaCl_3$) solution--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl. (CAUTION: Reaction is violent.) Dilute to 500 mL with DDI water.

8.10.1.2.2 Preparation of Magnesium Standard Solutions--

- Stock solution (500 mg/L Mg^{2+})--Dissolve 0.829 g magnesium oxide (MgO, spectroscopic grade) in 10 mL of HNO_3 and dilute to 1.00 L with DDI water.

- Dilute calibration standards--Daily, quantitatively prepare from the Mg^{2+} stock solution and in the correct matrix, a series of Mg^{2+} standards that spans the desired concentration range. Prepare all calibration standards in concentration units of milligrams per liter (mg/L).

8.10.1.2.3 Suggested Instrumental Conditions (General)--Magnesium hollow cathode lamp; wavelength, 285.2 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

8.10.1.2.4 Analytical Procedure--

1. 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).

2. Calibrate the instrument.

3. Analyze the samples.

4. Dilute and reanalyze any samples for which the concentration exceeds the linear range.

5. Record results as mg Mg^{2+}/L in the soil extract. (See Section 8.11.)

8.10.1.2.5 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 (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 °C rotation of the burner head will produce approximately one-eighth the normal sensitivity.

8.10.1.2.6 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati) evaluation using distilled water spiked at concentrations of 2.1 and 8.2 mg Mg^{2+}/L, the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100 percent.

8.10.1.3 Determination of Dissolved Potassium--

8.10.1.3.1 Preparation of Potassium Standard Solutions--

- Potassium stock solution (100 mg/L K) - Dissolve 0.1907 g KCl (spectroscopic grade, dried at 110 °C) in DDI water and dilute to 1.00 L.

- Dilute calibration standards--Daily, quantitatively prepare in the correct matrix a series of calibration standards spanning the desired concentration range. Prepare all calibration standards in concentration units of milligrams per liter (mg/L).

8.10.1.3.2 Suggested Instrumental Conditions (General)--

- Potassium hollow cathode lamp; wavelength, 766.5 nm; fuel, acetylene; oxidant, air; type of flame, slightly oxidizing.

8.10.1.3.3 Analytical Procedure--

1. Calibrate the instrument.

2. Analyze the samples.

3. Dilute and reanalyze any sample for which the concentration exceeds the calibrated range.

4. Record results as mg K^+/L in the soil extract. (See Section 8.11.)

8.10.1.3.4 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 can enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na^+ to K^+ is under 10. Any enhancement because of 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 (0.1 to 20 mg/L), it is suggested that the burner head be rotated. A 90 °C rotation of the burner head provides approximately one-eighth the normal sensitivity.

8.10.1.3.5 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati) evaluation using distilled water samples spiked at concentrations of 1.6 and 6.3 mg K^+/L, the standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103 percent and 102 percent, respectively.

8.10.1.4 Determination of Dissolved Sodium--

8.10.1.4.1 Preparation of Sodium Standard Solutions--

- Sodium stock solution (1,000 mg/L Na^+)--Dissolve 2.542 g NaCl (spectroscopic grade, dried at 140 °C) in DDI water and dilute to 1.00 L.

- Dilute calibration standards - Daily, quantitatively prepare a series of calibration standards in the correct matrix spanning the desired concentration range. Prepare all calibration standards in concentration units of milligrams per liter (mg/L).

8.10.1.4.2 Suggested Instrumental Conditions (General)--Sodium hollow cathode lamp; wavelength, 589.6 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

8.10.1.4.3 Analytical Procedure--

1. Calibrate the instrument.

2. Analyze the samples.

3. Dilute and reanalyze any samples for which the concentration exceeds the calibrated range.

4. Record results as mg Na^+/L. (See Section 8.11.)

8.10.1.4.4 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 ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1,000 mg/L) to both standards and samples.

8.10.1.4.5 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati) evaluation using distilled water samples spiked at levels of 8.2 and 52 mg Na^+/L, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102 percent and 100 percent.

8.10.2 Procedure for Determinations by Inductively Coupled Plasma

1. Set up the instrument as recommended by the manufacturer or as experience dictates. The instrument must be allowed to become thermally stable before analysis begins (10 to 30 minutes).

2. Profile and calibrate the instrument according to the recommended procedures of the 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.

3. Begin sample analysis, flushing the system with the calibration blank solution between each sample. Analyze QC samples as required.

4. Dilute and reanalyze any samples for which the concentration exceeds the calibration range.

8.10.3 Procedure for Determinations by Flame Photometry

Locate instrument in an area away from direct sunlight or constant light emitted by an overhead fixture and in an area free of drafts, dust, and tobacco smoke. Guard against contamination from corks, filter paper or pulp, perspiration, soap, cleansers, cleaning mixtures, and inadequately rinsed apparatus. Because of differences among instruments, it is impossible to formulate detailed operating instructions. Follow recommendation of the manufacturer for selecting proper photocell and wavelength, for adjusting slit width and sensitivity, for appropriate fuel and oxidant pressures, and for the steps for warm-up,

correcting for interferences and flame background, rinsing of burner, igniting sample, and measuring emission intensity.

8.10.3.1 Direct Intensity Measurement--

Starting with the highest calibration standard and working toward the most dilute, measure emission at 589 nm for sodium and 766.5 nm for potassium. Repeat the operation with calibration standards and samples enough times to secure a reliable average reading for each solution.

8.10.3.2 Internal Standard Measurement--

To a carefully measured volume of sample (or diluted portion), each sodium calibration standard, and a blank, add with a volumetric pipet an appropriate volume of standard lithium solution. Then follow all steps prescribed in 8.10.3.1 above for direct-intensity measurement.

8.10.3.3 Bracketing Approach--

If greater precision and accuracy are required from the calibration curve or if concentrations are automatically output by the instrument, select and prepare sodium standards that immediately bracket the emission intensity of the sample. Determine emission intensities of the bracketing standards, i.e., one standard slightly less than and the other slightly greater than the sample, and of the sample as simultaneously as possible. Repeat the determination on bracketing standards and sample.

8.11 Calculations

8.11.1 Solution Concentrations

Instruments may be calibrated to output sample or soil extract results directly in concentration units, i.e., mg/L. If the instrument is not so calibrated or programmed, then either (1) the slope of the linear calibration curve is calculated and sample concentrations are subsequently calculated, or (2) a manual calibration curve is prepared and sample concentrations are determined by comparing the sample signal to the calibration curve.

8.11.2 Dilutions

If dilutions are performed, the appropriate factor must be applied to sample values. The dilution factor is incorporated in equations 8-1 and 8-2.

8.11.3 Flame Photometry

If analyses are performed by flame photometry and the bracketing approach is used, the following equation and equations 8-1, 8-2, and 8-3 (Section 8.11.4) are required to determine meq/L:

$$\text{mg analyte/L} = \frac{[(B - A)(s - a) + A]\,D}{(b - a)}$$

where,

B = mg analyte/L in upper bracketing standard

A = mg analyte/L in lower bracketing standard

b = emission intensity of upper bracketing standard

a = emission intensity of lower bracketing standard

s = emission intensity of sample

$$D = \text{dilution ratio} = \frac{\text{mL sample} + \text{mL diluent}}{\text{mL sample}}$$

8.11.4 Atomic Absorption or Inductively Coupled Plasma

To convert mg/L to meq/L, multiply mg/L times 0.0256 for K^+ or by 0.0435 for Na^+.

After the meq/L values are obtained, calculate and report results in the original soil

sample on an oven-dried (OD) basis by using the following equation:

analyte concentration in soil (meq/100g) =

$$\left(\frac{\text{analyte conc. in extract (meq/L)}}{\text{OD soil sample wt (g)}}\right)\left(\frac{\text{extract volume mL}}{\text{1,000 mL/L}}\right)\left(\text{dilution factor if needed}\right)(100) \quad (8\text{-}1)$$

where,

$$\text{extract volume mL} = \frac{\text{weight of extract in reservoir tube (g)}}{\text{density of extraction solution (g/cm}^3\text{)}} \quad (8\text{-}2)$$

NOTE: Density of 1.0 N NH_4OAc = 1.0124 g/cm^3, 1.0 N NH_4Cl = 1.0105 g/cm^3

and,

$$\text{grams oven-dried (OD) sample} = \left(100 - \frac{\text{\% moisture content}}{100}\right)\left(\text{wt air-dried soil in g}\right) \quad (8\text{-}3)$$

Values should be reported to the nearest 0.001 meq.

8.12 Precision and Accuracy

The precision and accuracy information provided is based on analysis of water samples (U.S. EPA, 1983; APHA et al., 1985) and various types of waste samples (Patel et al., 1984). Analysis of soil extracts, which have different matrices and reflect different sample preparation procedures, may not supply results of the same precision and accuracy as cited here. The information in this section is supplied only as an indicator.

8.12.1 Determination by Atomic Absorption

Precision and accuracy for the instrumental portion of the procedure only were reported in the cation-specific discussions in sections 8.10.1.1.6 (Ca^{2+}), 8.10.1.2.6 (Mg^{2+}), 8.10.1.3.5 (K^+), and 8.10.1.4.5 (Na^+).

8.12.2 Determinations by Inductively Coupled Plasma

Precision and accuracy for synthetic standards prepared in distilled water are not available for the analytes of interest (Ca^{2+}, Mg^{2+}, and Na^+). The only precision and accuracy results available are for analysis of waste samples (Patel et al., 1984). It is not known how closely these results relate to those for soil sample extracts. The results (see Table 8-4) should not be compared to those by AA or flame photometry, however, because the matrices of the samples are not the same.

Table 8-4. Precision and Accuracy Data for Inductively Coupled Plasma (Patel et al., 1984)

	Precision (% RSD)	Accuracy (% Recovery)
Ca^{2+}	7.00	105.0
Mg^{2+}	6.62	100.5
Na^+	5.98	123.7

8.12.3 For Determinations by Flame Photometry

A synthetic sample containing 19.9 mg Na^+/L, 108 mg Ca^{2+}/L, 82 mg Mg^{2+}/L, 3.1 mg K^+/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L was analyzed in 35 laboratories by the flame photometric method, with %RSD of 17.3 and a relative error of 4.0 percent for solution determinations. A %RSD of 15.5 and a relative error of 2.3 percent were calculated for potassium determinations.

8.13 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.

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water*, D1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Blume, L. J., M. A. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I Field Sampling.* U.S. Environmental Protection Agency.

Fassel, V. A. 1982. *Analytical Spectroscopy with Inductively Coupled Plasmas - Present Status and Future Prospects.* In: *Recent Advances in Analytical Spectroscopy.* Pergamon Press, New York, New York.

Patel, B. R., G. A. Raab, D. Cardenas, and T. W. Riedy. 1984. *Report on a Single-Laboratory Evaluation of Inductively Coupled Plasma Optical Emission Method 6010.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes, Method 200.0, Atomic Absorption Methods; and 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. Environmental Protection Agency, Cincinnati, Ohio.

9 Exchangeable Acidity

9.1 Scope and Application

Exchangeable acidity refers to the hydrogen and aluminum ions held on soil colloids rather than to those ions present in the soil solution (active acidity). Because the ions migrate from the colloids to the soil solution when the pH is reduced, the conditions under which exchangeable acidity is quantitatively determined must be defined carefully.

The method most frequently used to determine exchangeable acidity and recommended by Fernandez (1983) involves treatment of the soil sample with a barium chloride ($BaCl_2$) solution buffered to pH 8.2 followed by titration of the extracted solution. This method actually measures total potential acidity, not the exchangeable acidity that actually occurs in field soils. Determination of exchangeable acidity by treatment of the soil sample with a solution of a neutral salt (KCl) and followed by subsequent titration of the extracted solution may be more indicative of actual field acidity. Methods for both $BaCl_2$- and KCl-exchangeable acidity are provided here, but the former is performed primarily to allow comparison with already existing data.

The KCl extract obtained from this procedure is analyzed for aluminum, as well as for exchangeable acidity, because the aluminum species that is extracted by the KCl solution is the species most likely to be toxic to fish and plants.

9.2 Summary of Method

Exchangeable acidic ions are extracted from two portions of a soil sample. One of the extractions is with a $BaCl_2$ extracting solution, and the other is with a KCl extracting solution. The extracts are then titrated, and the results are expressed as milliequivalents exchangeable acidity per 100 g soil. These extraction and titration procedures are performed with automated equipment. This method is modified from Thomas (1982) and USDA/SCS (1984).

The KCl extract is also analyzed for aluminum by inductively coupled plasma atomic emission spectrometry (ICP). This instrumental technique is summarized in Section 8.2.2.

9.3 Interferences

No specific interferences are identified for the extraction and titration procedures; use of automated equipment minimizes effects of variation in technique. Interferences influencing the determination of aluminum by ICP are described in Section 8.3.

9.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and ammonium hydroxide solutions should be restricted to a hood.

Follow the safety precautions provided by the manufacturer when operating the instruments.

Follow good laboratory practices when handling compressed gases. Cylinders should be chained or bolted in an upright position.

9.5 Apparatus and Equipment

9.5.1 General

- Mechanical extractor, 24 place, manufactured by Centurion, Inc. (Figure 7-1).
- Syringes, 60 mL, one sample tube and one extraction syringe per sample.

- Stirring rods, glass; one per sample.
- Pipettors, 2, volume adjustable to 25 mL.
- Filter pulp, Schleicher and Schuell, No. 289, washed according to the procedure given in Section 2.4.
- Erlenmeyer flasks, 250 mL and 125 mL.
- Reciprocating shaker.
- Tubes, glass, 25 mL, centrifuge or culture, with caps.
- Eppendorf or equivalent pipet, 5 mL with disposable plastic tips.
- Eppendorf or equivalent pipet, 5 μL with disposable plastic tips.
- Volumetric flasks, volumes as needed.
- Bottles, polyethylene (LPE), 25 mL, optional.
- Automatic titrator.
- pH meter and electrode.
- Fleakers.

9.5.2 Instrumentation for Determination by ICP

- Inductively coupled plasma atomic emission spectrometer, computer-controlled, with background correction capability.

9.6 Reagents and Consumable Materials

- Ascarite.
- Buffer solution (0.5 N $BaCl_2$/0.2 N $N(CH_2CH_2OH)_3$)--Dissolve 61.07 g $BaCl_2 \cdot 2H_2O$ and 29.8 g triethanolamine (TEA) in 1.00 L CO_2-free, DDI water. Adjust pH to 8.2 with 10 percent HCl. Protect solution from CO_2 contamination by attaching a drying tube containing Ascarite to the air intake of the storage vessel.
- Replacement solution (0.5 N with respect to $BaCl_2$)-Dissolve 61.07 g $BaCl_2 \cdot 2H_2O$ with 5 mL of above $BaCl_2$-TEA buffer solution and dilute to 1.00 L with DDI water.
- Hydrochloric acid, concentrated (12 M HCl)-Ultrapure grade (Baker Instra-Analyzed or equivalent).
- Hydrochloric acid (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL DDI water.
- Hydrochloric acid (0.1 N, standardized)--Dilute 8.32 mL concentrated HCl to 1.00 L with DDI water. Standardize as described in Section 7.6.2. This may also be purchased as certified, standardized 0.1 N HCl.
- Potassium chloride replacement solution (1.0 N)--Dissolve 74.56 g KCl in water and dilute to 1.00 L.
- Sodium hydroxide (NaOH), pellets or flakes.
- Sodium hydroxide (5 percent wt/vol) --Dissolve 50 g NaOH in DDI water and dilute to 1.000 L. This dissolution generates heat; therefore, a water- or ice-bath should be used to cool the dissolution vessel.
- Sodium hydroxide (0.01 N, standardized)--Dilute 6 to 7 mL of 5 percent NaOH to 1.00 L with CO_2-free DDI water. Titrate 20.00 mL with the 0.1 N standardized HCl titrant to a methyl orange endpoint (pH $\approx$ 4.4).
- Methyl orange solution, 0.1 percent aqueous solution--Dissolve 0.10 g methyl orange in 100 mL DDI water.

- Sulfuric acid, concentrated--Ultrapure grade.
- Nitric acid, concentrated--Ultrapure grade.
- Nitric acid (0.5 percent v/v HNO_3 Ultrapure grade)--Add 1 mL concentrated HNO_3 to DDI water and dilute to 200 mL.
- Primary aluminum standard.
- Dilute calibration standards--Prepare a series of aluminum standards to cover the concentration range desired by dilution of the primary aluminum standard. Prepare all calibration standards in concentration units of milligrams per liter (mg/L).
- NBS-traceable pH buffers of pH = 4, pH = 7, and pH = 10, for electrode calibration.

9.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the laboratory, all samples are kept sealed and are refrigerated at 4 °C when not is use.

9.8 Calibration and Standardization

9.8.1 Titration

Calibrate the titrator for volume of solution delivered. Calibrate the pH electrode by using two pH buffers that bracket the desired endpoint. (Refer to Section 6.8 for general information.)

9.8.2 Determination of Aluminum

Calibrate the instrument for aluminum by analyzing a calibration blank and a series of at least three standards within the linear range. Follow the instructions in the instrument operating manual. The concentration of standards should bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded.

9.8.3 Method of Standard Additions for Determination of Aluminum

Aluminum may be quantified by the method of standard additions. (Note: It is difficult to maintain a stable, concentrated solution of Al^{3+} for performing matrix spikes or standard additions.)

In this method, equal volumes of sample are added to a DDI water blank and to three standards that contain different known amounts of aluminum. The volume of the blank and of each standard must be the same. The emission 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 side 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 8-1. 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 emission plot of sample and standard 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 on 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.

9.9 Quality Control

QC procedures are specified in Section 2.6.

1. For the exchangeable acidity titration, three reagent blanks must be processed for each of the two extraction procedures. The average titration result for each kind of blank is subtracted from results for the samples in the same matrix. Matrix spikes and QCCS are not required for this titration.

2. For the aluminum determination, in addition to the QC inherent in the calibration procedures for ICP, three reagent blanks must be processed as described in Section 9.10.2. A detection limit QC sample and QCCS are required as described in Section 2.6.

9.10 Procedure

9.10.1 Barium Chloride ($BaCl_2$-TEA) Method

9.10.1.1 Preparation of Sample Tubes--

Tightly compress a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger. (To modify the plunger, remove the rubber portion and cut off the plastic protrusion.) Tamp the plunger and syringe assembly on a tabletop several times.

9.10.1.2 Preparation of Mineral Soils--

1. Weigh air-dried sample, equivalent to 2.00 g oven-dried soil, into tube. Place sample tube in upper disc of extractor and connect to inverted extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor. Attach pinch clamp to delivery tube of syringe barrel.

2. Add 10 mL $BaCl_2$-TEA *buffer* solution to sample. Stir the sample mixture with a glass stirring rod for 10 seconds. Leave stirring rod in syringe. Allow sample to stand for 30 minutes.

3. After 30 minutes, set extractor for a 30-minute rate and extract until 0.5 to 1.0 cm of solution remains above each sample. If necessary, turn off extractor to prevent soil from becoming dry. Continue at 9.10.1.5.

9.10.1.3 Preparation of Organic Soils--

1. Weigh air-dried sample, equivalent to approximately 2.00 g oven-dried soil, into small glass tube. Add 5 mL $BaCl_2$-TEA *buffer* solution to the sample, cap, and shake the tube and contents for 1 hour on a reciprocating shaker. Some organic soils have very high acidity, which may require reducing the amount of soil to 1.00 g to stay in the midrange of the titration procedure.

2. Place sample tube in upper disc of extractor and connect to inverted extraction syringe, with the syringe plunger inserted in the slot of the stationary disc of the extractor.

Attach pinch clamp to delivery tube of syringe barrel.

3. Quantitatively transfer contents of small glass tube to sample tube with 5 mL *buffer* solution. Set extractor at the 30-minute extraction rate and extract until only a small volume of solution remains above the sample.

9.10.1.4 Preparation of Reagent Blanks--

1. Run three reagent blanks for each batch of actual samples.

2. Place prepared sample tube in upper disc of extractor and connect to inverted extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor.

3. Add 10 mL $BaCl_2$-TEA *buffer* solution as described for mineral soils in Section 9.10.1.2, step 2. Continue with sections 9.10.1.2, step 3 and 9.10.1.5.

9.10.1.5 Principal Extraction--

Add a second 10-mL aliquot of $BaCl_2$-TEA *buffer* solution and continue extracting until nearly all solution has been pulled through sample. Add *replacement* solution from pipettor in two 20-mL aliquots, passing the first aliquot through the sample before adding the next. Total time for replacement should be approximately 30 minutes. Quantitatively transfer extract to an Erlenmeyer flask.

9.10.1.6 Titration--

1. Add 100 mL water to extract in Erlenmeyer flask. Use an automatic titrator to titrate with 0.1 N HCl to an endpoint pH of 4.60.

2. Titrate three reagent blanks, each containing 20 mL buffer solution and 40 mL replacement solution and extracted through 1 g of filter pulp, as described above for one batch of actual samples.

9.10.2 Potassium Chloride (KCl) Method

9.10.2.1 Preparation of Sample Tubes--

Tare each extraction syringe. Tightly compress a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger. (To modify the plunger, remove the rubber portion and cut off the plastic protrusion.) Tamp the plunger and syringe assembly on a tabletop several times.

9.10.2.2 Preparation of Mineral Soils--

1. Weigh air-dried sample, equivalent to 2.5 g oven-dried soil, into tube. Place sample tube in upper disc of extractor and connect to inverted, tared extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor.

2. Add a 10-mL aliquot of KCl replacement solution to sample. Mix for 10 seconds with a glass stirring rod. Leave stirring rod in syringe. Allow sample to stand for 30 minutes, then extract at a 30-minute rate until 0.5 to 1.0 cm of solution remains above each sample. If necessary, turn off extractor to prevent soil from becoming dry. Continue at 9.10.2.5.

9.10.2.3 Preparation of Organic Soils--

1. Weigh air-dried sample, equivalent to 2.50 g oven-dried soil, into small glass tube. Add 6 mL KCl replacement solution, cap, and shake the tube and contents on a reciprocating shaker for 1 hour.

If necessary, the sample weight may be reduced by half without changing the remaining procedure.

2. Place sample tube in upper disc of extractor and connect to inverted, tared extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor.

3. Quantitatively transfer sample and solution to a sample tube with 4 mL KCl replacement solution. Extract at a 30-minute rate until 0.5 to 1.0 cm of solution remains above each sample.

9.10.2.4 Preparation of Reagent Blanks--

1. Run three reagent blanks for each batch of actual samples.

2. Place prepared sample tube in upper disc of extractor and connect to inverted extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor.

3. Add KCl replacement solution as described for mineral soils in Section 9.10.2.2., i.e., add 10 mL KCl replacement solution. Allow syringe to stand for 30 minutes, then extract at a 30-minute rate until 0.5 to 1.0 cm solution remains above the filter pulp. If necessary, turn off extractor to prevent filter pulp from becoming dry. Continue at 9.10.2.5.

9.10.2.5 Principal Extraction--

Turn off extractor and add 40 mL KCl replacement solution to the reservoir syringe. Extract at a 40-minute rate. Disconnect syringes from sample tube, leaving rubber connector on sample tube, and weigh each syringe containing the extract to the nearest 0.01 g. The density factor to convert solution weight to volume is 1.0412 g/cm^3.

9.10.2.6 Removal of Aliquot for Aluminum Determination--

NOTE: Take each sample solution through this step before proceeding to the next sample.

Transfer the solution in the recovery syringe to a 125-mL Erlenmeyer flask but do not rinse the syringe at this time. With a plastic-tipped, fixed-volume pipet, transfer a 5-mL aliquot of the solution in the Erlenmeyer flask to another vessel and immediately acidify the aliquot by adding 5 μL of concentrated sulfuric acid. Complete the quantitative transfer of the solution from the recovery syringe to the Erlenmeyer flask, i.e., rinse the syringe with DDI water and add the rinsings to the solution in the flask. To determine KCl-exchangeable aluminum in the acidified 5-mL aliquot, continue at Section 9.10.3; to determine the exchangeable acidity of the solution in the Erlenmeyer flask, continue at Section 9.10.2.7.

9.10.2.7 Titration--

1. To the solution in the Erlenmeyer flask, add 2 or 3 drops of phenolpthalein indicator. Using an automatic titrator, titrate with 0.01 N NaOH to the first permanent pink endpoint, pH = 8.4.

Note: At the endpoint, it takes approximately 0.10 mL to go from pH = 8.0 to pH = 8.3. A deep pink is too far.

2. Titrate three reagent blanks, each containing 45 mL KCl replacement solution and extracted through 1 g of filter pulp as described above, for one batch of actual samples.

9.10.3 Determination of Aluminum

Determine aluminum by inductively coupled plasma (see Section 8.10.2). If

necessary, dilute sample to stay within linear dynamic range specified for the instrument.

9.11 Calculations

1. Calculate exchangeable acidity for the barium chloride method by using the following equation:

$$\text{Exchangeable acidity (meq/100 g)} = \left(\frac{\text{Reagent-blank titer (mL)} - \text{Sample titer (mL)}}{\text{oven-dried soil wt (g)}}\right)\left(\text{Normality of HCl}\right)(100) \quad (9\text{-}1)$$

Establish the blank titer by taking the mean of the titrations of three reagent blanks (see Section 9.10.2.7).

2. Calculate exchangeable acidity for the potassium chloride method as follows:

$$\text{Exchangeable acidity (meq/100 g)} = \left(\frac{\text{Sample titer (mL)} - \text{Reagent-blank titer (mL)}}{\text{oven-dried soil wt (g)}}\right)\left(\text{Normality of NaOH}\right)\left(\frac{\text{total volume}}{\text{total volume} - 5\text{mL}}\right)(100) \quad (9\text{-}2)$$

Again establish the blank titer by taking the mean of the titrations of three reagent blanks (see Section 9.10.2.7). The density factor to convert KCl solution weight to volume is 1.0412 g/cm³.

3. Calculate KCl-extractable aluminum as follows:

$$\text{Extractable } Al^{3+} \text{ (meq/100 g)} = \left(\frac{\text{mg } Al^{3+}/\text{L}}{\text{oven-dried soil wt (g)}}\right)\left(\frac{3 \text{ meq } Al^{3+}}{26.9815 \text{ mg Al}}\right)\left(\frac{1 \text{ L}}{1{,}000 \text{ mL}}\right)\left(\text{total volume of extract}\right)\left(\text{dilution factor as needed}\right)(100) \quad (9\text{-}3)$$

9.12 Precision and Accuracy

Precision and accuracy information is not available for the exchangeable acidity determinations. The precision and accuracy information that is available for determination of aluminum by ICP is given in Section 10.12.

9.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey*, U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity.* Technical Bulletin No. 404. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York.

Thomas, G. W. 1982. *Exchangeable Cations*, pp. 159-165. In: *Methods of Soil Analysis: Part 2 - Chemical and Microbiological Properties*, Second Edition, A. L. Page, R. H. Miller, and D. R. Keeney (eds.). American Society of Agronomy, Inc./Soil Science Society of America, Inc., Madison, Wisconsin.

10 Lime and Aluminum Potential

10.1 Scope and Application

Lime and aluminum potential are related to the concentrations of Ca^{2+} and Al^{3+}, respectively, that are extracted from a soil sample by a dilute $CaCl_2$ solution. Lime potential is defined as pH − 1/2 pCa. The p-function is defined as the negative logarithm (base 10) of the molar concentration of that species, or: pX = − log [X]. The advantage of using the p-function is that concentration information is available in terms of small positive numbers. Aluminum potential, K_A, is defined as: K_A = 3 pH − pAl. Extractable Mg^{2+}, K^+, and Na^+ are also determined for comparison to amounts determined in the CEC extracts. Fe^{3+} and Al^{3+} are determined for comparison to amounts obtained by the extractable iron and aluminum procedures in Section 11.

The procedure involves automated extraction of soil with 0.002 M $CaCl_2$ in a 1:2 ratio for mineral soils and in a 1:10 or 1:25 ratio for organic soils. The extract is analyzed by atomic absorption (AA) or inductively coupled plasma (ICP) emission for Ca^{2+}, Mg^{2+}, Na^+, and Fe^{3+}, by ICP for Al^{3+}, and by AA for K^+. Flame atomic emission (flame photometry) may be used for K^+ and Na^+.

Performance data such as instrumental detection limits are given in Section 8.1 for Ca^{2+}, Mg^{2+}, Na^+ and K^+ determinations. For Fe^{3+} and Al^{3+} determinations, the information in Tables 10-1 and 10-2 applies.

Table 10-1. Atomic Absorption Performance Data for Determination of Fe^{3+}

	Fe^{3+}
Optimum concentration range	0.3-5 mg/L
Sensitivity	0.12 mg/L
Detection Limit	0.03 mg/L

Table 10-2. Recommended Wavelengths and Estimated Instrumental Detection Limits for Determination of Fe^{3+} and Al^{3+} by Inductively Coupled Plasma

Element	Wavelength[a] (nm)	Estimated Detection Limit (µg/L)[b]
Iron	259.950	7
Aluminum	308.215	45

[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 if they are treated with the same corrective techniques for spectral interference.

[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.

10.2 Summary of Method

The procedure involves automated extraction of soil with 0.002 M $CaCl_2$. The soil-to-solution ratio is 1:2 for mineral soils and is 1:10 or 1:25 for organic soils. The extract is analyzed by atomic absorption (AA) or inductively coupled plasma (ICP) emission for Ca^{2+}, Mg^{2+}, Na^+, and Fe^{3+}, by ICP for Al^{3+}, and by AA for K^+. Flame atomic emission (flame photometry) may be used to analyze for K^+ and Na^+. These instrumental analytical techniques are summarized in Section 8.2.

10.3 Interferences

Chemical and spectral interferences can contribute to inaccuracies in analyses of the extracts by AA, ICP, or flame photometry. ICP and flame photometric analysis are subject to physical interferences as well. Interferences are discussed further in Section 8.3.

