manual on soil sampling and methods of analysis

Second Edition 1978

J.A. McKeague,
Editor

Prepared by the Subcommittee
on Methods of Analysis
of the Canada Soil Survey Committee

DR. D.F. ACTON



Canadian Society of Soil Science
Société canadienne de la science du sol

Rec'd 30/4/85 - P.O. 85-002L LRRI

MANUAL ON SOIL SAMPLING AND METHODS OF ANALYSIS

2nd Edition, 1978

Reprinted, 1981

Prepared by Subcommittee

(of Canada Soil Survey Committee)

on Methods of Analysis

J.A. McKeague, Ed.

Canadian Society of Soil Science

INTRODUCTION

This compilation of methods of soil analysis was prepared by a Subcommittee of the Canada Soil Survey Committee (CSSC) established in 1973. Members of the Subcommittee and others concerned with soil analysis studied the methodology for various determinations and either recommended certain methods or outlined those that were being used most commonly in Canada. Their recommendations were assembled, criticized by subcommittee members and others, and revised on the basis of the comments. Some methods used in soil testing laboratories were added. The resulting material was assembled in June, 1974 as a tentative Methods Manual for limited distribution. Users of the manual were urged to note errors, inconsistencies and ambiguities in the text, to consider desirable additions and deletions and to send to the Subcommittee chairman all suggestions for changes. Several suggestions were received and appropriate changes were made. In addition, a section on mineralogical analysis was added, and the section on soil testing methods expanded. A second draft of the manual was completed in August, 1975 and sent to the contributors for criticism. Users of the manual are requested to send suggestions for improvements to the chairman of the Subcommittee as it is the intention to update the manual every few years.

For a number of determinations, it was necessary to list several methods and this will probably continue to be the case. For example, depending upon the purposes involved, it is desirable to do particle-size analysis without removing carbonates in some cases, and after removing carbonates in others. It is important that the methods be identified and thus all methods are coded in a form convenient to CanSIS (Canadian Soil Information System), a computerized soil data storage and retrieval system. Our overall view of methodology for soil analysis hinges on the fact that most soil characteristics measured are not absolute, but method-dependent properties. These operationally-defined properties include: particle-size distribution, bulk density, pH, cation-exchange capacity. Thus, methods of analysis are chosen on the bases of convenience, ease of duplication of results by different analysts, and commonness of use, as well as on the basis of theoretical soundness. The purpose of this compilation is not to provide details on theory of the methods but some discussion of rationale and interpretations is included.

The format of this report and some sections of it, particularly Sample Collection and Preparation, follows Soil Survey Investigations Report No. 1 of SCS and our indebtedness to the authors of this report is acknowledged.

The Subcommittee wishes to thank the many soil scientists who contributed to the development of this methods manual either by studying and recommending methods or by criticizing the first draft of the material. Particular thanks are due to: W.B. McGill for preparing the material on total C, N, P and S; G.E. Byers, J.A. Carson, T.J. Heeg, R. Veinot and J.W. Hamm for supplying the initial material on soil testing

laboratory methods and to G.E. Byers for revising and expanding the latter material; H. Kodama, N.M. Miles and J.G. Ross for contributions to mineralogical methods; and to all those who are indicated as authors of methods. The subcommittee members who were active in the preparation of this manual were: A.J. Green - particle-size analysis; J.L. Bélair - bulk density; R. Eilers - soil water methods; V.E. Osborne - pH and exchangeable cations; A. Raad - carbonates; A.K. Ballantyne - soluble salts; C. Wang - extractable Fe, Al, Mn and Si; C.R. De Kimpe - mineralogical methods. The major contributors to the various sections are listed in cases where this is possible.

1978 edition

Corrections of the 1976 edition have been made and some new material has been added. C.R. De Kimpe has translated the revised Manual into french. We thank the many users of the Manual who have suggested corrections and other improvements; please continue to do this. Blank pages for noting corrections and other suggestions are included before the Table of Contents.

This edition in both english and french was published by the Canadian Society of Soil Science. It is available at a cost of $13.00 from: The Canadian Society of Soil Science, Suite 907, 151 Slater St., Ottawa, Ont. K1P 5H4.

J.A. McKeague, Chairman,
Subcommittee on Methods

TABLE OF CONTENTS

	Page
INTRODUCTION	i
1. SAMPLE COLLECTION AND PREPARATION	1
1.1 Field Sampling	1
1.2 Laboratory Preparation	2
1.3 Size-Fraction Base for Reporting Data	2
2. PHYSICAL ANALYSIS	4
2.1 Particle Size Analysis	4
2.11 Particles < 2 mm, pipet method	6
2.111 Pretreatments to remove carbonates, organic matter, soluble salts and iron oxides	6
2.112 Pretreatments to remove soluble salts, carbonates and organic matter	13
2.113 Pretreatments to remove soluble salts, and organic matter	14
2.114 Water-dispersible clay	14
2.115 Ultrasonic dispersion in water	14
2.12 Particles < 2 mm, hydrometer method	15
2.13 Sieve analysis (engineering test)	26
2.14 Particles coarser than 2 mm	27
2.2 Bulk Density and Particle Density	29
2.21 Core method	30
2.22 Saran coated clods	32
2.23 Paraffin clod method	34
2.24 Bulk density of organic soils	35
2.25 Particle density	36
2.3 Shrinkage	37
2.31 Linear extensibility, saran clod	38
2.32 Shrinkage by direct measurement	38
2.33 Shrinkage of disturbed soil and maximum dry density	39
2.4 Water Content and Water Retention (Porosity)	41
2.41 Water content	42
2.42 Water retention, tension table	43
2.43 Pressure plate extraction	45
2.44 Pressure membrane extraction	45
2.5 Saturated Hydraulic Conductivity	46
2.51 Core method	46
2.52 Clod method	47
2.53 Undisrupted soil block method	48

Page

2.6 Atterberg Limits 50

2.61 Liquid limit 50
2.62 Plastic limit 53
2.63 Plasticity Index 54

2.7 Specific Surface Area 55

2.8 Fiber Content 56

2.81 Unrubbed fiber 56
2.82 Rubbed fiber 57
2.83 Fiber content and particle size 59

2.9 Micromorphology 61

2.91 Stereomicroscope 61
2.92 Thin sections 61
2.93 Scanning electron microscopy 64

3. CHEMICAL ANALYSES 66

3.1 pH 66

3.11 pH in 0.01 M $CaCl_2$ 66
3.12 Field pH in $CaCl_2$ of moist peat 67
3.13 pH in water 67
3.14 pH of saturated soil paste 68
3.15 pH in 1 M NaF 68

3.2 Soluble Salts 68

3.21 Soluble salts in saturation extract 69
3.22 Soluble salts in 1:1 soil:water mixtures 70
3.23 Soluble salts in 1:5 soil:water mixtures 70
3.24 Soluble salts in groundwater 71
3.25 Gypsum 71
3.26 Sodium adsorption ratio (SAR) 71
3.27 Soluble sodium percentage 71

3.3 Cation Exchange Capacity and Exchangeable Cations 72

3.31 Permanent charge CEC, and exchangeable cations, NaCl extraction 72
3.32 CEC and exchangeable cations by NH_4OAc at pH 7 78
3.33 CEC by $Ca(OAc)_2$-$CaCl_2$ at pH 7 80
3.34 CEC by sodium acetate 82
3.35 Exchangeable H+ and CEC by $BaCl_2$-triethanolamine 83
3.36 Exchange capacity of organic samples by barium acetate 85

3.4 Carbonates 86

3.41 Gravimetric method, approximate 86
3.42 Gravimetric method, quantitative 87
3.43 Pressure method 88
3.44 Citrate buffer method 92
3.45 Titrimetric method 94

Page

3.5 Extractable Al, Fe and Mn (and Si) 98

3.51 Dithionite-citrate-bicarbonate method 98
3.52 Acid ammonium oxalate method 103
3.53 Sodium pyrophosphate method 104
3.54 Alkali-extractable Si and Al 106

3.6 Total C, N, S and P 109

3.61 Total carbon 109

3.611 - by dry combustion, induction furnace 109
3.612 - by wet oxidation (Allison) 112
3.613 - by wet oxidation (Walkley-Black) 115
3.614 - by dry combustion, resistance furnace 117
3.615 Pyrophosphate-soluble organic matter index 121

3.62 Total nitrogen 122

3.621 Semi-micro, NO_2^- & NO_3^- included 122
3.622 Semi-micro, NO_2^- & NO_3^- not included 125
3.623 Macro-Kjeldahl, NO_2^- & NO_3^- included 126
3.624 Macro-Kjeldahl, NO_2^- & NO_3^- not included 129

3.63 Total sulfur 130

3.631 $NaNO_3$-Na_2CO_3 fusion 131
3.632 Acid digestion 134
3.633 Alkaline hypobromite oxidation 134

3.64 Total phosphorous 137

3.641 Acid digestion 137
3.642 Sodium carbonate fusion 139

3.7 Total Major and Minor Elements (other than C, N, P & S) 140

3.71 Acid dissolution 140
3.72 Lithium metaborate fusion 141
3.73 Sodium carbonate fusion 142
3.74 Total mercury in soils 142
3.75 Total Se in soils 145

3.8 Loss on ignition 148

3.81 Loss on ignition at 420 C 149
3.82 Loss on ignition at 850 C 149

4. SOIL TESTING LABORATORY METHODS 151

4.1 pH and Conductivity 155

4.11 1:1 soil:water ratio 155
4.12 1:2 soil:water ratio 155
4.13 Saturated soil paste 155

Page

4.2 Organic matter 155

4.21 Wet Combustion, Colorimetric Method 155
4.22 Wet Combustion, Titration Method 157
4.23 Loss on Ignition 160

4.3 Nitrate and Ammonia 160

4.31 Incubated nitrate-N determination 160

4.311 Cadmium reduction method 161
4.312 Phenoldisulphonic acid method 162
4.313 Specific ion electrode for nitrate 162

4.32 Nitrate extractable by 0.02N $CuSO_4$ and 0.007N Ag_2SO_4 164
4.33 Nitrate extractable by 0.5 M $NaHCO_3$ 165
4.34 Nitrate in 1:1 soil:water suspensions 165
4.35 Nitrate and ammonium extractable by 2N KCl 165

4.4 Extractable Phosphorus and Sulfur 167

4.41 Sodium bicarbonate soluble P (Olsen & Dean) 167
4.42 Sodium bicarbonate soluble P (autoanalyzer) 169
4.43 Phosphorus extractable by "medium-strength Bray extract 172
4.44 Phosphorus extractable by 0.03 N NH_4F and 0.03 N H_2SO_4 173
4.45 Phosphorus extractable by 0.03 N NH_4F and 0.025 N HCl 174
4.46 Phosphorus extractable by "strong" Bray extract 0.05 N NH_4F and 0.1 N HCl. 174
4.47 Sulfate extractable by 0.1M $CaCl_2$ 176
4.48 Sulfate extractable by 0.01M $CaCl_2$ 177

4.5 Extractable K, Ca and Mg 179

4.51 Ammonium acetate extractable cations 179
4.52 Bicarbonate extractable K 181

4.6 Extractable Trace Elements 181

4.61 Hot water soluble boron - azomethine-H method 181
4.62 Hot water soluble boron - curcumin method 182
4.63 Hot water soluble boron - dianthrimide method 183
4.64 Al and Mn extractable in 0.02 M $CaCl_2$ 184
4.65 DTPA-TEA extractable elements 185
4.66 EDTA extractable elements 185
4.67 0.1N HCl extractable elements 186

4.7 Lime Requirement 186

4.71 Buffer method 186
4.72 Reaction with $Ca(OH)_2$ 187

4.8 Soil Texture, Hand Method 187

Page

5. MINERALOGICAL ANALYSES 189

5.1 Fractionation of Samples 189

5.11 Water dispersion 189
5.12 Dispersion involving chemical pretreatments 189
5.13 Clay collection and flocculation 190
5.14 Silt collection 190
5.15 Sand collection 191

5.2 X-Ray analysis 192

5.21 Ca-K sequence for clay-size fraction analysis 192

5.211 Sample preparation 192
5.212 Specimen preparation 192
5.213 Treatments 194
5.214 Criteria for identification 196
5.215 Semi-quantitative estimation of clay minerals 200

5.22 Mg-K sequence for clay-size fraction analysis 201
5.23 Ca-K sequence with removal of sesquioxides interlayer 201
5.24 Mg-K sequence with removal of sesquioxides interlayer 202
5.25 Silt analysis by X-ray diffraction 202

5.3 Chemical Analysis Related to Mineralogy 204

5.31 Exchange properties 204
5.32 Total elemental analysis 205
5.33 Selective dissolution of non-clay minerals 205

5.4 Thermal Methods 205

5.41 Nomenclature in thermal analysis 205
5.42 Differential thermal analysis 206
5.43 Thermogravimetric analysis 206
5.44 Characterization 206

5.5 Infrared Spectroscopy 208

5.51 Methods 208
5.52 Analysis of spectra and identification 209

5.6 Surface Area Determination 210

5.61 Low temperature gas adsorption 210
5.62 Ethylene glycol retention 210
5.63 Dye absorption 212

List of Tables

		Page
Table 1.	Settling times for 2 um clay at various temperatures (for 10 cm).	10
Table 2.	General guidelines on the weight of soil sample and the volume of suspension required to obtain an adequate clay sample for mineralogical analysis.	11
Table 3.	Values of y at $30^{o}C$ for the determination of particle size from observed hydrometer readings (Day, 1965).	17
Table 4.	Correction factor for y at various temperatures.	19
Table 5.	Particle diameter as a function of temperature and hydrometer reading (R) at various times.	19-25
Table 6.	Suggested times for equilibrating 7.6x7.6 cm cores at various tensions	43
Table 7.	Values of $(N/25)^{0.12}$ for calculating liquid limit	53
Table 8.	Calculated concentrations of different cations for AA determinations in NaCl extracts.	73
Table 9.	Canadian Soil Testing Laboratories	152
Table 10.	Soil Testing Laboratory Methods by province	154
Table 11.	Soluble salts in soils (1:2 soil:water ratio)	156
Table 12.	Organic matter from percent transmittance (Method 4.21)	158
Table 13.	Quantity of limestone in tons per acre required to raise soil pH to 6.5 to a 6 in. depth.	188

List of Figures

		Page
Fig. 1	A comparison of particle-size limits in 4 systems of particle-size classification.	5
Fig. 2	Summation curves for soils A and B plotted on a logarithmic scale of particle size.	18
Fig. 3	Modified syringe empty and containing peat sample, plastic sampling bottles and spatula for determination of fiber content.	58
Fig. 4	Apparatus for particle-size analysis and fiber content of peat (method 2.83).	60
Fig. 5	Apparatus for the determination of calcium carbonate equivaalent by method 3.42.	89
Fig. 6	Apparatus for the determination of inorganic carbon by method 3.45.	95
Fig. 7	Apparatus for determination of total carbon by method 3.612.	113
Fig. 8	Apparatus for total carbon determination by method 3.614.	119
Fig. 9	Steam distillation apparatus (Bremner, 1965) for nitrogen determination by method 3.621.	123
Fig. 10	Apparatus for $SO_4^=$ reduction to $S^=$ in method 3.631	133
Fig. 11	Digestion assembly for Hg determination (3.74)	143
Fig. 12	Flow diagram and flow cell for the determination of Hg (3.74)	146
Fig. 13	Flow diagram for organic matter determination by autoanalyzer.	159
Fig. 14	Flow diagram for the determination of nitrate by autoanalyzer (Method 4.311)	163
Fig. 15	Flow diagram for the determination of phosphorus by autoanalyzer (Method 4.42)	171
Fig. 16	Flow diagram for the determination of phosphorus by autoanalyzer (Method 4.43)	175
Fig. 17	Schematic summary of the assignments of infrared absorption bands in layer-lattice silicates.	211

1. - SAMPLE COLLECTION AND PREPARATION

1.1 FIELD SAMPLING

1.11 Site Selection

Select sample sites typical of the soils that the samples are intended to represent. The site should be away from roads, fences, abandoned farmsteads and other features that may have caused aberrant properties. Ideally, two or more sites several kilometers apart should be selected for each soil. The reasons for the selection of a particular site should be noted.

1.12 Soil Sampling

The method of sampling depends upon the purposes for which the samples are taken. These purposes should always be recorded when sampling. The methods described herein apply to soil characterization and genesis studies. Other kinds of samples include: Composite samples of surface soil for fertility tests and grab samples of a specific horizon for checking classification.

Take samples from freshly dug pits and not from roadcuts. Dig the pit wide enough to expose one face of a pedon and deep enough to expose part of the C horizon, or to the bottom of the control section (Canada Soil Survey Committee, 1978), whichever is deeper. Describe the pedon and any variations within the pedon. In laterally uniform pedons, sample from a face about 50 cm wide. Each sample should be representative of the entire cross section of each horizon. If horizons of a pedon are discontinuous or vary greatly in thickness or degree of expression, collect samples from different parts of the pedon or different locations on the pit face to ensure a representative sample of each horizon. Do not mix horizons if they are interfingered or discontinuous. If contrasting soil components are so small or so intimately associated that they cannot be sampled separately, estimate the proportion of each component and record it in the pedon description. Otherwise sample the contrasting materials separately and record their proportion. Make arbitrary subhorizons if morphologically recognizable subhorizons are more than 25 cm thick in the upper part of the pedon or more than 50 cm in the lower part. If coarse fragments (>20 mm) are present, follow the procedures outlined in 1.13. If convenient, start sampling at the bottom of the pit.

The characterization of several physical properties of soil, such as porosity and saturated hydraulic conductivity, requires undisturbed samples that are representative of the horizon being sampled. Suitable samples of friable, stone free soils can usually be obtained but problems arise with stony soils and with soils of coarse structure. For example, some fragipans have dense, prismatic structural units about 30 cm wide separated by more porous "gray streaks". A representative sample should include both the prismatic unit and the "gray streak" material in the proportions in which they occur. Such samples are difficult to obtain and very

bulky. An alternative approach is to sample the major part of the prismatic units and the "gray streaks" separately. No generally applicable methods can be specified for obtaining suitable undisturbed soil samples. The quality of the samples depends upon the judgement and ingenuity of the sampler and the reliability of many physical data depends more upon the quality of the "undisturbed" samples than on any other factor.

1.13 Stony Soils (Soil Conservation Service, 1972)

Volume estimates - In each horizon or group of horizons estimate the volume percentages of the 20 to 75 mm and the 75 to 250 mm fractions. Record the percentages in the pedon description. Collect a 5 to 7 kg sample of the <20 mm fraction and store it in an airtight plastic bag if field moisture content is to be determined. After drying, sieve and weigh the 2-20 mm material. Calculate the volume percentage of the 2-20 mm fraction (see 2.142).

Weight estimates - Estimate and record the volume percentages of the >75 mm fraction as outlined in volume estimates. Collect a 15 to 25 kg sample of the <75 mm fraction and weigh. Sieve out and weigh the 20 to 75 mm fraction. Record the weights of the 20 to 75 mm fractions and store the <20 mm material in an airtight plastic bag if field moisture content is to be determined. Calculate the weight percentage of coarse fractions (2.141).

1.2 LABORATORY PREPARATION

Spread the field samples on trays or on plastic sheeting and air-dry (except for special procedures requiring moist soil). Thoroughly mix and roll the samples to break up clods. Continue rolling or gently crushing and sieving until only coarse fragments (>2 mm) that do not slake in water or sodium metaphosphate remain on the sieve. (If the samples are to be analyzed for minor elements, nylon or stainless steel sieves should be used). Weigh and discard the >2 mm fraction. Calculate the percentages of the various fractions.

NOTE: Preparation of samples of strongly cemented soils is difficult as they are as hard as some rocks. No general method can be specified for such samples.

If C, total N, extractable Fe and Al, etc. are to be determined, grind a subsample of the <2 mm material to pass a 100 mesh sieve.

1.3 SIZE-FRACTION BASE FOR REPORTING DATA

1.31 Particles <2 mm

Unless otherwise specified report all data on the basis of <2 mm material.

1.32 Particles < specified size >2 mm

The maximum coarse-fragment size for the >2 mm base varies. The base usually includes fragments as large as 75 mm if they are

present in the soil. The maximum size for fragments larger than 75 mm is decided during sampling. It is established either because of the difficulty of handling larger material or because, by definition soil does not include material larger than 250 mm in diameter. Record the particle size set as the maximum for the soil being sampled. The base used to calculate the percentages of fractions >2 mm includes all material smaller than the maximum size specified for the sample.

References

(1) Canada Soil Survey Committee, 1978. The Canadian System of Soil Classification. Agr. Can. Publ. 1646.

(2) Soil Conservation Service, 1972. Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. Soil Survey Investigations Report No. 1 (Revised 1972). U.S.D.A. Washington, D.C.

2. - PHYSICAL ANALYSES

Only the more commonly-used physical methods are included. Some of these methods are used in the preparation of soils for mineralogical analysis. Other physical methods that apply mainly to mineralogical determinations are given in the section on mineralogical methods, e.g. heavy mineral separation.

2.1 PARTICE-SIZE ANALYSIS - A.J. Green

Particle-size analysis is the measurement of the proportions of the various sizes of primary soil particles as determined usually either by their capacities to pass through sieves of various mesh size or by their rates of settling in water. The proportions are usually represented by the relative weights of particles within stated size classes. The limits of these size classes differ in various commonly used systems of soil particle-size classification (Fig 1). In this Manual the CSSC system is used. For engineering interpretations, the AASHO and the Unified systems are used.

There is no general 'best' method of doing particle-size analysis. The best method in a particular case depends upon the nature of the soil being analyzed, the purposes of the analysis, time constraints, and the equipment available. No method yields absolute results, all methods are empirical. Different methods of pretreatment yield different results. Thus particle-size data must be operationally defined; the results depend upon the method. It is important to follow a specific method and to specify the method used when presenting the data. It is important also, to include reference samples with groups of unknown samples to ensure consistency of results.

A few points are listed that might aid the uninitiated in the choice of a method.

1. Pretreatments - The determination of the distribution of sizes of the primary particles of a soil sample should, ideally, involve no pretreatment because such treatments are likely to fragment some particles and to dissolve some others. However, pretreatments are necessary to break down aggregates in most soils. Chemical pretreatments are used commonly to remove materials that may bind primary particles together: acid - removes carbonates, hydrogen peroxide - removes organic matter, dithionite-citrate-bicarbonate - removes iron oxides. All of these pretreatments might alter or dissolve some primary soil minerals. Physical treatments such as violent stirring to break down aggregates can fragment primary particles. Ultrasonic treatment (Genrich and Bremner, 1974) has been used in recent years instead of chemical pretreatments but it is subject to the problem that a brief, low energy treatment may not disperse aggregates and a prolonged, high energy treatment will fragment primary particles. For most samples, the pretreatments indicated in 2.112 are adequate.

2. Purpose of analysis - If one of the purposes of particle-size analysis is to obtain a sample of the clay fraction of a soil for mineralogical analysis, the method should be chosen so as to ensure a suitable sample. Iron oxides should be removed (2.111) from some samples to permit the determination of phyllosilicate minerals by

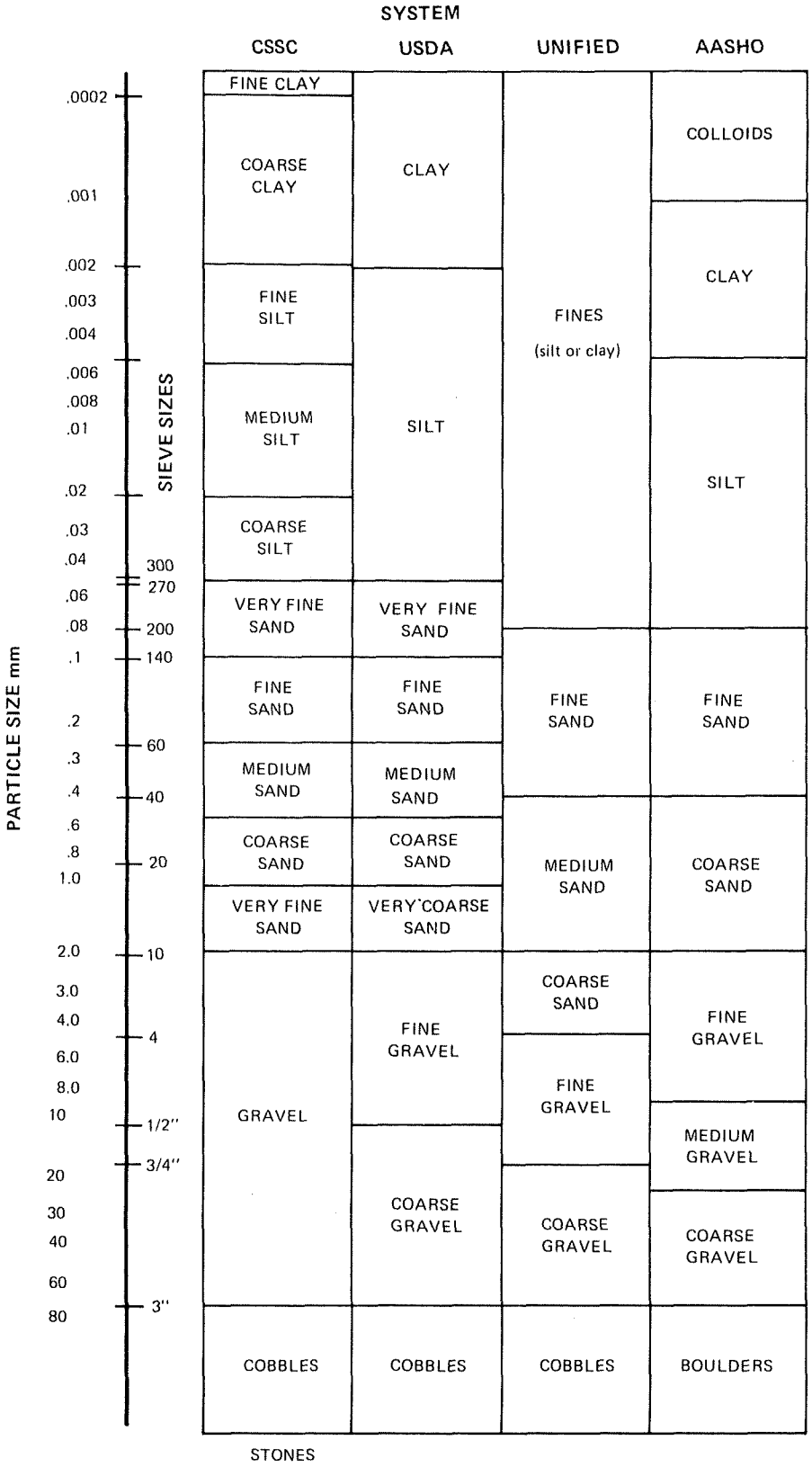


Fig. 1 A comparison of particle-size limits in 4 systems of particle-size classification.