10.4 Safety

The calibration standards, sample types, and most reagents pose little hazard to the

analyst. Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a hood.

10.5 Apparatus

10.5.1 General

- Mechanical extractor, 24 place, manufactured by Centurion, Inc. (see Figure 7-1).
- Syringes, disposable, 60 mL, polypropylene; one sample tube and extraction syringe for each sample.
- Rubber tubing, 1/8 by 1/4 inch; for connecting syringe barrels.
- Bottles, polyethylene (LPE), with cap: 25 mL for mineral soil; 50 mL for organic soil.
- Tubes, glass, 25 mL, centrifuge or culture, with caps.
- Reciprocating shaker.
- Balance, analytical, capable of weighing to ±1 mg.
- Volumetric pipets, volumes as needed.
- Volumetric flasks, volumes as needed.

10.5.2 Instrumentation for Determination by AA

- Atomic absorption spectrophotometer, single- or dual-channel, single- or double-beam, with grating monochromator, photomultiplier detector, adjustable slits, wavelength range of 190 to 800 nm, provisions for interfacing with a strip chart recorder.
- Burner, as recommended by the instrument manufacturer; for certain elements, nitrous oxide burner required.
- Hollow cathode lamps, single element lamps preferred, but multi element lamps acceptable; electrodeless discharge lamps may be used.
- Strip chart recorder.

10.5.3 Instrumentation for Determination by ICP

- Inductively coupled plasma atomic emission spectrometer, computer controlled, with background correction capability.

10.5.4 Instrumentation for Determination by Flame Photometry

- Flame photometer, either direct-reading or internal-standard type; or atomic absorption spectrometer in flame emission mode.

10.6 Reagents and Consumable Materials

- Stock calcium chloride solution (1.0 M $CaCl_2$)--Dissolve 55.493 g anhydrous $CaCl_2$ in DDI water and dilute to 500 mL. Two sources of high purity grade $CaCl_2$ are (1) SPEX Industries, Inc., Box 798, Metuchen, New Jersey 08840; telephone (201) 549-7144; and (2) Aesar Johnson Matthey, Inc., Eagles Landing, P.O. Box 1087, Seabrook, New Hampshire 03874, telephone (800) 343-1900.
- Calcium chloride ($CaCl_2$) 0.002 M--Dilute 4 mL 1.0 M $CaCl_2$ to 2.000 L with DDI water. If the pH of this solution is not between 5 and 6.5, adjust the pH by addition of dilute HCl (see Section 6.6) or saturated $Ca(OH)_2$ (see Section 6.6).

- Analytical filter pulp, Schleicher and Schuell, No. 289, washed according to the procedure given in Section 2.4.

- Calibration standards (Refer to Section 8.6 for Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}; Section 10.10.4 for Al^{3+} and Fe^{3+}.)

10.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not in use.

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.

10.8 Calibration and Standardization

Within each class of instruments (AA, ICP, and flame photometer), the calibration procedure varies slightly.

Calibrate by analyzing a calibration blank and a series of at least three standards within the linear range. If an ICP is used, a multi-element standard may be prepared and analyzed. For AA and flame photometric determinations, the instrument must be calibrated by single-element standards for each analyte.

The concentration of standards should bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded. An alternative, less sensitive line may be used, but the standards must bracket the samples.

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 that contain different known amounts of the analyte. The volume of the blank and of each standard must be the same. The absorbance or emission 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, or emission, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left side 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 8-1. 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 or emission 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 of 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.

10.9 Quality Control

The Ca^{2+} concentration of the extracting solution must be within 5 percent of 80 ppm. In addition to the QC inherent in the calibration procedures, the QC procedures described in Section 2.6 must be followed. These include detection limit QC samples, QCCS, duplicates, and matrix spikes.

10.10 Procedure

10.10.1 Preparation of Sample Tubes

Prepare sample tubes by tightly compressing 1 g of filter pulp into the bottom of a syringe barrel with a modified plunger. (Modify the plunger by removing the rubber portion and cutting off the plastic protrusion.) Wash the filter pulp with DDI water before use.

10.10.2 Sample Preparation

For mineral soils, weigh air-dried sample, equivalent to 10.00 g oven-dried soil, into sample tube. Place sample tube in upper disc of extractor and connect to inverted extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor.

Add 20 mL 0.002 M $CaCl_2$ and stir with glass stirring rod for 15 seconds. Leave stirring rod in syringe.

Let the sample mixture stand for 30 minutes and stir again for 15 seconds. Let the sample mixture stand for another 30 minutes, then continue at Section 10.10.3. This is a 1:2 extraction.

For organic soils, weigh air-dried sample, equivalent to 4.00 g oven-dried soil, into a small glass tube. Add 30 mL 0.002 M $CaCl_2$, cap, and shake for 1 hour.

Place a sample tube in the upper disc of the extractor and connect to inverted extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor.

Then quantitatively transfer the sample and 0.002 M $CaCl_2$ solution to a sample tube. Rinse shaking tube with 10 mL 0.002 M $CaCl_2$ into the sample tube. The total volume of 0.002 M $CaCl_2$ should equal 40 mL. This is a 1:10 extraction.

For extremely absorbent organic soils, use a 1.60 g sample and the same volumes of solution. This is a 1:25 extraction.

10.10.3 Extraction

Turn on extractor. Extract at the 17-hour rate (or overnight) until most of the available $CaCl_2$ solution is recovered.

Turn off extractor and pull plungers down as far as extractor will allow. Disconnect syringes from sample tube. Transfer extract to polyethylene containers.

If dilution is necessary, take an aliquot of known volume and dilute in a volumetric flask. Take this dilution factor into account when calculating the analyte concentrations.

10.10.4 Determination of Ca^{2+}, K^+ Mg^{2+}, Na^+, Fe^{3+}, and Al^{3+}

Analyze extract for Ca^{2+}, Mg^{2+}, Na^+, and Fe^{3+} by flame AA or ICP. K^+ must be determined by AA or flame photometry because ICP is not sufficiently sensitive in the determination of K^+ to quantify concentrations less than 100 mg/L. Al^{3+} must be determined by ICP because flame AA is not sufficiently sensitive in the determination of Al^{3+} to quantify concentrations less than 0.1 mg/L.

The procedures given in Section 8.10 are used for these determinations. However, the standard solutions are prepared with 0.002 M $CaCl_2$ rather than with 1.0 N NH_4Cl or NH_4OAc. For aluminum and iron determinations, the additional procedural detail given in sections 10.10.4.1 and 10.10.4.2 is required.

10.10.4.1 Determination of Aluminum--

10.10.4.1.1 Preparation of Aluminum Standard Solutions--

- Primary aluminum standard (1,000 mg/L Al)--Carefully weigh 1.000 g aluminum powder (spectroscopic 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 dilute to volume with DDI water. Alternatively, a commercially available, certified Al standard may be used.

- Nitric acid (HNO_3), concentrated--Ultrapure grade.

- Nitric acid (0.5 percent v/v HNO_3)--Add 1 mL concentrated HNO_3 (Ultrapure grade) to DDI water and dilute to 200 mL.

- Calibration standards--Prepare calibration standards at the time of analysis. The calibration standards should be prepared in 0.5 percent (v/v) HNO_3. To each 100 mL of standard and sample alike, add 2.0 mL potassium chloride solution.

10.10.4.1.2 Suggested Instrument Conditions (General)--Wavelength 308.215 nm.

10.10.4.1.3 Analytical Procedure--

1. Calibrate the instrument as directed by the instrument manufacturer.

2. Analyze the samples.

3. If a sample concentration exceeds the linear range, dilute with acidic media and reanalyze.

4. Record results as milligrams Al^{3+} per liter (mg Al^{3+}/L).

10.10.4.1.4 Precision and Accuracy--Refer to Table 10-3 for these data.

10.10.4.2 Determination of Iron--

10.10.4.2.1 Preparation of Iron Standard Solutions--

- Primary iron standard (1,000 mg/L Fe) --Carefully weigh 1.000 g pure iron powder (spectroscopic grade). Dissolve in 5 mL concentrated HNO_3 and warm if necessary. When iron is completely dissolved, dilute solution to 1.00 L with DDI water.

- Calibration standards--At the time of analysis, prepare calibration standards in the correct matrix spanning the desired concentration range.

10.10.4.2.2 Suggested Instrumental Conditions (General)--Iron hollow cathode lamp; wavelength, 248.3 nm; fuel, acetylene; oxidant, air; type of flame, oxidizing.

10.10.4.2.3 Analytical Procedure--

1. Calibrate the instrument.

2. Analyze the samples.

3. Dilute and reanalyze any samples for which the concentration exceeds the calibrated range.

4. Record results in milligrams Fe^{3+} per liter (mg Fe^{3+}/L). (See sections 8.11 and 10.11.)

10.10.4.2.4 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.

10.10.4.2.5 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

Table 10-3. Inductively Coupled Plasma Precision and Accuracy data (U.S. EPA, 1983)

	Sample 1			Sample 2			Sample 3		
Element	True Value (µg/L)	Mean Reported Value (µg/L)	Mean %RSD	True Value (µg/L)	Mean Reported Value (µg/L)	Mean %RSD	True Value (µg/L)	Mean Reported Value (µg/L)	Mean %RSD
Al	700	696	5.6	60	62	33	160	161	13
Fe	600	594	3.0	20	19	15	180	178	6.0

Note: Not all elements were analyzed by all laboratories.

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 Values µg/liter	Mean Value µg/liter	Deviation µg/liter	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

10.11 Calculations

1. Instruments may be calibrated to output sample results directly in concentration units, i.e., mg/L. If the instrument is not so calibrated or programmed, then either (1) the slope of the linear calibration curve is calculated, and sample concentrations are subsequently calculated, or (2) a manual calibration curve is prepared, and sample concentrations are determined by comparing the sample signal to the calibration curve.

2. If dilutions are performed, the appropriate factor must be applied to sample values.

3. Report Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Al^{3+}, and Fe^{3+} in units of meq/100 g oven-dried soil to the nearest 0.001 meq/100 g. To convert concentration of analyte in the extract to analyte in oven-dried soil, use equations 8-1 through 8-3 (see Section 8.11.4).

NOTE: Report Ca^{2+} without adjusting for the Ca^{2+} levels in the $CaCl_2$ extracting solution, i.e., do not subtract the blank.

$$\frac{\text{meq}}{100\text{ g soil}} = \left(\frac{\text{mg}}{\text{L}}\right)\left(\frac{\text{L}}{1{,}000\text{ mL}}\right)\left(\frac{\text{mmol}}{\text{Atomic wt. (mg)}}\right)\left(\frac{\text{meq}}{\text{mmol}}\right)\left(\frac{\text{mL extract}}{\text{g soil}}\right)(100) \qquad (10\text{-}1)$$

where:

Cation	Atomic wt.	meq/mmol
Ca^{2+}	40.080	2
Mg^{2+}	24.305	2
K^{+}	39.098	1
Na^{+}	22.990	1
Al^{3+}	26.982	3
Fe^{3+}	55.847	3

and

Soil Type	grams Soil	mL extract	ratio
mineral	10.00	20	1:2
organic	4.00	40	1:10
highly absorbent organic	1.60	40	1:25

10.12 Precision and Accuracy

Precision and accuracy for AA determinations are provided in the analyte-specific section (8.10.1.1.6 Ca^{2+}, 8.10.1.2.6 Mg^{2+}, 8.10.1.3.5 K^{+}, 8.10.1.4.5 Na^{+}, and 10.10.4.2.5 Fe^{3+}). Precision and accuracy for ICP determinations are given in part in Section 8.12.2; additional data are presented below:

In an EPA Round Robin Phase I study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 10-3 lists the results of this study.

Patel et al. (1984) report spike recovery percentages in seven wastes that average 102.3 percent for aluminum and 93.1 percent for iron.

Again, because of differences in matrices and in sample processing, neither of the above studies necessarily represents precision and accuracy for soil analyses, but simply indicates likely trends.

10.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey*, U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

Fassel, V. A. 1982. *Analytical Spectroscopy with Inductively Coupled Plasmas - Present Status and Future Prospects.* In: *Recent Advances in Analytical Spectroscopy.* Pergamon Press, New York, New York.

Patel, B. R., G. A. Raab, D. Cardenas, and T. W. Riedy. 1984. *Report on a Single-Laboratory Evaluation of Inductively Coupled Plasma Optical Emission Method 6010.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes. Method 200.0, Atomic Absorption Methods, and 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. Environmental Protection Agency, Cincinnati, Ohio.

11 Extractable Iron and Aluminum

11.1 Scope and Application

Iron and aluminum are extracted from soil into sodium pyrophosphate, citrate-dithionite, and acid-oxalate solutions. According to the Johnson and Todd (1983) iron and aluminum speciation scheme, the pyrophosphate extract contains organically bound iron (Fe-p) and aluminum (Al-p), the citrate-dithionite extract contains nonsilicate Fe (Fe-c) and Al (Al-c), and the acid-oxalate extract contains organic and amorphous oxides of Fe (Fe-o) and Al (Al-o).

In general, Al in these extracts does not indicate the readily available species that are known to cause fish kills. The exchangeable Al^{3+} from the unbuffered KCl extract (see Exchangeable Acidity, Section 9) is more indicative of readily available Al at field pH conditions. The Fe and Al values from the pyrophosphate, acid-oxalate, and citrate-dithionite extracts relate well to the sulfate adsorption capacity and have been used as an indication of this property (Fernandez, 1983).

Detection limits and related information for determination of Fe and Al in the extracts are provided in Table 10-2 and Table 11-1.

Table 11-1. Atomic Absorption Performance Data for Determination of Fe^{3+} and Al^{3+}

	Fe^{3+}	Al^{3+}
Optimum concentration range	0.3-5 mg/L	5-50 mg/L at 309.3 nm
Sensitivity	0.12 mg/L	1 mg/L
Detection Limit	0.03 mg/L	0.1 mg/L

11.2 Summary of Method

Each of three portions of a soil sample is treated with a different solution to extract iron and aluminum. The three extracting solutions are 0.1 M sodium pyrophosphate, a sodium citrate-sodium dithionite solution, and an oxalic acid-ammonium oxalate solution. After the extraction procedure, the three solutions are analyzed for iron and aluminum by atomic absorption spectrometry (AA) or by inductively coupled plasma atomic emission spectrometry (ICP). These instrumental techniques are summarized in Section 8.2. The method is modified from USDA/SCS (1984).

11.3 Interferences

Chemical and spectral interferences can contribute to inaccuracies in analysis of the extracts by AA or ICP. Analysis by ICP is subject to physical interferences as well. Interferences are discussed more completely in Section 8.3.

11.4 Safety

The calibration standards, sample types, and most reagents pose no hazard to the analyst. Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a hood.

Follow the safety precautions provided by the manufacturer when operating instruments.

Follow good laboratory practices when handling compressed gases. Cylinders

should be chained or bolted in an upright position.

11.5 Apparatus and Equipment

11.5.1 General

- Centrifuge bottles, 250 mL, polypropylene.
- Bottles, polyethylene (LPE), 25 mL.
- Reciprocating shaker.
- Centrifuge.
- pH meter and pH electrode.
- Mechanical extractor, 24 place, manufactured by Centurion, Inc. (Figure 7-1).
- Syringes, 60 mL, polypropylene, one sample tube, one reservoir tube, and one tared extraction syringe for each sample.
- Repipet or equivalent.
- Fleakers, or equivalent glassware.
- Volumetric pipets, volumes as needed.
- Volumetric flasks, volumes as needed.

11.5.2 Instrumentation for Determination by AA

- Atomic absorption spectrophotometer, single- or dual-channel, single- or double-beam, with grating monochromator, photomultiplier detector, adjustable slits, wavelength range of 190 to 800 nm, provisions for interfacing with a strip chart recorder.
- Burner as recommended by the instrument manufacturer; for certain elements, nitrous oxide burner required.
- Hollow cathode lamps, single element lamps preferred, but multielement lamps acceptable; electrodeless discharge lamps may be used.
- Strip chart recorder.

11.5.3 Instrumentation for Determination by ICP

- Inductively coupled plasma atomic emission spectrometer, computer-controlled, with background correction capability.

11.6 Reagents and Consumable Materials

11.6.1 Sodium Pyrophosphate Extraction

- NBS-traceable pH buffers of pH = 7 and pH = 10.
- Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$), 0.1 M--Dissolve 44.61 g $Na_4P_2O_7 \cdot 10\ H_2O$ in DDI water. Dilute to 1.0 L. Adjust to pH 10.0 by dropwise additions of 1 N NaOH or 1 N H_3PO_4.
- Sodium hydroxide (NaOH), 1 N--Dissolve 10 g NaOH in DDI water. Dilute to 250 mL. Store in polyethlene container.
- Phosphoric acid (H_3PO_4), concentrated.
- Superfloc 16, 0.2 percent solution (v/v) in DDI water (suggested source: American Cyanamid Co., P.O. Box 32787, Charlotte, NC 28232; telephone: 800/438-5615).

11.6.2 Citrate-Dithionite Extraction

- Sodium dithionite ($Na_2S_2O_4$).
- Sodium citrate ($Na_3C_6H_5O_7 \cdot 5H_2O$).

- Citrate-dithionite reagent--Dissolve 160 g sodium dithionite and 2,000 g sodium citrate into approximately 8 liters of DDI water. (This may require prolonged magnetic stirring or additional DDI water to totally dissolve the salts.) Dilute to 10 L. Store at 4 °C and use the same day.

- Superfloc 16, 0.2 percent solution (v/v) in DDI water.

11.6.3 Acid-Oxalate Extraction

- NBS-traceable pH buffers of pH = 4 and pH = 3 or pH = 2.

- Ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$].

- Oxalic acid ($H_2C_2O_4 \cdot H_2O$).

- Acid-oxalate reagent--Solution A: Dissolve 284 g ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$] in 10 L DDI water. Solution B: Dissolve 252 g oxalic acid ($H_2C_2O_4 \cdot H_2O$) in 10 L distilled water. Mix four parts solution A with three parts solution B. Adjust pH to 3.0 by adding either solution A or B.

- Analytical filter pulp, Schleicher and Schuell, No. 289.

11.6.4 Determination of Fe and Al

- Calibration standards--The matrix of the calibration standards should match the matrix of the soil extracts as closely as possible in order to assure maximum accuracy. Therefore, the calibration standards should be prepared with the extracting solution rather than water as the diluent. Refer to Section 11.10.4.1. for preparation of Al standard solutions and to Section 10.10.4.2.1 for preparation of Fe standard solutions.

11.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the laboratory, all samples are kept sealed and are refrigerated at 4 °C when not being used. The citrate-dithionite extractions should be analyzed within 24 hours after preparation; the pyrophosphate and acid-oxalate extracts, within 48 hours after preparation.

11.8 Calibration and Standardization

11.8.1 General

Within each class of instruments (AA and ICP), the calibration procedure varies slightly. Calibrate the instrument by analyzing a calibration blank and a series of at least three standards within the linear range. If an ICP is used, a multielement standard may be prepared and analyzed. For AA determinations, the instrument must be calibrated for each analyte. The concentration of standards must bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded.

11.8.2 Method of Standard Additions for Determination of Fe and Al

When indicated by the matrix spike analysis, the analytes must be quantified by the method of standard additions.

Note: It is difficult to maintain a stable, concentrated solution of Al^{3+} for performing matrix spikes or standard additions.

In this method, equal volumes of sample are added to a deionized water blank and to three standards that contain different known amounts of the test analyte. The volume of the blank and of each standard must be the same. The absorbance or emission 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 or emission, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left side 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 8-1. 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 or emission 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 of 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.

11.9 Quality Control

In addition to the QC inherent in the calibration procedures, the QC procedures described in Section 2.6 must be followed. These include detection limit QC samples, QCCS, duplicates, and matrix spikes.

11.10 Procedures

11.10.1 Sodium Pyrophosphate Extraction

1. Place 2.00 g of air-dried soil into a 250-mL centrifuge bottle. Add 200 mL 0.1 M $Na_4P_2O_7$, cap, and shake overnight (17 hours) on a reciprocating shaker.

2. Remove centrifuge bottle from shaker. Add 4 mL 0.2 percent Superfloc solution. Shake for 15 seconds and centrifuge at 510 G for 10 minutes.

3. Remove centrifuge bottle from centrifuge. Examine the supernatant for suspended clays. Because the pyrophosphate solution is relatively viscous and the clays are Na-saturated, the supernatant may not be clear. If it is not, repeat step 2.

4. Decant and save the supernatant. Store the supernatant at 4 °C. If dilution is necessary, take an aliquot of known volume and dilute in a volumetric flask. Take this dilution factor into account in calculating the concentration of Fe^{3+} and Al^{3+}.

5. Analyze for Fe^{3+} and Al^{3+} within 24 hours of the end of the extraction. (Refer to Section 11.10.4 for determination of Al^{3+} and to Section 10.10.4.2 for determination of Fe^{3+}.)

11.10.2 Citrate-Dithionite Extraction

1. Weigh approximately 4.00 ± 0.01 g air-dried soil into a 250-mL centrifuge bottle. Add 125 mL of the citrate-dithionite extraction solution, cap, and shake overnight (17 hours) on a reciprocating shaker.

   An alternative method: Add 2 g $Na_2S_2O_4$ and 20 to 25 g $Na_3C_6H_5O_7 \cdot 5H_2O$. Add 125 mL DDI water, cap,

and shake overnight (17 hours) on a reciprocating shaker.

2. Add 4 mL 0.2 percent Superfloc solution and shake vigorously for approximately 30 seconds. Centrifuge at 510 G for 10 minutes (higher speeds and longer times may be required for soils high in silts and clays).

3. Remove centrifuge bottle from centrifuge. Examine the supernatant for suspended clays. If the supernatant is not clear, repeat step 2.

4. Decant and save the supernatant for Fe^{3+} and Al^{3+} analysis. Store the supernatant at 4 °C. If dilution is necessary, take an aliquot of known volume and dilute in a volumetric flask. Take this dilution factor into account in calculating the concentration of Fe^{3+} and Al^{3+}.

5. Analyze for Fe^{3+} and Al^{3+} within 24 hours of the end of the extraction. (Refer to Section 11.10.4 for determination of Al^{3+} and to Section 10.10.4.2 for determination of Fe^{3+}.)

11.10.3 Acid-Oxalate Extraction

This extraction is sensitive to light and, therefore, should be performed under conditions of darkness. To minimize variability associated with different technicians, this procedure requires the use of a mechanical extractor.

1. For minerals soils, prepare sample extraction tubes by forcing a 1-g ball of filter pulp into the bottom of syringe barrel with syringe plunger. Weigh about 0.5 ± 0.001 g soil into tube.

   Place sample tube in extractor, attach extraction syringe, and add 15 mL acid-oxalate reagent from a repipet or equivalent unit, washing down sides of tubes. Attach reservoir tube and allow moistened sample to stand for 1 hour. Continue at step 3.

2. For organic soils, weigh about 0.5 ± 0.001 g soil into a small glass tube. Add 10 mL acid-oxalate reagent and shake for 1 hour on a reciprocating shaker.

   Prepare sample extraction tubes by forcing a 1-g ball of filter pulp into bottom of syringe barrel with syringe plunger. Place sample tube in extractor and attach extraction syringe.

   Quantitatively transfer soil to sample tube with 5 mL acid-oxalate reagent so that the total volume added to the soil equals 15 mL. Attach reservoir tube. Continue at step 3.

3. For mechanical extraction, extract at a setting of 1 hour until 0.5 to 1.0 cm of extracting solution remains above sample. Turn off extractor.

   Add 35 mL acid-oxalate reagent to the reservoir from a repipet or equivalent unit. Place a black plastic bag over the extractor to protect samples from light and other contamination. Extract overnight at a setting of 17 hours.

NOTE: Although the reagents are not sensitive to light, the combination of soil and acid-oxalate reagent is reactive to light. In the presence of light, the Fe^{3+} and Al^{3+} extracted are not limited to the organic and amorphous oxide species.

4. Remove syringe. Store the extract at 4 °C. If dilution is necessary, take an aliquot of known volume and dilute in a volumetric flask. Take this dilution factor into account in calculating the concentrations of Fe^{3+} and Al^{3+}.

5. Analyze for Fe^{3+} and Al^{3+} within 48 hours of the end of the extraction. (Refer to Section 11.10.4 for

determination of Al^{3+} and Section 10.10.4.2 for determination of Fe^{3+}.)

The procedures given in Section 8.10 are used for these determinations. However, the standard solutions are prepared with 0.002 M $CaCl_2$ rather than with 1.0 N NH_4Cl or NH_4OAc. For aluminum and iron determinations by AA, the additional procedural detail given in sections 10.10.4.1 and 10.10.4.2 is required. Samples should be analyzed within the holding times specified in Section 11.7.

11.10.4 Determination of Aluminum

11.10.4.1 Preparation of Aluminum Standard Solutions--

- Primary aluminum standard (1,000 mg/L Al)--Carefully weigh 1.000 g aluminum powder (spectroscopic 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 dilute to volume with DDI water. Alternatively, a commercially available, certified Al standard may be used.

- Nitric acid (HNO_3), concentrated--Ultrapure grade.

- Nitric acid (0.5 percent v/v HNO_3)--Add 1 mL concentrated HNO_3 (Ultrapure grade) to DDI water and dilute to 200 mL.

- Potassium chloride solution, ionization suppressant--Dissolve 95 g potassium chloride (KCl) in DDI water and dilute to 1.00 liter.

- Calibration standards--Prepare calibration standards at the time of analysis. The calibration standards should be prepared in 0.5 percent (v/v) HNO_3. To each 100 mL of standard and sample alike, add 2.0 mL potassium chloride solution.

11.10.4.2 Suggested Instrument Conditions (General)--

Aluminum hollow cathode lamp; wavelength 309.3 nm; fuel, acetylene; oxidant, nitrous oxide.

11.10.4.3 Analytical Procedure--

1. Calibrate the instrument as directed by the instrument manufacturer.

2. Analyze the samples.

3. If a sample concentration exceeds the linear range, dilute with acidic media and reanalyze.

4. Record results as milligrams Al^{3+} per liter (mg Al^{3+}/L).

11.10.4.4 Notes--

The following lines may also be used: 308.2 nm, relative sensitivity 1; 396.2 nm, relative sensitivity 2; 394.4 nm, relative sensitivity 2.5.

11.10.4.5 Precision and Accuracy--

An interlaboratory study of trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL-Cincinnati. Six synthetic concentrates that contained varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead, and zinc were added to natural water samples. The statistical results for aluminum were as follows:

Number of Labs	True Values µg/liter	Mean Value µg/liter	Deviation µg/liter	Accuracy as % Bias
38	1,205	1,281	299	6.3
38	1,004	1,003	391	-0.1
37	500	463	202	-7.4
37	625	582	272	-6.8
22	35	96	108	175
21	15	109	168	626

11.11 Calculations

Report percentage to 0.001 percent.

$$\%Al = (\text{mg Al/L})\left(\frac{\text{(mL extract)}}{\text{g oven-dried soil}}\right)\left(\frac{(1)}{10{,}000}\right)\left(\begin{array}{c}\text{dilution factor}\\ \text{as needed}\end{array}\right) \quad (11\text{-}1)$$

$$\%Fe = (\text{mg Fe/L})\left(\frac{\text{(mL extract)}}{\text{g oven-dried soil}}\right)\left(\frac{(1)}{10{,}000}\right)\left(\begin{array}{c}\text{dilution factor}\\ \text{as needed}\end{array}\right) \quad (11\text{-}2)$$

where,

mL extract = 204 for pyrophosphate extract
129 for citrate-dithionite extract
50 for acid-oxalate extract

11.12 Precision and Accuracy

Precision and accuracy information may be found in the following locations: for aluminum determinations by AA, Section 11.10.4.5; for iron determinations by AA, Section 10.10.4.2.5; for iron and aluminum determinations by ICP, Section 10.12.

11.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey*, U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity.* Technical Bulletin No. 404. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York.

Johnson, D. W., and D. E. Todd. 1983. Some Relationships among Fe, Al, C, and SO_4 in a Variety of Forest Soils. *Soil Sci. Soc. Am. J.*, Vol. 47, pp. 702-800.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

12 Extractable Sulfate and Nitrate

12.1 Scope and Application

Sulfur in the form of sulfate (SO_4^{2-}) is considered a major controlling factor in soil acidity. It is necessary, therefore, to determine both the quantity of sulfate held in the soil and how much of this sulfate is readily available to the soil solution. Sulfate on anion exchange sites, or loosely associated with cations, is readily removed. When strongly adsorbed to the soil surface or complexed with nonsoluble organic material, sulfate is not easily dislocated.

Nitrogen in the form of nitrate (NO_3) also may be influential in the acidification of soil. It is the thought that nitrate accumulates beneath the snow pack as a result of biological activity at the snow-soil interface. Then a relatively concentrated flush of nitrate moves through the soil profile after spring thaw. Therefore, samples collected in the spring, prior to heavy rains and before uptake of the nitrate by vegetation, should contain more nitrate than samples collected during the fall. Also, nitrogen may be a component of both dry and wet deposition.

Two extractions have been developed to determine the levels of sulfate and nitrate in the soil. The first extraction, for nitrate and readily available sulfate, utilizes DDI water. The water extraction will include the sulfate and nitrate on anion exchange sites and associated with cations. The phosphate (PO_4^{3-}) extraction will include the adsorbed and some complexed sulfate. In general, the trivalent charge on the phosphate ion enables phosphate to displace divalent sulfate from adsorbing and complexing sites. This, combined with mass action, will extract nearly all sulfate from the soil.

From the sulfate adsorption isotherm, an estimate of the inorganic sulfate retention capacity of the soil can be determined. The PO_4^{3-} extractable sulfate can be used to approximate the total amount of adsorbed sulfate. Because drying the soil prior to analysis allows oxidation of reduced forms of sulfur, the water extractable sulfate approximates both oxidized and reduced forms of sulfur which will readily enter the soil solution.