AASHO - American Association of State Highway Officials
USDA - United States Department of Agriculture
CSSC - Canada Soil Survey Committee

x-ray diffraction but this is not necessary for most samples. However, if the interest is in iron oxides or carbonates in the clay fraction, pretreatments with dithionite-citrate-bicarbonates and with acid must be avoided. Pretreatments involving the addition of sodium hexametaphosphate, $(NaPO_3)_6$ and sodium carbonate (pH of solution 9.5-10) to disperse the sample are not desirable if clay mineralogy is to be determined. Sodium hexametaphosphate was sold under the trade name 'Calgon' but the Calgon sold now does not contain soluble phosphates. A product sold as 'Instant Calgon' is largely sodium hexametaphosphate and it is suitable as a dispersant of soils (Veneman, 1977). Sieve analysis (2.13) is suitable if the purpose of the analysis is to make engineering interpretations, but this method is not suitable for studies of clay translocation in soils.

3. Newer methods than the hydrometer and pipette methods appear from time to time - plummet balance, falling drop method, etc. These are not listed but some of them might be preferable to older methods for some purposes. New methods should be checked against the pipette method which is considered as standard.

The methods outlined are listed in order of decreasing severity of pretreatment. References cited are listed at the end of the section on particle-size analysis.

2.11 Particles <2 mm, Pipet Method

2.111 Pretreatments to remove carbonates, organic matter, soluble salts and iron oxides

Apparatus

Beakers - 100 ml to 1000 ml; centrifuge bottles both glass and plastic - 250 ml

Centrifuges - low speed, about 1500 rpm; and preferably in addition - high speed, about 12000 rpm with 250 ml bottles

Shakers - end over end at about 30 rpm; sieve shaker; paint shaker; holders for 250 ml centrifuge bottles on paint shaker

Cylinders - 1000 ml

Stirrers - electric stirrers; hand stirrer made by joining a circular piece of perforated brass sheeting to the end of a brass rod about 50 cm long and placing a wide rubber band around the edge of the brass sheeting.

Constant temperature water bath with clips on base to hold cylinders in place.

pH Meter

Shaw Pipet rack - (no longer easily available) or similar device to permit sliding the pipet laterally, and lowering the pipet to a precise depth in the suspensions within the cylinders (Day, 1965; Clark, 1962)

Lowy Pipets - (Arthur H. Thomas Co.) or other source

Weighing Bottles - (beakers can be used)

Set of sieves with openings as follows (in mm) - 1.0, 0.5, 0.25, 0.105, 0.047 (300 mesh)

Reagents

Hydrogen peroxide, approx. 30%; HCl, 1N; citrate-bicarbonate buffer - prepare 0.3M sodium citrate (88.4 g/ℓ) and add 125 ml of 1M $NaHCO_3$ (84 g/ℓ) to each litre of citrate solution; sodium dithionite (hydrosulphite); saturated NaCl solution; 10% NaCl solution; acidified 1 M $CaCl_2$ (0.1 ml of 1N HCl per ℓ of solution).

Procedure

A. Removal of carbonates and soluble salts

(1) weigh 2 mm, air-dry soil into a 250 ml centrifuge bottle (10g for clays, 20g for loams, 40g for sandy loams and loamy sands, and 80g for sands). Weights are optional, but these are suitable if clay samples are required for mineralogy.

(2) either (a) add about 100 ml of water, mix and add 1N HCl dropwise until the pH falls to between 3.5 and 4.0 and remains below for 10 minutes. Centrifuge (about 10 minutes at 1500 rpm) until the centrifugate is clear and pour it off. Wash the soil twice by shaking with 50 ml of water, centrifuging and discarding the centrifugate if it is clear. If the centrifugate is not clear, proceed to step B. Soils containing high amounts of soluble salts and soils containing gypsum may require further centrifuge washing, or washing through a filter candle (Pasteur-Chamberlain filters, fineness F) to remove salts (check for salts by testing with $AgNO_3$ for Cl^- and $BaCl_2$ for SO_4^{-2}) or;

(b) add about 200 ml of 1N sodium acetate buffered at pH 5 (acetic acid), stir and heat to about 80°C for half an hour, or until CO_2 bubbles are no longer evident. Centrifuge, decant and repeat the treatment for samples high in carbonates until no further evolution of CO_2 occurs. Centrifuge and decant.

NOTE: Procedure 'b' is preferred by some for dissolving carbonate as the pH is maintained at 5 or more and there is thus less possibility of alteration of clay minerals than with treatment 'a'. However, unpublished work of Brydon indicated that the problem was more theoretical than real for the soils studied.

B. Removal of organic matter

(1) Add about 25 ml of water to the soils in the centrifuge bottles and shake on the paint shaker. Transfer samples containing high amounts of organic matter (> about 5%) to 1000 ml beakers. Retain the same centrifuge bottles, without washing, for further treatments.

(2) Add about 5 ml of H_2O_2 to the soil suspension, stir, cover, and observe closely for several minutes. If excessive frothing occurs, cool the container in cold water. Add more H_2O_2 when the reaction subsides. Heat to about 90°C when frothing has ceased to occur, remove cover when reaction has ceased and evaporate excess water (do not take to dryness). Continue additions of peroxide and evaporation when reaction subsides until most of the organic matter has been destroyed (as judged by the rate of reaction and the color of the sample). Rinse down the sides of the reaction vessel occasionally. Heat for about an hour after the final addition of peroxide to destroy excess peroxide. Transfer samples in beakers to centrifuge bottles.

(3) Add about 25 ml of 10% NaCl to the samples, mix, centrifuge and pour off the clear centrifugate. Add about 50 ml of 10% NaCl, shake to loosen the soil, centrifuge and pour off the supernatant solution if it is clear. If the centrifugate is not clear, continue with the next step.

C. Removal of iron oxides

(1) Add citrate-bicarbonate buffer to the samples in 250 ml glass centrifuge bottles to bring the total volume of solution to about 150 ml. Shake to disperse the soil. Add 3g of sodium dithionite ($Na_2S_2O_4$) gradually as some samples may froth. Put the bottles into a water bath at 80°C and stir the suspensions intermittently for 20 minutes. Remove the samples from the bath, add 10 ml saturated NaCl, mix, centrifuge and pour off the centrifugate. It may be combined with subsequent centrifugates,

if any, and analyzed for dithionite-extractable Fe, Al, Mn, etc. If the samples are completely gray (gleyed), proceed to (2). If brownish color remains, repeat (1).

(2) Wash the samples once with 50 ml of citrate-bicarbonate buffer plus 20 ml of saturated NaCl (shake, centrifuge and decant). Wash it twice with 50 ml of 10% NaCl, twice with about 50 ml of H_2O. If the wash solutions are not clear, transfer the samples to plastic centrifuge bottles and centrifuge at high speed. If this fails to yield clear centrifugates, add acetone, warm the samples and recentrifuge.

(3) Add about 150 ml of H_2O, shake the samples and check the pH. It should be above 8 as the soil is Na-saturated.

(4) Either, (a) transfer the suspensions to 1 ℓ shaker bottles, add water to about 400 ml and shake overnight on an end-over-end shaker, or (b) transfer the samples to a mechanical analysis stirrer cup (milkshake type) and stir for 5 minutes with an electric stirrer. Procedure (a) is preferred as the milkshake machine can break up primary particles.

D. Separation of the sand fractions

(1) Pour the suspensions through a 300 mesh (47 μm) sieve (or a 270 mesh, 53 μm, if a 300 mesh is unavailable) into a 1 ℓ sedimentation cylinder. A sieve of about 8 cm diameter is placed in a large funnel held by a stand above the cylinder. Tap the funnel gently and wash the sand thoroughly on the sieve. Collect the washings in the cylinder.

(2) Transfer the sand to a tared beaker or aluminum weighing dish, dry (105°C) and weigh.

(3) Transfer the dried sand to a nest of sieves (about 6 cm diameter) arranged as follows from top to bottom: 1 mm, 0.5 mm, 0.25 mm (60 mesh), 0.105 mm (140 mesh), 0.047 mm (300 mesh), pan. Put sand on the top and shake the sieves on a sieve shaker. The time of shaking depends on the shaker, 3 min. is suitable for some. Weigh each sand fraction and the residual silt that has passed through the 300 mesh sieve.

E. Determination of silt fractions

The <20 μm and the <5 μm fractions can be determined by pipette, if desired, by following the general procedure outlined in F for clay. The settling time for sampling at 10 cm at 20°C are: <20 μm

- 4.6 minutes; <5 μm - 74 minutes. The 20 to 50 μm silt can be separated by repeated sedimentation (9.2 min. for a depth of 20 cm at 20°C). See Jackson (1956) for details.

F. Determination of clay (0 to 2 μm)

(1) Place the cylinders containing the silt and clay suspensions in a water bath, make up to 1 ℓ with distilled water and cover with a watch glass. Let them stand several hours or overnight to equilibrate.

(2) In the morning, stir the suspensions thoroughly with an electric stirrer followed by 1/2 minute stirring with an up and down motion of the hand stirrer. Note the time at completion of stirring and the temperature of the water bath. It is convenient to complete stirring of adjacent suspensions at intervals of about 3 minutes.

(3) After the appropriate time interval depending upon the temperature (Table 1) lower the closed Lowy pipette carefully to a depth of 10 cm and turn on the vacuum so as to withdraw a 25 ml sample in about 12 seconds. A device for controlling the vacuum is required. Discharge the sample into a tared and numbered weighing bottle, or beaker, or aluminum dish. Rinse the pipet with distilled water and add the rinse water to the clay suspension in the weighing bottle. Evaporate the water, dry the clay at 105°C, cool in a desiccator and weigh.

Table 1. Settling Time for 2 μm Clay at Various Temperatures (for 10 cm)

Temperature	Time
20°	7 hr. 40 min.
21	7 hr. 33 min.
22	7 hr. 25 min.
23	7 hr. 17 min.
24	7 hr. 9 min.
25	7 hr.
26	6 hr. 51 min.

G. Sampling of 2 μm clay for X-ray analysis (if desired)

(1) About 300 mg of dry clay is required so the volume of suspension needed depends both upon the weight of sample and the percentage of clay. Table 2 serves as a general guide. If chemical as well as mineralogical analysis of the clay is to be done, more than 300 mg may be required.

Table 2. General guidelines on the weight of soil sample and the volume of suspension required to obtain an adequate clay sample for mineralogical analysis.

Wt. of Sample	Approx. % Clay	Approx. Time of Sampling	Volume of Sample	Depth of Sampling
20 g	>40	7 hr.	50 ml	8.5 cm
20 g	20-40	7 hr.	100 ml	8.5 cm
20 g	10-20	7 hr.	150 ml	8.5 cm
40 g	6-10	7 hr.	150 ml	8.5 cm
80 g	3- 6	7 hr.	150 ml	8.5 cm
80 g	0.5- 3	18 hr.	700 ml	25 cm

The samples to be taken at 8.5 cm (the depth depends upon the diameter of the cylinder) may be taken immediately after F. For samples to be taken at 25 cm, the cylinder should be shaken after F and the sample taken the next day. The samples must be siphoned or pipetted off with the least possible disturbance of the suspension. Measure and record the volume of suspension sampled.

(2) The clay in the suspensions is flocculated by adding 5 ml acidified 1M $CaCl_2$; the suspension is centrifuged and the centrifugate is discarded. (Use 1M $MgCl_2$ if Mg-clay is desired for mineralogical analysis; methods 5.22 and 5.24).

(3) Transfer the clay to 50 ml plastic centrifuge tubes. Add 5 ml acidified 1M $CaCl_2$, shake, centrifuge and decant.

(4) Wash the clay 2 or 3 times with about 10 ml of distilled water by shaking, high speed centrifuging and decanting. Check the last wash solution to ensure that Cl^- is absent (as indicated by the absence of a white precipitate when a saturated solution of $AgNO_3$ is added).

(5) Disperse the clay in 2 or 3 ml of water and freeze-dry, or air-dry and crush to a fine powder, or keep the clay in suspension.

H. Determining fine clay (<0.2 μm)

(1) Pour about 200 ml of suspension from the sedimentation cylinders into 250 ml centrifuge bottles. Shake the suspensions, and centrifuge at the appropriate speed for the time necessary to sediment particles coarser than 0.2 μm to a depth of 5 cm (54 minutes at 1500 RPM on an IEC Model V Centrifuge). The formula to use is based on Stoke's law:

$$t = \frac{63.0 \times 10^8 \; n \; 1\log R/S}{N^2 D^2 \Delta s}$$ where

n = viscocity in poises at the existing temperature

R = radius of rotation (cm) of the top of the sediment in the tube

S = radius of rotation (cm) of the surface of the suspension in the tube

N = revolutions per minute

D = particle diameter in μm

Δs = difference in specific gravity between the solvated particle and the suspending liquid (usually use $\Delta s = 1.65$)

t = time in minutes
(See Jackson, 1956 for tables of centrifuging times and speeds).

(2) Withdraw a 25 ml aliquot from a depth of 5 cm. Discharge the sample into a tared weighing bottle or beaker, rinse the pipette, add the rinsing to the weighing bottle, dry at 105°C, cool in a desiccator and weigh.

(3) Shake the centrifuge bottle and return the remaining suspension to the original sedimentation cylinder.

NOTE: Fine clay (<0.2 μm) may be separated for x-ray analysis as described above.

I. Separating <0.08 μm clay

This fraction is separated for mineralogical analysis in some studies. A supercentrifuge is used (see Whittig, 1965 and Jackson, 1956).

J. Determining the weight of treated soil

(1) Add 10 ml of 1M $CaCl_2$ and 1 ml of 1N HCl (to prevent $CaCO_3$ formation) to the suspension remaining in the cylinder. Siphon off the clear solution after flocculation has occurred. Transfer the soil from the cylinder to a tared beaker, evaporate, dry at 105°C and weigh.

(2) Weight of treated soils (Y) = weight of sediment remaining in cylinder + weight of <0.2 µm clay in 25 ml + (volume of suspension removed for determining 2 µm clay and for x-ray sample) x (1/25 weight of 2 µm clay in 25 ml) + weight of sand including residual silt.

(3) Calculate percentages of fractions:

Sand % = 100 x (weight of sand)/Y

Total clay % = 4000 x (weight of 2 µm clay in 25 ml)/Y

Fine clay % = 4000 x (weight of 0.2 µm clay in 25 ml)/Y

Silt % = 100 - (total clay % + sand %)

NOTES: (1) Calculations are made most conveniently by computer. All weights and volumes are recorded on coding sheets, a computer program is devised and all calculations are done automatically.

(2) Some of the steps may be omitted depending on the purposes of the analysis. For example, in some cases, it is not necessary to separate the sand fractions; in others, no sample is required for x-ray analysis.

2.112 Pretreatments to remove soluble salts, carbonates and organic matter

(1) Proceed as in 2.111 to the end of step B 2 (peroxide treatment).

(2) Centrifuge the H_2O_2 treated suspensions and decant. Add 50 ml distilled water, shake to disperse the soil, centrifuge and test the centrifugate for salts ($AgNO_3$ solution for chlorides; $BaCl_2$ for sulfates). Repeat centrifuge washing until the test for salts is negative.

(3) Transfer the samples to shaker bottles, add 10 ml of Instant Calgon solution (50.0g commercial Instant Calgon made to 1 ℓ with distilled water), add water to approximately 400 ml (if 1 ℓ bottles

are used). If "Instant Calgon" is not available use sodium hexametaphosphate with enough Na_2CO_3 added to bring the pH to 10 (35.7 g of $(NaPO_3)_6$ + 7.9 g of Na_2CO_3 per ℓ is suitable). Shake overnight on an end-over-end shaker. Alternatively, stir for 5 minutes with a mechanical analysis stirrer (See 2.111, C 4). Proceed as in steps D to H of 2.111 except that in H, the weight of clay must be corrected for the Calgon. To determine the correction factor, add 10 ml Calgon solution to a 1 ℓ cylinder, make to volume, stir thoroughly, withdraw duplicate 25 ml samples, dry and weigh (about .012g).

2.113 Pretreatments to remove soluble salts and organic matter

(1) Weigh out a sample as described in A1 of procedure 2.111. Samples high in organic matter should be weighed directly into large beakers.

Treat for organic matter removal with H_2O_2 as described in 2.111, step B 2. Neutral to alkaline samples containing MnO_2 will catalyze the decomposition of H_2O_2 and organic matter will not be oxidized. Such samples should be acidified (HCl) if carbonates are absent or if dissolution of carbonates is acceptable.

(2) Proceed as in steps (2) and (3) of procedure 2.112.

2.114 Water-dispersible clay

Weigh samples as outlined in 2.111, step A 1, into shaker bottles, half fill with distilled water, shake overnight on an end-over-end shaker, and proceed as in 2.111, steps D to H. Normally the sand fractions would not be separated.

2.115 Ultrasonic dispersion in water (Genrich & Bremner, 1974)

This specific procedure has not been tested in Canada.

Apparatus

Ultrasonic probe such as Bronson Model W-185C Sonifier (Heat Systems-Ultrasonic Inc., Plainview, N.Y.) with solid probe (tip diameter 1.27 cm).
Magnetic stirrer and teflon-coated stirring bar (3.8 cm long).
250 ml stainless steel beakers.
Cooling jacket to fit beakers.

Procedure

1. Weigh 60 g of air-dry, 2 mm soil into a 250 ml stainless steel beaker containing a stirring bar and add 150 ml of distilled water.

2. Fit the beaker with a cooling jacket and connect the jacket to a cold water tap.

3. Stir the soil magnetically, insert the tip of the ultrasonic probe about 3 cm below the surface of the stirred suspension and vibrate the suspension for 30 min. with the power output adjusted to obtain a meter reading of 100.

4. Proceed as in 2.111 steps D to H.

2.12 Particles <2 mm - Hydrometer Method

A hydrometer can be used to measure the density of a soil suspension after various times of settling and hence the particle-size distribution. Such measurements can be made of suspensions prepared by any of the pretreatments outlined in 2.11, but only one pretreatment is given here. The hydrometer method outlined is that of Day (1965). Simpler methods can be found in the literature (Bouyoucos, 1962).

2.121 Without pretreatment, except dispersion with Instant Calgon (see 2.112)

Apparatus and Reagents

Standard hydrometer, ASTM No. 152 H, with Bouyoucos scale in g/ℓ; electric stirrer; plunger; cylinders with 1 ℓ mark 36 ± 2 cm from the bottom of the inside; glassware; amyl alcohol, Calgon solution (50 g/ℓ); constant temperature room (if possible).

A. Calibration of hydrometer

(1) Add 100 ml of Calgon solution to the cylinder and make the volume to 1 ℓ with distilled water. Mix thoroughly with plunger and let stand until the temperature is constant; record temperature.

(2) Lower the hydrometer into the solution carefully, and determine the scale reading R_L at the upper edge of the meniscus surrounding the stem.

NOTE: If a constant temperature room is not used, measure R_L at the temperatures likely to occur.

B. Dispersion of soil

(1) Weigh 40.0g of soil (100g of loamy sand or sand) into a 600 ml beaker, add 100 ml of Calgon solution and about 300 ml distilled water and allow the sample to soak overnight.

(2) Weigh another sample of the same soil (about 10g) for determination of oven-dry weight. Dry overnight at 105°C, cool and weigh.

(3) Transfer the Calgon treated sample to a dispersing cup and mix for 5 minutes with the electric mixer (milkshake machine), or transfer the suspension to shaker bottles and shake overnight on an end-over-end shaker.

(4) Transfer the suspension to a cylinder, add distilled water to bring the volume to 1 ℓ. Move the cylinder to the constant temperature sedimentation room.

C. Stirring and hydrometer measurements

(1) Allow time for the suspensions to equilibrate with room temperature and record the temperature.

(2) Insert the plunger and move it up and down to mix the contents thoroughly. Dislodge sediment with strong upward strokes of the plunger near the bottom and by spinning the plunger while the disc is just above the sediment. Finish stirring with 2 or 3 slow, smooth strokes. Record the time of completion of stirring. Add a drop of amyl alcohol if the surface of the suspension is covered with foam.

(3) Lower the hydrometer carefully into the suspension and take readings after 30 seconds and again at the end of 1 minute.

(4) Remove the hydrometer carefully after the 1 minute reading, rinse it and wipe it dry.

(5) Reinsert the hydrometer carefully about 10 seconds before each reading and take readings at 3, 10, 30, 90, 270 and 1080 minutes (times of reading can be modified according to convenience and to the purpose of analysis). Carefully remove and clean the hydrometer after each reading. Record the reading R at each time.

D. Calculation of particle-size

(1) Calculate for each reading the concentration of suspension in g/ℓ from the equation $c = R-R_L$

(2) Calculate the summation percentage from the equation P = 100 c/co where co is the oven-dry weight of the sample analyzed (g/ℓ suspension, calculated from the water percentage of the sample that was oven-dried).

(3) Calculate the corresponding particle size by the equation X (μm) = $y/t^{1/2}$ where t is the sedimentation time in minutes and y is a sedimentation parameter (see Table 3).

(4) Plot P (summation percentage) against X on semilog paper and interpolate to read percentages less than particular diameters required such as 2, 5, 20, and 50 μm (Fig. 2).

(5) If desired, separate the sand fractions as described in 3.11.

Table 3. Values of y at 30°C for the determination of particle size from observed hydrometer readings (Day, 1965)

R	y	R	y	R	y
- 5	50.4				
- 4	50.1	11	46.4	26	42.2
- 3	49.9	12	46.2	27	41.9
- 2	49.6	13	45.9	28	41.6
- 1	49.4	14	45.6	29	41.3
0	49.2	15	45.3	30	41.0
1	48.9	16	45.0	31	40.7
2	48.7	17	44.8	32	40.4
3	48.4	18	44.5	33	40.1
4	48.2	19	44.2	34	39.8
5	47.9	20	43.9	35	39.5
6	47.7	21	43.7	36	39.2
7	47.4	22	43.4	37	38.9
8	47.2	23	43.1	38	38.6
9	47.0	24	42.8	39	38.3
10	46.7	25	42.5	40	38.0

NOTE: 1. For temperatures other than 30°C, the values of y can be corrected by multiplying by $(n/n_{30})^{\frac{1}{2}}$ where n is the viscosity of water at the temperature of measurement and n_{30}, the viscosity at 30°C is 0.008007 poise (Table 4).

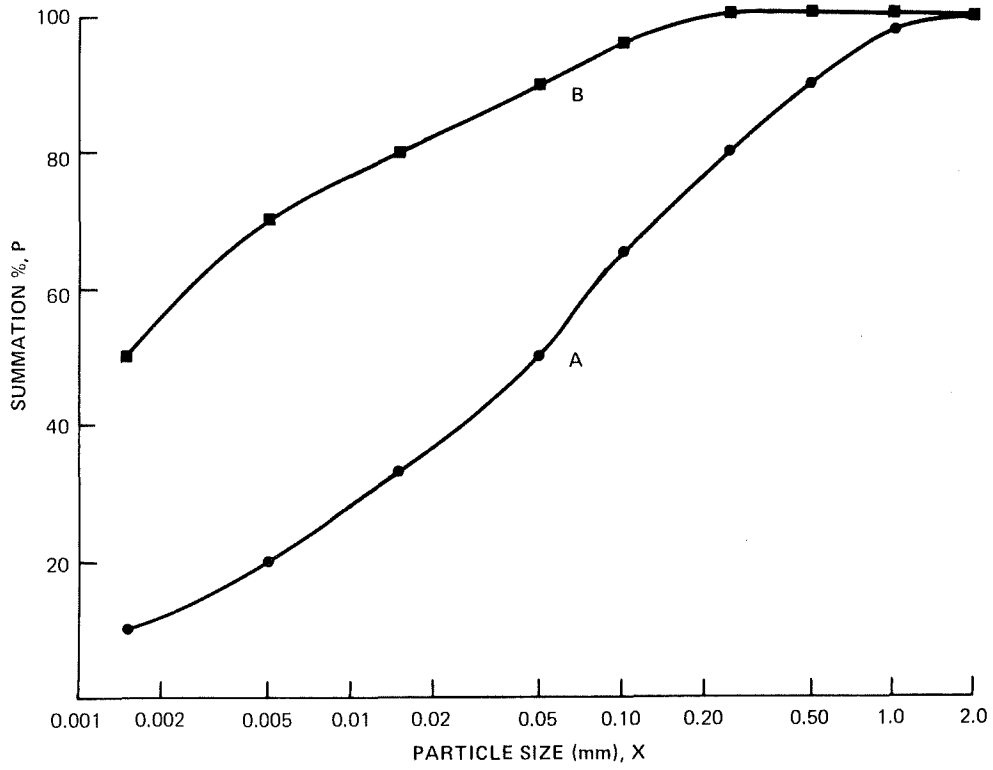


Fig. 2 Summation curves for soils A and B plotted on a logarithmic scale of particle size. Particle-size data for the soils are as follows;

	Percentage of soil finer than the indicated size limit (mm)								
	.0015	.005	.015	.050	.10	.25	.50	1.0	2.0
Soil A	10	20	33	50	65	80	90	98	100
Soil B	50	70	86	90	96	100	100	100	100

Table 4. Correction factors for y at various temperatures.