12.2 Summary of Method

Two portions of a soil sample are extracted. DDI water is the extracting matrix for nitrate and readily available sulfate. The extracting matrix for sulfate that is more difficult to dislocate is 0.016 M sodium phosphate (containing 500 mg P/L). After the extractions are completed, the analytes are determined by ion chromatography. This method is modified from Fernandez (1983) and Tabatabai (1982).

12.3 Interferences

An interference can occur during the ion chromatographic analysis of the 0.016 M NaH_2PO_4 (1500 mg PO_4^{3-}/L) extract. At such a high concentration, the phosphate peak overlaps the SO_4^{2-} peak under typical IC conditions (usually phosphate elutes prior to sulfate). By using the mixed eluent 0.0020 M Na_2CO_3/0.0020 M NaOH (an eluent whose pH is greater than the pK of HPO_4^{2} [pK = 12.37] and which is sufficiently buffered to maintain the pH in the presence of the eluting phosphate), phosphate elutes after SO_4^{2-}, and the interference is minimized or eliminated. Elution time for sulfate is increased by several minutes with this modification.

Soil extracts can rapidly degrade a column; therefore, frequent cleaning with dilute acid is recommended (after each 50 samples). Also, the use of guard columns is recommended. A guard column for organics should be used when analyzing PO_4^{3-} extracts.

12.4 Safety

Follow standard laboratory safety practices and wear gloves, safety glasses, and a laboratory coat when preparing and handling reagents. Follow the safety precautions of the manufacturer when operating the instruments.

12.5 Apparatus and Equipment

- Centrifuge tubes, with screw caps, 50 mL.
- Centrifuge.
- Filtration apparatus.
- Membrane filters, 0.20 μm pore.
- Reciprocating shaker.
- Vortex mixer (optional).
- Ion chromatograph, Dionex models 10, 12, 14, 16, or 2000 series or equivalent with AS3, AS4a, or equivalent anion separator column, anion fiber or micromembrane suppressor column or equivalent; appropriate guard column recommended to preserve the separator column.
- Automated injection system, commercially available from several manufacturers.
- Data recording system, integrator or strip chart recorder for recording ion chromatographs; the nominal output to recorder is 1.0 V. The Dionex plane parallel electrode conductivity detector or equivalent unit gives a linear response with concentration until electronic saturation occurs at approximately 4.0 V. Therefore, several analytical ranges on recorders set at different full-scale voltages can be monitored simultaneously.
- Volumetric pipets, volumes as needed.
- Volumetric flasks, volumes as needed.

12.6 Reagents and Consumable Materials

Unless stated otherwise, all chemicals must be ACS reagent grade or better. The concentrated and working eluents, as well as the regenerant used, are based on the recommendation of the manufacturer for the particular column and instrument used. These may be altered to increase resolution or decrease separation time. The eluents, suppressors, and regenerants are acceptable for a Dionex unit with an AS series anion separator column. These will change with the manufacturer and column used. Even individual columns may require variation. All modifications must be documented before routine analysis begins.

- Parafilm.
- Monobasic sodium phosphate ($NaH_2PO_4 \cdot H_2O$) 0.016 M (500 mg P/L)--Dissolve 2.227 g $NaH_2PO_4 \cdot H_2O$ in DDI water and dilute to 1.000 L.
- Sodium carbonate (Na_2CO_3).
- Concentrated eluent, 0.40 M Na_2CO_3--Dissolve 42.396 g Na_2CO_3 in DDI water and dilute to 1.000 L. Seal and store until use.
- Sodium hydroxide (NaOH), pellets or flakes.
- Sodium hydroxide (50 percent wt/v)--Dissolve 50 g NaOH in DDI water and dilute to 100 mL. This dissolution generates heat; therefore, a water- or ice-bath should be used to cool the dissolution vessel.
- Working eluent, 0.0020 M Na_2CO_3/0.0020 M NaOH - Dilute 20.0 mL concentrated eluent to 4.00 L and adjust pH to 12.5 with 50 percent NaOH. Other working eluents for the LECO type columns include: (1) 0.003 M Na_2CO_3 for water extractable sulfate and 0.002 M $NaHCO_3$/0.0025 M NaOH for phosphate extractable sulfate, and (2) 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3

for both sulfates. The eluent used must give clean separation of the peaks without excessive band broadening.

- Sulfuric acid (H_2SO_4), concentrated.

- Fiber suppressor regenerant--For water-extractable samples, H_2SO_4 (25 mM) - Dilute 10 mL of 2.5 M H_2SO_4 to 1.0 L with DDI water.

- Magnesium sulfate ($MgSO_4$).

- Sodium nitrate ($NaNO_3$).

- Stock resolution standard (1,000 mg SO_4^{2-}/L, 1,000 mg PO_4^{3-}/L, 1,000 mg NO_3^-/L)--Dissolve 1.2530 g $MgSO_4$, 1.3708 g $NaNO_3$, 3.5397 g $NaH_2PO_4 \cdot 12H_2O$ in DDI water and dilute to 1.00 L.

- Working resolution standard (10.0 mg NO_3^-/L, 10.0 mg SO_4^{2-}/L, and 10.0 mg PO_4^{3-}/L)--Dilute 10.00 mL of stock resolution standard to 1.00 L with DDI water.

- Primary mixed standard (1,000 mg SO_4^{2-}/L and 1,000 mg NO_3^-/L)--Dissolve 1.2530 g $MgSO_4$ and 1.3708 g $NaNO_3$ in DDI water and dilute to 1.00 L.

- Secondary standards:

  Solution A--Dilute 10.00 mL of primary mixed standard solution to 100.00 mL with DDI water (100.0 mg SO_4^{2-}/L and 100.0 mg NO_3^-/L).

  Standard Solution B--Dilute 5.00 mL primary mixed standard solution to 500.00 mL with DDI water (10.0 mg SO_4^{2-}/L and 10.0 mg NO_3^-/L).

- Calibration standards--Use secondary standard solutions A and B to prepare the calibration standards (see Table 12-1). Calibration standards are prepared by diluting a volume of standard solution A or B with DDI water.

Table 12-1. Example of Concentration of Calibration Standards Used for the Analysis of Water Samples by Ion Chromatography

Concentration in mg/L		Milliliters of Standard Solution per 100 mL of Calibration Standard
SO_4^{2-}	NO_3^-	
50	50	5.00 of primary (1,000 mg/L)
20	20	20.00 of A
10	10	100.0 of B
2	2	2.00 of A
0.5	0.5	5.00 of B

Calibration standards must be prepared daily. Calibration standards of concentrations other than those shown in Table 12-1 may be used as long as standard concentrations bracket the sample concentrations.

12.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the laboratory, all samples are kept sealed and are refrigerated at 4 °C when not in use.

12.8 Calibration and Standardization

Calibrate ion chromatograph as recommended by the manufacturer. Use the calibration standards in Table 12-1, and any additional standards needed, to bracket the sample concentrations. Nonlinear response can result when the separator column capacity is exceeded. Maximum column loading, for all anions, should not exceed about 400 ppm.

12.9 Quality Control

Quality control procedures are specified in Section 2.6. These include one resolution

check, a matrix spike determination, a detection limit QC sample, QCCS, and duplicate analysis for each analyte in each solution. The reagent blank is the DDI water used for water extraction procedure.

12.10 Procedure

12.10.1 Extraction of Sulfate and Nitrate by DDI Water

1. Weigh 4.00 g air-dried soil into 100-mL centrifuge tube. Add 80 mL DDI water and seal the tube.

2. Shake tube and contents for 1 hour on a reciprocating shaker. To ensure that soil is not accumulating at the base of each centrifuge tube, stop the shaker at 10 to 15 minute intervals and either invert each tube several times by hand or mix each tube on a vortex mixer.

3. Centrifuge for 10 minutes at 510 G. If the supernatant is not clear, repeat centrifugation. If it is clear, decant and save the supernatant.

4. Filter the supernatant solution through a 0.2 μm membrane filter.

5. Store the solution at 4 °C and analyze for sulfate and nitrate by ion chromatography within 24 hours (see Section 12.10.3). Immediate analysis is desirable, because biological activity may reduce the concentration of sulfate and nitrate in solution. The total volume of extract is 80 mL. If further dilution is necessary, take an aliquot of known volume and dilute in a volumetric flask. Take this dilution factor into account when calculating the concentration.

12.10.2 Extraction of Sulfate by Sodium Phosphate (NaH_2PO_4) Solution

1. Place 4.00 g of air-dried soil into a 100-mL centrifuge tube.

2. Add 20 mL 0.016 M NaH_2PO_4.

3. Shake tube and contents on a reciprocating shaker for 30 minutes. To ensure that soil is not accumulating at the base of each centrifuge tube, stop the shaker after 10 minutes and either invert each tube several times by hand or mix each tube on a Vortex mixer.

4. Centrifuge for 10 minutes at 510 G. If the supernatant is not clear, repeat centrifugation. If it is clear, decant supernatant into a clean beaker or LPE bottle.

5. Repeat extraction and centrifugation (steps 2, 3, and 4) three times for a total of four extractions. Combine all 4 supernatants and dilute to 100 mL.

6. Prior to analysis, filter the solution through a 0.2 μm membrane filter.

7. Store the solution at 4 °C and analyze for sulfate by ion chromatography within 24 hours (see Section 12.10.3). Immediate analysis is desirable, because biological activity in this nutrient-rich extract may reduce the concentration of sulfate in solution. The total volume of extract is 100 mL. If further dilution is necessary, take an aliquot of known volume and dilute in a volumetric flask. Take this dilution factor into account when calculating the concentration.

12.10.3 Determination of Sulfate (SO_4^{2-}) and Nitrate (NO_3^-) by Ion Chromatography

This procedure is based on methods using Dionex ion chromatographs. Other systems may be used with modifications to the columns, chromatographic conditions, and reagents. In these cases, follow the recommendations of the manufacturer. Analyze both the water and the phosphate extracts of the soil samples.

The following operating conditions are recommended for the Dionex-type system. Other systems require similar conditions.

- Recording system, 10 or 30 μS/cm full scale deflection; 100 μS/cm for some cases; linearity should be checked regularly since this may vary and cause error.
- Injection loop, 0.05 or 0.10 mL; 100 μL may be preferable for some PO_4^{3-} samples to reduce pH problems.
- Flow rate, 2.0 to 2.3 mL/min.
- Pressure gauge or similar device, used as pump-stroke noise suppressor, as required for unit.

Note: Make certain that pressure does not exceed the recommendations of the manufacturer for the column.

1. Operate the fiber suppressor as recommended by the manufacturer. Generally, the suppressor must be in an upright position with regenerant flowing from bottom to top.

2. Set up the recorders or integrators for the most sensitive setting for the sample range being analyzed. Set the second channel for a high range, or else perform dilutions when necessary. Operate integrators by following the instructions of the manufacturer.

3. Pump eluent through the columns. After a stable baseline is obtained, adjust the recorder zero to approximately 10 percent of the chart. Inject the highest standard. As the highest standard elutes, adjust the recorder range to approximately 90 percent of the chart. Repeat several analyses of the highest standard to be certain that the gain is stable and the peaks are reproducible. Analyze the resolution standard and determine the resolution. If the PO_4^{3-} - SO_4^{2-} or the NO_3^- - SO_4^{2-} resolution does not exceed 60 percent, replace or clean the separator column and repeat step 3.

4. Analyze the standards in random order. Load the injection loop, manually or via the autosampler, with the standard to be analyzed. Load five to ten times the volume required to flush the sample loop thoroughly; then inject the standard.

   If memory effects are noted for standards, blanks should be injected before each analysis. For each analysis, measure and record the peak height either manually or with a data system. If an integrator is available, record the peak area.

5. Repeat step 4 for analysis of QC samples, matrix spikes, blanks, and soil extracts. If using an autosampler, fill it with the samples.

6. Dilute and reanalyze each sample for which the concentration exceeds the calibrated range.

7. For each peak, draw a baseline. Measure the peak height with a clear plastic ruler and record the peak height on the strip chart and in a log book. If an integrator is used, manually check 5 percent or at least 2 per batch. Record these peak heights and peak areas in a log book or in a computer file. (See Figure 12-1.)

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 113

QUALITY CONTROL: ION CHROMATOGRAPHY RESOLUTION TEST

LAB NAME _____
BATCH ID _____ DATE OF ANALYSIS _____ MM/DD/YR

LAB MANAGER'S SIGNATURE _____

IC Make and Model: _____

	Concentration (mg/L)	Peak Area (integrator units)	Peak Height (cm)
SO_4^{2-}	_____	_____	_____
PO_4^{3-}	_____	_____	_____
NO_3^-	_____	_____	_____

Column Back Pressure (at max. of stroke): _____ psi

Flow Rate: _____ mL/min

Column Model: _____ Date of Purchase: _____

Column Manufacturer: _____

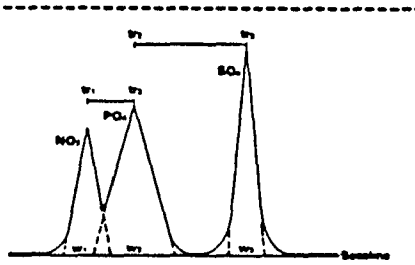
Column Serial No: _____

Precolumn in system ____ Yes ____ No

Percentage Resolution:
*$100 \times 2(tr_2-tr_1)/(W_1+W_2)$ $NO_3 - PO_4$ _____
$100 \times 2(tr_3-tr_2)/(w_2+W_3)$ $PO_4 - SO_4$ _____
$100 \times 2(tr_3-tr_1)/(w_1+W_3)$ $NO_3 - SO_4$ _____

The resolution must be greater than 60%.

Test Chromatogram:



(FACSIMILE)

*Calculations may change if order of elution is different from test chromatogram.

Figure 12-1. Ion chromatography resolution test.

12.11 Calculations

From the peak heights or peak areas, calculate the analyte concentration in the extract as follows:

- Using a graph--Construct a calibration curve by plotting concentration of standard versus peak height (or peak area) for each standard.

  Read the concentration of the analyte directly from the calibration curve.

- Using a linear least squares fit-- Equations used for calculation of the linear least squares fit are available in most elementary statistics books. The linear least squares fit yields the following parameters: slope (n), intercept (b), error of fit (e), and correlation coefficient (r). The slope and intercept define a relationship between concentration of standard i, (x_i), and the predicted instrument response, (y_i):

  $$y_i = mx_i + b \qquad (12\text{-}1)$$

  A simple rearrangement of Equation 12-1 yields the concentration (x_i) corresponding to an instrumental response of (y_i):

  $$x_i = (y_i - b)/m \qquad (12\text{-}2)$$

- For nonlinear calibration curves--A computer routine or microprocessor in the analyzer may be used to calculate concentration.

  Multiply results for concentration by the appropriate dilution factor if necessary. Then convert mg SO_4^{2-} to mg S by multiplying by 0.33379, and convert mg NO_3^- to mg N by multiplying by 0.22590.

  Convert concentration of analyte in the soil extract to concentration in the original soil sample by using the following equation:

$$\text{Analyte Concentration (mg/Kg soil)} = \left(\frac{\text{mg analyte}}{\text{L}}\right)\left(\frac{\text{mL extract}}{\text{g oven-dried soil wt*}}\right)\left(\frac{1\text{ L}}{1{,}000\text{ mL}}\right)\left(\frac{1{,}000\text{ g soil}}{\text{kg soil}}\right)$$

*converted from moisture percent procedure (12-3)

12.12 Precision and Accuracy

The precision and accuracy information provided is based on analysis of surface water samples (O'Dell et al., 1984). Analysis of soil extracts, which have different matrices and reflect different sample preparation procedures, may not yield results of the same precision and accuracy as cited here (Table 12-2). This information is supplied only as an indication of precision and accuracy.

Table 12-2. Single-Operator Precision and Accuracy (O'Dell et al., 1984)

Ion	Spike (mg/L)	Number of Replicates	Mean % Recovery	Standard Deviation (mg/L)
SO_4^{2-}	10.0	7	111.6	0.709
NO_3^--N	0.50	7	100	0.0058

12.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey*, U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity.* Technical Bulletin No. 404. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York.

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/ 600/4-84-017. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Tabatabai, M. A.. 1982. *Sulfur.* pp. 501-538 In: *Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties*, Agronomy Monograph No. 9, 2nd Edition. A. L. Page, R. H. Miller, and D. R. Keeney (Eds.) American Society of Agronomy, Inc./Soil Science Society of America, Inc., Madison, Wisconsin.

13 Sulfate-Adsorption Isotherms

13.1 Scope and Application

The ability of soil to adsorb sulfate (SO_4^{2}) is perhaps the most important factor in determining if a soil will show a direct or delayed response to SO_4^{2-} deposition. The higher the sulfate-adsorption capacity of a soil, the greater is its buffering capacity to SO_4^{2-} inputs.

Adsorption of inorganic sulfate is primarily affected by soil pH, quantity of Fe and Al sesquioxides, exchangeable cations, clay content, and type of clay minerals. Below a pH of 6.5, sulfate adsorption increases with decreasing pH; above this pH, sulfate adsorption is negligible (Tabatabai, 1982). Sulfate-adsorption capacity can be estimated indirectly by quantitative determination of the iron- and aluminum-oxide content (see Fernandez, 1983, and Johnson and Todd, 1983).

The most direct and effective way to determine sulfate-adsorption capacity utilizes sulfate-adsorption isotherms. For this study, sulfate-adsorption isotherms are developed by measuring the amount of SO_4^{2-} remaining in solution after contact with a soil sample.

These sulfate-adsorption isotherms allow relative comparisons to be made between horizons or between pedons. It should not be inferred that these isotherms quantify the in situ sulfate-adsorption of soil.

13.2 Summary of Method

Six portions of the same soil sample are shaken with solution containing 0, 2, 4, 8, 16, and 32 mg sulfur per liter, respectively. The mixtures are centrifuged and filtered, and the resulting filtrate is analyzed for SO_4^{2-} by ion chromatography. The difference between the original concentrations of the sulfur solutions and the concentrations after this procedure indicates the sulfur uptake by the soil.

13.3 Interferences

No interferences have been identified.

13.4 Safety

Follow standard laboratory safety practices and wear gloves, safety glasses, and a laboratory coat when preparing and handling reagents. Follow the safety precautions of the manufacturer when operating the instruments.

13.5 Apparatus and Equipment

- Centrifuge tubes, 100 mL, with screw caps (50 mL centrifuge tubes with screw caps, optional).
- Volumetric pipet, 50 mL (pipettor, optional).
- Vortex mixer.
- Reciprocating shaker.
- Centrifuge.
- Membrane filtration apparatus (Luer-Lok, glass syringes with membrane filters or equivalent).
- Ion chromatograph.

13.6 Reagents and Consumable Materials

- Membrane filters, 0.20 μm pore size.
- Primary sulfate (SO_4^{2-}) solution, (1,000 mg S/L)--Dissolve 3.754 g $MgSO_4$ in DDI water and dilute to 1.000 L.
- Adsorption solutions--Dilute 2.00, 4.00, 8.00, 16.00, 32.00 mL primary (1,000 mg S/L) solution to 1.000 L in separate volumetric flasks. It is most

convenient if 2- to 4-L batches of adsorption solution can be prepared. Each solution must be within 5 percent of its theoretical concentration.

13.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the laboratory, all samples are kept sealed and are refrigerated at 4 °C when not in use.

13.8 Calibration and Standardization

Calibrate the ion chromatograph as recommended by the manufacturer. Prepare working standards fresh daily and verify the concentrations by ion chromatography. Reprepare adsorption solutions if the concentrations are not within 5 percent of the theoretical concentrations. Calibration standards must be from a source independent of the primary SO_4^{2-} solution prepared for this analysis.

13.9 Quality Control

The concentration of each adsorption solution must be within 5 percent of its theoretical concentration. The quality control requirements are specified in Section 2.6 and include for each batch, a detection limit QC sample, QCCS, one resolution check, one SO_4^{2-} spike determination, and a duplicate isotherm, i.e., duplicate analysis of the 0-, 2-, 4-, 8-, 16-, and 32-mg S/L solutions after shaking them with portions of the same soil samples.

13.10 Procedure

1. Weigh air-dried sample, equivalent to 10.00 g ± 0.01 g oven-dried soil, and place it into 100-mL centrifuge tube. For highly absorbent organic soils, sample weight may be reduced to 2.50 g ± 0.01 g.

NOTE: If a 50-mL centrifuge tube is used, reduce sample weight to the equivalent of 5.00 g ± 0.01 g oven-dried soil and add 25.00 mL solution. For highly absorbent organic soils, sample weight may be reduced to 1.25 g ± 0.01 g.

2. Add 50.00 mL of DDI water to centrifuge tube, and cap it. Mix contents with vortex mixer until no soil adheres to the bottom of the centrifuge tube.

3. Repeat steps 1 and 2 and substitute 2-, 4-, 8-, 16-, and 32-mg S/L solutions for DDI water.

4. Shake the samples for 1 hour on a reciprocating shaker.

5. Centrifuge each sample for 30 minutes at 510 G, or as appropriate for the soil sample.

6. Filter supernatant through a 0.20 μm membrane filter. For some samples it may be necessary to use a larger pore pre-filter to prevent immediate clogging of the 0.20 μm filter.

7. Analyze solutions for SO_4^{2-} by ion chromatography as described in Section 12.10.3. Calibration standards must be from a source independent of the primary SO_4^{2-} solution prepared for this analysis.

13.11 Calculations

Express results as milligrams sulfur (mg S) remaining in the supernatant solution. Report data to three decimal places. If calibration standards are made in terms of mg SO_4^{2-} per liter, then:

amount of SO_4^{2-}
remaining in solution (mg S/L) =

$$\left(\text{concentration of } SO_4^{2-} \text{ remaining in solution as } \frac{\text{mg } SO_4^{2-}}{1{,}000 \text{ mL}}\right)(0.33379) \quad (13\text{-}1)$$

Calibration standards may be made in concentration units of milligrams sulfur per liter.

Also, record each sample weight so that results may be transformed to reflect milligrams sulfur adsorbed by the soil.

13.12 Precision and Accuracy

Precision and accuracy information for the ion chromatographic determination is given in Section 12.12.

13.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Soil Survey*, U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity.* Technical Bulletin No. 404. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York.

Johnson, D. W., and D. E. Todd. 1983. Some Relationships Among Fe, Al, C, and SO_4^{2-} in a Variety of Forest Soils. *Soil Sci. Soc. Amer. J.* 47:702-800.

Tabatabai, M. A. 1982. *Sulfur*, pp. 501-538 In: *Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties*, Agronomy Monograph No. 9, 2nd Edition. A. L. Page, R. H. Miller, and D. R. Keeney (Eds.), American Society of Agronomy, Inc./Soil Science Society of America, Inc., Madison, Wisconsin.

14 Total Carbon and Total Nitrogen

14.1 Scope and Application

Total carbon and total nitrogen in soil samples are determined with an automated CHN analyzer. There are many automated CHN analyzers currently available. The specific equipment and procedures required will vary with each model of CHN analyzer. This procedure is based on the operating instructions for a Perkin-Elmer 240C (McCracken, 1983; The Perkin-Elmer Corporation, 1981).

Total carbon and total nitrogen are used to characterize the amount of organic material in the soil, which is then correlated to other soil characteristics. Some nitrogen and carbon may occur in soluble forms such as NO_3^{2-}.

Heating the sample to 1,000°C will oxidize all organic materials and will also decompose carbonate minerals. This releases the nitrogen and carbon from all sources.

14.2 Summary of Method

A soil sample is oxidized at 1,000 °C for 2 minutes. CO_2, H_2O, and N_2 are then detected by thermal conductivity.

14.3 Interferences

Moisture in the sample can interfere with the analysis. Drying the soil at 50 °C prior to analysis removes most of the excess water without volatilizing excessive quantities of organic matter. Consult the instruction manual provided by the manufacturer for additional interferences for a specific instrument and procedure.

The helium must be kept flowing through the detectors whenever the power is on to prevent damage to the detectors. The helium will, however, remove surface water from the instrument if the instrument is left on standby. This is overcome by using conditioning samples before analyzing routine samples and standards. These condition samples recoat the system with water so that CO_2 and N_2 are not lost to adsorption.

14.4 Safety

Normal laboratory safety precautions should be followed. Wear protective clothing and safety glasses when handling reagents or operating instruments. Heat resistant gloves may be needed when placing samples in the furnace. The furnace must be adequately vented and protected from human contact and combustible materials.

Follow the safety precautions of the manufacturer when operating the instruments.

Gas cylinders should be bottled or chained in an upright position.

14.5 Apparatus and Equipment

NOTE: This list is general for CHN methods. The specific requirements will vary with the instrument and procedures used. Some additional apparatus may be required, other equipment may not be needed.

- Hammer mill, ball mill, shatterbox, agate or mullite mortar and pestle, or equivalent grinding device.
- Sieve, 60-mesh (0.25 mm).
- Convection oven, equilibrated at 50 °C; with thermometer, 0° to 100 °C range.
- Compressed air, for cleaning purposes only.
- CHN analyzer.

- Data station, micro processor equipped recording system and integrator, or equivalent digital or analog system.
- Forceps.
- Tamping rod.
- Bunsen burner.
- Desiccator.
- Microbalance, capable of weighing to ±0.001 mg (±1 μg).
- Vials, low carbon, low nitrogen vials specific for the equipment and procedures used.

14.6 Reagents and Consumable Materials

- Helium gas, high purity (99.995 mole percent minimum).
- Oxygen gas, high purity (99.99 mole percent minimum).
- Acetanilide ($CH_3CONHC_6H_5$), NBS-standard.
- Desiccant, anhydrous P_2O_5 or $Ca(OH)_2$.
- Alumina wool.

NOTE: Precondition alumina wool by holding it with forceps in a burner flame for a few seconds.

CAUTION: If heated too long, the alumina wool will become brittle. Store it in a desiccator.

14.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1986). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not in use.

14.8 Calibration and Standardization

The instrument must be calibrated once per day or once per batch, whichever is more frequent.

If (1) the instrument has been out of operation, (2) the system has been opened, (3) the combustion or reduction tube, traps, or scrubbers have been changed, (4) oxygen or helium has been changed, or (5) any other change in the gas system has been made which might affect the detectors, flush the system by running a blank without using a vial. When operating the instrument manually, i.e., without an autosampler, use no boat or ladle. Calibration checks include the acetanilide standard, a blank of alumina wool, and a quality control calibration standard.

14.8.1 Acetanilide Standards

Acetanilide standards are analyzed to determine the K-factor. The K-factor is the microvolts of response per microgram of sample (μV/μg) for the given standard.

Accurately weigh approximately 2 or 3 mg ± 0.1 mg acetanilide into sample vial. Record sample weight. Prepare 5 to 10 replicates. Analyze 2 acetanilide standards before each batch of approximately 42 samples, according to the procedure specified in Section 14.10.

K-factors should be reproducible within the ranges given in Table 14-1. Compute the mean and standard deviation of K-factors and note the spread by using the equations given in Section 14.11. In the absence of other criteria, Perkin-Elmer lists the following maximum deviations from the average K-factor for "an accuracy of ±0.3 percent absolute"; i.e.,

Table 14-1. Allowable Deviations in K-Factors[a]

Element	Level	Accuracy desired	Maximum deviation (μV/μg)	Equivalent range for acetanilide
N	5 % N	±0.10 % N	±0.15	10.16-10.57 % N
	5 % N	±0.05 % N	±0.08	10.25-10.47 % N
	2 % N	±0.05 % N	±0.20	10.10-10.62 % N
	1 % N	±0.05 % N	±0.40	9.85-10.87 % N
	0.5 % N	±0.05 % N	±0.70	9.32-11.40 % N
	0.5 % N	±0.01 % N	±0.15	10.16-10.57 % N
C	50 % C	±0.50 % C	±0.22	70.38-71.81 % C
	5 % C	±0.05 % C	±0.22	70.38-71.81 % C
	2 % C	±0.05 % C	±0.53	69.31-72.86 % C
	1 % C	±0.05 % C	±1.04	67.42-74.65 % C

[a] This table lists the maximum allowable deviations of the K-factors from the average factors.

Table 14-2. Allowable Blank Variations[a]

Element	Sample size (mg)	Accuracy desired	Maximum Variation (μV)
N	3	±0.05 % N	±11
C	3	±0.05 % C	±33
N	5	±0.05 % N	±19
C	5	±0.10 % C	±108
C	5	±0.05 % C	±54
N	20	±0.05 % N	±77
N	20	±0.01 % N	±15
C	20	±0.05 % C	±218

[a] This table lists the maximum allowable variation of the blank from the average blank, or from one blank run to the next.

consistently producing values for acetanilide within ±0.3 percent of the actual percent for each element.

	Element C	Element N
Typical K (rough)	20 μV/μg	7 μV/μg
Maximum deviation from average	±0.085 μV/μg	±0.20 μV/μg

NOTE: This is the deviation in one direction; therefore, the total variance may be up to twice the maximum deviation value.

14.8.2 Blank Samples

Analyze a blank consisting of a vial, alumina wool, ladle, and the oxygen donor specified by the manufacturer, if needed. Alternate blanks with the analysis of samples or standards to prevent a memory effect. When blanks are run consecutively, each blank result following the initial result is lower than when a blank is run after a sample.

Blanks should be reproducible within the allowable range given in Table 14-2. Use the equation given in Section 14.11 to compute average blank values and variation, and note the range. In the absence of other criteria, Perkin-Elmer lists the typical blank values and ranges as follows.

	Element C	Element N
Typical Blank	100 μV	50 μV
Maximum Range	50 μV	30 μV

14.8.3 Calibration Sequence

Analyze at least two acetanilide standards and two blanks for each batch of samples in the following sequence: (1) unweighed sample (~2 mg), (2) blank, (3) unweighed sample, (4) acetanilide standard (determine K-factor), (5) blank, continue to alternate determination of K-factors and blanks, and (6) acetanilide standard.

The blank values and K-factor must fall within limits specified in Tables 14-1 and 14-2.

14.8.4 Quality Control Calibration Standard

Analyze the QCCS after the calibration sequence is completed and before beginning routine sample analysis. The QCCS is a well characterized soil sample whose carbon and nitrogen values are known. This may be a purchased sample or one which has been evaluated many times in the laboratory with

little or no variation between replications. The analytical procedure is given in Section 14.10.

14.8.5 Linearity of Calibration Curve

Determine the linearity of the calibration curve by analyzing no fewer than three standards that bracket the expected concentration range of the samples. When only one standard material is used for calibration, at least three samples of standard material of different weights are prepared such that (1) the amount of analyte produced by the smallest sample is approximately equal to the instrumental detection limit, (2) the amount of analyte produced by the largest sample is just above that of the actual samples, and (3) the amount of analyte produced by the intermediate sample is in the midrange of the analyte content of the samples. The correlation coefficient of a graph of µg of analyte versus sample weight should not be less than 0.99.

Because elemental analyzers were developed for analysis of samples with a relatively high analyte concentration, it is especially important to verify linearity for low concentrations of analyte.

14.9 Quality Control

In addition to those analyzed during calibration, more blanks and QCCS are used during analysis of routine samples to assure that results continue to be valid. Analyze the blank sample after every 15 samples, after completion of analysis of each batch, and whenever an oxygen donor is added or changed. Blank values must fall within the limit specified in Table 14-2. Analyze QCCS after every ten or fewer samples. QCCS results must not have a relative standard deviation greater than 10 percent. If blank or QCCS values do not meet the specified criteria, recalibrate the instrument and reanalyze all samples analyzed since the last acceptable value was obtained for the QC sample type in question.

The QC requirements are specified in Section 2.6 and include a detection limit QC sample, one duplicate analysis, and a matrix spike determination.

14.10 Procedure

The specific procedural steps will vary with the instrument and manufacturer. Some units will not require all the steps, other units or methods will require additional steps.

14.10.1 Vial Preparation

1. If vials appear deformed, reform them prior to use. Misshaped vials may jam the autosampler. Handle vials with round-tipped forceps. When lifting a vial with forceps, place the forceps over the rim of the vial. Lifting the vial by placing the forceps around it may deform the vial.

2. Clean vials by blowing out the alumina wool plugs with compressed air. Heat the vials in a Bunsen burner flame until red hot. Store cleaned vials in a desiccator.

14.10.2 Sample Preparation

Crush a 2-g aliquot of soil to pass the 60-mesh sieve. Dry the entire aliquot of crushed soil in a convection oven at 50 °C for 24 hours to reduce excess water. Weigh a sample of approximately 50 mg accurately to three decimal places, i.e., ±1 µg. Adjust the sample size according to the estimated amount of organic material: less for high organic matter soils and more for low organic matter soils.

14.10.3 Determination of Total Carbon and Total Nitrogen

If the instrument has been on standby for more than 1 hour, analyze an unweighed conditioning sample of approximately 2 mg acetanilide and then recalibrate the instrument by using the following procedure:

1. Place vials in the numbered, lower sample-loading plate (or the equivalent for the instrument being used) with the open end up.

2. Using forceps, place approximately 1 mg preconditioned alumina wool into each vial. Gently push the alumina wool to the bottom of the vial with the flat-ended tamping rod. Caution: Compressing the fibers of the wool too much will break them.

NOTE: Not all systems require alumina wool.

3. Weigh the ~50 mg sample into the vial according to the instrument instruction manual.

4. Replace each weighed sample vial into lower plate.

CAUTION: Do not lift the tray and replace it on the table. This action may result in loss of sample from vial. Slide tray onto table if you must move it.

5. Place an additional 1 mg alumina wool on top of each sample. Use the tamping rod to gather the wool into the vial and to push it into place.

6. Inspect each vial for alumina wool strands that may extend outside the vial. Remove the extending strands or push them inside the vial. Holding the vial up to the light may reveal strands. Stray alumina wool strands may damage the autosampler.

7. Adjust sample magazine so that slot number 1 is over the loading hole. Place each vial into the magazine.

NOTE: If a sample must be added to the magazine while the instrument is in operation, wait until after a sample has loaded and the magazine has moved into the next position. Samples may then be added at any time until all samples in the batch are analyzed.

8. Analyze the samples according to the procedures in the instruction manual supplied by the instrument manufacturer.

9. After analysis is completed, clean the used vials as described in Section 14.10.1. Discard the used alumina wool. Place the instrument in the standby mode.

14.11 Calculations

If a data station or calculator system is linked to the analyzer, then sensitivity factors and analytical results for blanks and samples in weight percent are displayed. If a strip-chart recorder is used, this information must be calculated from the microvolt readings.

Report carbon and nitrogen as percent dry weight to 0.001 percent. Also report K-factors, blank values, and QCCS values.

The following equations are used to determine K-factors from acetanilide standard results:

+ Deviation =

$$\frac{[\text{level (\%)}]\ (\text{avg. K})}{\text{level (\%)} - \text{accuracy (\%)}} - \text{avg. K} \qquad (14\text{-}1)$$

– Deviation =

$$\text{avg. K} - \frac{[\text{level (\%)}]\ (\text{avg. K})}{\text{level (\%)} + \text{accuracy (\%)}} \qquad (14\text{-}2)$$

where:

$$\text{K-factor} = \frac{\mu\ \text{Volts}}{\mu\ \text{gram}} = \frac{\mu V}{\mu g}$$

Level (%) = % of C or N in the compound

The two deviations are not equal. The allowable negative deviation is less than the positive deviation. The negative deviation was used to tabulate values for the maximum deviation as given in Table 14-1.

$$\text{Equivalent range for Acetanilide} = \frac{(\text{actual acet. \%})\ (\text{avg. K})}{\text{avg. K} \pm \text{deviation}} \quad (14\text{-}3)$$

The calculated values for the equivalent range for acetanilide in Table 14-1 are based on the actual positive and negative deviations.

To determine allowable blank variations, the following equation is used:

Allowable variation (μV) =

$$\begin{pmatrix}\text{sample} \\ \text{wt } (\mu\text{g})\end{pmatrix}\left(\frac{\text{\% accuracy}}{100}\right)\ (\text{K-factor in } \mu\text{V}/\mu\text{g}) \quad (14\text{-}4)$$

14.12 Precision and Accuracy

Accuracy levels vary with sample size and weight percent for the analyte.

14.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

McCracken, R. E. 1983. *In-House Operations Manual for the Perkin-Elmer 240 CHN Analyzer.* Agronomy Analytical Laboratories, Cornell University, Ithaca, New York.

Perkin-Elmer Corporation, The. 1981. *Instructions: Model 240C Elemental Analyzer.* The Perkin-Elmer Corporation, Norwalk, Connecticut.

15 Inorganic Carbon

15.1 Scope and Application

This method is for the coulometric analysis of fine earth and rock fragment fractions for inorganic carbon. The analysis is performed if the qualitative test for inorganic carbon performed at the preparation laboratory is positive or if the water pH of the sample is greater than or equal to 6.0.

The effectiveness of the coulometric technique stems from its basic reliance on electrolytic measurement. Because it requires relatively large currents as compared with other methods and an unpolarized working electrode, a coulometric method is capable of precision to ±0.1 percent or better and is intrinsically accurate. The sensitivity of a coulometric method is high; by using low currents and microapparatus, good precision can be obtained at sample concentrations of 10^{-4} M and below (Strobel, 1973). There are some limitations on the use of the coulometric technique because of restrictions imposed by the electrolytic process, but these limitations are not of consequence in soil solution analysis.

15.2 Summary of Method

The less than 2-mm fraction and the rock fragment fraction of a soil sample are analyzed separately for inorganic carbon. Before analysis, the rock fragment fraction is crushed with a jaw crusher, then is powdered to pass a 60-mesh sieve by using either a pulverizer, a hammer mill, or an equivalent unit. The sample is placed in the sample tube of the coulometer, either directly or within a weighing boat, is treated with acid, and is heated to evolve carbon dioxide. When the coulometric reading in micrograms of carbon is relatively steady, the analysis is complete. The method is from Coulometrics, Inc., (1985).

15.3 Interferences

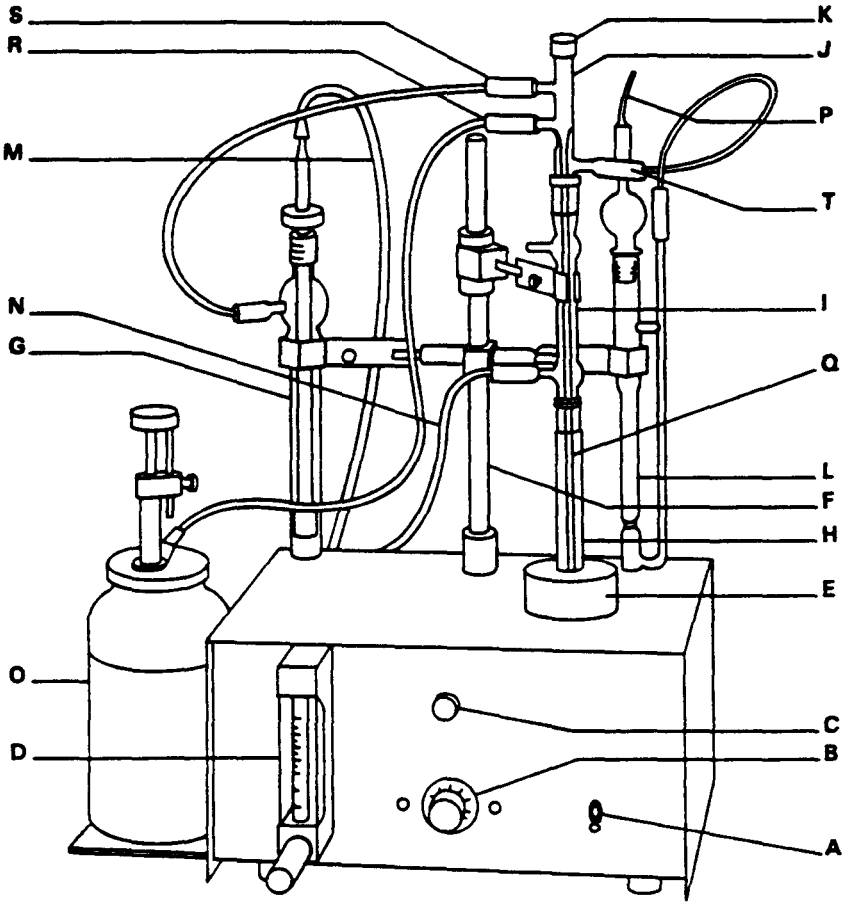
No interferences have been identified.

15.4 Safety

Wear protective clothing and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acid and hydroxide solutions should be restricted to a hood. Follow the safety precautions provided by the manufacturer when operating the coulometer.

15.5 Apparatus and Equipment

- Jaw crusher.
- Riffle splitter, Jones-type.
- Pulverizer, hammer mill, shatter box, or equivalent.
- Sieve, 60-mesh.
- Coulometer.
- Mineral carbon apparatus (see Figure 15-1).
- Weighing boats, carbonate-free.
- Sample tubes, as recommended by the manufacturer.
- Repipet, adjustable to 2 mL, or equivalent unit.
- Heating unit.
- Coulometer accessories as recommended by manufacturer.



A. Main Power	K. Septum
B. Heater Control	L. Sample Scrubber
C. Heat Indicator Light	M. Analysis Air Line
D. Flow Meter	N. Condenser Air Line
E. Heater and Shield	O. Acid Dispenser
F. Main Support	P. Scrubber Outlet to Coulometer
G. Air Scrubber	Q. Sample Purge Tube
H. Sample Tube	R. Acid Inlet
I. Condenser	S. Purified Air Inlet
J. Adaptor Tube	T. Sample Air Outlet

Figure 15-1. Mineral carbon apparatus.

15.6 Reagents and Consumable Materials

- DDI water--Water used for preparing or diluting reagents or samples must be double-distilled, double-deionized (DDI), or deionized and distilled to meet purity specifications for Type II Reagent Water given in ASTM D 1193 (ASTM, 1984).

- Acid solution for CO_2 evolution--A variety of mineral acids may be used for CO_2 evolution. Depending on the sample type, certain acids have advantages over others. One of the following acid solutions is suggested with the conditions noted.

  1. Sulfuric acid (H_2SO_4)--Add 58 mL of concentrated H_2SO_4 to 500 mL DDI water in a 1.00 L volumetric flask. Allow solution to cool, then dilute to volume with DDI water. This is about 2 N H_2SO_4. When H_2SO_4 solution is used for CO_2 evolution, precipitation of sulfates may tend to occlude some carbonate.

  2. Hydrochloric acid (HCl)--Add 200 mL of concentrated HCl to 600 mL DDI water in a 1.00 L volumetric flask. Allow solution to cool, then dilute to volume with DDI water. This is about 2 N HCl. When HCl solution is used for CO_2 evolution, care must be taken to ensure that HCl from the solution does not overload the scrubber and enter the coulometer.

- Calcium carbonate ($CaCO_3$), primary standard grade.

- Potassium hydroxide (KOH), solution for air scrubber--Dissolve 100 grams KOH in 100 mL CO_2-free DDI water to produce a solution that is 50 percent KOH by weight. This KOH solution remains effective for 1 to 2 weeks in regular use. The air bubbling through the solution must be well-dispersed for efficient removal of CO_2.

- Solution for sample scrubber tube--The common volatile acidic gases from acid treatment of mineral materials can be removed with either of the following:

  1. Saturated silver sulfate (Ag_2SO_4) containing 3 percent H_2O_2 and adjusted to pH 3--Dissolve about 1.5 grams Ag_2SO_4 in 90 mL DDI water to produce a saturated silver sulfate solution. Add 10 mL 30 percent H_2O_2. Adjust to pH 3 with H_2SO_4. Do not use HCl because it will precipitate AgCl.

  2. Potassium iodide (KI), 50 percent by weight adjusted to pH 3 Dissolve 100 g KI in 100 mL DDI water. Adjust to pH 3 with dilute HCl.

- Antifoam agent--Either of the following anti-oxidants may be added to the sample if there is a concern about rapid oxidation and foaming of organic materials because of H_2O_2.

  1. Stannous chloride ($SnCl_2$).

  2. Ferrous sulfate ($FeSO_4$).

15.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not in use.

15.8 Calibration and Standardization

Before and after each analytical batch, analyze a series of standards by following the procedure given in Section 15.10. The high and low standards should bracket the expected concentrations of inorganic carbon in the samples. Use the primary standard grade $CaCO_3$.

15.9 Quality Control

Quality control requirements are specified in Section 2.6 and include a detection limit QC sample, QCCS, a duplicate analysis, and a matrix spike determination.

15.10 Procedure

1. Pass the rock fragment fraction through the jaw crusher. By using the riffle splitter, obtain a 100-g subsample.

   Place the 100-g aliquot of rock fragments in the pulverizer or hammer mill and grind the fragments to a powder. Pass the powder through a 60-mesh sieve. If necessary, regrind any material retained by the sieve.

2. For both the powdered rock fragments and the <2-mm soil fraction, weigh an aliquot of sample that contains 1 to 3 mg of mineral carbon. Either weigh sample into a porcelain boat or other carbonate-free sample carrier and place the entire carrier into the sample tube; or weigh sample directly into the sample tube.

NOTE: The sample tube must be free of residual acid.

3. Check the system for leaks. The system must be leak-free for proper functioning.

4. Dispense approximately 2 mL acid into the sample tube from the repipet.

5. Place sample tube on the heating unit and adjust the temperature so that fumes from the acid do not overload the scrubber and enter the coulometer.

6. Allow CO_2 to evolve from the sample until the coulometer gives a relatively steady reading.

NOTE: The very high sensitivity of the coulometer can make a relatively stable end point appear somewhat unstable, e.g., for a 50-mg sample, 5 μg represents only 0.01% C.

7. Record the time required for analysis of the samples, standards, and blanks. Also, record the analyte concentration as weight percent carbon (wt % C).

8. Reset coulometer and analyze the next sample.

15.11 Calculations

$$\text{\% inorganic carbon} = \left(\frac{(\text{micrograms C} - \text{blank})}{\text{micrograms of sample.}}\right)(100)$$

15.12 Precision and Accuracy

No precision or accuracy data are currently available.

15.13 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water*, D1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report.*

Vol. I: Field Sampling. U.S. Environmental Protection Agency.

Coulometrics, Inc. 1985. *Coulometric Inorganic Carbon Determination*. Coulometrics Inc., Golden, Colorado.

Strobel, H.A. 1973. *Chemical Instrumentation: A Systematic Approach to Instrumental Analysis*, Second Edition. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts.

16 Total Sulfur

16.1 Scope and Application

Total sulfur in soil samples is determined with an automated sulfur analyzer by combustion of the sample at approximately 1,550 °C. This procedure is based on the operating instructions for a LECO 763-300 sulfur analyzer (LECO, undated).

The determination of total sulfur is necessary to establish a mass-balance relationship between naturally occurring sulfur and sulfur inputs from acidic deposition.

16.2 Summary of Method

The sample is placed in a ceramic crucible with Fe, Sn, and Cu catalysts, is covered with a porous cover, and is heated to a maximum of 1,550 °C in a high-frequency, timed induction furnace. The combustion of the sample liberates SO_2 which is then determined by an infrared detector or by another method which meets the required detection limit.

16.3 Interferences

If the soil has a high organic matter content, sample size must be reduced to prevent an explosion in the combustion furnace when heat and oxygen are added. Also, high organic matter content may delay combustion. Low recovery of sulfur may occur, since the organic matter will consume oxygen to produce CO_2 and nitrogen oxides in addition to SO_2.

If detection of the analyte is by titration, other volatile products may interfere with the titration of SO_2 by increasing the titer and, therefore, will produce high results.

16.4 Safety

Wear protective clothing and safety glasses when handling reagents or operating instruments. Heat resistant gloves may be needed when placing samples in the furnace. The furnace must be adequately vented and protected from human contact and combustible materials. Follow the safety precautions of the manufacturer when operating the instruments.

Gas cylinders should be bolted or chained in an upright position.

Fumes of magnesium oxide (MgO) are toxic. Magnesium perchlorate [$Mg(ClO_4)_2$] is a fire and explosion hazard when it comes in contact with organic materials.

16.5 Apparatus and Equipment

- Induction furnace (LECO model 763-300 or equivalent).
- Infrared gas analyzer.
- Chart recorder and integrator.
- Oxygen tank.
- Sampling scoops (LECO or equivalent).
- Balance, analytical, accurate to ±0.0001 g (±0.1 mg).

16.6 Reagents and Consumable Materials

- Crucibles with lids, sulfur free and appropriate for use with the equipment used.
- Anhydrous magnesium perchlorate [$Mg(ClO_4)_2$], 10 to 20 mesh, or equivalent desiccant specified by manufacturer for drying gases after combustion and prior to detection.

- Potassium aluminum sulfate [$KAl(SO_4)_2 \cdot 12H_2O$], standard, ACS reagent grade or other standard.

NOTE: Certain instruments may not require the following materials. Refer to the instructional manual for the specific instrument.

- Magnesium oxide (MgO), powder, ACS reagent grade, low in sulfur.
- Iron chip accelerator.
- Copper metal accelerator.
- Granular tin accelerator.

16.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. In the analytical laboratory, all samples are kept sealed and are refrigerated at 4 °C when not in use.

16.8 Calibration and Standardization

The instrument must be calibrated once per day or once per batch, whichever is more frequent. Analyze a series of $KAl(SO_4)_2 \cdot 12H_2O$ standards by the procedure given in the instruction manual for the specific instrument. $KAl(SO_4)_2 \cdot 12H_2O$ is 13.52 percent sulfur by weight. Determine the weights of standard to use so that the analytical results for the standard bracket the expected sulfur content of the samples.

If sulfur content of samples is low, other standard materials may be used. Cement or rock standards are suggested if clay or soil standards are unavailable.

Determine the linearity of the calibration curve by analyzing no fewer than three standards that bracket the expected concentration range of the samples. When only one standard material is used for calibration, at least three samples of standard material of different weights are prepared such that (1) the amount of sulfur produced by the smallest sample is approximately equal to the instrumental detection limit, (2) the amount of sulfur produced by the largest sample is just above that of the actual samples, and (3) the amount of sulfur produced by the intermediate sample is in the mid-range of the analyte content of the samples. The correlation coefficient of a graph of μg of sulfur versus sample weight should not be less than 0.99.

16.9 Quality Control

Quality control requirements are specified in Section 2.6 and include a detection limit QC sample, QCCS, one duplicate analysis, and a matrix spike determination.

16.10 Procedure

16.10.1 Sample Preparation

Note: The following steps outline a sample preparation procedure. Refer to the instruction manual for the instrument specific sample preparation procedure.

1. Place 1 large scoop of MgO, about 0.3 to 0.35 grams, in the bottom of the crucible. After adding each component, gently shake the crucible to distribute contents over the bottom.

2. Weigh 0.500 grams air-dried mineral soil into the crucible. A smaller sample may be needed if the soil is high in organic matter (see Section 16.3). A sample size of 0.200 to 0.300 g is suggested for organic soil. Material dried at 60 °C should not be used since some forms of sulfur may be volatile.

3. Add 1 more large scoop of MgO.

4. Add 1 small (0.2 mL) heaping scoop of Fe chips, evenly distributed to cover MgO.

5. Add 1 small (0.2 mL) heaping scoop of Sn granules, evenly distributed to cover Fe chips.

6. Add one Cu ring.

7. Place a porous cover on the crucible. (Cover may be turned over and reused once.)

16.10.2 Determination of Sulfur

Follow the procedure outlined in the operating manual of the specific instrument. Generally the following steps are necessary:

1. Up to five analyses are run to condition the instrument at the beginning of the day, whenever the instrument has been idle for a period of time, or whenever new desiccant has been installed.

2. Periodically, check the desiccant (magnesium perchlorate) in the drying tube and replace it whenever the first few centimeters become wet. If it becomes too wet, the baseline may shift as the sample starts to heat, and this shift will be integrated as sulfur.

3. To prolong the life of the combustion tube and refractory liner, the furnace should remain at operating temperature at all times; however, to conserve energy the furnace temperature may be reduced slightly. Refer to instructional manual for specific information.

4. If detection of analyte is by titration rather than by an infrared detector, the titration chamber and associated glassware should be cleaned with acetone or concentrated HCl periodically.

16.11 Calculations

An instrument with internal calibration may report results in weight percent sulfur (wt % S).

Data from other instruments may require a series of calculations to express results as weight precent sulfur. Compare the sample results to a standard curve (see Section 16.8). Determine the sulfur content in milligrams, then:

$$\% \text{ Sulfur} = \left(\frac{\text{mg S}}{\text{(g oven-dried soil) (1,000)}} \right) (100) \qquad (16\text{-}1)$$

16.12 Precision and Accuracy

No precision or accuracy information is available at this time.

16.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* U.S. Environmental Protection Agency, Las Vegas, Nevada. Appendix A In: *Direct/-Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency.

LECO. Undated. *Instruction Manual for LECO Sulfur Systems.* LECO Corporation, St. Joseph, Michigan.

17 Semiquantitative Analysis by X-Ray Powder Diffraction of the <2-mm and <0.002-mm Fractions of Soil

17.1 Scope and Application

This method is restricted to the analysis of the fine earth fraction (<2 mm) and the clay fraction (<0.002 mm) of soil. Nonclay minerals are often found in the <0.002-mm fraction, and their identification is essential to understanding the chemistry of the inorganic constituents of soil. Bulk soil mineralogy provides information about the weathering environment in the soil and about the parent materials from which the soil developed.

17.2 Summary of the Method

Randomly oriented powder mounts are prepared for a multiphase reference standard and for the fine earth and the clay mineral fractions of each soil sample. Each material is pulverized to a particle size of less than 2 mm and corundum is added as an internal standard. The mounted materials are analyzed by X-Ray diffraction (XRD). The resulting diffraction patterns, or diffractograms, are indexed and labeled for unambiguous identification of sample type and instrumental settings. By comparing the sample diffractograms with the diffractogram obtained for the multiphase reference standard, a semiquantitative estimate can be made for each mineral component of each sample.

Oriented mounts of the clay fraction of each soil sample are prepared from clay suspensions saturated with either Mg^{2+} or K^{+}. Standard treatments of glycolation or heating are performed on the oriented mounts. Each mount is then analyzed by XRD. The resulting diffraction patterns are indexed and used to identify the clay minerals occurring in each sample.

17.3 Interferences

To reduce the intensity variation due to particle size, all samples must be reduced to a particle size of <0.002 mm.

17.4 Safety

Follow standard laboratory safety practices and wear a laboratory coat, gloves, and safety glasses when preparing and handling reagents. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling any metal salts.

Follow the safety precautions of the manufacturer when operating instruments.

Personnel working with the X-Ray diffractometer must wear individual radiation badges. Check radiation badges on a monthly basis to assess exposure. In addition, on a monthly basis, use a detector to check for radiation leaks from the instrument.

17.5 Apparatus and Equipment

- Riffle-splitter, Jones-type.
- Ring and puck pulverizer, titanium carbide or equivalent.
- Automated mortar and pestle, agate or mullite.
- Graduated cylinder, 250 mL, fitted with a stopper.
- Ultrasound, bath or horn-type.

NOTE: If the horn type is used, use the lowest setting possible. The heat generated at the higher wattages can alter some clay types.

- Thermometer, range 0 to 50 °C.
- Sample holder for randomly oriented powder mounts.
- Glass slide, rectangular.
- X-Ray powder diffraction unit with Cu-radiation tube, x-, y-plotter, solid state pulse height analyzer, peak area integration capability, rotating and oscillating stage, diffraction pattern library, and data analysis software.
- Wiggle Bug mixer.
- Balance, accurate to ±0.1 g.
- Centrifuge tubes, plastic, 100 mL, with screw caps.
- Centrifuge tubes, glass, 50 mL.
- Centrifuge, International No. 2 with No. 240 head, or equivalent.
- Reciprocating shaker.
- Hypodermic syringes, plastic, 10 mL.
- Screen, 80-mesh.
- Diamond or carbide scribe.
- Glass slides, circular, 32 mm.
- Desiccator.
- Convection oven.
- Thermometer, range 0 to 100 °C.
- Muffle furnace.
- Eyedropper or pipet.
- Freeze-dryer.
- Dialysis tubing.

17.6 Reagents and Consumable Materials

- Reference minerals, as required to match the minerals identified or expected) in the samples.

1. Quartz.
2. Albite.
3. Orthoclase.
4. Hornblende.

NOTE: A source for these reference minerals is Wards Natural Science Establishment, Inc., 5100 West Henrietta Road, P.O. Box 92912, Rochester, New York 14692-9012, telephone: 716/359-2502; or 11850 East Florence Avenue, Santa Fe Springs, California 90670-4490, telephone: 213/946-2439.

5. Montmorillonite.
6. Illite.
7. Kaolinite.

NOTE: These reference clays are available from the Clay Minerals Society Source Clays Repository, Department of Geology, University of Missouri - Columbia, Columbia, Missouri 65201, telephone: 314/882-3785.

- Corundum, Linde semiconductor grade &-Al_2O_3, 1 micron (available from Union Carbide).
- Calibration standard.

1. Silicon powder, National Bureau of Standards (NBS) standard reference material SRM 640A or SRM 640B.
2. Arkansas novaculite, quartz standard.

NOTE: This standard is available from the Gem Dugout, 1652 Princeton Drive, State College, Pennsylvania 16803, telephone 814/865-5782.

- Double-deionized water (DDI H_2O) or equivalent.
- Sodium hexametaphosphate ($Na(PO_3)_6$), 10 percent solution--Dissolve 100 g $Na(PO_3)_6$ in DDI H_2O. Dilute to 1.0 L.
- Magnesium chloride ($MgCl_2$), reagent grade, 1.0 N--Dissolve 47.6 g $MgCl_2$ in DDI H_2O. Dilute to 1.0 L.
- Ethanol (C_2H_5OH), U.S.P. grade.
- Methanol (CH_3OH), reagent grade.
- Potassium chloride (KCl), reagent grade, 1.0 N--Dissolve 75.6 g KCl in DDI H_2O. Dilute to 1.0 L.
- Ethylene glycol (CH_2OHCH_2OH), technical grade.
- Cation exchange resin, Rexyn 101(H) (available from Fisher Scientific Co., Pittsburgh, PA 15219) or equivalent.
- Silica gel desiccant.
- Hydrogen peroxide (H_2O_2), reagent grade, 30% solution.
- Sodium acetate ($NaC_2H_3O_2$), reagent grade, 1.0 N--Dissolve 82.0 g $NaC_2H_3O_2$ in DDI H_2O. Dilute to 1.0 L.

17.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, all samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. Once the mineralogical samples are aliquoted, the mineralogical samples do not need to be refrigerated. In the mineralogical laboratory, all samples are kept sealed when not being used.

Label all slides prepared for XRD by etching the sample number on the back of the glass slide with a diamond or carbide scribe. Position the etching so that the vacuum seal on an automated XRD sample changer is not affected. Keep each slide in a desiccator or dry slide box, whichever is appropriate, when the slide is not being analyzed.

17.8 Calibration and Standardization

Use copper $K_{\alpha 1}$ radiation for XRD analysis. Set the power supply at an optimal setting according to the guidelines of the manufacturer. Set the goniometer speed to resolve low intensity peaks which are 10 percent of the maximum response.

Store the patterns in the computer for later printout.

Perform an initial alignment of the goniometer by X-Raying the silicon powder calibration standard NBS SRM Number 640 A or 640 B. To verify the alignment of the goniometer and the intensity of the X-Ray tube, the silicon powder calibration standard must be X-Rayed midway through the analyses and after the final sample. Corundum, i.e., Linde α-Al_2O_3, or an Arkansas novaculite standard are acceptable substitute calibration standards.