^{o}C	$(n/n_{30})^{\frac{1}{2}}$	^{o}C	$(n/n_{30})^{\frac{1}{2}}$	^{o}C	$(n/n_{30})^{\frac{1}{2}}$
18	1.148	22.5	1.088	27.0	1.033
18.5	1.142	23.0	1.082	27.5	1.026
19.0	1.135	23.5	1.075	28.0	1.021
19.5	1.128	24.0	1.070	28.5	1.015
20.0	1.121	24.5	1.063	29.0	1.010
20.5	1.114	25.0	1.055	29.5	1.005
21.0	1.109	25.5	1.050	30.0	1.000
21.5	1.100	26.0	1.045		
22.0	1.092	26.5	1.037		

2. The correction for temperature can be included in the calculation of diameter as follows:

$$\text{diameter } \mu m = \frac{y(n/n_{30})^{\frac{1}{2}}}{t^{\frac{1}{2}}}$$

Diameters as a function of temperature and hydrometer readings (R) at various times can be read directly from Table 5.

Table 5. Particle diameter as a function of temperature and hydrometer reading (R) at various times.

Diameter in microns at 30 sec.

T^{o}	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
R											
1	77.5	77.1	76.7	76.1	75.5	75.3	74.8	74.4	74.0	73.5	73.0
2	77.2	76.7	76.4	75.8	75.2	74.9	74.5	74.0	73.7	73.2	72.7
3	76.7	76.2	75.9	75.3	74.8	74.5	74.1	73.6	73.3	72.8	72.2
4	76.4	75.9	75.6	75.0	74.4	74.2	73.8	73.3	73.0	72.5	71.9
5	75.9	75.5	75.1	74.5	74.0	73.7	73.4	73.0	72.5	72.0	71.5
6	75.6	75.2	74.6	74.2	73.7	73.4	73.0	72.5	72.2	71.7	71.2
7	75.2	74.7	73.7	73.4	73.4	72.9	72.6	72.2	71.8	71.3	70.7
8	74.8	74.4	73.8	73.4	73.0	72.6	72.3	71.8	71.4	71.0	70.4
9	74.5	74.0	73.5	73.0	72.7	72.3	71.9	71.4	71.1	70.7	70.1
10	74.0	73.6	73.0	72.7	72.2	71.9	71.5	71.1	70.7	70.2	69.7
11	73.6	73.1	72.7	72.2	71.9	71.4	71.1	70.7	70.2	69.8	69.2
12	73.2	72.8	72.3	71.9	71.4	71.1	70.7	70.2	69.9	69.5	68.9
13	72.8	72.3	71.9	71.4	71.0	70.6	70.2	69.9	69.5	69.0	68.5
14	72.3	71.8	71.4	70.9	70.5	70.2	69 8	69.4	69.0	68.6	68.0
15	71.8	71.4	70.9	70.5	70.0	69.7	69.3	69.0	68.5	68.1	67.6
16	71.4	70.9	70.5	70.0	69.7	69.2	69.0	68.6	68.1	67.7	67.1
17	71.0	70.6	70.1	69.7	69.2	68.9	68.5	68.1	67.8	67.4	66.9
18	70.6	70.1	69.7	69.2	68.8	68.5	68.1	67.7	67.3	66.9	66.4

Table 5. (cont'd)

Diameter in microns at 30 sec.

T° / R	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
19	70.0	69.6	69.2	68.8	68.4	68.0	67.6	67.3	66.9	66.5	66.0
21	69.3	68.9	68.4	68.0	67.5	67.2	66.8	66.4	66.1	65.7	65.2
22	68.8	68.4	67.9	67.5	67.2	66.8	66.4	66.0	65.7	65.3	64.8
23	68.4	67.9	67.5	67.1	66.7	66.3	65.9	65.6	65.2	64.8	64.3
24	67.9	67.4	67.0	66.6	66.2	65.9	65.5	65.1	64.8	64.4	63.9
25	67.4	67.0	66.5	66.1	65.8	65.4	65.0	64.6	64.3	63.9	63.4
26	66.9	66.5	66.1	65.7	65.3	64.9	64.5	63.2	63.9	63.4	63.0
27	66.4	66.0	65.6	65.2	64.8	64.5	64.1	63.7	63.4	63.0	62.5
28	66.0	65.5	65.1	64.7	64.4	64.0	63.6	63.2	62.9	62.5	62.1
29	65.5	65.1	64.7	64.3	63.9	63.5	63.1	62.8	62.5	62.1	61.6
30	65.0	64.6	64.2	63.8	63.4	63.1	62.7	62.4	62.0	61.6	61.2
31	64.4	64.1	63.8	63.3	62.9	62.6	62.3	61.9	61.6	61.1	60.7
32	64.0	63.7	63.4	62.9	62.4	62.2	61.8	61.4	61.1	60.7	60.3
33	63.5	63.1	62.9	62.4	61.9	61.7	61.4	61.0	60.7	60.3	59.8
34	63.1	62.7	62.4	61.9	61.5	61.2	60.9	60.5	60.2	59.8	59.4
35	62.6	62.2	62.0	61.5	61.0	60.8	60.5	60.1	59.8	59.4	58.9
36	62.1	61.8	61.5	61.0	60.5	60.3	60.0	59.6	59.3	58.9	58.5
37	61.6	61.3	61.0	60.5	60.1	59.9	59.5	59.1	58.9	58.5	58.0
38	61.2	60.8	60.5	60.1	59.6	59.4	59.1	58.7	58.4	58.0	57.6
39	60.7	60.3	60.0	59.6	59.2	58.9	58.6	58.2	58.0	57.6	57.2
40	60.2	59.9	59.6	59.1	58.7	58.5	58.2	57.8	57.5	57.1	56.7

Diameter in microns at 1 min.

1	54.8	54.5	54.2	53.8	53.4	53.2	52.9	52.6	52.3	52.0	51.6
2	54.5	54.3	54.0	53.6	53.2	53.0	52.7	52.4	52.1	51.8	51.4
3	54.2	53.9	53.7	53.2	52.9	52.7	52.4	52.0	51.8	51.4	51.1
4	54.0	53.7	53.5	53.0	52.6	52.4	52.1	51.8	51.6	51.2	50.9
5	53.7	53.4	53.1	52.7	52.4	52.1	51.8	51.6	51.2	50.9	50.5
6	53.5	53.1	52.8	52.5	52.2	51.9	51.6	51.2	51.0	50.7	50.3
7	53.2	52.8	52.5	52.1	51.8	51.6	51.3	51.0	50.7	50.4	50.0
8	52.9	52.6	52.3	51.9	51.6	51.3	51.1	50.7	50.5	50.2	49.8
9	52.7	52.3	52.0	51.7	51.4	51.1	50.8	50.5	50.3	50.0	49.6
10	52.3	52.0	51.7	51.4	51.1	50.8	50.5	50.3	50.0	49.6	49.3
11	52.0	51.7	51.4	51.0	50.8	50.5	50.3	50.0	49.6	49.3	49.0
12	51.8	51.5	51.1	50.8	50.5	50.3	50.0	49.6	49.4	49.1	48.7
13	51.5	51.1	50.8	50.5	50.2	49.9	49.6	49.4	49.1	48.8	48.4
14	51.1	50.8	50.5	50.2	49.9	49.6	49.3	49.1	48.8	48.5	48.1
15	50.8	50.5	50.2	49.8	49.5	49.3	49.0	48.8	48.5	48.2	47.8
16	50.5	50.1	49.8	49.5	49.3	49.0	48.7	48.5	48.1	47.8	47.5
17	50.2	49.9	49.6	49.3	49.0	48.7	48.4	48.1	47.9	47.6	47.3
18	49.9	49.6	49.3	48.9	48.6	48.4	48.1	47.9	47.6	47.3	46.9
19	49.5	49.2	48.9	48.6	48.3	48.1	47.8	47.5	47.3	47.0	46.6
20	49.2	48.9	48.6	48.3	48.1	47.8	47.5	47.2	47.0	46.7	46.3
21	48.9	48.7	48.3	48.1	47.8	47.5	47.2	47.0	46.8	46.5	46.1
22	48.6	48.3	48.0	47.7	47.4	47.2	46.9	46.7	46.4	46.1	45.8
23	48.3	48.0	47.7	47.4	47.1	46.9	46.6	46.4	46.1	45.8	45.5
24	48.0	47.7	47.4	47.1	46.9	46.6	46.3	46.0	45.8	45.5	45.2

Table 5. (contd.)

Diameter in microns at 1 min.

T° / R	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
25	47.6	47.3	47.0	46.7	46.5	46.2	45.9	45.7	45.5	45.2	44.8
26	47.3	47.0	46.7	46.4	46.1	45.9	45.6	45.4	45.1	44.9	44.5
27	47.0	46.7	46.4	46.1	45.8	45.6	45.3	45.1	44.8	44.5	44.2
28	46.6	46.3	46.0	45.8	45.5	45.3	45.0	44.7	44.5	44.2	43.9
29	46.3	46.0	45.7	45.4	45.1	44.9	44.6	44.4	44.2	43.9	43.6
30	45.9	45.7	45.4	45.1	44.8	44.6	44.3	44.1	43.9	43.6	43.3
31	45.6	45.3	45.1	44.8	44.4	44.3	44.0	43.8	43.5	43.3	42.9
32	45.2	45.0	44.8	44.4	44.1	44.0	43.7	43.4	43.2	42.9	42.6
33	44.9	44.7	44.5	44.1	43.8	43.6	43.4	43.1	42.9	42.6	42.3
34	44.6	44.3	44.1	43.8	43.5	43.3	43.1	2.8	42.6	42.3	42.0
35	44.2	44.0	43.8	43.5	43.1	43.0	42.7	42.5	42.3	42.0	41.7
36	43.9	43.7	43.5	43.1	42.8	42.6	42.4	42.1	41.9	41.7	41.4
37	43.6	43.3	43.1	42.8	42.5	42.3	42.1	41.8	41.6	41.4	41.0
38	43.2	43.0	42.8	42.5	42.2	42.0	41.8	41.5	41.3	41.0	40.7
39	42.9	42.7	42.5	42.1	42.0	41.8	41.5	41.3	41.0	40.7	40.4
40	42.6	42.3	42.1	41.8	41.5	41.3	41.1	40.9	40.7	40.4	40.1

Diameter in microns at 3 min.

1	31.6	31.5	31.3	31.1	30.8	30.7	30.5	30.4	30.2	30.0	29.8
2	31.5	31.3	31.2	30.9	30.7	30.6	30.4	30.2	30.1	29.9	29.7
3	31.3	31.1	31.0	30.8	30.5	30.4	30.2	30.0	29.9	29.7	29.5
4	31.2	31.0	30.9	30.7	30.4	30.2	30.1	29.9	29.8	29.5	29.4
5	31.1	31.0	30.9	30.5	30.3	30.1	30.0	29.7	29.6	29.4	29.2
7	30.8	30.7	30.5	30.3	30.0	29.8	29.7	29.4	29.3	29.1	28.9
8	30.6	30.5	30.4	30.1	29.8	29.7	29.5	29.3	29.2	29.0	28.8
9	30.4	30.2	30.1	29.9	29.7	29.5	29.3	29.1	29.0	28.8	28.6
10	30.3	30.1	29.9	29.7	29.5	29.3	29.2	29.0	28.9	28.7	28.4
11	30.1	29.9	29.7	29.5	29.3	29.2	29.0	28.8	28.7	28.5	28.3
12	29.9	29.7	29.5	29.4	29.2	29.0	28.8	28.7	28.5	28.4	28.1
13	29.7	29.5	29.4	29.2	29.0	28.8	28.7	28.5	28.4	28.2	28.0
14	29.5	29.4	29.2	29.0	28.8	28.7	28.5	28.3	28.2	28.0	27.8
15	29.4	29.2	29.0	28.8	28.6	28.5	28.3	28.1	28.0	27.8	27.6
16	29.2	29.0	28.8	28.6	28.5	28.3	28.1	27.9	27.8	27.7	27.4
17	29.0	28.8	28.6	28.5	28.3	28.1	28.0	27.8	27.7	27.5	27.3
18	28.8	28.6	28.5	28.3	28.1	28.0	27.8	27.6	27.5	27.3	27.1
19	28.6	28.5	28.3	28.1	27.9	27.8	27.6	27.4	27.3	27.1	26.9
20	28.5	28.3	28.1	27.9	27.8	27.6	27.5	27.3	27.1	27.0	26.7
21	28.3	28.1	27.9	27.8	27.6	27.5	27.3	27.1	27.0	26.8	26.6
22	28.1	27.9	27.8	27.6	27.5	27.3	27.1	26.9	26.8	26.6	26.4
23	27.9	27.8	27.6	27.5	27.3	27.1	26.9	26.8	26.6	26.5	26.3
24	27.8	27.6	27.5	27.3	27.1	26.9	26.7	26.6	26.4	26.3	26.1
25	27.6	27.5	27.3	27.1	26.9	26.7	26.6	26.4	26.3	26.1	25.9
26	27.3	27.1	27.0	26.8	26.6	26.5	26.4	26.2	26.1	25.9	25.7
27	27.1	26.9	26.8	26.6	26.4	26.3	26.2	25.0	25.9	25.7	25.5
28	26.9	26.8	26.6	26.4	26.2	26.1	26.0	25.8	25.7	25.5	25.3
29	26.7	26.6	26.4	26.2	26.0	25.9	25.8	25.6	25.5	25.3	25.2

Table 5. (contd.)

Diameter in microns at 3 min.

R \ T°	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
30	26.5	26.4	26.3	26.0	25.8	25.8	25.6	25.4	25.3	25.2	25.0
31	26.3	26.2	26.1	25.8	25.7	25.6	25.4	25.3	25.1	25.0	24.8
32	26.1	26.0	25.9	25.7	25.5	25.4	25.2	25.1	25.0	24.8	24.6
33	26.0	25.8	25.7	25.5	25.3	25.2	25.1	24.9	24.8	24.6	24.4
34	25.7	25.6	25.5	25.3	25.1	25.0	24.9	24.7	24.6	24.4	24.2
35	25.5	25.4	25.3	25.1	24.9	24.8	24.7	24.5	24.4	24.2	24.1
36	25.3	25.2	25.1	24.9	24.7	24.6	24.5	24.3	24.2	24.1	23.9
37	25.1	25.0	24.9	24.7	24.5	24.4	24.3	24.1	24.0	23.9	23.7
38	25.0	24.8	24.7	24.5	24.3	24.2	24.1	24.0	23.8	23.7	23.5
39	24.8	24.6	24.5	24.3	24.1	24.0	23.9	23.8	23.7	23.5	23.3
40	24.6	24.4	24.3	24.1	24.0	23.9	23.7	23.6	23.5	23.3	23.1

Diameter in microns at 10 min.

1	17.3	17.2	17.2	17.0	16.9	16.8	16.7	16.6	16.5	16.4	16.3
2	17.2	17.1	17.1	17.0	16.8	16.8	16.7	16.6	16.5	16.4	16.2
3	17.1	17.0	17.0	16.9	16.7	16.7	16.6	16.5	16.4	16.3	16.1
4	17.1	17.0	16.9	16.8	16.6	16.6	16.5	16.4	16.3	16.2	16.0
5	17.0	16.9	16.8	16.7	16.6	16.5	16.4	16.3	16.2	16.1	16.0
6	16.9	16.8	16.7	16.6	16.5	16.4	16.3	16.2	16.1	16.0	15.9
7	16.8	16.7	16.6	16.5	16.4	16.3	16.2	16.1	16.0	15.9	15.8
8	16.7	16.6	16.6	16.4	16.3	16.2	16.2	16.1	16.0	15.9	15.7
9	16.6	16.6	16.4	16.3	16.2	16.2	16.1	16.0	15.9	15.8	15.7
10	16.5	16.5	16.4	16.2	16.2	16.1	16.0	15.9	15.8	15.7	15.6
11	16.4	16.4	16.3	16.2	16.1	16.0	15.9	15.8	15.7	15.6	15.5
12	16.3	16.3	16.2	16.1	16.0	15.9	15.8	15.7	15.6	15.5	15.4
13	16.2	16.2	16.1	16.0	15.9	15.8	15.7	15.6	15.5	15.4	15.3
14	16.1	16.1	16.0	15.9	15.8	15.7	15.6	15.5	15.4	15.3	15.2
15	16.0	16.0	15.9	15.8	15.7	15.6	15.5	15.4	15.3	15.2	15.1
16	15.9	15.8	15.8	15.7	15.6	15.5	15.4	15.3	15.2	15.1	15.0
17	15.8	15.7	15.7	15.6	15.5	15.4	15.3	15.2	15.2	15.1	14.9
18	15.7	15.6	15.6	15.5	15.4	15.3	15.2	15.1	15.1	15.0	14.8
19	15.6	15.6	15.5	15.4	15.3	15.2	15.1	15.0	15.0	14.9	14.7
20	15.5	15.5	15.4	15.3	15.2	15.1	15.0	14.9	14.8	14.8	14.6
21	15.4	15.4	15.3	15.2	15.1	15.0	14.9	14.9	14.8	14.7	14.6
22	15.3	15.3	15.2	15.1	15.0	14.9	14.8	14.8	14.7	14.6	14.5
23	15.2	15.2	15.1	15.0	14.9	14.8	14.7	14.7	14.6	14.5	14.4
24	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.6	14.5	14.4	14.3
25	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.4	14.3	14.2
26	14.9	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.3	14.2	14.1
27	14.8	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.2	14.1	14.0
28	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.1	14.0	13.9
29	14.6	14.6	14.5	14.4	14.3	14.2	14.1	14.0	14.0	13.9	13.8
30	14.5	14.4	14.4	14.3	14.2	14.1	14.0	13.9	13.9	13.8	13.7
31	14.4	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.8	13.7	13.6
32	14.3	14.2	14.2	14.1	14.0	13.9	13.8	13.7	13.7	13.6	13.5

Table 5. (cont'd.)

Diameter in microns at 10 min.

R \ T°	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
33	14.2	14.1	14.1	14.0	13.8	13.8	13.7	13.6	13.6	13.5	13.4
34	14.1	14.0	14.0	13.8	13.7	13.7	13.6	13.5	13.5	13.4	13.3
35	14.0	13.9	13.9	13.7	13.6	13.6	13.5	13.4	13.4	13.3	13.2
36	13.9	13.8	13.7	13.6	13.5	13.5	13.4	13.3	13.3	13.2	13.1
37	13.8	13.7	13.6	13.5	13.4	13.4	13.3	13.2	13.2	13.1	13.0
38	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.1	13.0	12.9
39	13.6	13.5	13.4	13.3	13.2	13.2	13.1	13.0	13.0	12.9	12.8
40	13.5	13.4	13.3	13.2	13.1	13.1	13.0	12.9	12.9	12.8	12.7

Diameter in microns at 30 min.

1	10.0	9.9	9.9	9.8	9.7	9.7	9.7	9.6	9.6	9.5	9.4
2	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.6	9.5	9.5	9.4
3	9.9	9.8	9.7	9.7	9.7	9.6	9.6	9.5	9.5	9.4	9.3
4	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.5	9.4	9.4	9.3
5	9.8	9.7	9.7	9.6	9.6	9.5	9.5	9.4	9.4	9.3	9.2
6	9.7	9.7	9.6	9.6	9.5	9.5	9.4	9.4	9.3	9.3	9.2
7	9.7	9.6	9.6	9.5	9.5	9.4	9.4	9.3	9.3	9.2	9.1
8	9.6	9.6	9.5	9.5	9.4	9.4	9.3	9.3	9.2	9.2	9.1
9	9.6	9.5	9.5	9.4	9.4	9.3	9.3	9.2	9.2	9.1	9.0
10	9.5	9.5	9.4	9.4	9.3	9.3	9.2	9.2	9.1	9.1	8.9
11	9.5	9.4	9.4	9.3	9.3	9.2	9.2	9.1	9.1	9.0	8.9
12	9.4	9.4	9.3	9.3	9.2	9.2	9.1	9.1	9.0	9.0	8.8
13	9.4	9.3	9.3	9.2	9.2	9.1	9.1	9.0	9.0	8.9	8.8
14	9.3	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7
15	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7
16	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6
17	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.8	8.7	8.6
18	9.1	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.7	8.6	8.5
19	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5
20	8.9	8.9	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4
21	8.9	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.5	8.4
22	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.5	8.4	8.3
23	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3
24	8.7	8.7	8.7	8.6	8.5	8.5	8.5	8.4	8.3	8.3	8.2
25	8.6	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2
26	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1
27	8.5	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.1
28	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0
29	8.4	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	8.0
30	8.3	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	8.0	7.9
31	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.9
32	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8
33	8.2	8.1	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7
34	8.1	8.1	8.1	8.0	7.9	7.9	7.9	7.8	7.8	7.7	7.7
35	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.7	7.6

Table 5. (contd.)

Diameter in microns at 90 min.

R / T^{o}	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
1	5.8	5.7	5.7	5.7	5.6	5.6	5.6	5.5	5.5	5.5	5.4
2	5.7	5.7	5.7	5.6	5.6	5.6	5.6	5.5	5.5	5.5	5.4
3	5.7	5.7	5.7	5.6	5.6	5.6	5.5	5.5	5.5	5.4	5.4
4	5.7	5.7	5.6	5.6	5.5	5.5	5.5	5.5	5.4	5.4	5.3
5	5.6	5.6	5.6	5.5	5.5	5.5	5.5	5.4	5.4	5.4	5.3
6	5.6	5.6	5.6	5.5	5.5	5.5	5.4	5.4	5.4	5.3	5.3
7	5.6	5.6	5.5	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.3
8	5.6	5.5	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.3	5.2
9	5.5	5.5	5.5	5.4	5.4	5.4	5.4	5.3	5.3	5.3	5.2
10	5.5	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.3	5.2	5.2
11	5.5	5.4	5.4	5.4	5.3	5.3	5.3	5.3	5.2	5.2	5.2
12	5.4	5.4	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.2	5.1
13	5.4	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.2	5.1	5.1
14	5.4	5.4	5.3	5.3	5.2	5.2	5.2	5.2	5.1	5.1	5.1
15	5.3	5.3	5.3	5.3	5.2	5.2	5.2	5.1	5.1	5.1	5.0
16	5.3	5.3	5.3	5.2	5.2	5.2	5.1	5.1	5.1	5.0	5.0
17	5.3	5.3	5.2	5.2	5.2	5.1	5.1	5.1	5.0	5.0	5.0
18	5.3	5.2	5.2	5.2	5.1	5.1	5.1	5.0	5.0	5.0	4.9
19	5.2	5.2	5.2	5.1	5.1	5.1	5.0	5.0	5.0	5.0	4.9
20	5.2	5.2	5.1	5.1	5.1	5.0	5.0	5.0	5.0	4.9	4.9
21	5.2	5.2	5.1	5.1	5.1	5.0	5.0	5.0	4.9	4.9	4.9
22	5.1	5.1	5.1	5.1	5.0	5.0	4.9	4.9	4.9	4.9	4.8
23	5.1	5.1	5.1	5.0	5.0	5.0	4.9	4.9	4.9	4.8	4.8
24	5.1	5.1	5.0	5.0	5.0	4.9	4.9	4.8	4.8	4.8	4.8
25	5.0	5.0	5.0	5.0	4.9	4.9	4.8	4.8	4.8	4.8	4.7
26	5.0	5.0	5.0	4.9	4.9	4.9	4.8	4.8	4.8	4.7	4.7
27	5.0	5.0	4.9	4.9	4.9	4.8	4.8	4.7	4.7	4.7	4.7
28	4.9	4.9	4.9	4.9	4.8	4.8	4.7	4.7	4.7	4.7	4.6
29	4.9	4.9	4.9	4.8	4.8	4.8	4.7	4.7	4.7	4.6	4.6
30	4.8	4.8	4.8	4.8	4.8	4.7	4.7	4.6	4.6	4.6	4.6
31	4.8	4.8	4.8	4.8	4.7	4.7	4.6	4.6	4.6	4.6	4.5
32	4.8	4.8	4.7	4.7	4.7	4.7	4.6	4.6	4.6	4.5	4.5
33	4.7	4.7	4.7	4.7	4.7	4.6	4.6	4.5	4.5	4.5	4.5
34	4.7	4.7	4.7	4.7	4.6	4.6	4.5	4.5	4.5	4.5	4.4
35	4.7	4.7	4.6	4.6	4.6	4.5	4.5	4.5	4.5	4.4	4.4

Diameter in microns at 270 min.

1	3.3	3.3	3.3	3.3	3.2	3.2	3.2	3.2	3.2	3.2	3.1
2	3.3	3.3	3.3	3.2	3.2	3.2	3.2	3.2	3.2	3.1	3.1
3	3.3	3.3	3.3	3.2	3.2	3.2	3.2	3.2	3.2	3.1	3.1
4	3.3	3.3	3.2	3.2	3.2	3.2	3.2	3.1	3.1	3.1	3.1
5	3.3	3.2	3.2	3.2	3.2	3.2	3.1	3.1	3.1	3.1	3.1
6	3.2	3.2	3.2	3.2	3.2	3.2	3.1	3.1	3.1	3.1	3.1
7	3.2	3.2	3.2	3.2	3.1	3.1	3.1	3.1	3.1	3.1	3.0
8	3.2	3.2	3.2	3.1	3.1	3.1	3.1	3.1	3.1	3.0	3.0
9	3.2	3.2	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.0	3.0

Table 5. (contd.)

Diameter in microns at 270 min.

R \ T°	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0	24.5	25.0
10	3.2	3.2	3.1	3.1	3.1	3.1	3.1	3.1	3.0	3.0	3.0
11	3.2	3.2	3.1	3.1	3.1	3.1	3.1	3.1	3.0	3.0	3.0
12	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.0	3.0	3.0	3.0
13	3.1	3.1	3.1	3.1	3.0	3.0	3.0	3.0	3.0	3.0	2.9
14	3.1	3.1	3.1	3.0	3.0	3.0	3.0	3.0	3.0	2.9	2.9
15	3.1	3.1	3.0	3.0	3.0	3.0	3.0	3.0	2.9	2.9	2.9
16	3.1	3.1	3.0	3.0	3.0	3.0	3.0	2.9	2.9	2.9	2.9
17	3.0	3.1	3.0	3.0	3.0	3.0	2.9	2.9	2.9	2.9	2.9
18	3.0	3.0	3.0	3.0	3.0	2.9	2.9	2.9	2.9	2.9	2.9
19	3.0	3.0	3.0	3.0	2.9	2.9	2.9	2.9	2.9	2.9	2.8
20	3.0	3.0	3.0	2.9	2.9	2.9	2.9	2.9	2.9	2.8	2.8
21	3.0	3.0	2.9	2.9	2.9	2.9	2.9	2.9	2.8	2.8	2.8
22	3.0	3.0	2.9	2.9	2.9	2.9	2.9	2.8	2.8	2.8	2.8
23	2.9	2.9	2.9	2.9	2.9	2.9	2.8	2.8	2.8	2.8	2.8
24	2.9	2.9	2.9	2.9	2.8	2.8	2.8	2.8	2.8	2.8	2.7
25	2.9	2.9	2.9	2.8	2.8	2.8	2.8	2.8	2.8	2.7	2.7

Diameter in microns at 1080 min (18 hr.)