Because each diffractometer yields slightly different patterns and reflection intensities, reference intensity ratios (RIR) must be established for the multiphase reference standard. This reference standard contains corundum as a matrix flushing agent (Chung, 1974). Other components are chosen to match those minerals identified (or expected) in the samples, and may include quartz, albite, orthoclase, hornblende, montmorillonite, illite, or kaolinite. When analyzing randomly oriented powder mounts of the <2-mm fractions and the <0.002-mm fractions, the reference standard must be X-rayed prior to sample analysis

and after every 60 samples. The calculation of RIR and the percentages of each mineral in each sample must be based on the average analyses of the reference standard that bracket the sample analyses.

17.9 Quality Control

17.9.1 Sample Preparation

Before removing an aliquot for preparation, each bulk sample must be passed seven times through a Jones-type riffle-splitter to achieve homogeneity.

Each batch of 26 samples must be prepared by the same technician.

A majority of the particles within each sample (approximately 70 percent by volume) must have a uniform particle size of <0.002 mm prior to analysis to reduce linear absorption and primary extinction effects. Use a ring and puck pulverizer of titanium carbide or equivalent for the initial particle size reduction to 0.040 mm. Use an automated mortar and pestle of agate or mullite for the final particle size reduction to <0.002 mm. Add ethanol to prevent excessive heating. In general, not more than 60 minutes grinding per sample is necessary. For each sample, perform a check on the particle size distribution of the first five of the pulverized samples in the first batch. The distribution will determine the average grinding time necessary to attain the required particle size.

17.9.2 Sample Analysis

For randomly oriented powder mounts, the multiphase reference standard and each of the routine samples contains corundum as an internal standard.

17.9.3 Indexing of Diffractograms

Each pattern must be indexed. Indexing includes marking the degrees 2θ in 1 degree increments from the starting point to the ending point of the pattern and labeling each peak with the degree 2θ position, the equivalent angstrom units, the mineral name, and the number of the JCPDS card (JCPDS, 1985/1986) used to identify each mineral.

In addition, the following must be recorded on each pattern:

- sample number.
- size fraction.
- type of mount, i.e., oriented or randomly oriented.
- treatments.
- date of analysis.
- goniometer speed.
- scale.
- millivolt (mV) or kilovolt (kV), milliampere (mA), and time constant settings.

17.10 Procedure

17.10.1 Preparation and Analysis of the Multiphase Reference Standard

NOTE: The reference standard contains corundum as a matrix flushing agent. Choose other components to match those minerals identified (or expected) in the samples. Match the crystallinity of the minerals in the reference standard as closely as possible to that of the minerals in the samples.

1. Pulverize each of the reference minerals to a particle size of <0.002 mm. Use a ring and puck pulverizer of titanium carbide or equivalent for the initial particle size reduction to 0.040 mm. Use an automated mortar and pestle of agate or mullite for the final particle size reduction to <0.002 mm. Add ethanol to prevent excessive heating. In general not more than 60

minutes grinding per sample is necessary.

2. Test the particle size distribution of each mineral by the sedimentation technique. This gravimetric technique allows particles to separate in a column of water according to their sizes.

   Add a 1.0-g aliquot of the pulverized material to a 250-mL graduated cylinder equipped with a stopper. Pour 5 mL sodium hexametaphosphate solution into the cylinder. Add DDI water to a depth of 11.0 cm. Place the unstoppered cylinder in an ultrasound bath for 5 minutes to disaggregate the particles.

   Place a mark on the graduated cylinder 10.0 cm below the surface of the suspension. Stopper the cylinder and invert it three times to thoroughly mix the suspension. Then set the cylinder down on a stable horizontal surface and immediately note the time. For the duration of the settling, the room temperature must be held at a constant 22 °C. If, by a visual estimate, more than 2 percent of the pulverized sample appears on the bottom of the graduated cylinder prior to 7 hours and 38 minutes elapsed time (Müller, 1967), the sample must be repulverized, and the particle size must be checked again.

NOTE: To accustom the analyst to visualizing 2 percent of 1.0 g, weigh 0.02 g of any sample composed of clay-sized particles, i.e., <0.002-mm diameter, to use as a comparison.

3. Weigh exactly 0.50 grams of each pulverized mineral including the corundum (alpha-Al_2O_3). Because it comes from the manufacturer in the 1 micron particle size, there is no need to pulverize the corundum. Combine the minerals in a polyethylene container and mix well. This mixture is the multiphase reference standard, subsequently referred to as the reference standard.

4. Utilize the free-falling method (NBS, 1971) to prepare a randomly oriented powder mount of the reference standard. Clamp a glass slide over the side of an open-ended sample holder to form a cavity. Allow the powdered standard to fall into the cavity while the holder is in a vertical position. Place the slide in the horizontal position (parallel to the plane of the holder) and remove the glass slide gently. Roughen the surface of the mounted sample with a single pass of emery paper to encourage random orientation of the surface layers.

5. X-Ray the sample from 2° to 65° 2θ while the stage is set to rotate and oscillate. The oscillation subjects the sample to travel in an arc which, combined with the rotation, causes the particles in the sample to approach a random orientation. This helps to eliminate some of the orientation caused by the sample preparation. Set the diffractometer to integrate the area under the peaks. Store the pattern digitally for later printing.

6. Determine the reference intensity ratios (RIR) for each mineral in the reference standard by measuring the integrated area under the curve of the strongest peak of each mineral (I_i) and of the matrix flushing agent, corundum (I_c). If there is overlap in the peaks, use the next strongest peak of the mineral being measured. Average duplicate readings for each peak and compute the RIR (equation 17-1) for the strongest peak of each mineral.

$$RIR = \frac{I_i}{I_c} \qquad (17\text{-}1)$$

This value is the RIR used for the SQXRD computations.

List the RIR values on DDRP Form 400 (see Appendix D).

17.10.2 Preparation of Randomly Oriented Powder Mounts from the <2-mm Fraction of Soil Samples

1. Homogenize the sample by passing it through a Jones-type riffle-splitter seven times.

2. Take 6.0 g of the <2-mm soil sample and pulverize it to a particle size of <0.002 mm in two steps. First, use a ring and puck pulverizer of titanium carbide or equivalent to reduce the particle size to about 0.040 mm. Then transfer the sample to an automated mortar and pestle of agate or mullite. Add 20 mL of ethanol to the soil sample and grind for 12 minutes. Allow the sample to air dry.

3. Check the particle size of the first five routine samples of the first batch by sedimentation, as described in Section 17.10.1, step 2.

4. Weigh 4.0 g of the <2-mm soil which has been pulverized to <0.002 mm, and add 1.0 g of corundum. Mix well in a Wiggle Bug mixer for approximately 20 to 30 seconds. Because mixing will generate enough heat to alter some clay minerals, excessive time in the mixer should be avoided.

5. Prepare a randomly oriented powder mount from the mixed sample in the same manner as described in Section 17.10.1, step 4.

6. X-Ray the sample from 2° to 65° 2θ while the stage is set to rotate and oscillate. Set the diffractometer to integrate the area under the strongest peak of each mineral in the sample. Store the pattern digitally for later printing.

17.10.3 Separation of <0.002-mm Fraction from the <2-mm Fraction of Soil Samples

1. Place 10.0 g of the <2-mm soil into each of four 100-mL centrifuge tubes. To each tube, add 5 mL sodium metaphosphate solution, and bring the volume of the suspension to 50 mL with DDI water. Disaggregate the material by shaking overnight (>15 hours) on a reciprocating shaker. Then hold the centrifuge tubes in the ultrasonic bath for 5 minutes to assure dispersion of the clay-sized particles.

2. Centrifuge the suspension for 4 minutes, 30 seconds at 750 rpm on an International No. 2 centrifuge with a No. 240 head. The supernatant will contain the <0.002-mm fraction, and the sediment will contain the >0.002-mm fraction.

3. Into a large container labeled with the sample number and "<0.002-mm," decant the supernatant to a depth of 10.0 cm as measured from the surface of the supernatant.

4. Add 5 mL sodium hexametaphosphate solution and DDI water to replace the solution decanted after each centrifuging. Resuspend the sediments in each centrifuge tube by sonicating the sample in the ultrasound bath.

5. Repeat steps 2, 3, and 4 until 3.0 g of <0.002-mm material is available for analysis.

6. Remove the sodium hexametaphosphate and other dissolved salts by dialysis, centrifugation, and decantation or by successive centrifugation, decantation, and resuspension. The <0.002-mm material produced here will be used to make both oriented mounts and randomly oriented mounts.

a. Pour the <0.002-mm suspension into dialysis tubing. Dialyze against DDI water for 96 hours. Change the water in the dialysis bath every 12 hours over that time period. Resuspend the <0.002-mm material by holding the dialysis tubing in an ultrasound bath of DDI water for 15 minutes. Pour the suspension into 100-mL test tubes, centrifuge the samples, decant the supernatant, and transfer the sediment to a holding container.

b. Pour the <0.002-mm suspension into four 100-mL test tubes and centrifuge the samples until the supernatant is clear. Decant and discard the supernatant. Add DDI water to replace the supernatant removed. Resuspend the sediment by holding the centrifuge tubes in an ultrasound bath for 15 minutes. Again centrifuge the suspension until the supernatant is clear. Again decant and discard the supernatant. Repeat this procedure a third time, then transfer the sediment to a holding container. Continue processing until the entire suspended <0.002-mm fraction has been washed.

7. When a sample contains a large amount of organic material it may be necessary to remove this material to eliminate an aggregating effect. Use the following technique:

   a. Remove the organic material by using a 30% solution of H_2O_2. The soil-to-water ratio of the sample should be 1:1 and not more than 1:2. H_2O_2 is most efficient in oxidizing the organics in a medium when the pH is slightly acidic. Use litmus paper to test the acidity of the suspension, and add a few drops of a 1.0 N solution of sodium acetate to acidify the suspension if necessary. Add H_2O_2 to the suspension in increments of 5 mL or less, stir the suspension during and after each addition, and allow any effervescence to subside before continuing the additions. Placing the suspension in a cold bath will help control strong reactions. Continue adding the H_2O_2 in small quantities until no more reaction is observed.

   b. Transfer the beaker to a hot plate set at 50 °C. Do not exceed 50 °C because some clays such as halloysite are susceptible to crystalline dehydration at temperatures of 60 °C or higher. Allow the beaker and its contents to heat for 15 to 20 minutes until all reaction has stopped. Add enough H_2O_2 to give a 10% solution.

   c. Transfer the suspension to 150-mL centrifuge tubes, filling the tubes to distribute their weight evenly, and centrifuge the samples at 2200 rpm for 10 minutes. Decant and discard the supernatant liquid. If clay is still suspended, add 2 to 3 drops of 1 N $MgCl_2$, mix the supernatant liquid, recentrifuge and decant the supernatant liquor.

17.10.4 Preparation and Treatment of Oriented Slides from the <0.002-mm Fraction of Samples for Identification of Clay Minerals (modified from USDA/SCS, 1984)

1. Prepare two syringes by placing a small circle of 80-mesh screen at the bottom of each. Fill each syringe with 3 cm^3 of exchange resin. Charge the exchange resin in one syringe with Mg^{2+} by drawing 2 mL of 1.0 N $MgCl_2$ solution into the syringe. Charge the resin in the second syringe with K^+ by using a 1.0 N KCl by solution. Allow

the exchange resin in each syringe to equilibrate for 10 minutes. Expel the used solution from each syringe and allow the syringe to stand for 10 minutes. Wash the exchange resin in each syringe three times with 5 to 8 mL DDI water to flush out the excess salt solutions.

After treating each 10 samples, recharge the resin in the same manner.

2. For each soil sample, clean four 32-mm circular glass slides with ethanol. This ensures good sample adhesion to the glass slide. Also, label the slides with the appropriate batch and sample numbers.

3. Prepare a desiccator for storage of the air-dried slides.

4. Using the syringe containing the Mg^{2+}-charged resin, withdraw 1 mL of the <0.002-mm suspension obtained in Section 17.10.3., step 6. Onto two clean 32-mm circular glass slides, slowly expel enough of the suspension to cover each slide. Allow the slides to air dry at room temperature, i.e., 22 °C. Use one slide for analysis and archive the other slide. Record the sample number of each pair of slides and record the treatment as "Mg-sat. AD" in the laboratory notebook. Since the slides will be analyzed in successive order, maintain the samples in sequence. X-Ray each sample from 2° to 30° 2θ. Store the patterns digitally for later printing.

NOTE: Do not set the XRD sample stage to rotate or oscillate when analyzing oriented slides.

5. Heat a desiccator containing 2 to 3 cm of ethylene glycol in a convection oven at 70 °C. Place one Mg-sat. AD slide from step 4 in the preheated desiccator and allow the slide to equilibrate for 1 hour. Note the sample number and the treatment as "Mg sat.gly" in the laboratory notebook. X-Ray the slide from 2° to 30° 2θ immediately after removal from the desiccator. Store the patterns digitally for later printing.

6. Using the syringe containing the K^{+}-charged resin, withdraw 1 mL of the <0.002-mm suspension obtained in Section 17.10.3, step 6. Onto two clean 32-mm circular glass slides, slowly expel enough of the suspension to cover each slide. Allow the slides to air dry at room temperature, i.e., 22 °C. Use one slide for analysis and archive the other slide. Record the sample number of each pair of slides and record the treatment as "K-sat. AD" in the laboratory notebook. X-Ray each sample from 2° to 30° 2θ. Store the pattern for later printing.

7. Place the K-sat. AD slide from step 6 in a cold furnace, then ramp the temperature to 110 °C for 1 hour. Allow the furnace to cool to room temperature slowly. Place the slide in a desiccator over silica gel desiccant prior to analysis. Note the sample number and the treatment as "K-sat. 110 °C" in the laboratory notebook. X-Ray the slide from 2° to 30° 2θ. Store the pattern digitally for later printing.

8. Place the K-sat. 110 °C slide from step 7 in a cold furnace, then ramp the temperature to 350 °C for 1 hour. Allow the furnace to cool to room temperature slowly. Place the slide in a desiccator over silica gel desiccant prior to analysis. Note the sample number and the treatment as "K-sat. 350 °C" in the laboratory notebook. X-Ray the slide from 2° to 30° 2θ. Store the pattern digitally for later printing.

9. Place the K-sat. 350 °C slide from step 8 in a cold furnace, then ramp the temperature to 550 °C for 1 hour. Allow the furnace to cool to room temperature slowly. Place the slide

in a desiccator over silica gel desiccant prior to analysis. Note the sample number and the treatment as "K-sat. 550 °C" in the laboratory notebook. X-Ray from 2° to 30° 2θ. Store the pattern digitally for printing.

17.10.5 Preparation of Randomly Oriented Powder Mounts from the <0.002-mm Fraction of Soil Samples

1. Freeze-dry the remaining suspension of <0.002-mm material from Section 7.10.3, step 6. Weigh the freeze-dried material. If there is less than 3.0 g, repeat Section 17.10.3 until there is more than 3.0 g of freeze-dried material. Record the total sample weight on DDRP Form 401 (see Appendix D).

2. Weigh 2.0 g of the <0.002-mm fraction and add 0.4 g of corundum. Mix well in a Wiggle Bug mixer for approximately 20 to 30 seconds. Because mixing will generate enough heat to alter some clay minerals, excessive time in the mixer should be avoided.

3. Prepare a randomly oriented powder mount from the mixed sample as described in Section 17.10.1, step 4. X-ray the sample from 2° to 65° 2θ while the stage is set to rotate and oscillate. Set the diffractometer to integrate the area under each of the three strongest peaks of each mineral. Store the pattern digitally for later printing.

17.11 Calculations

17.11.1 Mineral Identification and Quantification

Table 17-1, compiled from Brown and Brindley (1980), provides general guidelines for interpreting the X-Ray diffraction patterns and the effect of the various treatments. The analyst can find more detailed descriptions of the principles of X-Ray diffraction in Klug and Alexander (1974), of the characteristics of clay minerals in Weaver (1973), and of the identification of clay minerals in Brindley and Brown (1980), Carroll (1970), Jackson (1969), and Hutchison (1974). The final interpretation, however, must rely on the analyst's experience.

Index the peaks in angstrom units (Å) using Bragg's Law:

$$n\lambda = 2\,d \sin \theta$$

where:

- n = whole integer, assumed = 1,
- λ = wavelength of Cu $K_{\alpha 1}$ radiation = 1.540500 Å
- d = interplanar atomic distances in the crystal lattice,
- θ = angle of X-ray incidence = angle of diffraction.

Use the entries from the Powder Diffraction Files (a data base of references distributed solely by the Joint Committee for Powder Diffraction Standards [JCPDS, 1985/86]) stored in the computer and the software pattern library (see Section 17.8) to make the initial and final identification of the minerals. Differentiate the dioctahedral and trioctahedral clay minerals. Store the identified mineral phase data for final printing on DDRP Form 401 (see Appendix D).

Calculate the percentages of each mineral in the two randomly oriented powder mounts Sections 17.10.2 and 17.10.5 by using the following equation (after Chung, 1974):

$$x_i = \left(\frac{x_c}{k_i}\right)\left(\frac{I_i}{I_c}\right) \qquad (17\text{-}2)$$

where:

- x_i = weight fraction of component i,
- k_i = reference intensity ratio (determined in Section 17.10.1), X_c = weight percent of corundum standard added (20 percent),

Table 17-1. Effect of Some Diagnostic Treatments on Spacing of First Low Angle Reflection of Clay Minerals (Compiled from Brown and Brindley, 1980)

Mineral	Treatment				Temperature at which Reflection Disappears[b]	Remarks
	Air-Dried[a]	Ethylene Glycol[a]	300-350 °C[a,b]	500-600 °C[b]		
Kaolinite	7	7	7	Disappears	500-550 °C	Occasionally weak broad band at 12-14 Å at 500-550 °C.
Dickite	7	7	7	Disappears	550-650 °C	Usually broad reflection C. 14 Å at 550-700 °C.
Halloysite-7 A	7	7	7	Disappears	450-520 °C	
Halloysite-10 A	11	10	7	Disappears	450-520 °C	Dehydrates, usually irreversibly to 7 Å form at 50-100 °C.
Serpentine	7	7	7	Disappears	575-700 °C	Broad reflection 11-14 Å region at 550-650 °C; forms olivine and enstatite at 650-700 °C.
Mica	10	10	10	10	800-1000 °C+	
Smectite, Mg, Ca	15	17	10	10	700-1000 °C	Trioctahedral varieties more stable in 700-1000 °C range.
Smectite, Na	12.5	17	10	10	700-1000 °C	Trioctahedral varieties more stable in 700-1000 °C range.
Vermiculite, Mg, Ca	14.5	14.5	10	10	700-100 °C	
Vermiculite, Na	12.5	14.5	10	10	700-1000 °C	
Chlorite (magnesian)	14	14	14	14	800 °C	14 Å intensity increased at 500-600 °C; forms olivine at about 800 °C.
Chlorite(iron-rich)	14	14	14	14	600 °C	14 Å intensity increased at 500-600 °C; forms olivine at about 600-700 °C.
Swelling Chlorite	14	16-17	14	14		
Palygorskite	10.5	10.5	10.5+9.2	9.2	700 °C	Marked increase in 10.5 Å intensity at 150 °C.
Sepiolite	12.2	12.2	12.2+10.4	10.4	700 °C	

[a] Values are approximate in angstroms (Å).
[b] Temperature at which thermal changes occur is affected by size of crystals and duration of heating; larger crystals require higher temperature and longer time for reaction.

I_i = intensity of X-rays diffracted by a selected plane (hkl) of component i expressed as area under the peak (Sections 17.10.2 or 17.10.5),

I_c = intensity of X-rays diffracted by a selected plane (hkl) of the corundum standard expressed as area under the peak (Sections 17.10.2 or 17.10.5).

Record the percentage of each identified mineral on DDRP Form 401.

17.12 Precision and Accuracy

Because this semiquantitative method is relatively new, the actual precision is unknown. It is dependent upon both instrument and sample and must be calculated from the data. The precision of this method is estimated to be within 10 percent relative for minerals with low crystallinity in concentrations ≥50 percent. For minerals with low crystallinity in concentrations less than 50 percent, the precision is estimated to be within 50 percent relative (personal communication, Dr. Mike Holland, Terra Tek Core Services, Salt Lake City, Utah). Precision is directly dependent upon crystallinity: the higher the crystallinity of the mineral, the greater the precision. Using highly crystalline minerals, Chung (1974) was able to attain a precision of <1.0 percent between experimental and known mineral contents.

The accuracy of XRD is based on a statistical comparison of the intensity of diffracted X-Rays to the background radiation intensity. According to Klug and Alexander (1974), uncertainty in the net peak height strongly affects the absolute standard deviation of the peak height to background ratio when the background counting rate is appreciable. When background is low, the net percent standard deviation in the area under the peak (corrected for background) is 2.24 percent. Chung (1974) attained an accuracy of 1.7 percent.

17.13 References

Blume, L. J., M. L., Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

Brindley, G. W., and G. Brown. 1980. *Crystal Structures of Clay Minerals and Their X-Ray Identification.* Monograph No. 5. Mineralogical Society, London, England.

Brown, G., and G. W. Brindley. 1980. *X-Ray Diffraction Procedures for Clay Mineral Identification.* In: Brindley, G. W., and G. Brown, 1980. *Crystal Structures of Clay Minerals and their X-Ray Identification.* Monograph No. 5. Mineralogical Society, London, England.

Carroll, D. 1970. *Clay Minerals: A Guide to Their Identification.* Special Paper 126. The Geological Society of America, Boulder, Colorado.

Chung, F. H. 1974. Quantitative Interpretation of X-Ray Diffraction Patterns of Mixtures. I. Matrix-Flushing Method for Quantitative Multicomponent Analysis. *J. Applied Crystallogr.* v. 7, pp. 519-525.

Hutchison, C. S. 1974. *Laboratory Handbook of Petrographic Techniques.* John Wiley and Sons, New York, New York.

Jackson, M. L. 1969. *Soil Chemical Analysis - Advanced Course*, 2nd Ed. Published by the author, Department of Soil Science, University of Wisconsin, Madison, Wisconsin.

Joint Committee for Powder Diffraction Standards. 1985/86. *Powder Diffraction Files.*

International Centre for Diffraction Data, Swarthmore, Pennsylvania.

Klug, H. P., and L. E. Alexander. 1974. *X-Ray Diffraction Procedures*. John Wiley and Sons, New York, New York.

Müller, G. 1967. *Methods in Sedimentary Petrology*. E. Schweizerbart'sche Verlagsbuchhandlung/Hafner, New York.

National Bureau of Standards. 1971. *Standard X-Ray Diffraction Powder Patterns*. Monograph 25. p. 3. U.S. Department of Commerce, Gaithersburg, Maryland.

United States Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples*. Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

Weaver, C. E. 1973. *The Chemistry of Clay Minerals*. Developments in Sedimentology 15. Elsevier Scientific, New York, New York.

18 Wavelength-Dispersive X-Ray Fluorescence Spectrometry

18.1 Scope and Application

This method determines the elemental composition of the minerals in the <2-mm size fraction. These data are used to refine the semiquantitative data from the X-ray powder diffraction analysis (see Section 17) for the percentage of minerals in each soil sample.

18.2 Summary of Method

Bulk soil samples are pressed into pellets and are analyzed by wavelength-dispersive X-ray fluorescence (XRF) spectrometry. Twenty-five fixed channels are fitted to an instrument like the Phillips PW 1600 XRF unit to provide simultaneous analysis of twenty-five elements.

18.3 Interferences

Background signals are predicted and subtracted by commercially available software packages. The background signal is obtained by analyzing standards of pure element oxides, salts, and mixtures of oxides and salts and by measuring the continuum for other elements not present in the standards. Thirty standards are analyzed, and the resulting background signals are averaged to arrive at at final background signal value. For each fixed channel, the background signal depends on the average atomic number of the sample; the elements in the sample range in atomic number from 10 to 25.

This interval accurately represents the range in atomic number expected in naturally occurring samples such as soils, rocks, and marine sediments. The measured background signals (B_{peak}) for the fixed channel are related to measurements of the scattered continuum (B_{cont}) obtained at one of several 2θ angles; where:

$$B_{peak} = k\ (B_{cont})$$

$$k = B_{peak}/B_{cont}$$

Plots of k versus B_{cont} permit calculation of k if B_{cont} is known. For routine sample measurements, B_{cont} is measured and the software calculates k for each fixed channel. The background is automatically subtracted since $B_{peak} = k\ B_{cont}$.

Spectral interferences are minimized through the inherently high resolution of the wavelength-dispersive XRF; however, some peak overlaps are observed. For each overlap situation, preparation of a series of standards containing a fixed concentration of analyte and a varying concentration of the interfering element are prepared in order to characterize the contribution of the interfering element to the measured analyte signal. The appropriate functional relationships are developed to permit software to predict and subtract the contribution of an interfering element to the measured analyte signal.

Interelement effects are resolved by means of commercially available software packages, e.g., the software package developed by Criss Software Inc. Criss's XRFIIF software is used to convert measured X-ray fluorescence line intensities to chemical composition. XRFIIF employs measured net intensities from standards to establish a set of theoretical and empirical coefficients that fit the concentration versus intensity relationships over the range of compositions represented by the standards.

18.4 Safety

Follow standard laboratory safety practices and wear a laboratory coat, gloves, and safety glasses when preparing and handling reagents. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling metal salts.

Follow the safety precautions of the manufacturer when operating instruments.

Personnel working with the X-ray diffractometer must wear individual radiation badges. Check radiation badges on a monthly basis to assess exposure. In addition, on a monthly basis, use a detector to check for radiation leaks from the instrument.

18.5 Apparatus and Equipment

- Simultaneous wavelength-dispersive X-ray fluorescence spectrometer, Philips PW 1600 or equivalent.
- Hydraulic press, capable of producing pressure of 5 tons per square inch.
- Pellet die.
- Analytical balance.
- Desiccator.

18.6 Reagents and Consumable Materials

- Calibration Standards--Certified standards for the calibration of the EDXRF unit:

SY-3	CCRMP (Canadian Certified Reference Materials Project)
MRS-1	CCRMP
MAG-1	USGS (U.S. Geological Survey)
NOD A-1	USGS
BCR-3	USGS
GSP-1	USGS
RGM-1	USGS
SDC-1	USGS
PCC-1	USGS
DTS-1	USGS
SRM 97a	NBS (National Bureau of Standards)
SRM 278	NBS
SRM 688	NBS
SRM 1649	NBS

- Microcellulose powder.
- Desiccant.

18.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. Once the mineralogical samples are aliquoted, the mineralogical samples do not need to be refrigerated. In the mineralogical laboratory, all samples are kept sealed when not being used.

All pelletized samples must be kept in a desiccator when not being analyzed.

18.8 Calibration and Standardization

Follow the instructions of the manufacturer for calibration of the instrument. Generally, a suite of at least 25 certified standard rock and sediment samples are analyzed by the XRF using the same measurement parameters as are used for actual samples. Blank signals are subtracted, and signals are corrected for spectral interferences as described in Section 18.3. The operational software is then used to establish data files which contain the calibration information required to convert the measured net intensities of actual samples to elemental concentrations. Calibration using Criss software requires inputting the known elemental concentrations for the standards and their measured net intensities. Criss software allows the measured intensities for the standards to be scaled in any appropriate manner as long as the scaling is consistently applied. To ensure that the calibration is not affected by differences in instrument response which are due to factors such as replacement of a detector, changing of a tank of detector gas, or long term drift, all net element signals of samples and standards are divided by the

corresponding net element signal of the monitor standard; therefore, the instrument is calibrated in terms of signal ratios. The monitor standard is measured several times during the analysis of each suite of samples, and the same monitor standard is used for all samples and standard runs.

18.9 Quality Control

The quality control calibration sample or monitor standard is composed of a mixture of standard reference materials to obtain a standard containing all analytes in approximately the mid-concentration range for samples under study. The following mixture is suggested:

SY-3	(CCRMP)	41.29%	7.2899 g
MAG-1	(USGS)	42.75%	7.5473 g
SRM 1649	(NBS)	1.34%	0.2360 g
NOD A-1	(USGS)	14.63%	2.5825 g
total		100.01%	17.6557 g

To determine the result for each analyte, signal ratios are calculated between the monitor standard and the calibration standards and between the monitor standard and each sample. This minimizes the effect of instrumental variability.

If the carousel does not accommodate a full batch of 26 samples, analyze half-batch lots, i.e., 13 samples. In addition, include the monitor standard and a blank. The monitor standard is measured several times during the analysis of each group of samples. The monitor standard is analyzed as an actual sample so that its measured concentration can be checked after each set of samples has been analyzed. The blank is a pellet made of microcellulose only. Perform a duplicate analysis on a separate portion of each thirteenth routine sample or on one sample from each analytical run.

18.10 Procedure

18.10.1 Sample Preparation

1. Homogenize the <2-mm soil sample pulverized in Section 17.10.2, step 2, by passing it through a Jones-type riffle-splitter seven times.

2. Weigh 0.5 g soil sample and 2.0 g microcellulose powder. Mix sample, then place it into the 32-mm diameter pellet die. Do not mix the sample with the microcellulose; the microcellulose forms a supporting substrate that is not exposed directly to the X-rays. Assemble die and place it on hydraulic press at 5 tons pressure per square inch to form the pellet. Store the pellets in a desiccator when the pellets are not undergoing analysis.

3. The instrument is completely automated; therefore, load the sample carousel and log the samples into the analysis program. Place samples so that the monitor samples bracket the actual samples.

18.10.2 Instrumental Requirements

The instrumental detection limit must be established for each element. The concentration at the detection limit C_L as defined by Birks (1969, p. 54) is used: the amount of analyte which gives a net line intensity equal to three times the square root of the background intensity for a specified counting time.

The optimum combination of operating conditions is shown in Table 18-1.