1	1.7	1.7	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
2	1.7	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
3	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
4	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.5
5	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.5	1.5
6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.5	1.5	1.5
7	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5
8	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5
9	1.6	1.6	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.5
10	1.6	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.5	1.5
11	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5
12	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
13	1.6	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
14	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
15	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
16	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.4
17	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.4	1.4
18	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.4	1.4	1.4
19	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.4	1.4	1.4	1.4
20	1.5	1.5	1.5	1.5	1.5	1.5	1.4	1.4	1.4	1.4	1.4
21	1.5	1.5	1.5	1.5	1.5	1.4	1.4	1.4	1.4	1.4	1.4
22	1.5	1.5	1.5	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.4
23	1.5	1.5	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
24	1.5	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
25	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4

2.13 Sieve Analysis of Dry Soil (Engineering Test)

Apparatus

Set of sieves and pan. The following 20 cm diameter sieves are required No. 4 (4.76 mm), No. 10 (2.00 mm), No. 40 (.42 mm) and No. 200 (.074 mm); sieve brush; balance; drying oven.

(1) Weigh each clean sieve which is to be used to 0.1 g.

(2) Select (and weigh) a representative sample of approximately 500g of the soil to be tested; break the soil into individual particles with either the fingers or rubber-tipped pestle.

NOTE: If many of the soil particles are coarser than the openings of a No. 4 sieve, use a larger sample.

(3) Sieve the soil through this nest of sieves (No. 4; 10, 40 and 200) by shaking horizontally by hand or mechanically for at least 10 minutes.

(4) Weigh to 0.1g each sieve and the soil retained on these.

(5) Subtract the weights obtained in step 1 from those in step 4 to give weight of soil retained on each sieve. (Add these weights and check against original weight).

(6) If a large portion of the soil is retained on the No. 200 sieve, it should be washed. This is done by placing the sieve and retained soil in a pan and pouring clean water on the screen. Use a glass rod to stir the slurry. Recover the soil which is washed through, dry and weigh it. The weight of the soil recovered should be subtracted from the weight retained on the No. 200 sieve and added to the portion that passed through the No. 200 sieve.

(7) Calculate percentage retained on any sieve by:

$$\frac{\text{weight of soil retained} \times 100}{\text{total soil weight}}$$

For engineering interpretations the data are classified according to either the AASHO or the Unified System of soil particle-size classification (Fig. 1).

2.14 Particles Coarser than 2 mm

Sample size. The size of sample depends upon the the maximum size fragments present or to be analyzed.

Guidelines follow:

Particles up to 20 mm diameter - 5 kg

Particles up to 75 mm diameter - 20 kg

Particles up to 250 mm diameter - 100 kg or more

Because of the large samples required, the volume percentage of particles coarser than about 20 mm is usually estimated.

2.141 Weight estimates of coarse particles by field or laboratory weighings

(1) Weigh and sieve the entire sample through 75 mm and 20 mm screens. Weigh the >75 mm and the 75 to 20 mm fractions.

(2) Take a subsample of the <20 mm fraction for laboratory processing. Weigh the <20 mm sample before and after air-drying and correct the total sample weight for the loss in water from field conditions.

(3) Separate and weigh the 2 to 5 and the 5 to 20 mm fractions.

(4) If fine earth adheres to the coarse fraction, wash the coarse material, dry, reweigh and apply the appropriate corrections.

(5) Calculate the coarse fractions as a percentage of the <20 mm material (or the <75 or the <250 depending upon the size limit involved in sampling).

2.142 Volume estimates of particles coarser than 2 mm

(1) Record the volume estimates of particles >20 mm, >75 mm and >250 mm in the pedon description.

(2) To arrive at a volume percentage of all material >2 mm, convert the weight estimates of the fine earth to volume estimates.

$$Cm = \frac{Dp\ (1-y)(1-x)}{Dp\ (1-y)+Dbm\ (y)}$$

Dp = particle density (either measure or assume 2.65 g/cc)

Dbm = bulk density of moist <2 mm soil

$$x = \frac{\text{volume of fragments} > i \text{ mm}}{\text{volume of whole soil}}$$

$$y = \frac{\text{weight of material between 2 mm and } i \text{ mm}}{\text{weight material} < i \text{ mm}}$$

i = the size above which volume estimates are made and below which weight percentages are determined

Cm is the coarse-fragment conversion factor.

Cm x weight percentages based upon laboratory data converts these data to a field volume basis. Cm x 100 is the volume percentage of the less than 2 mm material in the whole soil. 100 minus this value is the volume percentage of >2 mm material.

NOTE: See Soil Conservation Service (1972) and Mehuys et al (1975) for further information on corrections for coarse fragments.

References (see also references cited in these publications)

(1) American Society for Testing and Materials. 1961. Tentative method for grain-size analysis of soils. pp. 1272-1283. in The 1961 Book of ASTM Standards. Am. Soc. Test. Mater., Philadelphia.

(2) Bouyoucos, G.J. 1962. Hydrometer method improved for making particle size analysis of soils. Agron. J. 54, 464-465.

(3) Clark, J.S. 1962. Note on a pipetting assembly for the mechanical analysis of soils. Can. J. Soil Sci. 42, 316.

(4) Day, P.R. 1965. Particle fractionation and particle-size analysis. pp. 545-567. in Methods of Soil Analysis, C.A. Black, ed. Agronomy, No. 9, Part 1. Am. Soc. of Agron., Madison, Wisconsin.

(5) Genrich, D.A. and Bremner, J.M. 1974. Isolation of soil particle-size fractions. Soil Sci. Soc. Am. Proc. 38, 222-225.

(6) Jackson, M.L. 1956. Soil Chemical Analysis - Advanced Course. Published by the author, Department of Soils, Univ. of Wisconsin, Madison 6, Wisconsin.

(7) Lavkulich, L.M. and Wiens, J.H. 1970. Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effect on selected mineral constituents. Soil Sci. Soc. Am. Proc. 34, 755-758. (See also Soil Sci. Soc. Am. Proc. 35, 514).

(8) Mehuys, G.R., Stelzy, L.H., Letey, J., and Weeks, L.V. 1975. Effect of stones on hydraulic conductivity of relatively dry desert soils. Soil Sci. Soc. Am. Proc. 39, 37-42.

(9) Soil Conservation Service. 1972. Soil Survey Laboratory Methods and Procedure for Collecting Soil Samples. Soil Survey Investigations, Report No. 1 (Revised 1972), U.S.D.A., Washington, D.C.

(10) Toogood, J.A. and Peters, T.W. 1953. Comparison of methods of mechanical analysis of soils. J. Agr. Sci. 33: 159-171.

(11) Veneman, P.L.M. 1977. "Calgon" still suitable. Soil Sci. Soc. Am. J. 41, 456.

(12) Whittig, L.D. 1965. X-ray diffraction techniques for mineral identification and mineralogical composition. pp. 671-698. in Methods of Soil Analysis, Ca. A. Black, ed. Agronomy No. 9, Part 1. Am. Soc. Agron., Madison, Wisconsin.

2.2 BULK DENSITY AND PARTICLE DENSITY

Soil bulk density is the ratio of the mass (g) of an oven-dry soil sample to the volume (cm^3) of that sample at a specified moisture condition, e.g., field-moisture, 1/3 bar, oven-dry, etc. It provides a measure of soil porosity and permits the recalculation on a volume basis of data expressed on a weight basis: % water in soil (by volume) = bulk density x % water in soil (by weight).

Only the commonly-used methods of measuring bulk density (core and clod methods) are presented. Other methods include: gamma ray attenuation, sand funnel, rubber balloon (Blake, 1965). For organic soils, mercury displacement by frozen soil cores is used by the Manitoba Soil Survey. In soil with well-developed structure, the clod method generally gives somewhat higher bulk density values than the core method as the larger inter-ped voids are not included in clod samples. However, for many soils lacking structure, clod and core methods yield closely similar results if the volume measurements are made at the same water contents. The choice of method depends upon the nature of the soil. For incoherent soils, cores should be used; for cemented or stony soils, the clod method is more suitable.

Several replicate samples (perhaps 5, see Toogood, 1961) are necessary to provide a good estimate of the bulk density of a soil

horizon. In reporting bulk density data, the water content at which the volume measurement was made should be stated. Also indicate whether or not the values were corrected for particles coarser than 2 mm.

The Saran clod method (2.22) has several advantages over the paraffin clod method (2.23). However, Tunny's (1970) results indicated that saran is not sufficiently flexible to permit full expansion of coated clods that are being wetted. Furthermore, in his tests, saran did not contract completely with the clod on drying. Bubbling of the saran coating is also a problem with some samples.

2.21 Core Method, Mineral Soils

Apparatus

Core sampler - hand operated core samplers such as the Uhland sampler (7.5 cm diameter cores) have been used commonly; truck-mounted, hydraulic core samplers are now coming into more general use.

2.211 Manually-powered double cylinder core sampler, bulk density (Db) uncorrected for coarse fragments

(1) Prepare a smooth, "undisturbed" vertical or horizontal soil surface at the depth to be sampled in moist soil (Good core samples are rarely obtained in dry or wet soils by this method).

(2) Drive or press in the sampler far enough to fill the inner metal cylinder but not so far as to compress the soil.

(3) Carefully remove the sampler so as to preserve the sample intact. Separate the 2 cylinders, retaining the "undisturbed" soil in the inner cylinder.

(4) Examine the sample in the inner cylinder. If there has been obvious disturbance; e.g., compression due to driving in too far; shattering of coherent material, hole left by a root or a stone that was displaced, discard the sample. If no or only slight disturbance is evident, trim the soil sample flush with each end of the inner cylinder.

(5) If only bulk density and water content are to be determined, the sample may be pushed out of the cylinder into a plastic bag. If the "undisturbed" core is to be used for other tests such as pore-size distribution, cover the bottom of the sample with a piece of nylon cloth, secure it with a

rubber band and put the core into a one-pint, cylindrical waxed-paper carton.

(6) Weigh the sample at field water content.

(7) Calculate the bulk density as follows:

(a) Measure diameter and hence radius (r) in cm of inside of cutting edge of sampler (with some samplers, this is slightly smaller than the inside diameter of the inner cylinder).

(b) Measure height (h) of cylinder in cm.

(c) Volume (cm^3) of sample (V) = $\pi r^2 h$

(d) Determine oven-dry weight of sample (W) in grams; dry to constant weight at 105°C (this may be done after the core has been used to make several other kinds of measurements).

(e) Calculate bulk density at field water content Dbm and the water content of the sample as follows:

$$Dbm = \frac{W}{V} \ g/cm^3$$

$$\text{Water content (weight basis) } Pw = \frac{(\text{Weight of moist soil sample}) - (\text{oven-dry weight of sample}) \times 100}{\text{oven-dry weight of sample}}$$

$$\text{Water content (volume basis) } Pv = Pw \times Dbm$$

2.212 Manually powered double cylinder core sampler, Dbm corrected for particles coarser than 2 mm

Proceed as in 2.211 except that after the sample has been oven-dried and weighed, it is crushed and sieved through a 2 mm sieve. The coarse material remaining is washed with water, dried and weighed (a). The volume (b) of coarse material is determined by measuring the displacement of water in a graduated cylinder when the material is added. The bulk density g/cm^3 of the fine fraction is calculated as follows:

$$Dbm = \frac{W-a}{V-b}$$

2.213 Cores taken with powered core sampler, Db uncorrected for coarse fragments

(1) Obtain a core to the depth required - Note any evidence of compression of the soil during sampling and discard if this is appreciable.

(2) Section the core into appropriate lengths depending upon horizonation of the soil. Measure and record the lengths of the samples, put them into plastic bags, label and seal.

(3) Determine Dbm and Pw as outlined in 2.211.

2.214 Cores taken with powered core sampler, Dbm corrected for coarse fragments

Follow 2.213 except that the coarse fragments are separated and the corrected Dbm calculated as outlined in 2.212.

2.215 Cores taken by pressing cylinder over exposed cylindrical-shaped volume of soil

This procedure is useful in some coherent soils that are compressed when core samplers are used. It is also useful in sampling some wet soils.

(1) Expose an "undisturbed" surface at the depth to be sampled.

(2) Remove soil to form a column about 20 cm in diameter to a depth of about 15 cm.

(3) Carefully cut away the sides of the column leaving it wider toward the base until the top is the same diameter as the inside of the metal cylinder.

(4) Press the cylinder gently over the column and continue to cut away soil below the cylinder and press gently until the cylinder is filled with soil.

(5) Proceed as in 2.211.

2.22 Saran Coated Clods

Reagents

Dow Saran Resin - F310 is dissolved in methyl-ethyl ketone by shaking on a paint shaker or by stirring with an electric stirrer under a fume hood. Prepare solutions with Saran-solvent ratios of 1:4 and 1:7. Keep the containers tightly closed and avoid breathing the vapour.

2.221 Clod bulk density uncorrected for coarse fragments

A. Sampling - the exact procedure must be chosen according to the nature of the soil but a general procedure is suggested.

(1) Collect clods of about 50 to 200 cm^3 by cutting out or chipping off a larger clod and by carefully trimming off protrusions and trimming off roots with scissors.

(2) Suspend the clod from a string or wire and dip it into the plastic solution (1:7 for most soils; 1:4 for porous soils).

(3) Suspend the clod from a line to allow it to dry.

(4) Put the clod into a plastic bag, label it, and pack the bag in a rigid container for transport.

NOTE: With highly coherent soil, no field treatment with plastic is required.

B. Laboratory Measurements

(1) Attach identification tags to string tied around sample. Determine the average weight of string and tag (W1).

(2) Weigh the fragment (W2). If the clod was not dipped in plastic in the field, dip it once in the laboratory and let dry before weighing (some soil may slake off during the first dip).

(3) Under a fume hood, dip the clod in plastic and let it dry for 15 minutes; repeat dipping and drying until a thin continuous coating is observed (3 to 7 times). Allow the final coat to dry for about 30 minutes.

(4) Weigh the sample in air (W3) and in water (W4) by suspending it below a balance.

(5) Oven dry the clod on a sheet of aluminum foil at 105°C for about 48 hours. Weigh the clod in air (W5) and in water (W6).

C. Calculation of Bulk Density

(1) Weight and volume of coatings

(a) Air-dry weight

$$(A1) = \frac{(W3-W2)}{(N-1)} + W3-W2$$

where N is the total number of coatings.

(b) Oven dry weight (A2) = 0.9 A1 (about 10% of the weight is lost on drying).

(c) Volume (cm^3) $(V1) = \frac{A1}{1.3}$

The density of saran is 1.3 g/cm^3

(2) Corrected weight of clods

(a) Field moisture (A3) = W3-A1-W1

(b) Oven-dry (A4) = W5-A2-W1

(3) Corrected volume of clod

(a) Field moisture (V2) = (W3-W4)-V1

(b) Oven-dry (V3) = (W5-W6)-V1

(4) Bulk density

(a) At field moisture $Dbm = \frac{A4}{V2}$

(b) Oven-dry $Dbod = \frac{A4}{V3}$

(5) Field water content (weight basis)

$Pw = \frac{A3-A4}{A4} \times 100$

Similarly bulk density may be determined at other water contents such as 1/3 bar, air dry, etc. by equilibrating the clod at that water content (peel off a portion of the Saran to equilibrate the clod on a sand tension table, etc.).

2.222 Clod bulk density corrected for coarse fragments

Follow procedure 2.221 except that, after oven-drying, the clod is broken open and the >2 mm material is separated by sieving. The weight (a) and volume (b) of the coarse material is measured as in 2.212 and the bulk density is corrected as follows:

e.g., Dbod (corrected for >2 mm material) $= \frac{A4-a}{V3-b}$

2.23 Paraffin Clod Method

This is essentially the same as the saran clod method except that melted paraffin (60 to 70°C) is used as the coating material. An uncoated soil sample is used to determine water content and thus to calculate the oven dry weight. Details of a procedure are given by Blake (1965).

2.231 Uncorrected for coarse fragments, as in 2.221.

2.232 Corrected for coarse fragments, as in 2.222.

2.24 Bulk Density of Organic Soils

2.241 Core samples

(1) Take an undisturbed core of organic soil with a piston-type sampler, or any other suitable core-sampler.

(2) With a sharp knife, cut sample about 5 cm long from the various layers included in the core. Measure the sample length to the nearest mm and put the sample into a plastic bag.

(3) Transfer the sample to a weighing can in the laboratory, weigh it moist, dry at 105°C for 1 to 2 days depending on sample size.

(4) Calculate bulk density as follows:

$$Dbm\ (g/cm^3) = \frac{\text{weight of dry sample in g}}{\pi r^2 L}$$

where r = radius of cutting edge of core sampler in cm
L = length of sample in cm.

(5) Calculate field water content, if desired as follows:

$$\text{weight percent } Pw = \frac{\text{Wet weight of sample (g) - Oven-dry weight (g)}}{\text{Oven-dry weight of sample (g)}}$$

Volume percent Pv = Dbm x Pw

2.242 McCauley peat auger samples

The auger removes a one-half cylinder of material that is relatively undisturbed. Bulk density is determined from the weight and volume of subsamples handled as indicated in 2.241.

2.243 Steel-pin sampling board (Lynn, SCS)

The sampling board has long steel pins fastened vertically in a square of selected side dimension (5 or 10 cm). The pins protrude from the board by at least the same length as the side dimension.

A block of peat is dug from a pit, trimmed flat on one surface and the trimmed surface is pushed onto the steel pins. With a sharp knife the block of peat is trimmed flush against the

steel pins to achieve a column of peat. Then the column of peat is lifted from the sampler and reinserted onto the pins carefully. The sixth side is trimmed flush against the pins to achieve a cube. The cube of peat is placed in a sample bag. Bulk density is calculated from weight and volume measurements as outlined in 2.241.

References

(1) ASTM. 1971. Annual Book of ASTM Standards, Part 2. Soc. for Testing and Materials, Philadelphia, Pa.

(2) Blake, G.R. 1965. Bulk density in Methods of Soil Analysis, C.A. Black, ed. Agronomy No. 9, Part 1, Madison, Wisconsin.

(3) Soil Conservation Service. 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Investigations Report No. 1 (Revised), U.S.D.A., Washington, D.C.

(4) Toogood, J.A. 1961. Use of soil cores in soil classification. Can. J. Soil Sci. 41, 241-246.

(5) Tunny, J. 1970. The influence of saran resin coatings on swelling of natural soil clods. Soil Sci. 109, 254-256.

2.25 Particle Density (after Blake, 1965)

Particle density of soils is expressed as the ratio of the total mass of solid particles to their total volume, excluding pore spaces between particles.

Apparatus

Pycnometer (specific gravity flask), or a volumetric flask if large samples (20 g or more) are used.

Procedure

(1) Weigh a clean, dry pycnometer, add about 10 g of air-dry soil, clean the outside of the pycnometer and weigh pycnometer plus contents. (If a 100 ml volumetric is used, weigh about 50 g of soil).

(2) Determine the water content of a duplicate soil sample by drying at 105 C (see method 2.412).

(3) Fill the pycnometer about half full with distilled water, working into the flask any soil adhering to the inside of the neck.

(4) Boil the water in the flask for several minutes with frequent gentle agitation. This removes entrapped air.

(5) Cool the pycnometer and its contents to room temperature, and add boiled, cooled distilled water to fill the pycnometer.

(6) Weigh the pycnometer and its contents and determine the temperature of the contents.

(7) Remove soil from the pycnometer and fill it with boiled, cooled distilled water at the same temperature as before.

(8) Thoroughly dry the outside of the pycnometer, weigh it, and measure the temperature.

(9) Calculate particle density as follows:

$$Dp = \frac{dw(Ws-Wa)}{(Ws-Wa)-(Wsw-Ww)}$$ where

dw = density of water in g/cm^3 at the temperature measured
Ws = weight of pycnometer and soil sample
Wa = weight of pycnometer filled with air
Wsw = weight of pycnometer filled with soil and water
Ww = weight of pycnometer filled with water at the temperature observed.

Reference

Blake, G.R. 1965. Particle density. pp. 371-373 in Methods of Soil Analysis, Part 1, Agronomy No. 9, C.A. Black, ed., American Society of Agronomy, Madison, Wisc.

2.3 SHRINKAGE

Shrinkage can be calculated from bulk density values, obtained by any method, for moist and dry samples of undisturbed soil. The bulk density of the moist soil should be measured at some standard point on the soil water content-tension curve, e.g., 0.1 bar. The results of "shrinkage" measurements are expressed in terms of expansibility because the basis of the measurement is the volume of dry soil. The linear shrinkage or expansion can be observed and measured directly by using a microscope (Warkentin and Bozozuk, 1961).

2.31 Linear Extensibility, Saran Clod (Soil Conservation Service, 1972)

Linear extensibility is a measure of the change in the dimensions of a clod from a dry to a moist state.

$$LE\ \% = 100\ \frac{(Lm-Ld)}{Ld}$$

Lm = length of clod, moist

Ld = length of clod, dry

LE can be estimated from laboratory data for bulk density, moist and dry, and the coarse fraction conversion factor (Cm).

$$LE\ \% = 100\ \left[\left(\frac{1}{Cm\ \frac{Dbm}{Dbd} + (1-Cm)}\right)^{\frac{1}{3}} - 1\right]$$

$$Cm = \frac{\text{Volume moist of <2 mm fabric}}{\text{Volume of whole soil}}$$

Dbm = Bulk density of <2 mm fabric at specified moisture conditions (1/10 bar, etc.)

Dbd = Bulk density of <2 mm fabric at oven- or air-dryness

If there is no coarse material, Cm = 1 and the equation reduces to:

$$LE\ \% = 100\left[\left(\frac{Dbd}{Dbm}\right)^{\frac{1}{3}} - 1\right]$$

2.32 Shrinkage by Direct Measurement of a Regularly-Shaped Sample (Rectangular or Cylindrical Block)

This method is satisfactory for soil materials that can be cut into regularly-shaped blocks. A general procedure is suggested.

(1) Cut out a block (or core) of moist soil, about a 10 cm cube, and place it in a plastic bag to prevent water loss.

(2) Take a sample for water determination adjacent to the sampling area and seal it in a plastic bag. Weigh, oven-dry and calculate the water percentage.

(3) In the laboratory, straighten any rough side of the block sample and measure its length, width and height (or diameter and height) with calipers. Measure at several places, record average dimensions and calculate volume Vm.

(4) Weigh the moist block (Wm).

(5) Allow the block to dry until it is air-dry and measure its dimensions as before and calculate the volume (Vd). Weigh the block (Wd).

(6) Oven-dry the block and reweigh it (Wod).

(7) Calculate volume expansibility as follows:

$$\text{Volume expansibility} = \frac{Vm-Vd}{Vd} \times \frac{100}{1}$$

Average linear expansibility is the cube root of volume expansibility. The change in water content between the moist sample and the air-dry sample should also be recorded.

2.33 Shrinkage of Disturbed Soil and Maximum Dry Density - R.G. Eilers (see ASTM, 1958).

Apparatus

Evaporating dish	Glass cup
Spatula	Glass plate
Shrinkage dish	Graduated cylinder
Straightedge	Balance

Reagents

Mercury

Procedure

(1) Weigh out about 30 g of 2.0 mm soil material and place in an evaporating dish.

(2) Add distilled water and mix thoroughly. Stop addition of water when the consistency of the soil is equal to or slightly greater than the liquid limit.

(3) Coat the inside of the shrinkage dish with a thin layer of vaseline or equivalent to prevent adhesion of soil to the dish.

(4) Place an amount of the wetted soil, equal to about 1/3 the volume of the dish, in the center of the dish.

(5) Cause soil to flow to the edges by tapping the dish on a firm surface.

(6) Add an approximately similar amount of soil, as outlined under step 4, to the dish and tap the dish again until the soil is thoroughly compacted and all included air has been brought to the surface.

(7) Repeat step 6 until the dish is completely filled and excess soil stands out about its edge.

(8) Remove excess soil with straightedge and clean the outside of the dish.

(9) Weigh dish plus soil and record value (W_W).

(10) Air-dry sample in dish until the sample color turns from dark to light, then oven-dry at 105°C and weigh (W_S).

(11) Determine the volume of the dry soil pat by removing it from the shrinkage dish and immersing it in the glass cup full of mercury in the following manner:

i) Fill the glass cup to overflowing with mercury.
ii) Remove the excess mercury by pressing the glass plate with the three prongs firmly over the top of the cup. Carefully wipe off any mercury which may be adhering to the outside of the cup.
iii) Place the cup (filled with mercury) in the evaporating dish.
iv) Place the soil pat on the surface of the mercury.
v) Carefully force the soil pat under the mercury by means of the glass plate with the three prongs, and press the plate firmly over the top of the cup. It is essential that no air be trapped under the soil pat.
vi) Measure the volume of the mercury displaced by means of the graduated cylinder and record it as the volume of the dry soil pat (V_S).

(12) Weigh the empty shrinkage dish and record (W_D).

(13) Determine the volume of the empty shrinkage dish -- which is also the volume of the wet soil pat -- by filling the dish to overflowing with mercury. Remove excess mercury by pressing a glass plate firmly over the top of the dish. Measure mercury in dish by means of a graduated glass cylinder and record as the volume of the wet soil pat (V).

Calculations

$$\text{Percent Moisture Content (M)} = \frac{(W_W - W_D) - W_S}{W_S} \times 100$$

$$\text{Shrinkage Limit (S)} = M - \frac{(V - V_S)}{W_S} \times 100$$

Shrinkage Ratio (R) (or maximum dry density) $= \frac{W_s}{V_s}$

Volumetric Change at field moisture (C_f) = (F-S)R
where F = field moisture equivalent

Lineal Shrinkage (L.S.) $= 100 \left(1 - \sqrt[3]{\frac{100}{C_f + 100}}\right)$

References

(1) ASTM. 1958. Procedures for testing soils. pp. 76-79.

(2) Grossman, R.B., Brasher, B.R., Franzmeier, D.P. and Walker, J.L. 1968. Linear extensibility as calculated from natural clod bulk density measurements. Soil Sci. Soc. Am. Proc. 32, 570-573.

(3) Holmgren, G.G.S. 1968. Nomographic calculation of linear extensibility in soils containing coarse fragments. Soil Sci. Soc. Am. Proc. 32, 568-570.

(4) Soil Conservation Service. 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Investigations Report No. 1 (Revised). U.S.D.A., Washington, D.C.

(5) Warkentin, B.P. and Bozozuk, 1961. Shrinking and swelling properties of two Canadian clays. Proc. 5th Intern. Conf. Soil Mechanics and Foundation Eng. 3A/49, 851-855.

2.4 WATER CONTENT AND WATER RETENTION (POROSITY) - R.G. Eilers

The capacity of a soil to retain water at various tensions is a property of major importance that can be measured in several ways. The methods listed are considered to be the most feasible for analyzing large numbers of samples with relatively simple equipment.

With samples having an appreciable volume of large pores (those that drain at a tension of 10 cm of water) it is virtually impossible to measure water content at saturation by the core method described. Total porosity (and hence pores coarser than those retaining water at 10 cm tension) can be calculated from bulk density and particle density (see Vomocil, 1965). For many soils, a particle density of 2.65 g/cm^3 can be assumed.

2.41 Water Content

2.411 Water Content, weight basis

(1) Weigh a sample of the moist soil (preferably 10 g or more) into a tared aluminum can or other suitable container. Record weight to the nearest mg.

(2) Dry the sample in an oven at 105°C to constant weight (usually 24 to 48 hours).

(3) Place the cover on the container and allow the samples to cool (to room temperature) in a desiccator.

(4) Weigh to the nearest mg.

(5) Calculate percentage water by weight

$$Pw = 100 \times \left(\frac{\text{Weight of moist soil}}{\text{weight of oven-dry soil}} - 1\right)$$

2.412 Hygroscopic water

This is the percentage of water (wt-basis) retained by air-dry soil based on oven-dry (105°C) weight. The procedure is the same as 2.411.

2.413 Water content, volume basis

Either, follow the procedure outlined in 2.411 using a known volume of undisturbed soils as a sample. Calculate percentage water by volume

$$Pv = \frac{(\text{weight of moist soil (g)} - \text{weight of oven-dry soil (g)}) \times 100}{\text{volume of soil (cm}^3\text{)}}$$

or, calculate Pv as follows:

Pv = Pw x Dbm if the bulk density of the moist soil is known.

NOTE: 1. Strictly speaking, the first formula for calculation of Pv should be multiplied by $1/\rho w$ (g/cm^3) where ρw is the density of water.

2.414 Ice content, volume basis

(1) Determine the volume of a core sample of the frozen soil.

(2) Follow the procedure outlined in 2.411. If the ice content is high, the excess water may be evaporated on a hot plate before oven drying the sample.

(3) Calculate percentage ice by volume:

$$Pv\ (ice) = \frac{(\text{weight of wet soil} - \text{weight of oven-dry soil}) \times 108.3}{\text{volume of frozen soil}}$$

2.42 Water Retention Using Tension Table and Undisturbed Samples

2.421 Core samples

Apparatus

Tension table as described by Vomocil (1965); Stakman, Valk and Harst (1969); Topp and Zebchuk (1978); cores, nylon bolting cloth, elastic bands.

Procedure

(1) Trim the soil cores flush with the cylinders as for bulk density measurements. Put a piece of nylon cloth over the bottom end and hold it in place with a rubber band.

(2) Presoak the samples for 1 to 2 days in water standing 1 cm below the surface of the soil. The water level should be raised slowly while the samples are being wetted. Samples that wet very slowly may have to be saturated under vacuum.

(3) Weigh the samples immediately after removing them from the water (W1). Also weigh an empty cylinder, with rubber band and nylon cloth, of the same size as used for the samples (blank core) immediately after removing it from the water tank (B1).

(4) Place the samples on a tension table with tension adjusted to 10 cm from the center of the cores. Cover the cores to prevent evaporation and allow them to equilibrate at that tension (see Table 6 for approximate times).

Table 6. Suggested times for equilibrating 7.6x7.6 cm cores at various tensions (Topp and Zebchuk, 1978)

Tension, cm H_2O	Time	Tension, cm H_2O	Time
0	16 h	80	4 days
5	16 h	100	4 days
10	1 day	150	6 days
20	3 days	225	10 days
40	3 days	300	10 days
60	4 days	500	12 days

(5) Weigh the samples (W2) and also the blank core equilibrated at 10 cm tension (B2).

(6) Moisten the surface of the tension table and replace the samples. Adjust the tension to 50 cm (or other tension) and proceed as in steps 4 and 5.

(7) Apply other tensions as required and follow the same general procedure. Tensions up to 500 cm of water can be measured by this method. Glass beads (diameter 30 μm) are used for tensions up to 100 cm and aluminum oxide (diameter 9 μm) for tensions of 100 to 500 cm (Topp and Zebchuk, 1978). The time required to achieve equilibrium increases with the tension. Thus cores only a few cm high are preferable for the higher tensions.

(8) When the measurements have been completed, oven dry the sample at 105°C to constant weight (Wd). Drying takes about 2 days for cores 8 cm. high. Also weigh the blank core with cloth and rubber band after oven drying (Bd) and obtain the oven dry weight of each cylinder after removing the soil sample. Thus determine Wd corr. (oven dry weight of soil corrected for the weight of the core & cloth & rubber band).

Calculations

Water Retention at a Given Tension

$$Pw = \frac{W1-(B1-Bd)-Wd}{Wd\ corr.} \times \frac{100}{1}$$

Similarly the water retention at various tensions can be calculated.

Porosity

Air-filled pores as a percent of the total volume can be calculated as follows:

e.g., at 10 cm tension, $$Porosity = \frac{W1-(B1-B2)-W2}{V} \times 100$$

where V is volume of sample. (See note following 2.413)

Note 1. Aluminum oxide is preferable to kaolin-sand as a tension medium. Better contact between sample and medium is obtained and saturated hydraulic conductivity is much higher.

2.422 Clod samples

Coherent clods can be used on a sand tension table as described by Stakman, Valk and Harst (1969). The clod enclosed in nylon bolting cloth can be pressed into the sand lightly so as to ensure a good contact. The procedure is basically the same as 2.421.

2.43 Pressure Plate Extraction (1/10, 1/3, 1 bar, etc.)

2.431 With disturbed (2 mm) samples (not desirable below 1 bar)

Apparatus

Pressure-plate apparatus with system for controlling pressure, retainer rings (about 1 cm high by 4 cm diameter), balance, oven, drying cans.

Procedure

(1) Place numbered retainer rings on porous plate and put about a teaspoon-full of sample in each ring.

(2) Cover the plate with water to wet the samples from below, cover the plate with a plastic sheet and let the samples stand overnight.

(3) Remove excess water, place the plate in the pressure pot and apply the required pressure until no more water is extracted (about 2 to 6 days).

(4) Transfer the samples to moisture tins, weigh, dry at 105°C and weigh again. Calculate water content as percent of oven-dry weight as in 2.411.

2.432 With undisturbed core samples

Proceed as in 2.431 except that cores 1 to 3 cm thick are used instead of disturbed samples.

2.433 With clods

Clods (about 2.5 cm diameter) are placed on a small piece of Kimwipe on top of the 2 mm disturbed sample in 2.431. They are saturated etc. as described in 2.431. If the clods contain material coarser than 2 mm, a correction is made as described in 2.212.

2.44 Pressure Membrane Extraction (15 bars)

Apparatus

Pressure membrane apparatus with ceramic plate or cellulose membrane, retainer rings about 1 cm high and 6 cm in diameter, balance, oven, moisture cans.

Procedure

(1) Install a wet cellulose membrane (or preferably an appropriate ceramic plate) in the pressure apparatus, add water and fill the rings with 2 mm soil samples.

(2) Add further water if necessary to maintain free water on the membrane, cover with plastic and allow to soak overnight.

(3) Remove excess water, close the apparatus carefully, and gradually apply pressure to the desired level.

(4) After about a day, apply a 4 psi pressure differential to the rubber diaphragm above the samples (if there is such a diaphragm on the apparatus used).

(5) When outflow has ceased (approximately 2 to 6 days normally) remove the samples, transfer them to moisture cans, weigh, oven dry and reweigh. Report water as a percentage of the oven dry weight.

References

(1) Richards, L.A. ed. 1954. Diagnosis and improvement of saline and alkali soils. U.S. Salinity Laboratory, U.S.D.A., Handbook 60.

(2) Soil Conservation Service. 1972. Soil survey methods and procedures for collecting soil samples. Soil Survey Investigations Report No. 1 (Revised 1972). U.S.D.A., Washington, D.C.

(3) Soil Moisture Equipment Corp., Technical notes on equipment. (P.O. Box 30025, Santa Barbara, Calif.)

(4) Stakman, W.P., Valk, G.A. and Van der Harst, G.G. 1969. Determination of soil moisture retention curves 1. Sandbox apparatus, Range pF 0-2.7, 3rd ed. Inst. for Land and Water Management Res., P.O. Box 35, Wageningen, Netherlands.

(5) Topp, G.C. and Zebchuk, W. 1978. The determination of soil-water desorption curves for soil cores. Can. J. Soil Sci. 58 (in press).

(6) Vomocil, J.A. 1965. Porosity, in Methods of Soil Analysis, Part 1, C.A. Black, ed., pp. 299-314.

(7) Young, K.K. 1962. A method of making moisture desorption measurements on undisturbed soil samples. Soil Sci. Soc. Am. Proc. 26, 301.

2.5 SATURATED HYDRAULIC CONDUCTIVITY

Saturated hydraulic conductivity is a measure of the ability of a saturated soil to transmit water. Either core or clod samples can be used but it is simpler to work with core samples if good cores can be obtained.

2.51 Core Method - W. Zebchuk

1. Core samples are taken as outlined in 2.21 and trimmed flush with the cylinder at both ends. The top and bottom of

the core are covered by filter paper discs (the top paper is notched to let air escape) and by stiff metal screens. The screens are sealed to the metal cylinder with paraffin. An empty metal cylinder is sealed with paraffin to the top of the cylinder containing the soil core.

2. Place the cores in a water bath filled to the level of the top of the soil core and allow them to soak overnight or until saturated.

3. Support the saturated core above a funnel leading to a beaker or graduated cylinder. Carefully, add water to the cylinder above the core and maintain a constant head of water by means of a constant head system (Klute, 1965).

4. Measure the volume of water that passes through the sample during a measured time interval. Repeat the measurements several times. Measure the hydraulic head (water level to base of core).

5. Calculate the hydraulic conductivity, K

$K(cm/hr) = QL/ATΔH$
where Q = water outflow in ml.
L = height of core in cm.
A = cross sectional area of core, cm^2
T = time in hours (or other unit)
ΔH = hydraulic head difference in cm.

2.52 Clod method - (R.K. Guertin)

This method is useful for cemented horizons for which undisturbed cores are difficult to obtain with the normal soil sampling tools.

1. Select a clod of reasonably uniform thickness and trim it to a regular shape, circular or rectangular.

2. Measure the thickness, length and width (or diameter) as accurately as possible. Use calipers and make several measurements of each dimension.

3. Melt a large amount of paraffin wax. Coat the sides of the sample with hot wax (100°C) using a brush.

4. Support the sample, inside a plastic cylinder open at both ends so that the bottom of the clod is flush with the end of the cylinder. Using a spatula, fill the gap between the soil clod and the cylinder wall with wax of a soft plastic consistency. Avoid dropping any wax on the bottom of the clod. Allow the wax to cool.

5. Invert the cylinder and pour melted wax carefully into the cylinder (down the side) until the thickness of the wax is approximately three-quarters the thickness of the sample.

6. After the wax has cooled, heat a metal rod and melt the wax along the edge of the sample to prevent leaking. Cover the bottom of the cylinder with cheesecloth and seal the cheesecloth to the cylinder with wax.

7. Mark the outside of the cylinder in centimeters measured from the bottom of the cylinder. Place the sample in water and let it saturate overnight.

8. Support the cylinder above a funnel leading to a graduated cylinder. Apply a head of water 10 to 20 cm above the base of the cylinder using a constant head device as in 2.51, or by adding water manually to maintain a constant head ± 1 cm. Allow to flow for about 15 minutes before taking readings.

9. Measure the outflow of water during measured time intervals at a constant head of water (or while the head falls 1 cm). Take several readings for each clod.

10. Determine the hydraulic conductivity, K

$K(cm/hr) = Q\ L/At\Delta H$

where Q = water outflow (ml)
L = thickness of clod (cm)
A = cross sectional area of clod (cm^2)
t = time during which outflow was measured (hr)
ΔH = hydraulic head difference (cm), measured from the water level to the bottom of the clod.

NOTE: If a constant head device is not used, record ΔH as the average head during the interval when the outflow was collected. The error is slight if the drop in head is small in relation to ΔH (10% or so).

References

Klute, A. 1965. Laboratory measurement of hydraulic conductivity of saturated soil, in Methods of soil analysis, C.A. Black, ed. Agronomy No. 9., Part 1. Am. Soc. Agron., Madison, Wisconsin.

2.53 Undisrupted Soil Block method for uncemented soils - G.R. Mehuys

This procedure is useful for soil having characteristics such that good core samples cannot be obtained.

Field Procedure

(1) Dig by hand or with back-hoe a large pit at the sampling site.

(2) Establish a flat horizontal surface in one side of the pit at the desired sampling depth.

(3) Carve out a soil block with a butcher knife until the cross-section is approximately 10 x 10 cm and the height is 12 to 15 cm.

(4) Trim the block carefully with a paring knife so that it fits loosely (2 to 3 mm on each side) into a waxed milk carton ($\frac{1}{2}$ imp. gal. size, 10 x 10 cm sides). These are available at any dairy.

(5) Cut the carton to the same height as the soil block and place it over the block.

(6) Dam the outside of the carton at the base with a slurry of fine soil and water (wet sand will work also).

(7) Pour melted paraffin into the space between the soil block and the carton and allow to set (each block requires approximately 200g of paraffin).

(8) Carefully cut through the base of the soil block and remove it from the pit. Trim excess soil from the bottom surface.

(9) Enclose the soil block in a labelled plastic bag.

NOTE: (1) The soil should be moist during sampling.

(2) Minor protuberences such as gravel fragments may be allowed to remain in the sample.

(3) The shape of the cross section of the block is not critical but the sides must be vertical & parallel.

(4) The procedure can be adapted for sampling larger blocks if necessary.

Laboratory Procedure

(1) Slit one side of the carton and remove it from the block.

(2) Repair holes in the paraffin walls of the block with melted paraffin.

(3) Measure the height of the soil block to the nearest millimeter.

(4) Attach a piece of milk carton to the top of the soil block so as to form a water trough for K measurements. Seal it on the outside with paraffin applied with a paint brush. Seal the inside by pouring a small amount of paraffin down each side while tilting the block.

(5) Saturate the soil block from the bottom, increasing the level of water slowly while the sample is being wetted.

(6) Measure K according to the constant head method, as in 2.51.

(7) Remove the water trough and seal the top and bottom surfaces of the block with paraffin. Do not allow the soil block to dry.

(8) Determine the moist volume of block and the bulk density as in 2.23.

(9) From the volume determination, calculate the cross-sectional area of the block by dividing volume by measured height. Calculate hydraulic conductivity according to

$K = QL/AT\Delta H$ as in 2.51

2.6 ATTERBERG LIMITS

2.61 Liquid Limit (ASTM, D 423-66)

2.611 General method for liquid limit

The liquid limit of a soil is the water content, expressed as a percentage of the weight of the oven-dried soil, at the boundary between the liquid and plastic states. The water content at this boundary is arbitrarily defined as the water content at which two halves of a soil cake will flow together over a distance of 1/2 inch (13 mm) along the bottom of the groove separating the two halves, when the cup is dropped 25 times for a distance of 1 cm at the rate of 2 drops per second.

Apparatus

Evaporating dishes, spatula, liquid limit device as depicted in ASTM, D 423-66, grooving tool, moisture cans, balance sensitive to 10 mg. The liquid limit device should be checked and adjusted before use as described in ASTM, D 423-66.

Procedure

(1) Put a 100 g sample of soil that has passed a No. 40 (425 μm) sieve (prepared from 2 mm soil by dry sieving and crushing aggregates but not primary particles) into an evaporating dish. Mix thoroughly with 15 to 20 ml of distilled water by alternately and repeatedly stirring, kneading and chopping with a spatula.

(2) Make further additions of water (a few ml at a time) and mix thoroughly each increment until the mixture is nearly liquid.

(3) When the consistency has reached a point such that the mixture is almost liquid, place a portion of the mixture in the cup. Squeeze it down and spread it evenly with as few strokes of the spatula as possible. Level the soil and trim it to a maximum thickness of 1 cm. Return the excess soil to the evaporating dish.

(4) Divide the soil in the cup by firm strokes of the grooving tool along the diameter of the centerline to form a clean, sharp groove of the proper dimensions.

Up to six strokes may be used to make the groove, each one penetrating a little deeper until the last stroke scrapes the bottom of the cup clean. Make the groove with as few strokes as possible.

(5) Lift and drop the cup by turning the crank at the rate of two revolutions per second, until the two halves of the soil cake come in contact at the bottom of the groove along a distance of about 1/2 inch (13 mm). Record the number of drops required to close the groove (see data sheet).

(6) Remove a slice of the soil approximately the width of the spatula (2 cm) from edge-to-edge of the soil cake at right angles to the groove and including the portion where the groove closed. Place the sample in a tared container, weigh, oven-dry at 105°C, cool in a desiccator, reweigh. Record oven dry weight of soil and loss of water on drying.

(7) Transfer the soil remaining in the cup to the evaporating dish. Wash and dry the cup and grooving tool, and re-attach the cup to the carriage.

(8) Repeat step 3 to 7 adding water as necessary to obtain at least 3 readings between 15 and 35 drops with at least one above and another below 25 drops. Always proceed from dryer to wetter soil.

(9) Calculate the water content of the soil for each test as follows:

$$\frac{\text{weight of water}}{\text{weight of oven-dried soil}} \times \frac{100}{1}$$

(10) Plot a graph of water content vs number of drops on semilog paper with water content on the arithmetic scale. Draw a straight line as nearly as possible through the 3 or more points (see data sheet for Atterberg limits).

(11) Read the liquid limit as the water content corresponding to the point of intersection of the 25 drop ordinate with the line plotted in step 10. Record the liquid limit as the nearest whole number.

2.612 <u>One point method for liquid limit</u>

(1) Proceed exactly as in 2.511 except that a moisture content sample is taken only for a trial requiring between 20 and 30 drops. Before the sample is taken, two consistent, consecutive closures must be obtained with the same sample in the cup. Proceed from dryer to wetter as in 2.511 until a test occurs requiring between 20 and 30 drops.

ATTERBERG LIMITS DATA SHEET

Date: _____

Sample No. _____ Tested by: _____

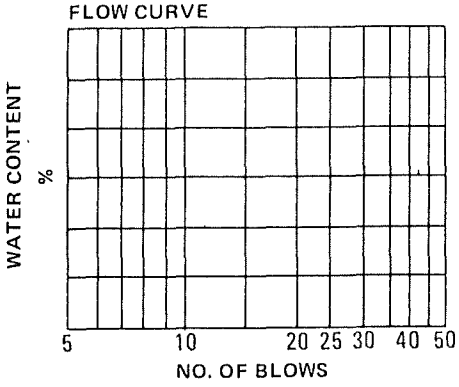
LIQUID LIMIT

Determination no.	1	2	3	4	5	6	7
No. of blows							
Container no.							
Wt. container & wet soil							
Wt. container & dry soil							
Wt. water, W_w							
Wt. container							
Wt. dry soil, W_s							
Water content % W_p							

PLASTIC LIMIT

Determination no.	1	2	3
Container no.			
Wt. container & wet soil			
Wt. container & dry soil			
Wt. water			
Wt. container			
Wt. dry soil			
Water content, W, in % (W_L)			

FLOW CURVE



SUMMARY

Liquid limit, W_L _____ %

Plastic limit, W_p _____ %

Plasticity index, $W_L - W_p$ _____ %

(2) Calculate the water content "w" for the accepted trial, as in 2.511.

(3) Determine the liquid limit by using the formula:

Liquid limit = $w(N/25)^{0.12}$ (see Table 7) where N = the number of drops required to close the groove at water content w.

Table 7. Values of $(N/25)^{0.12}$ for calculating liquid limit

N	$(N/25)^{0.12}$	N	$(N/25)^{0.12}$
20	0.974	26	1.005
21	0.979	27	1.009
22	0.985	28	1.014
23	0.990	29	1.018
24	0.995	30	1.022
25	1.000		

NOTES:

(1) The results are influenced by the time required to make the test and the water content at which the test is begun. The ASTM procedure for referee purposes calls for a mixing period of 5 to 20 minutes (the longer period for the more plastic soils); seasoning 24 hours in a humidifier; remixing before placing in the cup; adding water in increments of 1 ml; placing in cup, testing and weighing - 3 minutes; washing cup and grooving tool, adding water and remixing - 3 minutes.

(2) Usually a portion of the soil taken for the liquid test is used for the plastic limit test. The sample is taken before the water content has reached the liquid limit.

2.62 Plastic Limit (After ASTM, D 424-59)

The plastic limit of a soil is the water content (as a percentage of the weight of oven-dry soil) at the limit between plastic and semi-solid states. It is the lowest water content at which the soil can be rolled into threads 1/8 inch (3 mm) in diameter without the threads breaking into pieces.

Apparatus

Evaporating dish, spatula, ground glass plate or glazed paper, moisture cans, balance sensitive to 10 mg.

Procedure

(1) Put about 15 g of soil that has passed a No. 40

(425 μm) sieve, prepared from 2 mm soil by dry sieving and crushing aggregates but not primary particles, into an evaporating dish. Mix thoroughly with distilled water until the mass becomes plastic enough to be shaped into a ball. Take a portion of the ball weighing about 8 g for the test sample. Alternatively an 8 g portion of the soil material prepared for the liquid limit test 2.61 may be used.

(2) Squeeze and form the 8 g sample into an ellipsoidal-shaped mass. Roll the mass between the fingers and a ground glass plate (or glazed paper) with just enough pressure to form a thread of uniform diameter throughout its length. The rate of rolling should be 80 to 90 strokes per minute (a stroke is 1 complete back and forth motion).

(3) When the diameter of the thread reaches about 3 mm, break the thread into 6 or 8 pieces. Squeeze the pieces together between the thumbs and fingers and form a uniform ellipsoidal shape and re-roll as before.

(4) Repeat step 3 until the thread crumbles under the pressure required for rolling and the soil can no longer be rolled into a 3 mm thread. The soil may crumble when the thread has a diameter greater than 3 mm.

(5) Collect the pieces of crumbled soil together, place them in a tared container, weigh, oven-dry at 105°C and re-weigh (see data sheet for Atterberg limits).

(6) Calculate the plastic limit as the water content in percentage of the weight of the oven-dry soil:

$$\text{Plastic limit} = \frac{\text{weight of water}}{\text{weight of oven-dry soil}} \times \frac{100}{1}$$

Report the plastic limit to the nearest whole number.

2.63 Plasticity Index

Calculate the plasticity index as follows:

(liquid limit - plastic limit) = plasticity index (%).

Under the following conditions, the plasticity index cannot be calculated and it is reported as NP (non-plastic).

(1) When either the liquid limit or the plastic limit cannot be determined.

(2) When the plastic limit is equal to or greater than the liquid limit.

(3) When the soil is extremely sandy, the plastic limit test should be made before the liquid limit. If the plastic limit cannot be determined, report both plastic limit and liquid limit as NP.

References

(1) American Society for Testing and Materials. 1971. The annual book of ASTM standards. Part II, 225-232.

(2) Sowers, G.F. 1965. Consistency. pp. 391-399 In Methods of Soil Analysis, C.A. Black, ed. Agronomy No. 9, Part 1. Am. Soc. Agron., Madison, Wisconsin.

2.7 SPECIFIC SURFACE AREA - J.G. Ross

Total surface area is a fundamental soil property which is closely related to several soil physical and chemical properties. The conventional methods in which ethylene glycol is used as the adsorbed phase have the common disadvantage of being very time consuming. The method (1) in which the adsorbed phase is ethylene glycol monoethyl ether (EGME) is similar to, but much more rapid, than the ethylene glycol methods.

Reagents

1. Ethylene glycol monoethyl ether

2. Calcium chloride, 1N solution

3. Hydrogen peroxide (30-35%)

Procedure

(1) Grind air-dry samples to pass a 60 mesh sieve.

(2) Destroy organic matter with H_2O_2 (2.111 to the end of step B2).

(3) Saturate samples with Ca by washing three times with 1N $CaCl_2$. Remove excess salt by washing with distilled H_2O until the test with $AgNO_3$ is negative. Washings may be done using the centrifuge or Buchner funnels.

(4) Dry samples in air and again grind to pass a 60 mesh sieve.

(5) Weigh 1.1 g soil sample (or 0.3 g clay sample) and transfer into shallow aluminum weighing cans. Dry to constant weight over P_2O_5 in an evacuated desiccator.

(6) At the beginning of a working day treat samples with approximately 3 ml of EGME to form a soil-EGME slurry, place in a desiccator over $CaCl_2$ and allow to equilibrate for 30 minutes. Then evacuate desiccator for 45 minutes.

(7) About one hour before the end of the working day, weigh samples and re-evacuate the desiccator for 45 minutes.

(8) At the beginning of the next working day weigh samples again. Generally this latter weight will agree closely with the previous weight.

(9) Return samples that have not attained a constant weight to the desiccator and evacuate. Weigh again about midday or at the end of the working day. Repeat this step until weight is constant.

(10) The total surface area for each sample is calculated by dividing the grams of adsorbate retained per gram of soil by 0.000286 g/m^2 (2).