Table 18-1. Optimum Combination of Operational Conditions* (Philips Electronic Instruments, 1982)

Item	Parameter	
Exciting radiation	Rh	
Kilovolts	50	
Milliamperes	50	
Detector	-	gas flow proportional counters for atomic numbers 11 to 19
	-	sealed Xe counters for atomic numbers > 22
	-	sealed Kr detectors for Ti and Ca
Measurement time 120 seconds		

*Detector power supplies and pulse height analyzers are set according to the manufacturer's instructions.

18.11 Calculations

Raw data files are generated by the software that operates the XRF unit. Net intensity data files are generated, and final elemental concentrations are provided by XRFIIF software or equipment. All spectral data must be recorded and printed out to be included in the data package. Each sample printout must be labeled with the sample number, date of analysis, instrument detection limits, reference standard maximum intensity, concentration of element in percent or ppm, and concentration of oxide in percent or ppm.

18.12 Precision and Accuracy

Precision is defined (Jenkins et al., 1981) as the degree of mutual agreement between repeated individual measurements made on the same sample. The precision of a well-designed X-ray spectrometer is typically on the order of one-tenth of a percent (Jenkins, 1984).

Accuracy is defined (Jenkins et al., 1981) as the degree of agreement between a measurement made on a reference standard and the "true result" for an accepted reference standard. In quantitative terms, this corresponds to approximately 0.1 percent absolute (Jenkins, 1984).

18.13 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report. Vol. I: Field Sampling.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

Jenkins, R., R. W. Gould, and D. Gedcke. 1981. *Quantitative X-Ray Spectrometry.* Marcel-Dekker, New York, New York.

Jenkins, R. 1984. X-Ray Fluorescence Analysis. *Anal. Chem.,* v. 56, n 9, pp. 1099-1106.

Philips Electronic Instruments, Inc. 1982. *Operations Manual for Philips PW-1600 XRF.* Philips Electronic Instruments, Mahwah, New Jersey.

19 Scanning Electron Microscopy with Energy-Dispersive X-Ray Fluorescence Analysis

19.1 Scope and Application

Pictures obtained from scanning electron microscopy (SEM) will provide information about crystal morphology, such as form, habit, and possibly crystal system, the type of weathering, i.e., chemical or physical, and the degree of weathering. The quantitative energy dispersive X-ray fluorescence (EDXRF) analysis of individual mineral grains will provide microchemical compositions of the specific mineral grains analyzed.

19.2 Summary of Method

The heavy minerals and light minerals of the very fine sand fraction, i.e., 0.105- mm to 0.053-mm fraction, are separated gravimetrically by a heavy liquid separation using sodium polytungstate (density = 2.95). The clay-sized fraction is separated gravimetrically from the soil samples (see Section 17.10.3) and is freeze-dried (see Section 17.10.5). A three- to five- milligram aliquot of each fraction is mounted on doublesided tape for examination by SEM and analysis by EDXRF.

The SEM electron beam excites with known secondary energies (fluorescence) and produces measurable data that are directly dependent on elemental concentrations and that are mathematically convertable into elemental concentrations. Peak intensities are determined by one or more of three methods: (1) simple integration of the area under the peaks, (2) spectral peak-fitting to stored reference peaks, and (3) Gaussian deconvolution by means of a program such as one developed by the Kevex Corporation.

19.3 Interferences

Spectral interferences, interelemental interferences, and background corrections are automatically calculated by the Kevex Corporation or equivalent software.

19.4 Safety

Follow standard laboratory safety practices and wear a laboratory coat, gloves, and safety glasses when preparing and handling reagents. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling metal salts.

Follow the safety precautions of the manufacturer when operating instruments.

Personnel working with the X-ray diffractometer must wear individual radiation badges. Check radiation badges on a monthly basis to assess exposure. In addition, on a monthly basis, use a detector to check for radiation leaks from the instrument.

19.5 Apparatus and Equipment

- Scanning electron microscope (SEM), with 200- to 300-angstrom resolution in the secondary electron mode.
- Gold-palladium sputter-coater, with an argon diffusion chamber.
- Energy-dispersive X-ray fluorescence (EDXRF) analytical unit and software, Kevex or equivalent, which can interface with the SEM.
- Separatory funnel, 250 mL.
- Fritted funnel, 50 mL.
- Sieves, 60-mesh and 270-mesh.
- Polaroid camera.

19.6 Reagents and Consumable Materials

- Gold-palladium wire, metal for coating the specimen.
- Film, 35-mm or 4x5-inch format.
- Film, Polaroid type 55.
- Certified microprobe mineral and rock standards--available from Tousimis Company, Rockville, Maryland.
- Sodium polytungstate, density = 2.95, reagent grade.
- Filter paper, Whatman No. 1.
- Double-deionized water (DDI H_2O) or equivalent.
- Double-sided cellophane tape.
- Silver conducting paint.

19.7 Sample Collection, Preservation, and Storage

Sample collection is discussed in Blume et al. (1987). No preservatives are added to the samples. Within 24 hours of collection, samples are delivered to the preparation laboratory and are refrigerated at 4 °C. If this time requirement cannot be met, the samples are placed in a cooler after they are collected. Once the mineralogical samples are aliquoted, the mineralogical samples do not need to be refrigerated. In the mineralogical laboratory, all samples are kept sealed when not being used.

Each prepared sample must be kept in a desiccator when not undergoing analysis.

19.8 Calibration and Standardization

Follow the calibration procedure supplied by the instrument manufacturer.

Prior to sample analysis by EDXRF, use pure Al and Cu standards to check the peak-to- peak spacings and peak position of each channel. Store the spectra at the laboratory for audit purposes.

Build a library of reference spectra by collecting three spectra from each certified reference standard. Keep a copy of each spectrum for audit purposes.

Analyze the reference standard three times by EDXRF and compare the results against those from the previous EDXRF analysis. If the change in peak height is greater than 10 percent, recalibrate the instrument with the reference standards.

19.9 Quality Control

The SEM must be serviced within the month prior to the start of analysis. Retain a copy of the service report for audit purposes.

Perform a duplicate EDXRF analysis on a separate portion of every fifteenth sample. Each batch of 15 samples and the duplicate must be prepared by the same technician.

The detection limit is defined by operating conditions such as specimen/ beam/ detector geometry, excitation voltage, and acquisition time. The slope of the line relating X-ray intensity in counts to elemental concentration is expressed algebraically as follows:

$$Y = mX + b$$

The change in the Y axis is equal to the counts per second per percent elemental concentration (mX) added to the point at which the line intersects the Y axis (b). From this simple formula, the relationship that predicts the mean detection limit for an element within a specific specimen matrix is derived.

$$\text{Mean Detection Limit} = 3/m \sqrt{\frac{\text{background counts/second}}{\text{time}}}$$

where:

3 = standard deviations from background level (approximately equivalent to a one percent significance level);

m = counts per second per percent elemental concentration;

background counts per second = counts per second seen in the background under the peak representing the element;

time = seconds during which the data are acquired.

The factors in the equation include a sensitivity factor, i.e., 3/m, which addresses the statistical significance of the peak and the intensity vs. concentration relationship, and a background factor, i.e., the square root of the background intensity over time, which estimates the noise level or interference present in the analysis. The sensitivity factor gives the slope of the line relation (intensity and concentration); the background factor represents the intercept of the line and gives the detection limit for the element within the specific matrix. To be detected, an element must emit enough characteristic radiation to cause a peak that is statistically significant above background (from Alfred Soeldner, 1986, unpublished manuscript).

New film must be used. All film must be refrigerated when not in use. Allow the refrigerated film time to equilibrate to room temperature before use.

Daily, take two high resolution pictures at 30,000x magnification of the sample undergoing analysis, one picture at the beginning of the analyses and one at the end. These pictures are a record indicating that the resolution of the instrument has been maintained. Keep the pictures on file at the laboratory for audit purposes.

Collect two spectra per day from the same spot on a reference standard; the reference standard contains as many elements as possible. Collect one spectra at the beginning of the analyses and one at the end of the analyses. For each required element, include a verification printout of all the collected spectra for calibration. Record pertinent geometry and instrument settings daily on DDRP Form 403 (see Appendix D).

19.10 Procedure

1. Separate up to 5 g of the 0.105-mm to 0.053-mm fraction by wet sieving. Dry this fraction at 105 °C.

2. Transfer the dried 0.105-mm to 0.053-mm fraction to a 250-mL separatory funnel containing 200 mL sodium polytungstate (SPT) with a density of 2.95. The minerals separate gravimetrically according to their densities. Those minerals with densities <2.95 are referred to as "light minerals," and minerals with densities >2.95 are referred to as "heavy minerals." As the separation takes place, occasionally stir the light portion with a spatula to disperse air bubbles and to free some of the heavier minerals from possible aggregation.

3. After the separation is complete, open the stopcock of the separatory funnel and allow the heavy mineral portion to flow into a beaker. Pour the contents of this beaker (SPT + heavy minerals) into a fritted funnel lined with filter paper and seated on a vacuum flask. Turn on the vacuum, and filter the SPT through the heavy fraction. After the SPT has filtered through the minerals, move the funnel containing the heavy minerals to a second vacuum flask. Wash the heavy minerals with DDI H_2O until they are free of SPT. Tap the side of the fritted funnel. When the grains fall apart from one another, they are free of SPT.

NOTE: The SPT in the first flask is clean and reusable and has the original density.

4. Allow the light mineral portion still in the separatory funnel to flow into a

beaker. Pour the contents of this beaker into a fritted funnel lined with filter paper and seated on a vacuum flask. Vacuum filter the SPT from the solids, and wash the light mineral portion in the same manner as the heavy mineral portion. Transfer the heavy and light fractions to clean, preweighed containers labeled "Heavy Minerals" and "Light Minerals," respectively.

5. Prepare samples by placing 3 mg of the light mineral fraction on a slide covered with doubled-sided tape. Repeat this preparation for the heavy and the clay fractions. Use the clay fraction (<0.002 mm) produced by the procedure described in Section 17.10.3, step 6, and freeze-dried as described in Section 17.10.5.

6. Place the slide in the sputter-coater, seal the argon diffusion chamber, evacuate the chamber, bleed in argon, and coat the slide with gold-palladium. After the slide is coated, equalize the chamber, remove the slide, and check the coating for electrical continuity. If necessary, use silver conducting paint to complete the continuity. The slide is ready for analysis.

7. Place the slide on the stage of the SEM. Connect the ground wire to the slide. Use silver-conducting paint if the connection is weak. Seal the stage in the chamber and evacuate the chamber. Raise the stage to the proper height for coarse focus of the electron beam. Turn on the beam and adjust beam current for proper focus.

8. Conduct a survey scan of the sample at a magnification of 50x to 5,000x. During the scanning of the sample, have a second analyst record observations concerning areas photographed and particles analyzed by EDXRF. The analyst must record observations in a laboratory notebook or on a Dictaphone and must be experienced in geological specimen microanalysis and interpretation. Record this commentary on DDRP Form 404 (see Appendix D).

All photographs must include the magnification, a scale, and the name of the object photographed. After an EDXRF analysis is completed and the area of the specimen is photographed, the area analyzed must be labeled on the photograph. Record the data on DDRP Form 405 (see Appendix D). The EDXRF spectra must be attached to the form.

19.11 Calculations

The EDXRF software automatically counts and corrects for background, spectral, and interelemental interferences (see Bertin, 1978; Jenkins et al., 1981; Jenkins, 1984; Lakowicz, 1983; and Müller, 1972).

19.12 Precision and Accuracy

The precision of current X-ray spectrometers is typically on the order of 0.1 percent (Jenkins, 1984).

For this type of analysis, the accuracy is estimated at 10 percent (personal communication, Alfred Soeldner, Oregon State University).

19.13 References

Bertin, E. P. 1978. *Introduction to X-Ray Spectrometric Analysis.* Plenum Press, New York, New York.

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, and D. S. Coffey. 1987. *Soil Sampling Manual for the Direct/Delayed Response Project Soil Survey.* Appendix A In: *Direct/Delayed Response Project Southern Blue Ridge Province Field Sampling Report: Vol. I: Field Sampling.* U.S. Environmental Protection Agency, Las Vegas, Nevada.

Jenkins, R., R. W. Gould, and D. Gedcke. 1981. *Quantitative X-Ray Spectrometry.* Marcel-Dekker, New York, New York.

Jenkins, R. 1984. X-Ray Fluorescence Analysis. *Anal. Chem.*, v. 56, n. 9, pp. 1099-1106.

Lakowicz, J. R. 1983. *Principles of Fluorescence Spectroscopy.* Plenum Press, New York, New York.

Müller, R. O. 1972. *Spectrochemical Analysis by X-Ray Fluorescence.* Plenum Press, New York, New York.

Appendix A

Atomic Absorption Spectroscopy Methods

1 Scope and Application

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments, and other solid type samples may also be analyzed after proper pretreatment.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table A-1, however, provide some indication of the actual concentration ranges measurable by direct aspiration and by using furnace techniques. In the majority of instances, the concentration range shown in the table by direct aspiration may be extended much lower with scale expansion and conversely extended upwards 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 through solvent extraction techniques. Lower concentrations may also be determined using the furnace techniques, or both. The concentration ranges given in Table A-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 using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To insure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see 5.2.1) and if detected, must treat the matrix accordingly by using either successive dilution, matrix modification, or the method of standard additions (see 8.5).

1.3 Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, in addition to the furnace procedure, reference is made to specialized procedures such as the gaseous hydride method for arsenic and selenium, the cold vapor technique for mercury, and the chelation-extraction procedure for selected metals. Reference to approved colorimetric methods is also made.

1.4 Atomic absorption procedures are provided as the methods of choice; however, other instrumental methods have also been shown to be capable of producing precise and accurate analytical data. These instrumental techniques include emission spectroscopy, X-ray fluorescence, spark source mass spectroscopy, and anodic stripping to name but a few. The analyst should be cautioned that these methods are highly specialized techniques requiring a high degree of skill to interpret results and to obtain valid data. These above mentioned techniques are presently considered as alternate test procedures, and approval must be obtained prior to their use.

Table A-1. Atomic Absorption Concentration Ranges[a]

	Direct Aspiration			Furnace Procedure[b,c]	
Metal[d]	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
Antimony	0.2	0.5	1-40	3	20-300
Arsenic[e]	0.002	—	0.002-0.02	1	5-100
Barium(p)	0.1	0.4	1-20	2	10-200
Beryllium	0.005	0.025	0.05-2	0.2	1-30
Cadmium	0.005	0.025	0.05-2	0.1	0.5-10
Calcium	0.01	0.08	0.2-7	—	—
Chromium	0.05	0.25	0.5-10	1	5-100
Cobalt	0.05	0.2	0.5-5	1	5-100
Copper	0.02	0.1	0.2-5	1	5-100
Gold	0.1	0.25	0.5-20	1	5-100
Iridium(p)	3	8	20-500	30	100-1500
Iron	0.03	0.12	0.3-5	1	5-100
Lead	0.1	0.5	1-20	1	5-100
Magnesium	0.001	0.007	0.02-0.5	—	—
Manganese	0.01	0.05	0.1-3	0.2	1-30
Mercury[f]	0.0002	—	0.0002	0.01	—
Molybdenum(p)	0.1	0.4	1-40	1	3-60
Nickel(p)	0.04	0.15	0.3-5	1	5-50
Osmium	0.3	1	2-100	20	50-500
Palladium(p)	0.1	0.25	0.5-15	5	20-400
Platinum(p)	0.2	2	5-75	20	100-2000
Potassium	0.01	0.04	0.1-2	—	
Rhenium(p)	5	15	50-1000	200	500-5000
Rhodium(p)	0.05	0.3	1-30	5	20-400
Ruthenium	0.2	0.5	1-50	20	100-2000
Selenium[e]	0.002	—	0.002-0.02	2	5-100
Silver	0.01	0.06	0.1-4	0.2	1-25
Sodium	0.002	0.015	0.03-1	—	
Thallium	0.1	0.5	1-20	1	5-100
Tin	0.8	4	10-300	5	20-300
Titanium(p)	0.4	2	5-100	10	50-500
Vanadium(p)	0.2	0.8	2-100	4	10-200
Zinc	0.005	0.02	0.05-1	0.05	0.2-4

[a] The concentrations shown are not contrived values and should be 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.
[d] The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.
[e] Gaseous hydride method.
[f] Cold vapor technique.

2 Summary of Method

2.1 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.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (*Spectrochim Acta, 24B* 53, 1969), the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is necessitated, the process should include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined, and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection, and the filtrate should be acidified immediately.

2.2.3 The total sample may also be treated with acid without prior filtration to measure what may be termed "total recoverable" concentrations.

2.3 When using 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, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than 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 which causes 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.

3 Definition of Terms

3.1 Optimum Concentration Range--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 condition employed.

3.2 Sensitivity--The concentration in milligrams of metal per liter that produces an absorption of 1%.

3.3 Detection Limit--Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used, while the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above but close to blank absorbance measurement. The detection limit values listed in Table A-1 and on the individual analysis sheets are to be considered minimum working limits achievable with the procedures given in this manual. These values may differ from the optimum detection limit reported by the various instrument manufacturers.

3.4 Dissolved Metals--Those constituents (metals) which will pass through a 0.45 μ membrane filter.

3.5 Suspended Metals--Those constituents (metals) which are retained by a 0.45 μ membrane filter.

3.6 Total Metals--The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals determined in both the dissolved and suspended fractions.

3.7 Total Recoverable Metals--The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Section 4.1.4).

4 Sample Handling and Preservation

4.1 For the determination of trace metals, 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. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and by (b) depleting concentrations through absorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle whether borosilicate glass, polyethylene, polypropylene or Teflon should be thoroughly washed with detergent and tap water, should be rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and finally deionized distilled water in that order.

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product--NOCHROMIX--available from Godax Laboratories, 6 Varick St. New York, N.Y. 10013, may be used in place of chromic acid. (Chromic acid should not be used with plastic bottles.)

NOTE 2: If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure. Before collection of the sample, a decision must be made as to the type of data desired, i.e.,

dissolved, suspended, total or total recoverable. For container preference, maximum holding time, and sample preservation at time of collection, see Table 2 in the front part of this manual. Drinking water samples containing suspended and settleable material should be prepared by using the total recoverable metal procedure (section 4.1.4).

4.1.1 For the determination of dissolved constituents, the sample must be filtered through a 0.45 μ membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 mL of (1:1) acid per liter should be sufficient to preserve the sample (See Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and should be analyzed as soon as possible by using Method 218.4. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 3: If a precipitate is formed upon acidification, the filtrate should be digested by using 4.1.3. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 mL of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

4.1.2 For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45 μ membrane filter. When considerable suspended material is present, as little as 100 mL of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 mL Griffin beaker and add 3 mL conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. redistilled HNO_3. Cover and continue heating until the digestion is complete; generally complete digestion is indicated by a light colored residue. Evaporate to near dryness (DO NOT BAKE), add 5 mL distilled HCl (1:1), and warm the beaker gently to dissolve any soluble material. (If the sample is to be analyzed by the furnace procedure, 1 mL of 1:1 distilled HNO_3 per 100 mL dilution should be substituted for the distilled 1:1 HCl). Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended." (See Note 4.)

NOTE 4: Certain metals such as antimony, arsenic, gold, iridium, mercury, osmium, palladium, platinium, rhenium, rhodium, ruthenium, selenium, silver, thallium, tin, and titanium require modification of the digestion procedure, and the individual sheets for these metals should be consulted.

4.1.3 For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much

suspended material is present, as little as 50-100 mL of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.) Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 mL of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3 mL portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return the beaker to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating and add additional acid as necessary until the digestion is complete (generally indicated by a light colored residue or by no change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HCl (5 mL/100 mL of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. (If the sample is to be analyzed by the furnace procedure, substitute distilled HNO_3 for 1:1 HCl so that the final dilution contains 0.5% (v/v) HNO_3). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total." (See Note 4.)

4.1.4 To determine total recoverable metals, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 mL/L. At the time of analysis, a 100-mL aliquot of well mixed sample is transferred to a beaker or flask. Five mL of distilled HCl (1:1) is added, and the sample is heated on a steam bath or hot plate until the volume has been reduced to 15-20 mL; be certain that the samples do not boil. (If the sample is being prepared for furnace analysis, the same process should be followed except HCl should be omitted.) After this treatment the sample is filtered to remove silicates and other insoluble material that could clog the atomizer, and the volume is adjusted to 100 mL. The sample is then ready for analysis. Concentrations so determined shall be reported as "total." (See Notes 4, 5, and 6).

NOTE 5: The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy certain metal complexes if a colorimetric procedure is to be employed for the final determination. When this is suspect, the more vigorous digestion given in 4.1.3 of this appendix should be followed.

NOTE 6: For drinking water analyses by direct aspiration, the final volume may be reduced to effect up to a 10X concentration of the sample; provided that the total dissolved solids in the original sample do not exceed 500 mg/L, the determination is corrected for any non-specific absorbance, and there is not loss by precipitation.

5 Interferences

5.1 Direct Aspiration

5.1.1 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, calcium, and

barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.2 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.

5.1.3 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solids type samples should be extracted (see 5.1.1 and 9.2).

5.1.4 Ionization interferences occur where 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.

5.1.5 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 multielement lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

5.2 Flameless Atomization

5.2.1 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 those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or of chemical interference, use 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 multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference should be treated in one or more of the following ways.

a. The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b. The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses (*Atomic*

Absorption Newsletter Vol. 14, No. 5, p. 127, Sept.-Oct. 1975). The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

c. Analyze the sample by method of standard additions while noting the precautions and limitations of its use (see 8.5).

5.2.2 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. Nonspecific broad band absorption interference can also be compensated for with background correction.

5.2.3 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 analysis element.

5.2.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

5.2.5 From anion interference studies in the graphite furnace, it is generally accepted that nitrate is the preferred anion. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

5.2.6 Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced, and the sensitivity is increased with the use of pyrolytically-coated graphite.

5.2.7 Ionization interferences have to date not been reported with furnace techniques.

5.2.8 For comments on spectral interference, see Section 5.1.5.

5.2.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in section 6.9. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks both in analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

6 Apparatus

6.1 Atomic absorption spectrophotometer--Single or dual channel, singleor 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 stripchart recorder.

6.2 Burner--The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

6.3 Hollow cathode lamps--Single element lamps are to be preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available.

6.4 Graphite furnace--Any furnace device capable of reaching the specified temperatures is satisfactory.

6.5 Stripchart recorder--A recorder is strongly recommended for furnace work so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

6.6 Pipets--Microliter with disposable tips. Sizes can range from 5 to 100 microliters as required.

NOTE 7: Pipet tips, which are white in color, do not contain CdS, and have been found suitable for research work, are available from Ulster Scientific, Inc., 53 Main St., Highland, NY 12528 (914) 691-7500.

6.7 Pressure-reducing valves--The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.8 Separatory flasks--250 mL, or larger, for extraction with organic solvents.

6.9 Glassware--All glassware, linear polyethylene, polypropylene or Teflon containers, including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and, deionized distilled water in that order. [See Notes 1 and 2 under (4.1) concerning the use of chromic acid and the cleaning procedure.]

6.10 Borosilicate glass distillation apparatus.

7 Reagents

7.1 Deionized distilled water--Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc.)--If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus or use a spectrograde acid.

CAUTION: Distillation should be performed in hood with protective sash in place.

7.2.1 Nitric Acid (1:1)--Prepare a 1:1 dilution with deionized, distilled water by adding the conc. acid to an equal volume of water.

7.3 Hydrochloric acid (1:1)--Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus or use a spectrograde acid.

7.4 Stock standard metal solutions--Prepare as directed in 8.1 and under the individual metal procedures. Commercially available stock standard solutions may also be used.

7.5 Calibration standards--Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 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.

7.7 Special reagents for the extraction procedure.

7.7.1 Pyrrolidine dithiocarbamic acid (PDCA)--[The name pyrrolidine dithiocarbamic acid (PDCA), although commonly referenced in the scientific literature, is ambiguous. From the chemical reaction of pyrrolidine and carbon disulfide a more proper name would be 1-pyrrolidine.] Prepare by adding 18 mL of analytical reagent grade pyrrolidine to 500 mL of chloroform in a liter flask. (See Note 8.) Cool and add 15 mL of carbon disulfide in small portions and with swirling. Dilute to 1 liter with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

NOTE 8: An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI 53233, (414) 273-3850.

7.7.2 Ammonium hydroxide, 2N--Dilute 13 mL conc. NH_4OH to 100 mL with deionized distilled water.

7.7.3 Bromophenol blue indicator (1 g/liter)--Dissolve 0.1g bromophenol blue in 100 mL of 50 percent ethanol or isopropanol.

7.7.4 HCl, 2.5% v/v--Dilute 2 mL redistilled HCl (6N) to 40 mL with deionized distilled water.

8 Preparation of Standards and Calibration

8.1 Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic spectroscopic grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used.

8.2 Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and should be discarded after use. Prepare a blank and at least four calibration standards in graduated amounts in the appropriate range. The *calibration standards* should be prepared by using the same type of acid or combination of acids and at the same concentration as will result in the samples after following processing. As filtered water samples are carbodithioic acid, PCDA (CAS Registry No. 25769-03-3) preserved

with 1:1 redistilled HNO_3 (3 mL per liter), calibration standards for these analyses should be similarly prepared with HNO_3. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

8.3 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample--the absorbance difference between those and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in 8.5.

8.4 For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and to plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log (100/\%T) = 2 - \log \% T$$

$$\text{where: } \% T = 100 - \% \text{ absorption}$$

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

8.5 *Method of Standard Additions*--In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and of the standards 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 back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left side 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 8-1, earlier in this manual. The method of standard additions can be very useful; however, for the results to be valid the following limitations must be taken into consideration:

a. 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%), caution should be exercised.

b. 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.

c. The determination must be free of spectral interference and corrected for non-specific background interference.

9 General Procedure for Analysis by Atomic Absorption

9.1 *Direct Aspiration:* Differences between 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 provided by the manufacturer for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the 'amp 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 of the manufacturer. Subsequently, light the flame and 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 construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration, set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples are run.

9.1.1 Calculation--Direct determination of liquid samples: Read the metal value in mg/L from the calibration curve or directly from the readout system of the instrument.

9.1.1.1 If dilution of sample was required:

$$\text{mg/L metal in sample} = A \left(\frac{C+B}{C} \right)$$

where:

A = mg/L of metal in diluted aliquot from calibration curve
B = mL of deionized distilled water used for dilution
C = mL of sample aliquot

9.1.2 For samples containing particulates:

$$\text{mg/L metal in sample} = A \left(\frac{V}{C} \right)$$

where:

A = mg/L of metal in processed sample from calibration curve
V = final volume of the processed sample in mL
C = mL of sample aliquot processed

9.1.3 For solid sample: report all concentrations as mg/kg dry weight.

9.1.3.1 Dry sample

$$\text{mg metal/kg sample} = \left(\frac{(A)(V)}{D} \right)$$

where:

A = mg/L of metal in processed sample from calibration curve
V = final volume of the processed sample in mL
D = weight of dry sample in grams

9.1.3.2 Wet sample

$$\text{mg metal/kg sample} = \left(\frac{(A)(V)}{(W)(P)}\right)$$

where:

A = mg/L of metal in processed sample from calibration curve
V = final volume of the processed sample in mL
W= weight of wet sample in grams
P = % solids

9.2 *Special Extraction Procedure:* When the concentration of the metal is not sufficiently high to determine directly or when considerable dissolved solids are present in the sample, certain metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) [The name ammonium pyrrolidine dithiocarbamate (APDC) is somewhat ambiguous and should more properly be called ammonium 1-pyrrolidine carbodithioate (APCD), CAS Registry No. 5108-96-3] in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead, and chromium^{+6}. Trivalent chromium does not react with APDC unless it has first been converted to the hexavalent form *(Atomic Absorption Newsletter* 6, p. 128, 1967). This procedure is described under Method 218.3. Aluminum, beryllium, barium, and strontium also do not react with APDC. While the APDCMIBK chelating-solvent system can be used satisfactorily, it is possible to experience difficulties. (See Note 9.)

NOTE 9: Certain metal chelates, manganese-APDC in particular, are not stable in MIBK and will redissolve into the aqueous phase on standing. The extraction of other metals is sensitive to both shaking rate and time. As with cadmium, prolonged extraction beyond 1 minute will reduce the extraction efficiency, whereas 3 minutes of vigorous shaking is required for chromium. Also, when multiple metals are to be determined, either larger sample volumes must be extracted or individual extractions must be made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen [*(Atomic Absorption Newsletter* 5, p. 17 (1966)] (see 7.7.1) has been found to be most advantageous. In this procedure the more dense chloroform layer allows for easy combination of multiple extractions which are carried out over a broader pH range favorable to multielement extractions. Pyrrolidine dithiocarbamic acid in chloroform is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The following procedure is suggested.

9.2.1 Extraction Procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

9.2.1.1 Transfer 200 mL of sample into a 250 mL separatory funnel, add 2 drops bromophenol blue indicator solution (7.7.3), and mix.

9.2.1.2 Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 mL with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

9.2.1.3 Adjust the pH by addition of 2N NH_4OH solution (7.7.2) until a blue color persists. Add HCl (7.7.4) dropwise until the blue color just disappears; then add 2.0 mL HCl (7.7.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of by using indicator.)

9.2.1.4 Add 5 mL of PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 mL beaker. (See NOTE 10.)

NOTE 10: If hexavalent chromium is to be extracted, the aqueous phase must be readjusted back to a pH of 2.3 after the addition of PDCA-chloroform and must be maintained at that pH throughout the extraction. For multielement extraction, the pH may be adjusted upward after the chromium has been extracted.

9.2.1.5 Add a second portion of 5 mL PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate. Drain the chloroform phase and combine with that obtained in step (9.2.1.4).

9.2.1.6 Determine the pH of the aqueous phase and adjust to 4.5.

9.2.1.7 Repeat step (9.2.1.4) again combining the solvent extracts.

9.2.1.8 Readjust the pH to 5.5, and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.

9.2.1.9 Hold the beaker at a 45 degree angle and slowly add 2 mL of conc. distilled nitric acid while rotating the beaker to effect thorough contact of the acid with the residue.