Note

1. The calcium saturation and the H_2O_2 oxidation treatments could be omitted for samples having high base (Ca and Mg) saturation and low organic matter content.

References

(1) Hielman, M.D., Carter, D.L. and Gonzalez, C.L. 1965. The ethylene glycol monoethyl ether (EGME) technique for determining soil surface area. Soil Sci. 100:409-413.

(2) Carter, D.L., Heilman, M.D., and Gonzalez, C.L. 1965. Ethylene glycol monoethyl ether for determining surface aera of silicate minerals. Soil Sci. 100:356-360.

2.8 FIBER CONTENT (of organic soil)

This provides a measure of the degree of decomposition of the material. The syringe method (2.81) can be used in the field or the laboratory. Method 2.83 is a laboratory method that provides a measure of the particle-size distribution of fibers as well as total fiber content.

2.81 Unrubbed Fiber Content, syringe method. (from unpublished procedure of W. Lynn, SCS, Lincoln, Nebraska.)

Apparatus

Modified plastic hypodermic syringe as illustrated in Fig. 3. The syringe is modified by cutting away half of the cylinder wall, in a longitudinal direction, between the zero and 6 ml marks. The plunger end, the needle end and the piston are not altered. Only those brands of syringes (e.g., Brunswick, Monoject) that have calibration marks embedded in the plastic are suitable for extended use.

8 cm diameter 100 mesh sieve, paper towelling.

Preparation of sample

Place about 25 cm^3 of moist sample on a strip of paper towel and form the sample into a cigar shape. Roll up the sample in the paper towel and squeeze lightly to express surplus water. The objective is to dry the sample until it does not glisten but is still very moist. Unroll the towel and, using scissors, cut the sample into about 6 mm lengths.

Mix the cut-up sample to ensure random selection of sub-samples.

Procedure

(1) Pack the modified syringe adjusted to 5 ml capacity level full with sample pressing hard enough to express air but not water.

(2) Transfer all of the soil material in the syringe, using the rounded end of a 6 mm wide spatula, onto the 100 mesh sieve.

(3) Wash the sample with cold water from a faucet adjusted to deliver about 400 ml in 5 seconds until the water passing through the sieve appears clean when observed against a white surface. Collect the sample together at one side of the sieve, and dry it by pressing a finger against the sample while holding a wad of paper towel against the bottom of the sieve.

(4) Transfer the sample completely into the modified syringe and pack it level into the smallest volume by simultaneously pushing the syringe piston and levelling the surface with a spatula. Ensure that the water content is about the same as that of the intial sample (step 1). Water can be withdrawn if necessary by lightly pressing a piece of paper towel onto the sample surface.

(5) Read the volume of sample in the syringe and express it as a percentage of the initial volume. This percentage is the unrubbed fiber content.

(6) Transfer the sample onto the 100 mesh sieve for determination of rubbed fiber content.

2.82 Rubbed Fiber Content - (Lynn, unpublished, see 2.81).

Sample

Use the sample remaining after the unrubbed fiber content determination (step 6 in 2.81).

(1) Rub the sample lightly between thumb and finger(s) under a stream of water until the water passing through

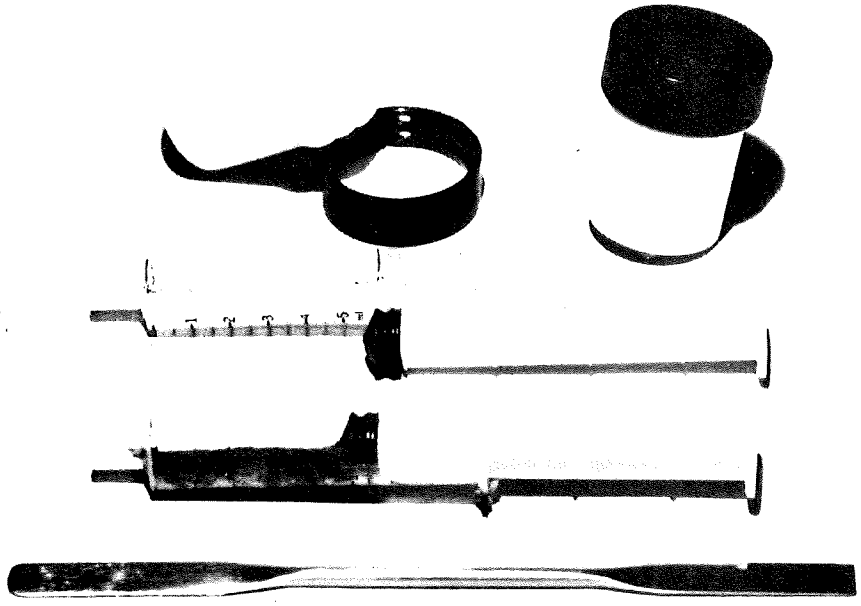


Fig. 3. Seringue modifiée vide et contenant un échantillon de tourbe, flacon d'échantillonnage en matière plastique et spatule pour la détermination de la teneur en fibres.

the sieve is clean. Clean fibers will roll between thumb and fingers like fragments of string rather than glide or smear.

(2) Dry the sample residue on the sieve as outlined in step 3 of 2.81. Transfer the sample residue completely to the modified syringe and measure its volume as in step 4 of 2.81. Calculate this volume as a percentage of the initial volume of sample taken in step 1 of 2.81 (5 ml). This percentage is the rubbed fiber content. Discard the residue.

NOTES:

(1) This procedure is rapid and the precision is adequate for most purposes. It can be used in the field or in the laboratory. It is being used both in Canada and the United States.

(2) A more rigorous procedure was outlined by Sneddon, Farstad and Lavkulich (1971). See Can. J. Soil Sci. 51, 138-141.

2.83 Fiber content and particle-size distribution - (Dinel and Lévesque, 1975).

Apparatus (Fig. 4)

The apparatus consists of a cylinder with an interior diameter of 14.5 cm and a height of about 46 cm. with a hole near the base for entry of air (A) and outlet of water (B).

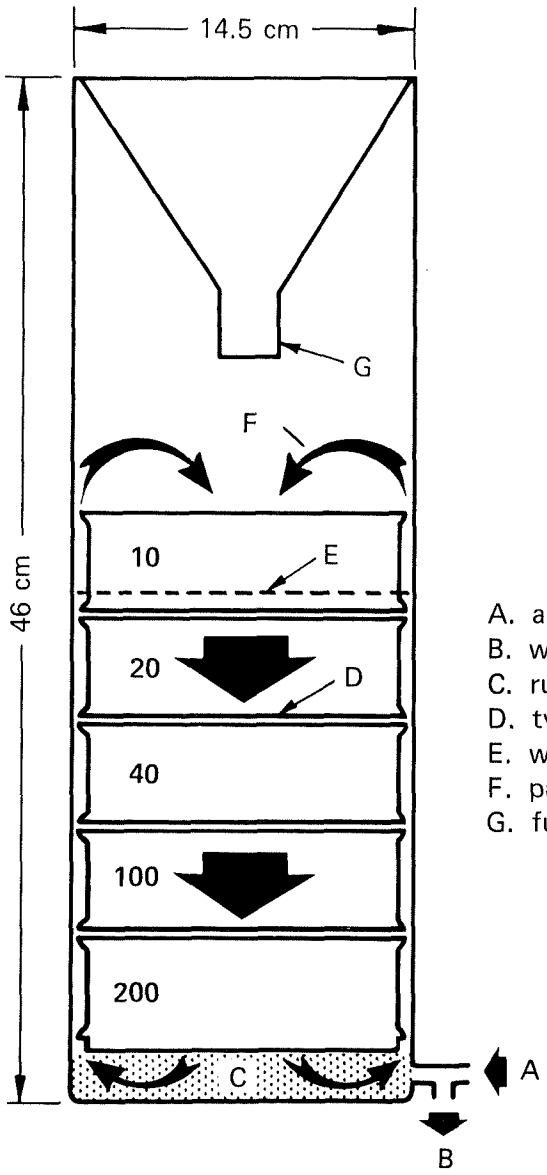
A piece of rubber tubing about 1.5 cm in diameter and 45 cm long is formed into a ring (C) and placed at the bottom of the cylinder. A nest of sieves (10, 20, 40, 100 and 200 mesh), 13.5 cm in diameter is assembled with a "gasket" (D) made from thin (2 mm) tygon tubing between sieves to provide a seal. The sieves are held together with an elastic band. The top of the cylinder is closed with a funnel (G).

Procedure

(1) Place 25 g of moist sample broken into small pieces, in 300 ml of water and shake the suspension for 16 hr. Determine the water content of duplicate 25 g samples by weighing, drying at 70°C and reweighing.

(2) Pour the suspension onto 200 mesh sieve and wash with water to remove the material finer than 200 mesh.

(3) Assemble the apparatus and place the material retained on the 200 mesh sieve on the top sieve (10



A. air inlet
B. water outlet
C. rubber tubing, 1.5 cm diameter
D. tygon tubing gasket
E. water level
F. path of air
G. funnel

Fig. 4 Apparatus for particle-size analysis and fiber content of peat (Method 2.73)

mesh).

(4) Fill the cylinder with water to just above the level of the screen in the top sieve.

(5) Introduce air through A at a rate sufficient to shake the nest of sieves and continue bubbling air through vigorously for 1 hr.

(6) Remove the nest of sieves, recover the fibres remaining on each sieve by washing the fibres onto a funnel fitted with a coarse filter paper, dry the various fractions at 70°C and weigh.

(7) Calculate the proportion of the sample in each particle size range, as a percentage of the dry weight of the total sample.

References

Dinel, H. and Lévesque, M. 1976. Une technique simple pour l'analyse granulométrique de la tourbe en milieu aqueaux. Can. J. Soil Sci. 56, 119-120.

2.9 MICROMORPHOLOGY - R.K. Guertin and J.A. McKeague

Soil micromorphology may be defined broadly as the study of soils with the aid of microscopes; thus it includes the range of magnification from 10 x or less with a light microscope to more than 10,000 x with an electron microscope. The major activity in soil micromorphology is the study of soil fabric in thin section using a polarising light microscope.

2.91 Stereomicroscope, magnification of about 10 to 30 times

This procedure may be considered as the next step after description of the macromorphology of the soil. It is useful in revealing the distinctness, class and size of secondary peds and of fine structural features in general. Features, such as clay skins and other cutans, can be seen much more clearly than under a hand lens. Examination of freshly-taken soil monoliths under a stereomicroscope complements macro-descriptions of the soil and aids in the selection of features for more detailed micromorphological study (McKeague, Bourbeau and Cann, 1967). Relatively undisturbed bulk samples and peds may also be studied in this way.

2.92 Thin Sections

Apparatus

Soil thin sections can be made using equipment that ranges tremendously in sophistication and cost. Generally, the best results are obtained with good equipment but the skill of the technician is at least as important. Minimum equipment includes

a hack saw, sandpaper, cold setting plastic from a hobby shop, microscope slides and a polarizing microscope. Almost essential are: a diamond saw, a good source of vacuum, a lap, various abrasives, a slide warmer, glass plates for hand grinding of sections. Preparation of good thin sections, especially large sections, is facilitated by the availability of diamond laps with different grit sizes and an automatic section grinder and polisher (Jongerius and Heintzberger, 1963). Many different plastics are used to impregnate soil samples.

Reagents

Acetone
A polyester resin such as Polylite (Reichhold Chemicals)
Lupersol DDM catalyst, methyl ethyl ketone peroxide (Harchem)
1% cobalt nepthenate
Canada balsam

Sample Collection

Undisturbed samples are required. They may be obtained in a variety of ways: clods of coherent or cemented soil, cores of loose soil, rectangular metal boxes (Kubiena boxes) of non-cemented, reasonably stone-free soils. Open galvanized iron boxes measuring 8 x 6 x 5 cm (or other size) are pushed or cut into the horizon to be sampled, trimmed, and covered with plywood pieces held in place by masking tape. The orientation of samples is marked.

Impregnation of Samples

(1) For most work, the samples are dried at 100°C and placed in a desiccator. The dried samples are placed in a suitable container (aluminum foil loaf pan, double paper hot drink cup, etc.) and evacuated in a modified desiccator (Guertin and Bourbeau, 1971) or other device. The plastic mixture (2 ℓ polylite, 2 ℓ acetone, 1 ml Lupersol, 0.2 ml 1% cobalt naphthenate) is added slowly to the evacuated sample and the vacuum is adjusted to avoid boiling of the plastic mixture. Plastic is added until it covers the sample by about 3 cm.

(2) The samples are removed from the desiccator and placed in a fume hood. Plastic is added periodically to compensate for volume loss due to evaporation of acetone. Containers may be covered with foil to reduce the rate of evaporation, if necessary. The samples remain in the fume hood until the plastic hardens (about 2 weeks to 2 months).

(3) The samples are placed in an oven in the fume hood and the temperature is raised gradually over a period of a few days from 40° to 100°C. Remove the samples from the oven.

Cutting, Grinding and Mounting

(1) Cut the cured samples in half using a diamond saw. If water is used as a lubricant, use the minimum amount possible and dry the sample in a jet of compressed air immediately after

sectioning. Kerosene or preferably an oil of low viscosity and low volatility should be used for poorly-impregnated samples.

(2) Check the quality of impregnation of the sample. If it is poor, set the sample aside for re-impregnation. Cut impregnated samples into chips about 7 mm thick and the size of a petrographic slide.

(3) Re-impregnation of soil chips is done as follows: the chip is placed on a piece of aluminum foil and the surface of the chip is covered with polylite resin mix. The plastic is cured in an oven at 60°C.

(4) The impregnated chips are ground on one side using diamond laps, alundum powders on a lap, or sanding discs. Progressively finer abrasives are used.

(5) Clean the chip by placing it in water in an ultrasonic bath and dry the surface with a jet of air.

(6) Cement the polished surface of the chip to a petrographic slide using epoxide and hardner. Mix the epoxy thoroughly, allow to stand for 5-10 min. for bubbles to pop, and place epoxy on the soil chip. Warm chip on hot plate to help get rid of bubbles. Place one edge of a glass slide on the chip and carefully lower the slide onto the chip, wedging out air bubbles and excess plastic. Place chip with glass slide on top of a flat surface and allow epoxy to harden. If the chip is wedged-shaped, put it on a styrofoam sheet and hold the glass slide in place with pins.

Finishing

(1) Label the section with a diamond pen, sample no. and orientation. Place the bonded glass slide and chip in a resectioning holder (Copeland, 1965), and cut off the excess material with a diamond saw leaving a section of soil about 0.5 mm thick.

(2) Insert the slide in a holder (Cochran and King, 1957) and grind the section on a lap using progressively finer diamond grit or other abrasive. Grinding may be completed by hand using a glass plate and 600 grit abrasive. Thickness of the section is judged by examination under a polarizing microscope - quartz white indicates about 30 μm.

(3) Clean the section in an ultrasonic bath.

(4) Cement a cover glass to the slide using Canada balsam and taking precautions to exclude air bubbles. Heat gently to cure. Remove excess balsam, and clean the slide in xylene.

(5) Label the section using a fine-tipped black marker. This makes the sample no. and orientation easily visible.

Microscopic Study of Thin Sections

The exact procedure depends upon the purpose of the work. In general, it is desirable to study the whole slide at low magnification (5 to 25 x) to note major features. Other magnifications up to about 400 x are used to identify particular features. For most studies of general soil fabric, magnifications of 50 to 100 x are used. Fabric classification is generally done accordingly to the system of Brewer (1964) including modifications by Brewer and Pawluk (1975). Numerous features such as argillans, papules, voids, sesquioxidic nodules, various minerals, may be estimated qualitatively, or quantitatively by point counting. A microprobe may be used to determine the chemical composition of unknown features.

2.93 Scanning Electron Microscopy

This instrument makes it possible to obtain stereoscopic pictures of soil surfaces at magnifications from about 50 to 30,000 times. The sample must be polished and coated with a thin metallic layer.

Notes

(1) Scotchcast, an epoxy resin, is suitable for impregnating soil samples. See Innis and Pluth (1970).

(2) Wet samples may be impregnated. Polyethylene glycol (carbowax) used for organic samples (Mackenzie and Dawson, 1961) and an acetone exchange procedure followed by plastic for mineral samples (Miedema et al., 1974). This has the advantage of avoiding changes in fabric due to shrinkage or drying.

(3) Preparation of good thin sections is achieved only through experience. This outline of methods does not indicate all the details of procedure.

(4) Good thin sections are essential if quantitative estimates of pores, argillans etc. are to be done.

(5) Large thin sections (15 cm by 10 cm) are useful in some studies (Jongerius and Heintzberger, 1963). However, small sections (3 x 2 cm) are easier to prepare by hand and they are adequate for many purposes. Equipment for preparation of large sections is costly.

(6) Impregnation may be improved by applying pressure to the soil-plastic mix after adding the plastic under vacuum.

References

(1) Brewer, R. 1964. Fabric and mineral analysis of soils. Wiley, New York.

(2) Brewer, R. and Pawluk, S. 1975. Investigations of some soils developed in hummocks of the Canadian sub-Arctic and southern-Arctic regions. 1. Morphology and Micromorphology. Can. J. Soil Sci. 55, 301-319.

(3) Cochran, M. and King, A.G. 1957. Two new types of holders used in grinding thin sections. Amer. Mineral. 42, 422-425.

(4) Copeland, D.A. 1965. A simple apparatus for trimming thin sections. Amer. Mineral. 50, 1128-1130.

(5) Guertin, R. and Bourbeau, G.A. 1971. Dry grinding of soil thin sections. Can. J. Soil Sci. 51, 243-248.

(6) Innes, R.P. and Pluth, D.J. 1970. Thin section preparation using epoxy impregnation for petrographic and electron microprobe analysis. Soil Sci. Soc. Am. Proc. 34, 483-484.

(7) Jongerius, A. and Heintzberger, G. 1963. The preparation of mammoth-sized thin sections. Soil Survey Papers, Neth. Soil Survey Inst. 1, 37 pp.

(8) Mackenzie, A.F. and Dawson, J.E. 1961. The preparation and study of thin sections of wet organic soil materials. J. Soil Sci. 12, 142-144.

(9) McKeague, J.A., Bourbeau, G.A., and Cann, D.B. 1967. Properties and genesis of a bisequa soil from Cape Breton Island. Can. J. Soil Sci. 47, 101-110.

(10) Miedema, R., Pape, Th., and Van de Waal, G.J. 1974. A method to impregnate wet soil samples, producing high-quality thin sections. Neth. J. Agric. Sci. 22, 37-39.

(11) Soil Conservation Service. 1972. Revised. Soil survey laboratory methods and procedures for collecting soil samples. Method 4E, pp. 18-21 S.C.S., Washington, D.C.

(12) Wang, C., Nowland, J.L., and Kodama, H. 1974. Properties of two fragipan soils in Nova Scotia including scanning electron micrographs. Can. J. Soil Sci. 54, 159-170.

3. - CHEMICAL ANALYSES

The chemical methods outlined are used in soils laboratories in Canada but the coverage of methods is not complete and all minor modifications of methods are not included. Opinions are given, in some cases, on the preferred method for a given purpose, but such opinions are not shared by all soil scientists in Canada. Several of the chemical methods outlined are used in mineralogical analysis. Other chemical methods used specifically in mineralogical determination are given in the section on mineralogical analysis.

3.1 pH - V.E. Osborne

Measurement of soil pH in 0.01 M $CaCl_2$ (3.11) is the preferred method for most purposes because of advantages pointed out by Peech (1965).

1. The pH is almost independent of dilution over a wide range.

2. The pH measured is almost independent of the concentration of soluble salt present in non-saline soils.

3. It provides a good approximation of the pH of the soil solution under field conditions.

4. Errors due to the liquid junction potential are minimized because the soil suspensions are flocculated.

Measurement of the pH of a saturated soil paste (3.14) is not recommended because of theoretical (junction potential) and practical (difficulty of obtaining reproducible results) disadvantages. It is included because saturated soil pastes are prepared commonly in the analysis of saline soils and the pH of the pastes is usually measured.

There is no point in measuring the pH of most soils containing free carbonates of Ca or Mg as the value obtained depends upon the partial pressure of CO_2 which is generally uncontrolled during pH measurements (Turner and Clark, 1956). It is, however, useful to measure the pH of saline, calcareous soils as values above about 8.5 indicate sodium carbonate (Richards, 1954).

3.11 pH in 0.01 M $CaCl_2$ (Peech, 1965).

Reagents

0.01 M $CaCl_2$ - If large volumes are required, make a stock solution of 3.6 M $CaCl_2$ (1059 g of $CaCl_2.2H_2O$ to 2 ℓ with distilled water, and dilute 50 ml of this stock solution to 18 ℓ with distilled water. Check the pH; it should be between 5.0 and 6.5. If it is not, adjust by adding $Ca(OH)_2$ or HCl. To check the concentration of the solution, measure its conductivity; the specific conductivity should be 2.32 ± 0.08 millisiemens per cm (ms/cm) at 25°C.

Procedure

(1) Place about 10 g of soil into a 50 ml beaker, or a disposable paper or plastic cup, add about 20 ml of 0.01 M $CaCl_2$ solution and stir the suspension several times during the next 30 minutes. For organic soils that absorb all of the solution use a 4 to 1 solution:soil ratio.

(2) Let the suspension stand for 30 minutes to allow most of the sediment to settle.

(3) Measure the pH by immersing the glass electrode into the partly settled suspension (do not immerse it to the bottom of the container) and placing the calomel electrode in the clear supernatant solution. If a combination electrode is used immerse it in the supernatant solution. The pH meter is adjusted by setting it to the pH of buffer solutions at the same temperature as the soil suspension. The meter should be checked against two buffers one of which has a pH at the lower and the other at the upper end of the range of pH of the soils being measured.

(4) Record the pH in $CaCl_2$ to one decimal place.

3.12 Field pH, in $CaCl_2$, of Moist Peat Samples

(1) Place 4 ml of 0.015 M $CaCl_2$ solution in a small plastic screw top bottle. Transfer $\frac{1}{2}$ teaspoonful of moist peat sample into the bottle and shake the mixture.

(2) After about 15 minutes, read the pH on narrow gauge test paper or by pH meter.

NOTE:

The 0.015 M $CaCl_2$ is used to allow for the water in the moist peat sample. If the $\frac{1}{2}$ teaspoonfull of moist peat contains 2 ml of pure water, the pH is measured in 0.01 M $CaCl_2$.

3.13 pH in Water

(1) To 20 g of soil in a 50 ml beaker or plastic cup, add 20 ml of distilled water and stir the suspension several times during the next 30 minutes. For samples with a high content of organic matter, use a 1:2 or a 1:4 soil:water ratio.

(2) Allow the suspension to settle for 30 minutes.

(3) Measure the pH as outlined in 3.11, step 3.

3.14 pH of Saturated Soil Paste (Handbook 60, U.S.D.A.)

(1) Prepare a saturated soil paste by adding water to soil, stirring thoroughly and tapping.

(2) Allow the mixture to stand for an hour.

(3) Insert the electrodes into the paste and raise and lower repeatedly until a representative pH reading is obtained.

3.15 pH in 1M NaF (Brydon and Day, 1970)

This procedure, originally devised as a test for allophane, is useful in indicating soils having an appreciable content of reactive Al(OH) groups such as podzolic B horizons. Podzolic B horizons usually give a fluoride pH greater than 10.3.

3.151 Field test with pH paper

Place 10 mg of dry, crushed soil, (estimated by the size of a 3-mm cone, or the amount easily seen on the tip of a pocket-knife blade), in the well of a spot plate. Add 1 drop of a saturated NaF solution (approximately 1 M) and stir with the knife blade. After 2 min, determine the pH using pH test paper (Accutint narrow range, pH 8.9-10.0 and pH 10.1-12, Anachemia Co., or equivalent).

3.152 Laboratory test

Add 25 ml of 1M NaF to 0.5 g of soil ground to pass a 100 mesh sieve. Stir and read the pH of the suspension after 2 min.

References

(1) Brydon, J.E. and Day, J.H. 1970. Use of the Fieldes and Perrott sodium fluoride test to distinguish the B horizons of Podzol in the field. Can. J. Soil Sci. 50, 35-41.

(2) Peech, M. 1965. Hydrogen-ion activity in Methods of Soil Analysis Part 2; C.A. Black, ed. pp. 914-926.

(3) Richards, L.A., ed. 1954. Diagnosis and Improvement of Saline and Alkali Soils. U.S. Salinity Laboratory, U.S. Dept. Agr., Hbk. 60, 160 pp.

(4) Turner, R.C. and Clark, J.S. 1956. The pH of Calcareous Soils. Soil Sci. 82, 337-341.

3.2 SOLUBLE SALTS - A.K. Ballantyne

Determination of soluble salts in a saturation extract is the preferred method as this gives a closer approximation of the salinity

of the natural soil solution than does analysis of extracts of wider water to soil ratios. However, for some purposes, other ratios are suitable. If the amount of soil sample is limited a 1 to 5 soil to water ratio might be the best choice. Sparingly soluble salts such as gypsum result in an overestimation of salinity when high ratios of water to soil are used.

Some suggestions on the preparation of a saturated soil paste are:

(1) Dry samples of organic soils require an overnight wetting period. Pastes of such soils usually stiffen on standing and require addition of water and remixing to obtain a stable saturated paste.

(2) Coarse-textured soils are oversaturated readily. Further soil should be added if free water stands at the surface after the equilibration period.

(3) With fine-textured soil, sufficient water should be added immediately with little mixing to bring the sample rapidly to near saturation. This helps to prevent puddling and results in a more definite endpoint.

3.21 Soluble Salts in Saturation Extract (conductivity, cations and anions)

(1) Weigh 200 to 1000 g (usually 250 g yields an adequate volume of extract) of air-dry soil of known water content into a plastic or metal container with lid.

(2) Add distilled water from a large burette and stir the mixture with a spatula until the soil is saturated. Consolidate the mixture by tapping the container periodically on the bench during mixing. At saturation, the soil paste glistens as it reflects light, flows slightly when the container is tipped, and slides freely off a spatula for all soils except those of high clay content.

(3) Cover the container and allow the samples to stand for at least an hour; then re-check the criteria for saturation. If the paste has stiffened markedly or lost its glisten, add water and mix again. If free water has accumulated at the surface, add a weighed amount of dry soil and remix.

(4) Record the volume of water added and calculate the saturation percentage as the total weight of water in the sample (that added and hygroscopic water) as a percentage of the oven-dry weight of soil. Alternatively, the saturation percentage may be determined by taking a subsample of the saturated paste, oven-drying it at 105°C and reweighing. If this method is used it is not necessary either to weigh the initial soil sample or to measure the water added.

(5) Allow the saturated paste to stand 4 hours or more and transfer it to a Buchner funnel fitted with a low ash, highly retentive filter paper. Apply vacuum and collect the filtrate in a test tube or bottle. If the initial filtrate is turbid, refilter it. Terminate filtration when air begins to pass through the filter. One drop of 0.1% sodium hexametaphosphate solution may be added for each 25 ml of extract (to prevent precipitation of $CaCO_3$).

(6) Measure the conductivity of the saturation extract using a Wheatstone bridge or other conductivity bridge and a conductivity cell with cell constant of about 1 cm^{-1}. (See Bower and Wilcox for details). Report conductivity as millimhos/cm at 25°C. Standardize the cell against 0.01 N KCl (0.7456 g of KCl made to 1 ℓ with distilled water at 25°C). At 25°C, the conductivity of this solution is 1.4118 mmhos/cm.

(7) Determine cations in solution by standard flame emission or atomic absorption procedures. Alternatively complexometric methods may be used for Ca, Mg, etc. (see Bower and Wilcox, 1965; or Richards, 1954). Reliability of data should be checked by analyzing extracts of standard soil samples and comparing the results obtained with "best" values. The cations that are usually determined are: Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}.

(8) Determine anions in solution by standard methods given by Bower and Wilcox, 1965. The anions commonly determined are: CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-}. As with cations, reliability of data should be checked by analysis of standard soil samples of known salt content.

3.22 Soluble Salts in Extracts of 1:1 Soil:Water Mixtures

(1) Weigh the required amount of air-dry soil (100 g) and transfer it to a bottle or flask. Add the required amount of water to give a 1:1 mixture (correction should be made for hygroscopic water in soil having high contents of organic matter or clay).

(2) Shake the mixture on a mechanical shaker for 1 hour. End-over-end shaking ensures thorough mixing. If a mechanical shaker is not available, shake the container vigoursly by hand for 1 minute at least 4 times at 30 minute intervals.

3.23 Soluble Salts in Extracts of 1:5 Soil:Water Mixtures

Follow the procedure outlined in 3.22 except that the ratio of soil to water is 1 to 5.

3.24 Soluble Salts in Groundwater

Samples of groundwater taken from piezometers, etc. may be analyzed for soluble salts in the same way as soil extracts.

3.25 Gypsum

(1) Weigh 15 g of air-dry 2 mm soil into a 500 ml flask, add 300 ml of distilled water and shake overnight.

(2) Filter the suspension and determine Ca in the filtrate by atomic absorption or titration.

(3) Calculate gypsum in me/100 g soil as follows: (soluble Ca in the above filtrate in me/100 g soil) - (soluble Ca at the saturation percentage in me/100 g soil).

NOTES:

(1) Do not determine gypsum in any soil with a conductivity of less than 2 mmhos/cm or less than 20 me of Ca per liter of saturation extract, as none is present.

(2) Other methods of determining gypsum are given in Richards ed. 1954.

3.26 Sodium Adsorption Ratio (SAR)

This ratio is useful in relating the concentrations of cations in solution to exchangeable cations (Richards, 1954). It may be calculated from data obtained in 3.21, 3.22, 3.23 or 3.24. The soil:water ratio involved should be specified.

$$SAR = Na^{+} / \sqrt{(Ca + Mg)/2}$$

where Na^{+}, Ca^{2+} and Mg^{2+} concentrations are expressed in me/ℓ.

3.27 Soluble Sodium Percentage

This calculated value is useful in indicating the degree of dominance of Na^{+} as a soluble cation. It is useful as a supporting criterion in the distinction of Solonetzic from Chernozemic soils (Ballantyne and Clayton, 1963). Soluble sodium percentage $= \frac{Na^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \times 100$

where cation concentrations are expressed in me/ℓ. Use of a low soil:water ratio is desirable.

References

(1) Ballantyne, A.K. and Clayton, J.S. 1963. The relationship of water-soluble cations to field separations of Chernozemic and Solonetzic soils. Can. J. Soil Sci. 43, 359-369.

(2) Bower, C.A. and Wilcox, L.V. 1965. Soluble salts In Agronomy No. 9. Methods of Soil Analysis, Part 2, Black, C.A. ed., pp. 933-951.

(3) Richards, L.A. ed. 1954. Diagnosis and Improvement of Saline and Alkali soils. U.S. Salinity Laboratory, U.S. Dept. Agr. Hbk. 60, 160 pp.

3.3 CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS - V.E. Osborne

The cation exchange capacity (CEC) of a soil varies with pH. Thus, there are two general approaches to the measurement of CEC: 1) to extract the soil with a neutral salt and thus measure CEC at the pH of the soil, 2) to extract the soil with a solution buffered at a given pH, often 7, and thus measure CEC at a fixed pH. The preferred method for most purposes is to determine CEC at the pH of the soil using NaCl as extractant. However ammonium acetate at pH 7 has been widely used for determining CEC despite the problem of ammonium fixation by some soils. The use of NaCl as an extractant has the disadvantage that exchangeable Na^+ cannot be determined. For many acid soils exchangeable Na^+ values are low, and Na^+ is commonly not determined. For soils of arid areas and especially those developed in saline materials, however, the determination of exchangeable Na^+ is important. It can be extracted with other suitable salts.

Sodium acetate has been used for determining the CEC of saline and alkali soils because some of these soils fix considerable amounts of NH_4^+ (Richards, 1954). For saline soils, the determinations of soluble salts and of CEC are generally adequate. Exchangeable cations in such soils can be estimated from soluble salt data (Richards, 1954), and there is no generally accepted way of determining exchangeable cations in saline soil.

3.31 Permanent charge CEC and exchangeable cations by NaCl extraction - S.S. Singh

The cation exchange capacity (CEC) of a soil is not a fixed, unique characteristic but may be changed by external conditions prior to and during the procedure for the determination of exchangeable cations or the CEC. However, many physicochemical properties of soils and clays appear to be determined by the equilibrium of electro-statically bonded ions. The sum of cations measured by extraction with neutral salts has greater significance than the so-called total CEC measured by buffered salts.

The method was developed by Singh based upon Clark's (1965) studies. It is designed for convenience of determination of exchangeable Ca, Mg and K by atomic absorption. Clark's procedure, which has been used for the determination of CEC and base saturation, involves equilibration of soil with 0.01 M $CaCl_2$ before extraction with NaCl. It was designed to determine relationships among pH, solubility of Al compounds and base saturation. Clark's procedure is not suitable for the determination of exchangeable cations because some of the exchangeable Mg, K, Al are replaced by Ca in the initial step.

3.311 Extraction and determination of exchangeable cations by atomic absorption

Sample Size

Sample size is based upon an estimate of the pH and CEC of the soil. Table 8 gives appropriate sample weights for different exchange capacities and indicates the concentration of different cations expected in diluted NaCl extracts. Estimates of cation exchange capacity may be made on the basis of the clay and organic matter content of soil samples. For completely unknown soil samples, assume a CEC of 5 me/100g.

Table 8. Calculated concentrations of different cations for AA determination in NaCl extracts (based on Ca=50%; Mg=10%; K=5% and Al=35% of the exchange complex)

C.E.C. meq/100g	Sample weight	Ca	Mg	K	Al*
			ppm		
	Extractant Conc. 2N NaCl; Dilution 1:50				
20	5.0g	4.0	0.5	0.8	1.25
	2.5g	2.0	0.25	0.4	-
10	10g	4.0	0.5	0.8	1.25
	5g	2.0	0.25	0.4	-
5	20g	4.0	0.5	0.8	1.25
	10g	2.0	0.25	0.4	-
2.5	30g	3.0	0.37	0.6	0.95
	20g	2.0	0.25	0.4	-
	Extractant Conc. 1N NaCl; Dilution 1:25				
1.0	30g	2.4	0.30	0.48	0.75
	20g	1.6	0.20	0.32	
0.5	30g	1.2	0.15	0.24	-

*Experience has shown that the 8-hydroxyquinoline method for the determination of Al is reliable and more sensitive.

Procedure

(1) Transfer appropriate weight of soil into 90 ml plastic centrifuge tube and shake with 50 ml of 1N or 2N NaCl solution on a mechanical shaker. Shake for four hours when exchangeable aluminum is present (pH <5.5) and only two hours for soils having a pH of 5.5 or more.

(2) Centrifuge the suspension at 1500 to 2000 rpm for 15 to 20 min. and filter the centrifugate through Whatman No. 42 filter paper into a 25 to 50 ml. flask. Analyze for exchangeable cations within a few days.

(3) Dilute an aliquot of the extract (usually 1:50 for Ca and Mg and usually 1:10 for K) and determine Ca, Mg and K by atomic absorption. Note the following points:

a) The concentration of Na in test solutions and standards should be approximately the same.

b) Add lanthanum (to 2000 ppm) to both samples and standards to avoid interferences.

c) For most samples, the weights and dilution suggested will result in concentrations of Ca, Mg and K in the optimum range for determination by AA. CEC (me/100g) may be estimated as (-11+0.2 clay%+2 organic C%+2.5 pH in $CaCl_2$).

d) Standards for Ca, Mg and K can be either purchased or prepared from suitable salts. Always check new standards against another standard.

(4) If the pH of the soil in 0.01 M $CaCl_2$ is less than 5.5 determine exchangeable Al, preferably by 8-hydroxyquinoline (see 3.312). Determination of Al in 2N NaCl solutions by AA results in erratic readings and burner clogging unless much water is aspirated between samples. For samples high in exchangeable Al, the extracts can be diluted before determination Al. Samples and standards should have approximately the same concentration of Na. Values for exchangeable Al measured by AA are usually higher than those by 8-hydroxyquinoline.

Calculations

(1) In general, exchangeable cations in me/100 g = (ppm measured / 1000 x equivalent wt of cation) x (volume of extractant ml)x(dilution factor) x (100/wt of sample in g).

For the following conditions: 5 g sample, 50 ml. of 2N NaCl, 2 ml diluted to 100 before determining cations and 3 ppm Ca measured:

$$\text{Exchangeable Ca} = \frac{3}{20 \times 1000} \times \frac{50}{1} \times \frac{100}{2} \times \frac{100}{5} = 7.5 \text{ me/100g}$$

Similar calculations apply for the other cations. The equivalent weights are: Ca - 20, Mg - 12.16, Al - 9, K - 39.

(2) CEC can be calculated as the sum of exchangeable Ca + Mg + K + Al in me/100g.

Notes

(1) If 50 ml centrifuge tubes are used, change the sample weight to 60% of that suggested in Table 8 and add 30 ml of NaCl solution.

(2) If dilution of the extract to 1:50 results in concentrations of Ca, Mg etc. too low to measure, other dilutions may be made (1:25 etc.). Another set of standards having the same concentration of NaCl would be required.

3.312 Ca and Mg by Titration, Al by Colorimetry

Reagents for Ca and Mg

- Tartaric acid, 2% solution
- Triethanolamine, 50% solution
- Buffer solution, (67.5 g NH_4Cl in 200 ml H_2O+570 ml conc. NH_4OH diluted to 1 ℓ with H_2O).
- Eriochrome Black T indicator, (0.5 g E Black T and and 4.5 g hydroxylamine hydrochloride in 100 ml of 95% ethanol).
- Versene solution, (disodium EDTA) - 0.01 N solution. Dissolve 2.00 g Na - EDTA and 0.05 g $MgCl_2$-$6H_2O$ in water and make to 1 ℓ. Standardize against 0.01 N Ca^{2+} standard using E Black T indicator.
- NaOH, 8N solution
- Hydroxylamine hydrochloride, 6% solution
- KCN, 3% solution
- Cal-red indicator (Moss, 1961).

Procedure for Ca + Mg

(1) Pipet a 1 to 15 ml aliquot (about 0.1 me of Ca + Mg) of the 2N NaCl extract into a 100 ml beaker.

(2) Add 1 ml 2% tartaric acid.

(3) Add 20 ml 50% triethanolamine.

(4) Add 1 ml of 3% KCN.

(5) Add 3 ml buffer solution.

(6) Add 6 drops E Black T solution.

(7) Stir using a magnetic stirrer and titrate with the EDTA solution under a good white light to the blue endpoint.

(8) Titrate a blank containing water instead of the aliquot of NaCl extract.

(9) Calculation: Ca + Mg (me/100 g of soil) =

mls versene (corrected for blank) x Normality x 30/aliquot x 100/weight of soil

Procedure for Ca

(1) Pipet 1 to 1.5 ml aliquot (about 0.1 me of Ca) of the 2N NaCl extract into a 100 ml beaker.

(2) Add 4 ml of 8N NaOH, 0.5 ml of 3% KCN and 0.5 ml of 6% hydroxylamine hydrochloride.

(3) Add 1 scoopful (40 to 50 mg) of Cal-red indicator.

(4) Titrate with 0.01 N versene solution, standardized with Ca using Cal-red indicator, to blue endpoint.

Calculations

(1) Exchangeable Ca (me/100g of soil) = mls. versene (corrected for blank) x N x 30/aliquot x 100/wt. of soil.

(2) Exchangeable Mg = (exchangeable Ca+ Mg) - (exchangeable Ca).

Al by 8-hydroxyquinoline

Reagents

1. Reagent grade chloroform

2. Sodium acetate, 1 M solution

3. 8-hydroxyquinoline solution: dissolve 5g of 8-hydroxyquinoline in 12.5 ml glacial acetic acid and dilute to 500 ml with distilled water.

4. Composite 8-hydroxyquinoline-sodium acetate solution: Mix 1 part 8-hydroxyquinoline solution, 1 part sodium acetate solution and 5 parts water (1:1:5).

5. Aluminum standard:
Stock solution: Dissolve 1.8976 g of reagent grade $A\ell K(SO_4)_2 \cdot 12H_2O$ (FW 474.404) in 40 ml of 6 N HCl and dilute to 1 ℓ with distilled water (4×10^{-3}M Al solution)

Standard: Dilute 25 ml of stock solution to 1 ℓ with distilled water (10^{-4}M Al solution).

6. Hydroxylamine hydrochloride, 5% solution

7. O-phenanthroline, 0.2% solution

Procedure

(1) Place 2 ml of hydroxylamine hydrochloride and 2 ml of O-phenanthroline in a separatory funnel (125 ml).

(2) Add an aliquot of the soil extract (0 to 2 micromoles Al) and shake the funnel.

(3) Add 10 ml chloroform and 14 ml of the composite 8-hydroxyquinoline-sodium acetate solution.

(4) Stopper the funnel immediately and shake the mixture for 10 sec.

(5) Allow the layers to separate and collect the yellow chloroform containing the Al-quinolate complex.

(6) Measure the absorbance at 395 mu against standards prepared in the same way as the samples. The standards should contain 0 to 2.5 micromoles of Al (0 to 25 ml of the standard solution).

Al by pyrocatechol violet

Reagents

Hydroxylamine hydrochloride - 10% solution

ortho-phenanthroline - 0.10% solution

Pyrocatechol violet - 0.15% solution

Ammonium acetate buffer, pH 6.2 - 10% solution

Procedure

(1) Pipet an aliquot of the NaCl extract into a 100 ml volumetric flask (usually 1 ml; 50 µg or less of Al).

(2) Add 2 ml 10% hydroxylamine hydrochloride.

(3) Add 3 ml 0.10% ortho-phenanthroline.

(4) Add 2 ml pyrocatechol violet solution.

(5) Make to volume with NH_4OAc buffer, mix and after 2 hours read absorbance at 580 mµ.

(6) Calculate me Al per 100 g soil =

$$\frac{\mu g}{9} \times \frac{30}{\text{aliquot}} \times \frac{100}{\text{weight soil}} \times \frac{1}{1000} = \frac{\mu g}{9 \times \text{aliquot}}$$

if a 3 g sample is used.

Permanent charge CEC is approximately equal to Ca + Mg + Al (except for soils high in exchangeable Na).

Base saturation percentage is $\frac{Ca + Mg}{Ca + Mg + Al} \times \frac{100}{1}$

Preferably, exchangeable K is determined and the calculation of base saturation is:

$$\frac{Ca + Mg + K}{Ca + Mg + Al + K} \times \frac{100}{1}$$

References

(1) Clark, J.S. 1965. The extraction of exchangeable cations from soils. Can. J. Soil Sci. 45, 311-322.

(2) Clark, J.S. and Hill, R.G. 1968. Vessel for long term soil-solution equilibration. Can. J. Soil Sci. 48, 221.

(3) Moss, P. 1961. Limits of interference by iron, manganese, aluminum and phosphate in the EDTA determination of calcium in the presence of magnesium using Cal-red as indicator. J. Sci. Food. Agric. 12, 30-34.

(4) Wilson, A.D. and Sergeant, G.A., 1963. The Colorimetric determination of aluminum minerals by pyrocatechol violet. Analyst, 88, 109-112

3.32 CEC and Exchangeable Cations by NH_4OAc at pH 7 (Chapman, 1965)

3.321 CEC determined by NH_4 displacement and macro-Kjeldahl distillation

A. Ammonia saturation and displacement of exchangeable cations.

Reagents

(1) Ammonium acetate (NH_4OAc) 1 N, pH 7.0. Either:

(a) Dissolve 1386 g of NH_4OAc in distilled water and make to 18 ℓ or,

(b) Mix 68 ml NH_4OH (specific gravity 0.90) and 57 ml 99.5% acetic acid per liter of solution required.

Cool and dilute to volume and adjust pH to 7.0 by adding acetic acid or ammonium hydroxide.

(2) Isopropyl alcohol, 99% (ethanol may be used but isopropyl is preferred - see Chapman).

(3) Ammonium chloride (NH_4Cl), 1 N, adjusted to pH 7 with NH_4OH.

(4) Ammonium chloride (NH_4Cl), 0.25 N, adjusted to pH 7 with NH_4OH.

(5) Silver nitrate ($AgNO_3$), 0.10 N.

Procedure

(1) Weigh 10 g of 2 mm, air-dried soil (25 g for soils having a CEC of <5 me/100 g) into a 250 ml Erlenmeyer flask and add 50 ml of neutral 1 N NH_4OAc.

(2) Shake the flask thoroughly and allow to stand overnight.

(3) Filter the soil with gentle suction using a 55 mm Buchner funnel fitted with Whatman No. 42 filter paper. Do not allow the soil to become dry or cracked.

(4) Leach the soil with small portions of NH_4OAc until the total volume of extract is 200 to 225 ml.

(5) Transfer the leachate to a 250 ml volumetric flask, make to volume with NH_4OAc and keep for determination of exchangeable cations, by atomic absorption.

(6) Leach the soil four times with neutral 1 N NH_4Cl and once with 0.25 N NH_4Cl.

(7) Wash out the electrolyte with 150 to 200 ml of 99% isopropyl alcohol. When the test for Cl^- in the leachate ($AgNO_3$) becomes negative, allow the soil to drain thoroughly.

B. Displacement and determination of adsorbed NH_4^+

Reagents

(1) Sodium chloride (acidified); 10% solution (ammonia free) acidified with enough HCl to make the solution approximately 0.005 N with respect to acidity.

(2) Sodium hydroxide, 1 N.

(3) Boric acid, 2% solution.

(4) Standard sulfuric acid (H_2SO_4), 0.1 N.

(5) Bromocresol green - methyl red mixed indicator: Triturate 0.1 g of bromocresol green with 2 ml of 0.1 N NaOH in an agate mortar, and add 95% ethyl alcohol to obtain a total volume of 100 ml. Triturate 0.1 g of methyl red with a few ml of 95% ethyl alcohol in an agate mortar. Add 3 ml of 0.1 N NaOH, and dilute the solution to a volume of 100 ml with 95% alcohol. Mix 75 ml of the bromocresol green solution with 25 ml of the methyl red solution, and dilute the mixture to 200 ml with 95% ethyl alcohol.

Procedure

(1) Leach the ammonium-saturated soil prepared in 3.321 A, before it dries, with 10% acidified NaCl adding small portions at a time and allowing each portion to pass through the sample before more is added, until about 225 ml of extract has been collected.

(2) Transfer the leachate quantitatively to an 800 ml Kjeldahl flask, add 25 ml of 1 N NaOH and distill 60 ml of the solution into 50 ml of 2% boric acid solution.

(3) Add 10 drops of bromocresol green-methyl red indicator and titrate the boric acid solution with 0.1 N H_2SO_4. The color change is from bluish green through bluish purple to pink at the end point.

(4) Titrate reagent blank, correct the titration reading for the blank and calculate me of ammonia per 100 g of soil as (ml H_2SO_4 for sample - ml for blank) x (N of H_2SO_4) x (10) if 10 g of soils is used. Alternatively, NH_4 can be determined by autoanalyser.

3.322 CEC determined by Kjeldahl distillation of NH_4^+ saturated soil (Chapman, 1965).

3.323 CEC determined by NH_4^+ replacement and micro-Kjeldahl distillation (see 3.621).

3.324 CEC determined by NH_4 replacement and nesslerization (Jackson, 1958).

References

(1) Chapman, H.D. 1965. Cation-exchange capacity, In Agronomy No. 9. Methods of Soil Analysis, Part 2, Black, C.A. ed., pp. 891-901.

(2) Jackson, M.L. 1958. Soil Chemical Analysis. Prentice-Hall Inc., Englewood Cliffs, N.J. p. 195.

3.33 CEC at pH 7 by $Ca(OAc)_2$-$CaCl_2$ (Clark et al., 1966)

This procedure has some advantages over NH_4^+ saturation for the determination of CEC at pH 7:

(a) Ca can be determined readily by atomic absorption,

(b) Ca is the dominant exchangeable cation in many soils,

(c) Ammonium fixation is a problem in some soils.

The measurement of CEC both at the pH of the soil (neutral salt, 3.31) and at pH 7 permits the calculation of the pH dependent charge. The pH dependent charge is generally high in acid soils containing appreciable amounts of either organic matter or amorphous inorganic substances.

Reagents

0.9 N $Ca(OAc)_2$-0.1 N $CaCl_2$ at pH 7.
Combine 1426 g of $Ca(OAc)_2$ and 101 g of $CaCl_2$, dissolve and make to 18 ℓ with distilled water. Check pH and adjust to 7.0 by adding 0.5 N $Ca(OH)_2$ or HCl. The $Ca(OH)_2$ solution is made up with freshly distilled water.

- Disodium EDTA - 0.1 N standardized against 0.1 N Ca^{+2} solution.

- Cal-red indicator

- 8 N, NaOH, 6% hydroxylamine hydrochloride.

Procedure

(1) Weigh 3 g of 2 mm soil into a 50 ml centrifuge tube. Extract with six successive portions of 15 ml (ratio 1:5) each of 0.9 N Ca(OAc) + 0.1 $CaCl_2$ solution at pH 7.0 using 30 minute shaking intervals except for the fourth one when the mixture is shaken end-over-end overnight. The samples are washed free of Cl^- with exactly 12 ml of water (ratio 1:4) using high speed centrifuge.

(2) Extract once with 40 ml 2 N NaCl shaking thirty minutes on paint shaker and centrifuging. Decant and save supernatant in 100 ml flask. Add 40 ml 2 N NaCl, shake for 5 minutes on paint shaker, then overnight end-over-end, centrifuge and decant saving supernatant in same 100 ml flask.

(3) Make extract to volume with water and take an aliquot (20-50 ml) for determination of Ca using Cal-red indicator and EDTA as in 3.12, or by atomic absorption.

Reference

(1) Clark, J.S., McKeague, J.A. and Nichol, W.E. 1966. The use of pH-dependent cation-exchange capacity for characterizing the B horizons of Brunisolic and Podzolic soils. Can. J. Soil Sci. 46, 161-166.

3.34 CEC by Sodium Acetate (NaOAc) (Chapman, 1965)

This method has been used for determining the CEC of saline and alkali soils because some of these soils fix considerable amounts of NH_4^+ (Richards, 1954).

Reagents

- NaOAc, 1 N, pH about 8.2; 136 g of $NaOAc.3H_2O$ per ℓ. Adjust pH to 8.2 using acetic acid or NaOH.

- Isopropyl alcohol.

- Ammonium acetate (NH_4OAc), pH 7.0 (see 3.3[2]1).

Procedure

(1) Weigh 5 g sample of 2 mm soil and place in 50 ml centrifuge tube.

(2) Add 30 ml NaOAc, stopper the tubes and shake for 5 minutes. Remove stopper and centrifuge until the centrifugate is clear (usually about 5 minutes). Decant the supernatant solution as completely as possible and discard.

(3) Repeat step 2 three times making sure that the soil mass in the bottom of the tube is dispersed each time (total of 4 NaOAc treatments). After the last treatment, wash the stoppers and use absorbant paper to remove any acetate crystals remaining on the lip of the centrifuge tube.

(4) Add about 30 ml of isopropyl alcohol to each tube, stopper, shake for 5 minutes, remove stopper and centrifuge until the centrifugate is clear. Decant and discard the clear centrifugate.

(5) Repeat step 4 two times (total of 3 alcohol washes). The conductivity of the centrifugate from the last washing should be between 55 and 40 µs/cm.

(6) Replace the adsorbed Na^+ by extracting the soil with three 30 ml portions of NH_4OAc solution (shake, centrifuge, decant and keep centrifugate). Dilute the combined centrifugate to 100 ml and determine Na by flame photometry or atomic absorption.

(7) Calculate CEC (me/100 g) =

$$\frac{\text{me/ℓ Na from curve}}{\text{g sample}} \times \text{dilution} \times 10$$

References

(1) Chapman, H.D. 1965. Cation-exchange capacity. In Agronomy No. 9. Methods of Soil Analysis, Part 2. Black, C.A. ed. pp. 891-901.

(2) Richards, L.A. ed. 1954. Diagnosis and Improvement of Saline and Alkali Soils. U.S. Salinity Laboratory, U.S. Dept. Agr. Hbk. 60, 160 pp.