9.2.1.10 Place the beaker on a low temperature hotplate or steam bath and evaporate just to dryness.

9.2.1.11 Add 2 mL of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 mL volumetric flask, and bring to volume with distilled water. The sample is now ready for analysis.

9.2.2 Prepare a calibration curve by plotting absorbance versus the concentration of the metal standard (µg/L) in the 200 mL extracted standard solution. To calculate sample concentration, read the metal value in µg/L from the calibration curve or directly from the readout system of the instrument. If dilution of the sample was required, use the following equation:

$$\mu g/L \text{ metal in sample} = Z\left(\frac{C+B}{C}\right)$$

where:

Z = µg/L of metal in diluted aliquot from calibration curve
B = mL of deionized distilled water used for dilution
C = mL of sample aliquot

9.3 *Furnace Procedure:* Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between 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 on the individual analysis sheets which are recommended for the Perkin-Elmer HGA-2100. In addition, the following points may be helpful.

9.3.1 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. It can be caused by the presence of gaseous molecular species, salt particules, 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.

9.3.2 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 as needed at regular intervals in the analytical scheme.

9.3.3 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 using lower atomization temperatures for shorter time periods than those listed in this manual.

9.3.4 Although prior digestion of the sample in many cases is not required when a representative aliquot of sample can be pipeted into the furnace, it will provide for a more uniform matrix and possibly will lessen matrix effects.

9.3.5 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 reanalyzed. The use of multiple injections can improve accuracy and can help detect furnace pipetting errors.

9.3.6 To verify the absence of interference, follow the procedure as given in 5.2.1.

9.3.7 A check standard should be run approximately after every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating would extend that estimate by a factor of 3.

9.3.8 Calculation--For determination of metal concentration by the furnace: Read the metal value in µg/L from the calibration curve or directly from the readout system of the instrument.

9.3.8.1 If different size furnace injection volumes are used for samples than for standards:

$$\mu g/L \text{ of metal in sample} = Z \left(\frac{S}{U}\right)$$

where:

Z = µg/L of metal read from calibration curve or readout system
S = µL volume standard injected into furnace for calibration curve
U = µL volume of sample injected for analysis

9.3.8.2 If dilution of sample was required and if sample injection volume is the same as for the standard:

$$\mu g/L \text{ of metal in sample} = Z \left(\frac{C+B}{C}\right)$$

where:

Z = µg/L metal in diluted aliquot from calibration curve
B = mL of deionized distilled water used for dilution
C = mL of sample aliquot

9.3.9 For sample containing particulates:

$$\mu g/L \text{ of metal in sample} = Z \left(\frac{V}{C}\right)$$

where:

Z = µg/L of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in mL
C = mL of sample aliquot processed

9.3.10 For solid samples: Report all concentration as mg/kg dry weight.

9.3.10.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{(Z)(V)}{(1000)(D)}$$

where:

Z = µg/L of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in mL
D = weight of dry sample in grams

9.3.10.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{(Z)(V)}{(W)(P)(1000)}$$

where:

Z = µg/L of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in mL
W= weight of dry sample in grams
P = % solids

10 Quality Control For Drinking Water Analysis

10.1 Minimum requirements

10.1.1 All quality control data should be maintained and should be available for easy reference or inspection.

10.1.2 An unknown performance sample (when available) must be analyzed once per year for the metals measured. Results must be within the control limit established by EPA. If problems arise, they should be corrected, and a follow-up performance sample should be analyzed.

10.2 Minimum Daily Control

10.2.1 After a calibration curve composed of a minimum of a reagent blank and three standards has been prepared, subsequent calibration curves must be verified by use of at least a reagent blank and one standard at or near the MDL. Daily checks must be within ±10 percent of original curve.

10.2.2 If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the MDL every 20 samples. Checks must be within ±10 percent of original curve.

10.3 Optional Requirements

10.3.1 A current service contract should be in effect on balances and on the atomic absorption spectrophotometer.

10.3.2 Class S weights should be available to make periodic checks on balances.

10.3.3 Chemicals should be dated upon receipt of shipment and replaced as needed or before shelf life has been exceeded.

10.3.4 A known reference sample (when available) should be analyzed once per quarter for the metals measured. The measured value should be within the control limits.

10.3.5 At least one duplicate sample should be run every 10 samples or with each set of samples to verify precision of the method. Checks should be within the control limits established by EPA.

10.3.6 Standard deviation should be obtained and documented for all measurements being conducted.

10.3.7 Quality control charts or a tabulation of mean and standard deviation should be used to document validity of data on a daily basis.

Appendix B

Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

1 Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps *must* be taken to correct for potential interference effects. (See 5.)

1.4 Table B-1 lists elements for which this method applies along with recommended wavelengths for sequential instruments and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various 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.

2 Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized, and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra 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 and are controlled by a computer system. 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 on samples during 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 posititon used must be free of spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional

Table B-1. Recommended Wavelengths[a] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, µg/L [b]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see[c]
Selenium	196.026	75
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a] The wavelengths listed are recommended for sequential instruments because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and if they are treated with the same corrective techniques for spectral interference. (See 5.1.1.)
[b] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. 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.
[c] Highly dependent on operating conditions and plasma position.

interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized, and appropriate corrections should be made.

3 Definitions

3.1 *Dissolved*--Those elements which will pass through a 0.45 µm membrane filter.

3.2 *Suspended*--Those elements which are retained by a 0.45 µm membrane filter.

3.3 *Total*--The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations (Section 9.1 plus 9.2).

3.4 *Total recoverable*--The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*--The concentration equivalent to a signal due to the analyte and which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*--The slope of the analytical curve, i.e., functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*--A multielement standard of known concentrations prepared by the analyst to monitor and to verify instrument performance on a daily basis. (See Section 7.6.1.)

3.8 *Interference check sample*--A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See Section 7.6.2.)

3.9 *Quality control sample*--A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See Section 7.6.3.)

3.10 *Calibration standards*--A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See Section 7.4.)

3.11 *Linear dynamic range*--The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*--A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See Section 7.5.2.)

3.13 *Calibration blank*--A volume of deionized, distilled water acidified with HNO_3 and HCl. (See Section 7.5.1.)

3.14 *Method of standard addition*--The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See Section 10.6.1.)

4 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, 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 (14.7, 14.8, and 14.9) for the information of the analyst.

5 Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 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 requiring 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 multielement 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 B-2 are some interference effects for the recommended wavelengths given in Table B-1. The data in Table B-2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory [Ames Laboratory, USDOE, Iowa State University, Ames, Iowa 50011], is expressed as analyte concentration eqivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table B-2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table B-2 and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated, and the blank spaces in Table B-2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table B-3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table B-3.

At present, information on the listed silver and potassium wavelengths are not available, but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids or acid concentrations, or both. 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. Another problem which can occur from high dissolved solids is 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. Also, 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.

5.1.3 Chemical Interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique; however, if observed, they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and

Table B-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	Y
Aluminum	308.215	—	—	—	—	—	—	0.21	—	—	1.4
Antimony	206.833	0.47	—	2.9	—	0.08	—	—	—	.25	0.45
Arsenic	193.696	1.3	—	0.44	—	—	—	—	—	—	1.1
Barium	455.403	—	—	—	—	—	—	—	—	—	—
Beryllium	313.042	—	—	—	—	—	—	—	—	0.04	0.05
Boron	249.773	0.04	—	—	—	0.32	—	—	—	—	—
Cadmium	226.502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317.933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267.716	—	—	—	—	0.003	—	0.04	—	—	0.04
Cobalt	228.616	—	—	0.03	—	0.005	—	—	0.03	0.15	—
Copper	324.754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259.940	—	—	—	—	—	—	0.12	—	—	—
Lead	220.353	0.17	—	—	—	—	—	—	—	—	—
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	—	—	—	—
Molybdenum	202.030	0.05	—	—	—	0.03	—	—	—	—	—
Nickel	231.604	—	—	—	—	—	—	—	—	—	—
Selenium	196.026	0.23	—	—	—	0.09	—	—	—	—	—
Silicon	288.158	—	—	0.07	—	—	—	—	—	—	0.01
Sodium	588.995	—	—	—	—	—	—	—	—	0.08	—
Thallium	190.864	0.30	—	—	—	—	—	—	—	—	—
Vanadium	292.402	—	—	0.05	—	0.005	—	—	—	0.02	—
Zinc	213.856	—	—	—	0.14	—	—	—	0.29	—	—

Table B-3. Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table B-2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Nn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

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 the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference which would distort effects the accuracy of the reported values are operative on any of the analyte elements.

5.2.1 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 (14.3) that has been established for that matrix]. If not, a chemical or physical interference effect should be suspected.

5.2.2 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 suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See Section 5.2.3).

5.2.3 Comparison with alternate method of analysis--When investigating a new sample matrix, a comparison test may be performed with other analytical techniques such as atomic absorption spectrometry or other approved methodology.

5.2.4 Wavelength scanning of analyte line region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6 Apparatus

6.1 Inductively Coupled Plasma Atomic Emission Spectrometer.

6.1.1 Computer-controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply, welding grade or better.

6.2 Operating conditions--Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7 Reagents and Standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity spectroscopic grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid, conc. (sp gr 1.06).

7.1.2 Hydrochloric acid, conc. (sp gr 1.19).

7.1.3 Hydrochloric acid, (1+1)--Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

7.1.4 Nitric acid, conc. (sp gr 1.41).

7.1.5 Nitric acid, (1+1)--Add 500 mL conc. HNO3 (sp. gr 1.41) to 400 mL deionized distilled water and dilute to 1 liter.

7.2 Deionized, distilled water--Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards, and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105 °C unless otherwise specified.

CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow:

7.3.1 Aluminum solution, stock, 1 mL = 100 µg Al--Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a 1 liter volumetric flask, add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.2 Antimony solution stock, 1 mL = 100 µg Sb--Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.3 Arsenic solution, stock, 1 mL = 100 µg As--Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.4 Barium solution, stock, 1 mL = 100 µg Ba--Dissolve 0.1516 g $BaCl_2$ (dried at 250° for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.5 Beryllium solution, stock, 1 mL = 100 µg Be--*Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ in deionized, distilled water, add 10.0 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.6 Boron solution, stock, 1 mL = 100 µg B--*Do not dry.* Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 Cadmium solution, stock, 1 mL = 100 µg Cd--Dissolve 0.1142 g CdO in a minimum amount of(1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.8 Calcium solution, stock, 1 mL = 100 µg Ca--Suspend 0.2498 g $CaCO_3$, dried at 180 °C for 1 h before weighing, in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.9 Chromium solution, stock, 1 mL = 100 µg Cr--Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.10 Cobalt solution, stock, 1 mL = 100 µg Co--Dissolve 0.1000 g of colbalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.11 Copper solution, stock, 1 mL = 100 µg Cu--Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.12 Iron solution, stock, 1 mL = 100 µg Fe--Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.13 Lead solution, stock, 1 mL = 100 µg Pb--Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.14 Magnesium solution, stock, 1 mL = 100 µg Mg--Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.15 Manganese solution, stock, 1 mL = 100 µg Mo--Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.16 Molybdenum solution, stock, 1 mL = 100 µg Mo--Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 Nickel solution, stock, 1 mL = 100 µg Ni--Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool, and dilute to 1,000 mL with deionized, distilled water.

7.3.18 Potassium solution, stock, 1 mL = 100 µg K--Dissolve 0.1907 g KCl, dried at 110 °C, in deionized, distilled water and dilute to 1,000 mL.

7.3.19 Selenium solution, stock, 1 mL = 100 µg Se--*Do not dry.* Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

7.3.20 Silica solution, stock, 1 mL = 100 µg SiO_2--*Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.21 Silver solution, stock, 1 mL = 100 µg Ag--Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

7.3.22 Sodium solution, stock, 1 mL = 100 µg Na--Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.23 Thallium solution, stock, 1 mL = 100 µg Tl--Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.24 Vanadium solution, stock, 1 mL = 100 µg V--Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.25 Zinc solution, stock, 1 mL = 100 µg Zn--Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.4 Mixed calibration standard solutions--Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See Sections 7.4.1 thru 7.4.5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified by using a quality control sample and must be monitored weekly for stability (see Section 7.6.3). Although not specifically required, some typical calibration standard combinations follow which use those specific wavelengths listed in Table B-1.

7.4.1 Mixed standard solution I--Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 Mixed standard solution II--Barium, copper, iron, vanadium, and colbalt.

7.4.3 Mixed standard solution III--Molybdenum, silica, arsenic, and selenium.

7.4.4 Mixed standard solution IV--Calcium, sodium, potassium, aluminum, chromium, and nickel.

7.4.5 Mixed standard solution V--Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and must contain the same acid concentration in the final solution as in the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8), and a quality control sample (3.9) are also required for the analyses.

7.6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See Section 12.1.1.)

7.6.2 The interference check sample is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest but a known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/L or 5 times the estimated detection limits given in Table B-1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See Section 12.1.2.)

7.6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See Section 12.1.3.)

8 Sample Handling and Preservation

8.1 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 measure ment 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. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample, a decision must be made as to the type of data desired, i.e., is dissolved, suspended, or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements, the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve sample.

8.2.2 For the determination of suspended elements, a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

9 Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid or by heat (as described in 9.3), or both.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL concentrated HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of concentrated HNO_3. Cover and continue heating until the digestion is complete; digestion

is generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution, and warm the beaker gently for 15 minutes to dissolve any precipitate or residue. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water, and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

NOTE 4: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured volume of the well-mixed, acid-preserved sample appropriate for the expected level of elements and transfer it to a Griffin beaker. (See Note 5.) Add 3 mL of concentrated HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of concentrated HNO_3. Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of (1+1) HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool; wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

NOTE 5: If low determinations of boron are critical, quartz glassware should be used.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in 9.4 but does not introduce a physical interference or affect the analytical result the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well-mixed, acid-preserved sample appropriate for the expected level of elements and transfer it to a Griffin beaker. (See Note 5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

10 Procedure

10.1 Set up instrument with proper operating parameters as established in Section 6.2. The instrument must be allowed to become thermally stable before analysis begins. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to recommended procedures of the manufacturer, using the typical mixed calibration standard solutions described in Section 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 µg/L, extended flush times of 1 to 2 minutes may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run, flushing the system with the calibration blank solution (7.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) after each 10 samples.

10.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal and thus produces a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_b V^s C_s}{(S_a - S_b)\, V_x}$$

Where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x. If a concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

11 Calculation

11.1 Reagent blanks (7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place, and all results should be reported in mg/L up to three significant figures.

12 Quality Control (Instrument)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

12.1.1 Analyze an appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ±5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated. Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of 2 standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem, and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors, analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem, and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor the instrument stability. If the results are not within ±5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

13 Precision and Accuracy

13.1 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 B-4 lists the true value, the mean reported value, and the mean % relative standard deviation.

Table B-4. ICP Precision and Accuracy Data

Element	Sample 1 True Value µg/L	Sample 1 Mean Reported Value µg/L	Sample 1 Mean Percent RSD	Sample 2 True Value µg/L	Sample 2 Mean Reported Value µg/L	Sample 2 Mean Percent RSD	Sample 3 True Value µg/L	Sample 3 Mean Reported Value µg/L	Sample 3 Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

14 References

14.1 Winge, R.K., V.J. Peterson, and V.A. Fassel, *Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines*, EPA/600/479-017.

14.2 Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements," *Chemical Analysis* Vol. 46 pp. 41-42.

14.3 *Handbook for Analytical Quality Control in Water and Wastewater Laboratories*, EPA/600/4-79-019.

14.4 Garbarino, J.R., and Taylor, H.E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," *Applied Spectroscopy* 33 No. 3(1979).

14.5 *Methods for Chemical Analysis of Water and Wastes*," EPA/600/4-79-020.

14.6 *Annual Book of ASTM Standards*, Part 31.

14.7 *Carcinogens - Working With Carcinogens*, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

14.8 OSHA Safety and Health Standards, General Industry, *(29 CFR 1910)*, Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

14.9 *Safety in Academic Chemistry Laboratories*, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

Appendix C

Forms for Reporting Analytical Laboratory Data

The following forms are used for recording raw data and results form the analytical procedures detailed in Section 3 through 16.

An index of data forms is presented as Table 2-5. Form 102 is a shipping form that is used to confirm sample shipment and receipt. Forms 103a and 103b summarize pH, moisture, and particle size analysis results. Forms 109 through 114 contain quality control data. The 200-series forms summarize data that are corrected for both blanks and dilutions. Raw data are recorded on forms 115, 116, 303b, 306, and 308.

NATIONAL ACID DEPOSITION SOIL SURVEY (NADSS)
SHIPPING FORM 102

DATE RECEIVED
BY DATA MGT. D D M M M Y Y

Prep Lab ID _____ Date Received D D M M M Y Y
Batch ID _____ Date Shipped
Analytical Lab ID _____

Sample Number	Sample (Identify By Check) Shipped	Received	Soil Type (Identify By Check) Organic	Mineral	Inorganic Carbon Y - Yes N - No	Rock Fragments Shipped Check if Yes
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

Signature of Preparation Laboratory Manager: _____
Comments:

White - SMO Canary - Analytical with copy to SMO Pink - Analytical with copy to EMSL-LV Gold - Analytical Lab

SUMMARY OF pH AND MOISTURE DATA
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 103a

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Sample Number	pH in H_2O	pH in 0.01M $CaCl_2$	pH in 0.002M $CaCl_2$	Moisture, Weight %
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				
31				
32				
33				
34				
35				
36				
37				
38				
39				
40				
41				
42				

PARTICLE SIZE ANALYSIS DATA
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 103b

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Particle Size Analysis, Weight %

Size Class and Particle Diameter (mm)

				Sand					Silt	
Sample Number	Sand (2.0-0.05)	Silt (0.05-0.002)	Clay (<0.002)	Very Coarse (2.0-1.0)	Coarse (1.0-0.5)	Medium (0.5-0.25)	Fine (0.25-0.1)	Very Fine (0.1-0.05)	Coarse (0.05-0.02)	Fine (0.02-0.002)
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										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										
42										

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 109a

QUALITY CONTROL: DETECTION LIMITS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Reporting Units	Contract-Required Detection Limit	Instrumental Detection Limit	Date Determined (DD MMM YY)
Total S	wt. %	0.010%		
Total N	wt. %	0.010%		
Total C	wt. %	0.010%		
Inorganic C	wt. %	0.010%		
CEC (FIA)	meq/100 g	0.140 mg N/L		
CEC (titration)	meq/100 g	0.010 meq NH_4^+*		
Exchangeable Acidity:				
$BaCl_2$-TEA	meq/100 g	0.40 meq*		
KCl	meq/100 g	0.25 meq*		
KCl-Al^{3+}	meq/100 g	0.10 mg/L		

*For titrations, the instrumental detection limit is a calculated value based upon a minimum titration.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 109b
QUALITY CONTROL: DETECTION LIMITS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Calculated Reporting Units	Contract-Required Instrumental Detection Limit	Instrumental Detection Limit	Date Determined (DD MMM YY)
NH_4OAc Extract:				
Ca^{2+}	meq/100 g	0.050 mg/L		
Mg^{2+}	meq/100 g	0.020 mg/L		
K^+	meq/100 g	0.020 mg/L		
Na^+	meq/100 g	0.020 mg/L		
NH_4Cl Extract:				
Ca^{2+}	meq/100 g	0.050 mg/L		
Mg^{2+}	meq/100 g	0.020 mg/L		
K^+	meq/100 g	0.020 mg/L		
Na^+	meq/100 g	0.020 mg/L		
0.002 M $CaCl_2$ Extract:				
Ca^{2+}	meq/100 g	---*		
Mg^{2+}	meq/100 g	0.020 mg/L		
K^+	meq/100 g	0.020 mg/L		
Na^+	meq/100 g	0.020 mg/L		
Fe^{3+}	meq/100 g	0.050 mg/L		
Al^{3+}	meq/100 g	0.050 mg/L		

*Report the standard deviation of 10 non-consecutive blank analyses.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 109c

QUALITY CONTROL: DETECTION LIMITS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Calculated Reporting Units	Contract-Required Instrumental Detection Limit	Instrumental Detection Limit	Date Determined (DD MMM YY)
SO_4^{2-} Adsorption	mg S/L	0.10 mg SO_4^{2-}/L		
SO_4^{2-} (H_2O extract)	mg S/Kg	0.1 mg SO_4^{2-}/L		
NO_3^- (H_2O extract)	mg N/Kg	0.10 mg NO_3^-/L		
SO_4^{2-} (PO_4^{3-} extract)	mg S/Kg	0.10 mg SO_4^{2-}/L		
Pyrophosphate Extract:				
Fe^{3+}	wt. %	0.50 mg/L		
Al^{3+}	wt. %	0.50 mg/L		
Acid-Oxalate Extract:				
Fe^{3+}	wt. %	0.50 mg/L		
Al^{3+}	wt. %	0.50 mg/L		
Citrate-Dithionite Extract:				
Fe^{3+}	wt. %	0.50 mg/L		
Al^{3+}	wt. %	0.50 mg/L		

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 110a

QUALITY CONTROL: MATRIX SPIKES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extractant	1.0 M NH_4OAc				1.0 M NH_4Cl				0.002 M $CaCl_2$						NONE
Parameter	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	Fe, mg/L	Al, mg/L	CEC NH_4*,
First Matrix Spike Sample ID:															
Sample Result															
Spike Result															
Spike Added															
% Recovery															
Second Matrix Spike Sample ID:															
Sample Result															
Spike Result															
Spike Added															
% Recovery															
Third Matrix Spike Sample ID:															
Sample Result															
Spike Result															
Spike Added															
% Recovery															

*CEC units are instrument and method dependent: Fill in mg N/L for flow injection analysis or meq for distillation/titration.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 110b

QUALITY CONTROL: MATRIX SPIKES

LAB MANAGER'S SIGNATURE _____ BATCH ID _____

LAB NAME _____

Extractant	Pyrophosphate		Acid-Oxalate		Citrate-Dithionite		KCl
Parameter	Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L	Al, mg/L
First Matrix Spike Sample ID:							
Sample Result							
Spike Result							
Spike Added							
% Recovery							
Second Matrix Spike Sample ID:							
Sample Result							
Spike Result							
Spike Added							
% Recovery							
Third Matrix Spike Sample ID:							
Sample Result							
Spike Result							
Spike Added							
% Recovery							

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 110bb

QUALITY CONTROL: MATRIX SPIKES

LAB MANAGER'S SIGNATURE _____ BATCH ID _____

LAB NAME _____

Extractant	Deionized H_2O		500 mg P/L
Parameter	NO_3^- mg/L	SO_4^{2-}, mg/L	SO_4^{2-}, mg/L
First Matrix Spike Sample ID			
Sample Result			
Spike Result			
Spike Added			
% Recovery			
Second Matrix Spike Sample ID			
Sample Result			
Spike Result			
Spike Added			
% Recovery			
Third Matrix Spike Sample ID			
Sample Result			
Spike Result			
Spike Added			
% Recovery			

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 110c

QUALITY CONTROL: MATRIX SPIKES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Total S, Weight %	Total N, Weight %	Total C, Weight %	Inorganic C, Weight %	
				<2 mm	2-20 mm
First Matrix Spike Sample ID:					
Sample Result					
Spike Result					
Spike Added					
% Recovery					
Second Matrix Spike Sample ID:					
Sample Result					
Spike Result					
Spike Added					
% Recovery					
Third Matrix Spike Sample ID:					
Sample Result					
Spike Result					
Spike Added					
% Recovery					

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 110d

QUALITY CONTROL: MATRIX SPIKES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Sulfate remaining in solution, mg S/L Initial solution concentration, mg S/L					
	0	2	4	8	16	32
First Matrix Spike Sample ID:						
Sample Result						
Spike Result						
Spike Added						
% Recovery						
Second Matrix Spike Sample ID:						
Sample Result						
Spike Result						
Spike Added						
% Recovery						
Third Matrix Spike Sample ID:						
Sample Result						
Spike Result						
Spike Added						
% Recovery						

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111a

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	pH in H_2O	pH in 0.01 M $CaCl_2$	pH in 0.002 M $CaCl_2$	Specific Surface, m^2/g
Triplicate Sample ID:				
First Replicate Result				
Second Replicate Result				
Third Replicate Result				
Average				
Standard Deviation				NA
% RSD	NA	NA	NA	

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111b

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Particle Size Analysis, Weight %

Size Class and Particle Diameter (mm)

Parameter	Sand (2.0-0.05)	Silt (0.05-0.002)	Clay (<0.002)	Sand: Very Coarse (2.0-1.0)	Sand: Coarse (1.0-0.5)	Sand: Medium (0.5-0.25)	Sand: Fine (0.25-0.1)	Sand: Very Fine (0.1-0.05)	Silt: Coarse (0.05-0.02)	Silt: Fine (0.02-0.002)
Duplicate Sample ID:										
Sample Result										
Duplicate Results										
% RSD										
Second Duplicate Sample ID:										
Sample Result										
Duplicate Result										
% RSD										
Third Duplicate Sample ID:										
Sample Result										
Duplicate Result										
% RSD										

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111c

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extractant	1.0 M NH_4OAc				
Parameter	Ca, meq/100 g	Mg, meq/100 g	K, meq/100 g	Na, meq/100 g	CEC, meq/100 g
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					

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111d

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extractant	1.0 M NH_4Cl				
Parameter	Ca, meq/100 g	Mg, meq/100 g	K, meq/100 g	Na, meq/100 g	CEC, meq/100 g
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					

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111e

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extractant	0.002 M $CaCl_2$					
Parameter	Ca, meq/100 g	Mg, meq/100 g	K, meq/100 g	Na, meq/100 g	Fe, meq/100 g	Al, meq/100 g
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						

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111f

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extract	Pyrophosphate		Acid-Oxalate		Citrate-Dithionite	
Parameter	Fe, Weight %	Al, Weight %	Fe, Weight %	Al, Weight %	Fe, Weight %	Al, Weight %
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						

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111g

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extract	Extractable Nitrate, mg N/kg	Extractable Sulfate, mg S/kg		Exchangeable Acidity, meq/100 g		Extractable Al, meq/100 g
	H_2O	H_2O	PO_4	$BaCl_2$	KCl	KCl
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						

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111h

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Sulfate Remaining in Solution, mg S/L					
	Initial Solution Concentration, mg S/L					
	0	2	4	8	16	32
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						

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 111i

QUALITY CONTROL: REPLICATES

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Total S, Weight %	Total N, Weight %	Total C, Weight %	Inorganic C, Weight %	
				<2 mm	2-20 mm
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					

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112a

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter		pH in H_2O	pH in 0.01M $CaCl_2$	pH in 0.002M $CaCl_2$
Reagent Blank*				
DL QCCS	Theoretical	NA	NA	NA
	Measured	NA	NA	NA
Low QCCS True Value				
Low QCCS Upper Limit				
Low QCCS Lower Limit				
Initial				
Continuing				
Continuing				
Continuing				
Continuing				
Final				
High QCCS True Value				
High QCCS Upper Limit				
High QCCS Lower Limit				
Initial				
Continuing				
Continuing				
Final				

*Reagent blank is the solution being added to the soil.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112b

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Particle Size Analysis, Weight %										
Size Class and Particle Diameter (mm)										
				Sand					Silt	
Parameter	Sand (2.0-0.05)	Silt (0.05-0.002)	Clay (<0.002)	Very Coarse (2.0-1.0)	Coarse (1.0-0.5)	Medium (0.5-0.25)	Fine (0.25-0.1)	Very Fine (0.1-0.05)	Coarse (0.05-0.02)	Fine (0.02-0.002)
Reagent Blank	NA	NA		NA	NA	NA	NA	NA	NA	NA
DL QCCS Theoretical	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Measured	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Low QCCS True Value										
Low QCCS Upper Limit										
Low QCCS Lower Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Final										
High QCCS True Value										
High QCCS Upper Limit										
High QCCS Lower Limit										
Initial										
Continuing										
Continuing										
Final										

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112c

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extractant	1.0 M NH_4OAc					1.0 M NH_4Cl				
Parameter	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	CEC, *_____	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	CEC, *_____
Calibration Blank										
Reagent Blank 1										
Reagent Blank 2										
Reagent Blank 3										
DL QCCS Theoretical										
DL QCCS Measured										
Low QCCS True Value										
Low QCCS Upper Limit										
Low QCCS Lower Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Final										
High QCCS True Value										
High QCCS Upper Limit										
High QCCS Lower Limit										
Initial										
Continuing										
Continuing										
Final										

*CEC reporting units are instrument and method dependent. Fill in mg N/L for flow injection analysis or meq for distillation/titration.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112d

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME_____ BATCH ID_____ LAB MANAGER'S SIGNATURE _____

Extractant		0.002 M $CaCl_2$					
Parameter		Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	Fe, mg/L	Al, mg/L
Calibration Blank							
Reagent Blank*							
DL	Theoretical						
QCCS	Measured						
Low QCCS True Value							
Low QCCS Upper Limit							
Low QCCS Lower Limit							
Initial							
Continuing							
Continuing							
Continuing							
Continuing							
Final							
High QCCS True Value							
High QCCS Upper Limit							
High QCCS Lower Limit							
Initial							
Continuing							
Continuing							
Final							

*Analyze 0.002 M $CaCl_2$ solution that has been extracted through filter pulp.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112e

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extractant		Pyrophosphate		Acid-Oxalate		Citrate-Dithionite	
Parameter		Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L
Calibration Blank							
Reagent Blank							
DL	Theoretical						
QCCS	Measured						
Low QCCS True Value							
Low QCCS Upper Limit							
Low QCCS Lower Limit							
Initial							
Continuing							
Continuing							
Continuing							
Continuing							
Final							
High QCCS True Value							
High QCCS Upper Limit							
High QCCS Lower Limit							
Initial							
Continuing							
Continuing							
Final							

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112f

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter		Extractable Nitrate, mg/L	Extractable Sulfate, mg/L		Exchangeable Acidity, meq		Extractable Al, mg/L
Extractant		H_2O	H_2O	PO_4^{3-}	$BaCl_2$	KCl	KCl
Calibration Blank					NA	NA	
Reagent Blank 1*							
Reagent Blank 2		NA	NA	NA			
Reagent Blank 3		NA	NA	NA			
DL	Theoretical				NA	NA	
QCCS	Measured				NA	NA	
Low QCCS True Value							
Low QCCS Upper Limit							
Low QCCS Lower Limit							
Initial							
Continuing							
Continuing							
Continuing							
Continuing							
Final							
High QCCS True Value							
High QCCS Upper Limit							
High QCCS Lower Limit							
Initial							
Continuing							
Continuing							
Final							

*Reagent blank is the extracting solution.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112g

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter		Total S, Weight %	Total N, Weight %	K Factor µV/µg	Total C, Weight %	K Factor µV/µg	Inorganic C, Weight %	
							<2 mm	2-20 mm
Calibration Blank				NA		NA		
Reagent Blank		NA		NA		NA		
DL QCCS	Theoretical							
	Measured							
Low QCCS True Value								
Low QCCS Upper Limit								
Low QCCS Lower Limit								
Initial								
Continuing								
Continuing								
Continuing								
Continuing								
Final								
High QCCS True Value								
High QCCS Upper Limit								
High QCCS Lower Limit								
Initial								
Continuing								
Continuing								
Final								

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112h

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Specific Surface, m^2/g (at equilibrium)	Day*	Weight of EGME in mg		
			Blank 1	Blank 2	Blank 3
Low QCCS True Value		0			
Low QCCS Upper Limit		1			
Low QCCS Lower Limit		2			
Initial		3			
Continuing		4			
Continuing		5			
Continuing		6			
Continuing		7			
Continuing		8			
Continuing		9			
Continuing		10			
Continuing		11			
Continuing		12			
Continuing		13			
Final		14			
High QCCS True Value		15			
High QCCS Lower Limit		16			
Initial		17			
Continuing		18			
Continuing		19			
Continuing		20			
Continuing		21			
Continuing		22			
Continuing		23			
Continuing		24			
Continuing		25			
Continuing		26			
Continuing		27			
Final		28			

*Measurements may be taken less frequently than daily, but record the results on the day actually performed.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 112i

QUALITY CONTROL: BLANKS AND QCCS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Parameter	Sulfate remaining in solution, mg S/L Initial solution concentration, mg S/L					
	0	2	4	8	16	32
Reagent Blank		N/A	N/A	N/A	N/A	N/A
Low QCCS True Value						
Low QCCS Upper Limit						
Low QCCS Lower Limit						
Initial						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Final						
High QCCS True Value						
High QCCS Upper Limit						
High QCCS Lower Limit						
Initial						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Continuing						
Final						

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 113

QUALITY CONTROL: ION CHROMATOGRAPHY RESOLUTION TEST

LAB NAME _____
BATCH ID _____
LAB MANAGER'S SIGNATURE _____ DATE OF ANALYSIS _____
MM/DD/YR

IC Make and Model: _____

	Concentration (mg/L)	Peak Area (integrator units)	Peak Height (cm)
SO_4^{2-}	_____	_____	_____
PO_4^{3-}	_____	_____	_____
NO_3^-	_____	_____	_____

Column Back Pressure (at max. of stroke): _____ psi

Flow Rate: _____ mL/min

Column Model: _____ Date of Purchase: _____

Column Manufacturer: _____

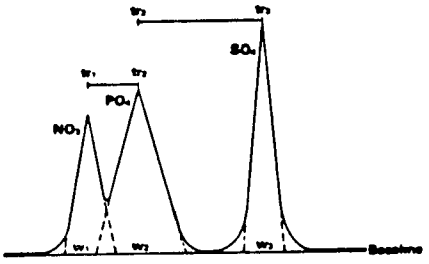
Column Serial No: _____

Precolumn in system ____ Yes ____ No

Percentage Resolution:
*$100 \times 2(tr_2-tr_1)/(W_1+W_2)$ $NO_3 - PO_4$ _____
$100 \times 2(tr_3-tr_2)/(w_2+W_3)$ $PO_4 - SO_4$ _____
$100 \times 2(tr_3-tr_1)/(w_1+W_3)$ $NO_3 - SO_4$ _____

The resolution must be greater than 60%.

Test Chromatogram:



(FACSIMILE)

*Calculations may change if order of elution is different from test chromatogram.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 114a

QUALITY CONTROL: STANDARD ADDITIONS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extract	1.0 M NH_4OAc				1.0 M NH_4Cl			
Parameter	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L
Original Sample ID:								
Single Response								
Spike Added Concen-tration								
Sample Spike 1 Response								
Spike 2 Concen-tration								
Sample Spike 2 Response								
Sample Con-centration for Original Sample (calc.)								

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 114b

QUALITY CONTROL: STANDARD ADDITIONS

LAB NAME _____ BATCH ID _____ LAB MANAGER'S SIGNATURE _____

Extract	0.002 M $CaCl_2$						Pyrophosphate		Acid-Oxalate		Citrate-Dithionite	
Parameter	Ca, mg/L	Mg, mg/L	K, mg/L	Na, mg/L	Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L	Fe, mg/L	Al, mg/L
Original Sample ID:												
Single Response												
Spike Added Concentration												
Sample Spike 1 Response												
Spike 2 Concentration												
Sample Spike 2 Response												
Sample Concentration for Original Sample (calc.)												

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 114c

QUALITY CONTROL: STANDARD ADDITIONS

LAB NAME _____ BATCH ID _____

LAB MANAGER'S SIGNATURE _____

Extract	H_2O	PO_4^{3-}	KCl	None	Solid				
Parameter	SO_4^{2-} mg/L	SO_4^{2-} mg/L	Al mg/L	SO_4^{2-} mg/L	Total S, wt %	Total N, wt %	Total C, wt %	Inorganic C, wt% <2mm	Inorganic C, wt% 2-20mm
Original Sample ID:									
Single Response									
Spike Added Concentration									
Sample Spike 1 Response									
Spike 2 Concentration									
Sample Spike 2 Response									
Sample Concentration for Original Sample (calc.)									

AIR DRY SAMPLE WEIGHT IN GRAMS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 115a

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Moisture[a]				Particle Size Analysis[d]	CEC and Exchangeable Cations	
	Dup 1		Dup 2				
	Air	Oven	Air	Oven		NH_4OAc	NH_4Cl
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							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							
Rep 1[b]			NA	NA			
Rep 2			NA	NA			
Rep 3[c]			NA	NA			

[a]Moisture is performed in duplicate; place one sample weight in each column. First column is air-dry weight, second column is oven-dry weight.
[b]Replicates are recorded here; the sample weight recorded by the sample number is repeated as Rep 1.
[c]Not all methods require three replicates.
[d]Oven-dry weight after organic matter removal.

AIR DRY SAMPLE WEIGHT IN GRAMS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 115b

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Exchangeable Cations in 0.002 M $CaCl_2$	Exchangeable Acidity	
		$BaCl_2$	KCl
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			
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
Rep 1 *			
Rep 2			
Rep 3**			

*Replicates are recorded here; the sample weight recorded by the sample number is repeated as Rep 1.
**Not all methods require three replicates.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 115c

QUALITY CONTROL: AIR DRY SAMPLE WEIGHT IN GRAMS

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Extractable Fe and Al			H_2O Extractable SO_4^{2-} and NO_3^-	PO_4^{3-} Extractable SO_4^{2-}
	Pyrophosphate	Acid-Oxalate	Citrate-Dithionite		
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					
31					
32					
33					
34					
35					
36					
37					
38					
39					
40					
41					
42					
Rep 1*					
Rep 2					
Rep 3**					

*Replicates are recorded here; the sample weight recorded by the sample number is repeated as Rep 1.

**Not all methods require three replicates.

AIR DRY SAMPLE WEIGHT IN GRAMS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 115d

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Sulfate Adsorption Isotherm Initial Solution Concentration, mg S/L					
	0	2	4	8	16	32
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
Rep 1*						
Rep 2						
Rep 3**						

*Replicates are recorded here; the sample weight recorded by the sample number is repeated as Rep 1.
**Not all methods require three replicates.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 115e

QUALITY CONTROL: AIR DRY SAMPLE WEIGHT

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Total S, mg	Total N, mg	Specific Surface,[a] g	Total C, mg	Inorganic C, mg	
					<2 mm	2-20 mm
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
Rep 1[b]						
Rep 2						
Rep 3[c]						

[a] P_2O_5 - dry weight.
[b] Replicates are recorded here; the sample weight recorded by the sample number is repeated as Rep 1.
[c] Not all methods require three replicates.

EXCHANGEABLE BASIC CATIONS IN NH_4OAc
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116a

Lab Name _____ Batch ID _____

Lab Manager's Signature

	Exchangeable Basic Cations in NH_4OAc												
Sample Number	Solution Recovered in Syringe (mL)	Aliquot Volume (mL)*				Total Dilution Volume (mL)*				Solution Concentration (mg/L)			
		Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na
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													
31													
32													
33													
34													
35													
36													
37													
38													
39													
40													
41													
42													

Blank	Total Volume in Sample (mL)	Aliquot Volume in Dilution (mL)	Total Volume of Dilution (mL)	Dilution Blank Concentrations (mg/L)			
				Ca	Mg	K	Na
D-Blank							
D-Blank							
D-Blank							
D-Blank							
D-Blank							
D-Blank							

*Enter U if no dilution is made.

EXCHANGEABLE BASIC CATIONS IN NH_4Cl
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116b

Lab Name _____ Batch ID _____

Lab Manager's Signature

Sample Number	Exchangeable Basic Cations in NH_4Cl												
	Solution Recovered in Syringe (mL)	Aliquot Volume (mL)*				Total Dilution Volume (mL)*				Solution Concentration (mg/L)			
		Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na
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													
31													
32													
33													
34													
35													
36													
37													
38													
39													
40													
41													
42													

Blank	Total Volume in Sample (mL)	Aliquot Volume in Dilution (mL)	Total Volume of Dilution (mL)	Dilution Blank Concentrations (mg/L)			
				Ca	Mg	K	Na
D-Blank							
D-Blank							
D-Blank							
D-Blank							
D-Blank							
D-Blank							

*Enter U if no dilution is made.

CATION EXCHANGE CAPACITY
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES; TITER AND NORMALITY
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116c

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Titrant used: NH_4OAc NH_4Cl

Sample Number	Cation Exchange Capacity (FIA)							Cation Exchange Capacity (Titration)			
	Total Volume in Sample (mL)	Aliquot Volume (mL)*		Total Dilution Volume (mL)*		Solution Conc. mg N/L)		NH_4OAc		NH_4Cl	
		NH_4OAc	NH_4Cl	NH_4OAc	NH_4Cl	NH_4OAc	NH_4Cl	Titer (Volume in mL)	Normality of Titrant	Titer (Volume in mL)	Normality of Titrant
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											
31											
32											
33											
34											
35											
36											
37											
38											
39											
40											
41											
42											

Blank	Cation Exchange Capacity (FIA)				
	Total Volume in Sample (mL)	Aliquot Volume (mL)	Dilution Volume (mL)	Dilution Conc. (mg N/L)	
				NH_4OAc	NH_4Cl
D-Blank					
D-Blank					
D-Blank					

*Enter U if no additional is made.

KCl-EXCHANGEABLE ACIDITY AND EXTRACTABLE ALUMINUM
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES; TITER AND NORMALITY
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116cc

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number		KCl-Extractable Al			KCl-Exchangeable Acidity	
	Solution Recovered in Syringe (mL)	Aliquot Volume (mL)*	Total Dilution Volume (mL)*	Solution Conc. (mg/L)	Titer (Volume in mL)	Normality of Titrant
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

Blank	Total Volume in Sample (mL)	KCl-Extractable Al			
		Aliquot Volume (mL)	Total Dilution Volume (mL)	Dilution Conc. (mg/L) KCl	
D-Blank					
D-Blank					
D-Blank					

*Enter U if no dilution is made.

EXCHANGEABLE BASIC CATIONS IN $CaCl_2$
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116d

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Exchangeable Basic Cations in $CaCl_2$												
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]				Total Dilution Volume (mL)[b]				Solution Concentration (mg/L)			
		Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na
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													
31													
32													
33													
34													
35													
36													
37													
38													
39													
40													
41													
42													

Blank	Total Volume in Sample (mL)	Aliquot Volume in Dilution (mL)	Total Volume of Dilution (mL)	Dilution Blank Concentrations (mg/L)			
				Ca	Mg	K	Na
D-Blank							
D-Blank							
D-Blank							
D-Blank							
D-Blank							
D-Blank							

[a]Volume added for extraction.
[b]Enter U if no dilution is made.

EXTRACTABLE Fe AND Al IN $CaCl_2$
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116e

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Extractable Fe and Al in $CaCl_2$								
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]		Total Dilution Volume (mL)[b]		Solution Conc. (mg/L)		Soil Type Mineral (M) or Organic (O)	Extraction Ratio[c]
		Fe	Al	Fe	Al	Fe	Al		
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									
31									
32									
33									
34									
35									
36									
37									
38									
39									
40									
41									
42									

Blank	Extractable Fe and Al in $CaCl_2$				
	Total Volume in Sample (mL)	Aliquot Volume (mL)	Dilution Volume (mL)	Dilution Conc. (mg/L)	
				Fe	Al
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					

[a]Volume added for extraction.
[b]Enter U if no dilution is made.
[c]Soil to solution ratio is expressed as 1:x; enter the value of x.

EXTRACTABLE Fe AND Al IN PYROPHOSPHATE
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116ee

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Extractable Fe and Al in Pyrophosphate						
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]		Total Dilution Volume (mL)[b]		Solution Conc. (mg/L)	
		Fe	Al	Fe	Al	Fe	Al
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							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							

Blank	Extractable Fe and Al in Pyrophosphate				
	Total Volume in Sample (mL)	Aliquot Volume (mL)	Dilution Volume (mL)	Dilution Conc. (mg/L)	
				Fe	Al
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					

[a]Volume added for extraction.
[b]Enter U if no dilution is made.

EXTRACTABLE Fe AND Al IN ACID-OXALATE
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116f

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Extractable Fe and Al in Acid-Oxalate						
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]		Total Dilution Volume (mL)[b]		Solution Conc. (mg/L)	
		Fe	Al	Fe	Al	Fe	Al
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							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							

Blank	Extractable Fe and Al in Acid-Oxalate				
	Total Volume in Sample (mL)	Aliquot Volume (mL)	Dilution Volume (mL)	Dilution Conc. (mg/L)	
				Fe	Al
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					

[a]Volume added for extraction.
[b]Enter U if no dilution is made.

EXTRACTABLE Fe AND Al IN CITRATE-DITHIONITE
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116ff

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Extractable Fe and Al in Citrate-Dithionite						
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]		Total Dilution Volume (mL)[b]		Solution Conc. (mg/L)	
		Fe	Al	Fe	Al	Fe	Al
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							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							

Blank	Extractable Fe and Al in Citrate-Dithionite				
	Total Volume in Sample (mL)	Aliquot Volume (mL)	Dilution Volume (mL)	Dilution Conc. (mg/L)	
				Fe	Al
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					
D-Blank					

[a]Volume added for extraction.
[b]Enter U if no dilution is made.

WATER EXTRACTABLE SULFATE AND NITRATE
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116g

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	H_2O Extractable Nitrate				H_2O Extractable Sulfate		
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]	Total Dilution Volume (mL)[b]	Solution Concentration (mg/L)	Aliquot Volume (mL)[b]	Total Dilution Volume (mL)[b]	Solution Concentration (mg/L)
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							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							

Blank	Total Volume in Sample (mL)	Aliquot Volume in Dilution (mL)	Total Volume of Dilution (mL)	Dilution Blank Concentrations	
				NO_3^-	SO_4^{2-}
D-Blank					
D-Blank					
D-Blank					

[a]Volume added for extraction.
[b]Enter U if no dilution is made.

PHOSPHATE EXTRACTABLE SULFATE
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116gg

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	PO_4^{3-} Extractable Sulfate			
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]	Total Dilution Volume (mL)[b]	Solution Concentration (mg/L)
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				
31				
32				
33				
34				
35				
36				
37				
38				
39				
40				
41				
42				

Blank	Total Volume in Sample (mL)	Aliquot Volume in Dilution (mL)	Total Volume of Dilution (mL)	Dilution Blank Concentration (mg/L)
D-Blank				
D-Blank				
D-Blank				

[a]Volume added for extraction.
[b]Enter U if no dilution is made.

SULFATE ADSORPTION ISOTHERMS
DILUTION FACTORS AND DILUTION REAGENT BLANK VALUES
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 116h

Lab Name _____ Batch ID _____

Lab Manager's Signature _____

Sample Number	Sulfate Adsorption Isotherm																		
	Total Volume in Sample (mL)[a]	Aliquot Volume (mL)[b]						Total Dilution Volume (mL)[b]						Solution Concentration (mg/L)					
		0	2	4	8	16	32	0	2	4	8	16	32	0	2	4	8	16	32
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																			
31																			
32																			
33																			
34																			
35																			
36																			
37																			
38																			
39																			
40																			
41																			
42																			

[a]Volume added for adsorption.
[b]Enter U if no dilution is made.

SUMMARY OF EXCHANGEABLE CATIONS IN NH_4OAc
CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 204a

Analytical Lab ID _____

Batch ID _____ Date Form Completed _____

Prep Lab Name _____ Date Batch Received _____

Lab Manager's Signature _____

Remarks _____

Sample Number	Exchangeable Cations in NH_4OAc, meq/100g			
	Ca	Mg	K	Na
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				
31				
32				
33				
34				
35				
36				
37				
38				
39				
40				
41				
42				

SUMMARY OF EXCHANGEABLE CATIONS IN NH_4Cl
CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 204b

Analytical Lab ID _____

Batch ID _____ Date Form Completed _____

Prep Lab Name _____ Date Batch Received _____

Lab Manager's Signature _____

Remarks _____

Sample Number	Exchangeable Cations in NH_4Cl, meq/100g			
	Ca	Mg	K	Na
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				
31				
32				
33				
34				
35				
36				
37				
38				
39				
40				
41				
42				

SUMMARY OF EXCHANGEABLE CATIONS IN 0.002 M $CaCl_2$
CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 204c

Analytical Lab ID _____

Batch ID _____ Date Form Completed _____

Prep Lab Name _____ Date Batch Received _____

Lab Manager's Signature _____

Remarks _____

Sample Number	Exchangeable Cations in 0.002 M $CaCl_2$, meq/100g					
	Ca*	Mg	K	Na	Fe	Al
01						
02						
03						
04						
05						
06						
07						
08						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

*Reported data may be negative.

SUMMARY OF CATION EXCHANGE CAPACITY (CEC)
CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 204d

Analytical Lab ID _____

Batch ID _____ Date Form Completed _____

Prep Lab Name _____ Date Batch Received _____

Lab Manager's Signature _____

Remarks _____

Sample Number	CEC, meq/100g			CEC, meq/100g		
	NH_4OAc	NH_4Cl			NH_4OAc	NH_4Cl
01				22		
02				23		
03				24		
04				25		
05				26		
06				27		
07				28		
08				29		
09				30		
10				31		
11				32		
12				33		
13				34		
14				35		
15				36		
16				37		
17				38		
18				39		
19				40		
20				41		
21				42		

SUMMARY OF EXTRACTABLE IRON AND ALUMINUM DATA
CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 205

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Sample Number	Pyrophosphate Extractable, Weight %		Acid-Oxalate Extractable, Weight %		Citrate-Dithionite Extractable, Weight %	
	Fe	Al	Fe	Al	Fe	Al
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

SUMMARY OF EXTRACTABLE SULFATE, EXCHANGEABLE ACIDITY, AND
EXTRACTABLE ALUMINUM DATA, CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 206

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Sample Number	Extractable Nitrate mg N/kg	Extractable Sulfate, mg S/kg		Exchangeable Acidity, meq/100g		Extractable Al, meq/100g
Extract	H_2O	H_2O	PO_4^{3-}	$BaCl_2$	KCl	KCl
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

SUMMARY OF SULFATE-ADSORPTION ISOTHERM DATA
CORRECTED FOR BLANKS* AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 207

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Sample Number	Sulfate Remaining in Solution, mg S/L					
	Initial Solution Concentration, mg S/L					
	0	2	4	8	16	32
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

*Blanks are double-deionized water.

SUMMARY OF TOTAL C, N, S, SPECIFIC SURFACE, AND INORGANIC CARBON DATA
CORRECTED FOR BLANKS AND DILUTIONS
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 208

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Sample Number	Total S, Weight %	Total N, Weight %	Specific Surface, m^2/g	Total C, Weight %	Inorganic C, Weight %	
					<2 mm	2-20 mm
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						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						

PARTICLE SIZE ANALYSIS RAW DATA
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 303b

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____
Cylinder Volume (mL) _____ Pipet Volume (mL) _____

Weight of Fraction, grams								
Size Class and Particle Diameter (mm)								
				Sand				
Sample Number	Sand (2.0-0.05)	Clay and Fine Silt (<0.02)	Clay (<0.002)	Very Coarse (2.0-1.0)	Coarse (1.0-0.5)	Medium (0.5-0.25)	Fine (0.25-0.1)	Very Fine (0.1-0.05)
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								
31								
32								
33								
34								
35								
36								
37								
38								
39								
40								
41								
42								

SUMMARY OF $BaCl^2$ - EXCHANGEABLE ACIDITY RAW DATA
DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY REPORT FORM 306

Analytical Lab ID _____ Lab Manager's Signature _____
Batch ID _____ Date Form Completed _____
Prep Lab Name _____ Date Batch Received _____
Remarks _____

Sample Number	$BaCl_2$ - Exchangeable Acidity	
Extract	Titer (Volume in mL)	Normality of Titrant
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		
31		
32		
33		
34		
35		
36		
37		
38		
39		
40		
41		
42		

SUMMARY OF TOTAL C, N, S, SPECIFIC SURFACE, AND INORGANIC CARBON RAW DATA
DIRECT/DELAYED RESPONSE PROJECT (DDRP) REPORT FORM 308

Analytical Lab ID _____ Lab Manager's Signature _____

Batch ID _____ Date Form Completed _____

Prep Lab Name _____ Date Batch Received _____

Remarks _____

Sample Number	Total S, µg	Total N, µg	Specific Surface, mg EGME		Total C, µg	Inorganic C, µg	
			added	retained		<2 mm	2-20 mm
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							
31							
32							
33							
34							
35							
36							
37							
38							
39							
40							
41							
42							

Appendix D

Forms for Reporting Mineralogical Laboratory Data

The following forms are used for recording data from the mineralogical procedures detailed in sections 17 through 19.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 400
Data from Randomly Oriented Powder Mounts

Analytical Lab ID: _____ Batch No.: _____

Analyst: _____ Date Received: _____

Date Completed: _____

Lab Manager's Signature: _____

Sample Number: _____ Size Fraction: <2-mm <0.002-mm (circle one)

°2θ	d(Å)	I/I_1	Mineral Name	JCPDS Card Number	hkl	Integrated Area	RIR	Half-Height Peak Width

Minerals (in order of highest to least abundance)	%	Major Peaks 1		Major Peaks 2		Major Peaks 3		Confirming Peak		Degree of Match
		d(A)	I/I	d(A)	I/I	d(A)	I/I	d(A)	I/I	
1										
2										
3										
4										
5										
6										
7										
8										
9										

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 401
Data from Oriented Pipet Mounts

Analytical Lab ID: _____ Batch No.: _____

Analyst: _____ Date Received: _____

Date Completed: _____

Lab Manager's Signature: _____

Treatment: (circle one)

Mg - sat.	A D	GLY		
K - sat.	A D	110°C	350°C	550°C

°2θ	d(Å)	I/I	Mineral Name	JCPDS Card Number	hkl	Response to Treatment

Weight from Section 17.10.5 _____g freeze-dried <0.002-mm material.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 402a
Chemical Composition of Minerals by Wavelength-dispersive XRF

Analytical Lab ID:_____ Batch No.:_____

Analyst: _____ Date Received:_____

Date Analyzed:_____

Lab Manager's Signature:_____

Sample No.:_____

Elements Major	Oxide	Concentration Elemental, wt%	Concentration Oxide, wt%	2 σ error	I/I(b)	Detection Limit
Sodium	Na_2O					
Potassium	K_2O					
Rubidium	Rb_2O					
Magnesium	MgO					
Calcium	CaO					
Strontium	SrO					
Aluminum	Al_2O_3					
Silicon	SiO_2					
Phosphorus	$P2O_5$					
Iron*	Fe_2O_3					
Manganese	MnO_2					
Titanium	TiO_2					
TOTAL		NA		NA	NA	NA

*The iron value represents both the $^{+}2$ and $^{+}3$ states of iron.

Comments:

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 402b
Chemical Composition of Minerals by Wavelength-Dispersive XRF

Analytical Lab ID:_____ Batch No.:_____

Analyst: _____ Date Received:_____

Date Analyzed:_____

Lab Manager's Signature:_____

Sample No.:_____

Minor and Trace Elements		Concentration Elemental, (wt% or ppm)	Concentration Oxide, (wt% or ppm)	2 σ error	I/I(b)	Detection Limit
Sulfur	S					
Chloride	Cl					
Barium	Ba					
Lead	Pb					
Nickel	Ni					
Copper	Cu					
Cobalt	Co					
Chromium	Cr					
Zinc	Zn					
Uranium	U					
Thorium	Th					
Zirconium	Zr					
Niobium	Nb					
Cerium	Ce					

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 403
Pertinent Geometry and Instrument Settings Specific to the System

Analytical Lab ID:_____

SEM Machine Name:_____ EDXRF Machine Name:_____

Operator:_____ Date Completed:_____

Lab Manager's Signature:_____

1. X-ray detector to specimen fixed angle and azimuth_____

2. X-ray detector to specimen distance_____

3. X-ray detector active area_____

4. X-ray detector window_____

5. Specimen tilt angle and tilt azimuth_____

6. Specimen to SEM pole piece working distance (adjusted on the electron beam axis to the main constant for every spectral collection).
_____

7. SEM operating voltage:_____

8. SEM beam current (±10%):_____

9. SEM spot size:_____

10. SEM scan rate (preferred as fast as possible):_____

11. Specimen area fluoresced:_____; volume excited:_____

12. Magnification:_____; full frame or partial field:_____

13. Spectral acquisition time (dead-time corrected):_____

14. Spectrometer pulse shaping time constant:_____
electron volts/channel:_____

15. Average absorbed current:_____

16. Average input count rate:_____

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 404
Comments on Observations, Photographs, and Areas of Analysis

Analytical Lab ID:_____ Batch No:_____

Analyst: _____ Date Received:_____

Date Completed:_____

Lab Manager's Signature:_____

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY FORM 405
SEM Photograph and Chemical Composition of Minerals

Analytical Lab ID:_____ Batch No:_____
Analyst: _____ Date Received:_____
Date Completed:_____
Lab Manager's Signature:_____
Clay Mineral: yes no (circle one)
Light Mineral: yes no (circle one)
Heavy Mineral: yes no (circle one) If yes, include:
Wt % Heavy Minerals_____ Wt % Light Minerals_____
Sample Number:_____ Mineral Name:_____

(Attach Photograph Here)

Magnification:_____

Composition: (Attach spectrum to the back of this sheet)

Appendix E

Glossary

Air-dried soil	-- Soil that has reached equilibrium with the air; the moisture content does not change by more than 5 percent in a 40-g sample over a 24-hour period.
Aluminum potential (K_A)	-- 3 pH − pAl.
Base saturation percentage	-- Extent to which the adsorption complex of a soil saturated with exchangeable cations other than hydrogen; expressed as a percentage of the total cation exchange capacity.
Batch	-- A group of as many as 42 samples including 1 preparation duplicate, at least 2 audit samples, and as many as 39 routine samples and field duplicates.
Capacity-protected systems	-- Watersheds in which surface waters will not become acidic for centuries to millennia.
DDI water	-- Water which meets ASTM Type II reagent grade specifications; prepared by double distillation, double deionization, or a combination of distillation and deionization; having a conductivity of less than 1.0 μmho/cm at 298° K (28°C).
Delayed response systems	-- Watersheds in which surface waters will become acidic in the time frame of a few mean water residence times to several decades (10 to 100 years).
Direct response systems	-- Watersheds with surface waters that either are presently acidic (alkalinity <0) or will become acidic within a few (3 to 4) mean water residence times.
Endogenous level	-- Naturally occurring concentration of analyte within the sample.
Instrumental detection limit	-- Three times the standard deviation of ten nonconsecutive replicate calibration blank analyses run on separate days. If a signal is not obtained for a blank analysis, then the instrumental detection limit is defined as 3 times the standard deviation of 10 nonconsecutive replicate analyses of a standard whose concentration is 4 times the lesser of the actual detection limit or the required detection limit.
K-factor	-- The number of μV/μg for acetanilide standard for carbon and nitrogen determinations.
Lime potential	-- pH − 1/2 pCa.

Mean water residence time	-- Maximum amount of time for complete replacement of all the water within the permeable strata of the watershed.
Mineral soil	-- Soil that contains greater than 80 percent mineral matter.
Organic soil	-- Soil that contains greater than 20 percent organic matter.
Oven-dried (OD) soil	-- Soil that has been dried for 24 hours at the prescribed temperature in a convection oven: 105 °C for mineral soils, 60 °C for organic soils.
Sesquioxides	-- Generally considered to be iron (Fe_2O_3) and aluminum (Al_2O_3) oxides. More specifically, sesquioxides are combinations of these two minerals in a one-to-two ratio.
Set	-- A group of samples that were sampled by an individual crew on one day.
Soil	-- Unconsolidated mineral and organic material on the immediate surface of the earth that serves as a natural medium for the growth of land plants.

U.S. GOVERNMENT PRINTING OFFICE 1990/748-159/00449