3.35 Exchangeable Hydrogen and Exchange Capacity by $BaCl_2$-Triethanolamine (Peech, Cowan and Baker, 1962)

This procedure provides a direct measure of exchangeable acidity to pH8 and a measure of the exchange capacity at pH8. It is not widely used in Canada. The preferred method for the determination of exchangeable acidity (aluminum) is 3.31 and the preferred method for pH dependent CEC is 3.33.

3.351 Exchangeable hydrogen (acidity)

Reagents

(1) 0.5 N $BaCl_2$-0.05 N triethanolamine adjusted to pH 8. Weigh 1220g $BaCl_2.2H_2O$ into a 20 ℓ pyrex bottle and dissolve in CO_2-free water. Add 133.3 ml of C.P. concentrated triethanolamine. Add 36 ml of concentrated HCl. Mix well and make volume to 20 ℓ with CO_2-free water. Adjust pH to 8.00 ± 0.02 with HCl or triethanolamine. The solution is 0.03 N with respect to free base. Protect the solution from CO_2 by providing a siphon and connecting a soda-lime tube to the air inlet.

(2) Mixed indicator solution: Dissolve 0.22 g of bromocresol green and 0.075 g of methyl red in 96 ml of 95% ethanol, add 3.5 ml of 0.1 N NaOH and mix. (Alternatively the endpoint can be determined potentiometrically).

(3) HCl-0.1 N, standardized to 4 significant figures.

Procedure

(1) To sample (2g for organic and 10 to 25g for mineral soil) in a 125 ml Erlenmeyer flask, add 100 ml of extracting solution, stopper, mix and allow to stand overnight.

(2) Transfer the contents of the flask to a Buchner funnel fitted with filter paper. Filter and rinse the flask several times with extracting solution (about 90 ml in total). Allow each portion of the solution to drain before adding the next portion of rinse solution but do not allow the soil to dry sufficiently to crack.

(3) Make the leachate to 200 ml.

(4) Take an aliquot of the leachate (all of it for soils of low acidity), add a few drops of indicator and titrate with 0.1 N HCl to the endpoint of the indicator or to pH 5.1. An automatic titrimeter may also be used.

(5) Titrate a blank containing an equivalent volume of extracting solution.

Calculations

Exchangeable acidity me/100 g =

(ml HCl for blank - ml HCl for sample) x N of HCl x

$$\frac{200}{\text{aliquot titrated in ml}} \times \frac{100}{\text{sample weight in g}}$$

3.352 Exchange capacity

(1) Leach the soil from the exchangeable hydrogen determination with about 100 ml of water, added in four portions, to remove the excess barium. Discard washings and wash suction flasks.

(2) Leach the Ba saturated soil with about 190 ml of N NH_4OAc.

(3) Make the volume of the leachate up to 200 ml and determine Ba either by:

A. atomic absorption, or

B. gravimetrically as follows:

(a) Take an aliquot of the NH_4OAc extract and place it in a 400 ml beaker (if less than 200 ml is used, make the aliquot to about 150 ml with NH_4OAc).

(b) Heat to boiling and add 5 ml of 15% $(NH_4)_2\ Cr_2O_7$. A yellow precipitate of $BaCrO_4$ forms. Cool to room temperature.

(c) Decant the clear supernatant liquid into a Gooch crucible fitted with a glass wool or asbestos mat, dried at 105°C and weighed.

(d) Wash precipitate, by decantation, with dilute NH_4OAc (20 ml of N diluted to 1 ℓ).

(e) Transfer all of precipitate from beaker to crucible using rubber policeman.

(f) Dry crucible at 105°C and weigh.

Calculations

$$\text{CEC (me/100 g)} = \frac{\text{weight } BaCrO_4}{.1267} \times \frac{200}{\text{aliquot (ml)}} \times \frac{100}{\text{weight of soil (g)}}$$

Reference

(1) Peech, M., Cowan, R.L. and Baker, J.H. 1962. A critical study of the $BaCl_2$-triethanolamine and ammonium acetate methods for determining the exchangeable hydrogen content of soils. Soil Sci. Soc. Am. Proc. 26, 37-40.

3.36 Exchange Capacity of Organic Samples by Barium Acetate (AOAC, 1975)

This AOAC method is the preferred method for CEC of organic soil materials. It yields somewhat higher values than the ammonium acetate method (MacLean et al., 1964).

Reagents

Hydrochloric acid, 0.5 N (42 ml of conc. HCl per ℓ)
Barium acetate, 0.5 N. Dissolve 64g of $Ba(OAc)_2$ per ℓ of solution required
Silver nitrate soln., 1%. Dissolve 1g $AgNO_3$ in 100 ml H_2O
Sodium hydroxide std. soln., 0.1N. Use 4g NaOH per ℓ of solution. Protect from contamination by CO_2. Standardize acid potassium phthalate dried at 120°C (see AOAC, 1975, p. 946 for details).

Procedure

(1) Mix air-dried, ground sample and place 2.00 g in a 300 ml erlenmeyer.

(2) Add 100 ml 0.5N HCl, stopper flask and shake on a mechanical shaker for 30 min.

(3) Filter through rapid paper in a large funnel.

(4) Wash with 100 ml portions of H_2O until 10 ml wash shows no ppt with 3 ml 1% $AgNO_3$. Discard filtrate.

(5) Immediately transfer sample to 300 ml erlenmeyer by puncturing filter paper and washing sample through funnel with a fine spray from a wash bottle containing 0.5N $Ba(OAc)_2$. Add a total of 100 ml.

(6) Shake flask mechanically for 15 min.

(7) Filter and wash sample with three 100 ml portions of H_2O. Discard sample.

(8) Titrate washings with 0.1N NaOH, using 5 drops phenolthalein, to first pink.

Calculations

CEC, me/100g air-dry sample = (ml x normality NaOH x 100)/g sample

References

(1) AOAC (Association of Official Agricultural Chemists) 1975. Methods of Analysis. pp. 32 and 946.

(2) MacLean, A.J., Halstead, R.L., Mack, A.R. and Jasmin, J.J. 1964. Comparison of procedures for estimating exchange properties and availability of phosphorus and potassium in some eastern Canadian organic soils. Can. J. Soil Sci. 44, 66-75.

3.4 CARBONATES - A.A. Raad

Several methods are outlined for the determination of carbonates in soils. The best method depends upon the purpose of the analysis. Method 3.41 is suitable if a rapid, approximate result is adequate. Method 3.42 is considerably more quantitative than 3.41 and it is adequate for most routine determinations of the $CaCO_3$ equivalent. Method 3.43 is quantitative and it permits the differentiation of calcite and dolomite. However it requires some specialized equipment and it is more time-consuming than 3.42. Method 3.44 permits the determination of calcite but it is relatively time-consuming. Method 3.45 is quantitative for $CaCO_3$ equivalent, but it is relatively time-consuming. Some other procedures are indicated in the references. In general 3.42 is preferred for routine determinations of $CaCO_3$ equivalent and 3.43 for quantitative determination of calcite and dolomite.

3.41 Gravimetric Method (Allison and Moodie, 1965), approximate

The accuracy of this semiquantitative method depends upon the accuracy of weighing and the degree to which CO_2 retained in solution is compensated for by loss of water vapor. Calcite and dolomite cannot be distinguished but if the weight decreases markedly after 30 min., some dolomite is present.

Reagents

(1) Hydrochloric acid (HCl), 4 N.

(2) Hydrochloric acid - ferrous chloride (HCl - $FeCl_2$-$4H_2O$). Dissolve 3 g of $FeCl_2.4H_2O$ per 100 ml of 4 N HCl immediately before use.

Procedure

(1) Weigh to nearest mg a stoppered, 50 ml Erlenmeyer flask containing 10 ml of HCl-$FeCl_2$ solution.

(2) Transfer a 1 to 10 g soil sample containing 0.1 to 0.3 g of carbonate to the flask gradually to prevent excessive frothing.

(3) After effervescence has subsided, replace the stopper loosely in the flask and set it aside, swirling it occasionally for about 30 minutes. Replace stopper and weigh the flask, and its contents.

(4) At intervals of about 30 minutes, remove the stopper and swirl the flask for 10 to 20 seconds to displace any accumulated CO_2 with air, replace the stopper and weigh the flask and its contents.

(5) Repeat swirling and weighing about every 30 minutes until the weight change is 3 mg or less. The reaction is usually complete within 2 hours and commonly within 30 minutes.

(6) Calculate the $CaCO_3$ equivalent and carbonate C:

(a) Weight of CO_2 lost = Difference in initial and final weights of (flask + stopper + acid + soil);

(b) $CaCO_3$ equivalent, % = $\frac{\text{g } CO_2 \text{ lost}}{\text{g soil}} \times 228$

(c) C as carbon, % = $\frac{\text{g } CO_2 \text{ lost}}{\text{g soil}} \times 27.3$

Reference

(1) Allison, L.E. and Moodie, C.D. 1965. Carbonate, In Methods of Soil Analysis, Part 2. Black, C.A. ed. pp. 1379-1396.

3.42 Gravimetric method with trap to catch water, quantitative (Soil Conservation Service, 1972. Method 6E1c)

The water vapour evolved with CO2 is trapped by anhydrone and the CO_2 in solution is swept out with dry air. The method is quantitative within the limits of weighing errors. With several units (Fig. 5) in operation at a time, it is quite rapid.

(1) Weigh a sample of soil (preferably 100 mesh, oven-dry soil) containing less than 1 g $CaCO_3$ equivalent into a 125 ml Erlenmeyer flask (usually between 1 and 10 g).

(2) Wash down the sides of the flask with 10 ml of water.

(3) Place 7 ml of HCl-$FeCl_2$ solution (3 g of $FeCl_2.4H_2O$ added to 100 ml of 6 N HCl just before use) into vial C (Fig. 5) and place the vial upright in the flask without spilling any acid.

(4) Moisten stopper G with glycerin, sprinkle it with a small amount of 180 mesh abrasive to overcome slipperiness, and assemble the apparatus as in Fig. 5 except that the U tube is not connected. Make sure that stoppers and stopcocks are firmly in position, close stopcocks D and E and place the apparatus beside the balance.

(5) Wait about 30 minutes before weighing to allow the temperature to equilibrate. Weigh to the nearest 0.1 mg with stopcock D open, and immediately close D. Handle the apparatus with tongs. Check the weight after 10 min.

(6) Open stopcock D and shake the flask to upset vial C, thus allowing the acid to react with the soil.

(7) After 10 minutes, attach the airdrying tube H to the apparatus, open stopcock E and apply gentle suction at stopcock D to give 5 to 10 bubbles per second at tube J to sweep out the CO_2. Shake the flask after 10 min. and again after 20 min.

(8) After 30 minutes sweeping time (dolomitic soils may require longer) stop the suction, close stopcocks D and E and place apparatus beside the balance.

(9) Weigh after one hour with stopcock D open and check the weight after 10 min.

Calculations

$CaCO_3$ equivalent (%) = 228 (initial wt. of apparatus, g - final wt, g) /sample wt., g

Reference

(1) Soil Conservation Service. 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Investigations Report No. 1, (Revised) U.S.D.A., Washington, D.C.

3.43 Pressure Method Using Pressure Transducer (S.R.I. Procedure Modified from Skinner et al., 1959)

This is a quantitative method capable of detecting as little as 5 mg $CaCO_3$ and of determining as much as 1 g of $CaCO_3$ with the apparatus described. If dolomite is present, the sample must be run for about an hour. If only calcite is present, the determination takes about 5 min. Clay-sized dolomite is not distinguished from calcite by this method (Turner and Skinner, 1960). With samples containing no carbonate, there is generally a small peak at about 5 sec. probably due to the heat of wetting. Then the pen goes below the zero line, perhaps due to the absorption of components of the air in the bottle by HCl.

A. Glass wool plugs
B. Anhydrone, $Mg(ClO_4)_2$
C. Vial containing 6N HCl
D. Stopcock
E. Stopcock
F. 125–ml Erlenmeyer flask
G. Stopper
H. U tube
I. Calcium chloride tube (shortened)
J. Glass tube

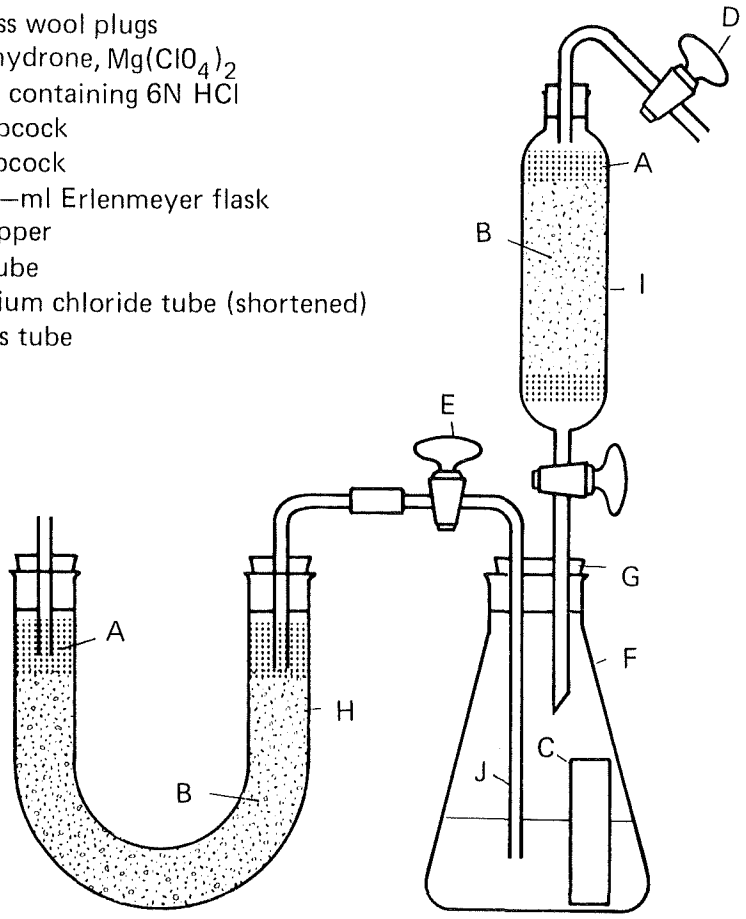


Fig. 5. Apparatus for the determination of calcium carbonate equivalent by method 3.42

Apparatus

Pressure transducer 0 to 10 PSIG. Alternatively a mercury manometer can be used to measure pressure (see Skinner, Halstead and Brydon, 1959).

Power supply, 6 V

Recorder - 10 mv full scale

Wrist action shaker

Constant temperature water bath

Reaction bottle - thick walled, wide-mouth glass bottle, about 1 ℓ capacity, fitted with 2 hole stopper.

Procedure

(1) Weigh the oven-dry sample ground to pass a 0.5 mm sieve (100 mesh is also suitable) into a 1/2 oz. lily cup (paper cup). The sample weight depends upon the carbonate content and the volume of the reaction vessel. For a 1 ℓ reaction vessel estimate the weight of soil that contains 0.2 to 0.6 g of $CaCO_3$.

(2) Measure 50 ml of 4 N HCl into the shaker bottle and add about 1 g of $FeCl_2.4H_2O$. Place a rubber stopper, about No. 6, in the acid at the bottom of the bottle and avoid splashing acid on the top of the stopper. Put the cup containing the soil sample on top of the stopper.

(3) Turn on the power supply and recorder and allow at least 10 min. warmup time. Set the recorder's mv span at 10, and the power supply at 6 v. Set the gain as high as possible without causing vibration of the pen, and adjust the pen to read 5 units on the chart paper.

(4) Clamp the shaker bottle to the arm of a wrist-action shaker and immerse the bottle up to the neck in a water bath maintained at a constant temperature (about room temperature, the exact temperature is not important but samples and standards must be run at the same temperature).

(5) Stopper the bottle tightly with a dry 2-hole stopper. From one of the holes, a tube goes to the transducer. The tube from a stopcock is inserted into the other hole; the stopcock is left open until the stopper is fully inserted and then closed. (This avoids an increase in pressure due to insertion of the stopper).

(6) Set the recorder chart on "fast" (about 5 in/ minute) and turn on the power. When the pen reaches a line on the chart, turn on the shaker and mark the starting point, sample weight and sample no. on the chart. Check to ensure that the sample has mixed completely with the acid.

(7) After the sample has shaken for 1 or 2 minutes, turn the speed to "medium" (1 inch/minute) and mark the chart where the change was made. For samples containing dolomite, set the chart speed on "slow" (0.2 inch/minute) after the sample has shaken for about 10 minutes and mark the chart where the change was made.

(8) Run the samples until the reading is constant for 5 minutes or more. Stop shaking, release the pressure and check the zero reading after the stopper is removed. Turn off the recorder.

(9) Remove the stopper and the shaker bottle and wash out the bottle with water at about the temperature of the bath. Dry the mouth of the bottle and proceed with the next sample.

(10) Prepare a standard curve by running 0 to 1.0 g samples of oven-dry $CaCO_3$ in exactly the same way as the soil samples. The reaction is complete in about a minute.

Calculations

(1) Record the final reading (Hf) on the chart and also a reading (Hfc) corrected for any deviation from the zero setting (5.0 units) after the pressure is released. For example, if Hf = 50.0 and if the reading is 4.5 after the stopper is removed, Hfc = 50 + (5-4.5) = 50.5.

(2) Record readings (Ht) from 1 to 8 minutes from the beginning of shaking at 1 minute or 1/2 minute intervals. If the pen was not zeroed exactly at 5 units before starting, correct Ht accordingly (Htc). For example, if Ht at 1 min is 10.5 and if the pen was zeroed at 5.5 instead of 5.0, Htc is (10.5 - 0.5) = 10.

(3) Subtract Htc from Hfc for each time and plot (Hfc - Htc) on a log scale against time on a linear scale. Draw a line through the points and extrapolate it to 0 time. Frequently these points do not all fall on a straight line; in this case, construct the line through the points from about 1.5 to 5 minutes. The intercept of this line on the (Hfc - Htc) axis is the reading for dolomite.

(4) The weight of $CaCO_3$ corresponding to Hfc is read from the standard curve prepared by plotting Hfc against g of $CaCO_3$. The weight of $CaCO_3$ corresponding to the dolomite reading obtained in (3) is read from a line through 0 parallel to the standard graph.

(5) The $CaCO_3$ equivalent of the sample and the $CaCO_3$ equivalent attributable to calcite and to dolomite are calculated. The percentage of dolomite is 0.92 x the $CaCO_3$ equivalent attributable to dolomite, e.g., suppose that a 5.000 sample is used, Hfc is 60 and the dolomite reading from (3) is 20. The standard graph (which does not pass through the origin) shows that the Hfc reading is equivalent to 0.540 g of $CaCO_3$. The parallel curve through the origin shows that a dolomite reading of 20 is equivalent to 0.185 g of $CaCO_3$.

Thus the $CaCO_3$ equivalent of the sample is

$$\frac{0.540}{5.000} \times \frac{100}{1} = 10.8\%; \quad \frac{0.185}{5.000} \times \frac{100}{1} = 3.7\%$$

is attributable to dolomite and (10.8 - 3.7) = 7.1% to calcite. The percentage of dolomite in the sample is 0.92 x 3.7 = 3.4%

References

(1) Skinner, S.I.M., Halstead, R.L. and Brydon, J.E. 1959. Quantitative manometric determination of calcite and dolomite in soils and limestones. Can. J. Soil Sci. 39, 197-204.

(2) Turner, R.C. and Skinner, S.I.M. 1960. An investigation of the intercept method for determining the proportions of dolomite and calcite in samples consisting of a number of crystals. Can. J. Soil Sci. 40, 232-241.

3.44 Citrate Buffer Method (Peterson and Chesters, 1966; Modified by Rostad and St. Arnaud, 1970)

This method involves the selective dissolution of calcite in a citrate buffer solution, analysis of Ca and Mg in the solution, calculation of calcite dissolved, determination of total carbonate in the sample by another method and calculation of dolomite by difference. The calculations involve the assumption that the Ca:Mg ratio of dolomite is 1:1. This is not necessarily the case (St. Arnaud and Herbillon, 1973). It also involves the assumption that all of the Ca and Mg in the solution come from calcite and dolomite. Results of Peterson, Chesters and Lee (1966) show that this assumption is reasonably valid for the soils they studied. The method is useful

if clay-size dolomite occurs in the sample and if the differentation of calcite and dolomite is required. Otherwise 3.42 or 3.43 are preferable.

Reagents

Citrate buffer - Titrate a 1 N citric acid solution to pH 5.85 with concentrated NH_4OH.

Sodium chloride-ethanol - Dissolve 58.5 g NaCl in 30% ethanol and make the volume to 1 ℓ.

Sodium dithionite.

Procedure

(1) Weigh 0.0500 to 0.500 g of oven-dried soil ground to pass a 100 mesh sieve into a 50 ml centrifuge tube.

(2) Wash the soil twice with NaCl-ethanol solution and discard washings.

(3) Add 25 ml of citrate buffer solution and heat the sample in a water bath at 80°C. Add about 0.5 g of sodium dithionite and heat with stirring a total of 15 minutes.

(4) Centrifuge, decant the centrifugate into a 250 ml volumetric flask. Wash the residue once with 25 ml of citrate buffer, centrifuge and add the washing solution to the initial centrifugate. Make to volume with distilled water.

(5) Determine Ca and Mg in solution by atomic absorption using a flooding solution containing La at 1000 ppm to avoid interferences. The standards are made up in the same concentrations of citrate buffer, dithionite and La as the sample solutions.

(6) Determine total carbonate in another subsample by 3.42 or another quantitative procedure and calculate percentages of calcite and dolomite.

Calculations

If citrate-soluble Ca = x me, citrate-soluble Mg = y me and total CO_3 = z me.

The me calcite Ca = x-y and % calcite = $\frac{50(x-y)}{\text{mg sample}} \times \frac{100}{1}$

me dolomite = z-(x-y) so percentage dolomite is

$$\frac{46.1[z-(x-y)]}{\text{mg sample}} \times \frac{100}{1}$$

The $CaCO_3$ equivalent of the dolomite present is

$$\frac{50[z-(x-y)]}{\text{mg sample}} \times \frac{100}{1}$$

References

(1) Peterson, G.W. and Chesters, G. 1966. Quantitative determination of calcite and dolomite in pure carbonates and limestones. J. Soil Sci. 17, 317-327.

(2) Peterson, G.W., Chesters, G. and Lee, G.B. 1966. Quantitative determination of calcite and dolomite in soils. J. Soil Sci. 17, 328-338.

(3) Rostad, H.P.W. and St. Arnaud, R.J. 1970. Nature of carbonate minerals in two Saskatchewan soils. Can. J. Soil Sci. 50, 65-70.

(4) St. Arnaud, R.J. and Herbillon. 1973. Occurrence and genesis of secondary magnesium-bearing calcites in soils. Geoderma 9, 279-298.

3.45 Titrimetric Method Involving Absorption of CO_2 in NaOH

Apparatus

The apparatus (Fig. 6) consists of an NaOH tower to remove CO_2 from the intake air, a mercury valve, a reaction vessel consisting of a wide-mouthed Erlenmeyer fitted with a dropping funnel through which reagents are added, a condenser and an H_2SO_4 tube to remove water from the gas, a mercury valve and an NaOH tower to absorb the CO_2 produced in the reaction. The units of the apparatus are connected to a suction line and the rate of aspiration is controlled by a screw clamp. Three of these apparatuses can be used simultaneously.

Reagents

(1) Approximately 0.5 N NaOH.

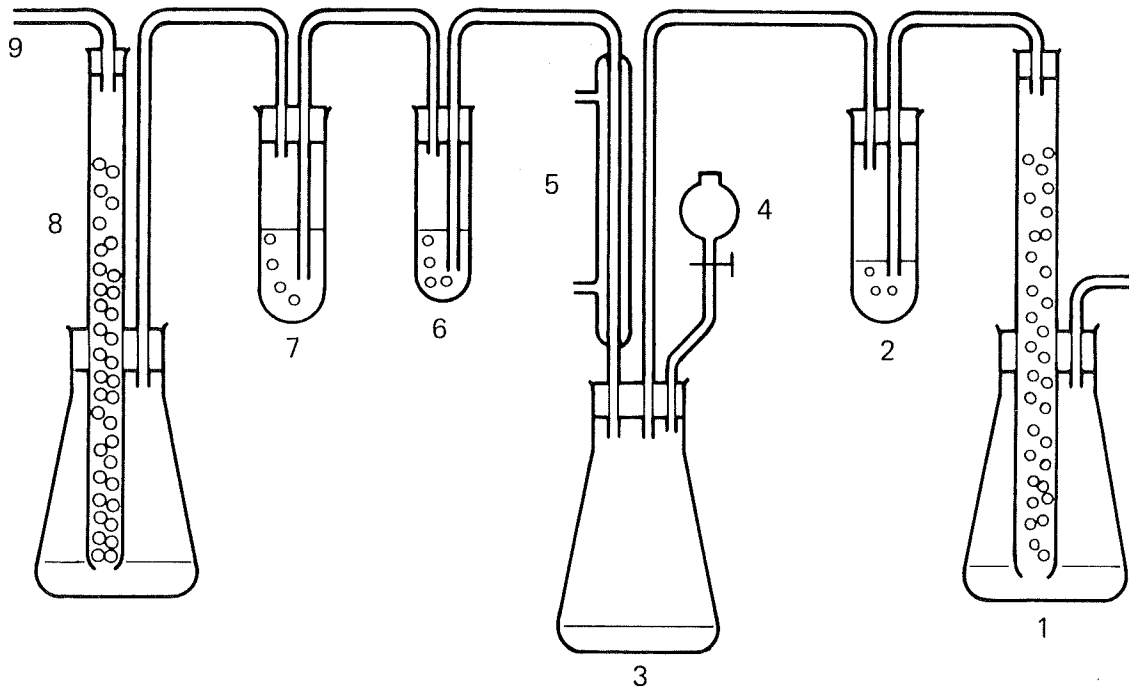
(2) Standard 0.5 N HCl.

(3) 15% $BaCl_2$.

(4) Phenolphthalein indicator (1% in 95% alcohol).

(5) HCl about 2 N (1:5) containing 10 drops of $SnCl_2$ solution per 50 ml.

(6) $SnCl_2$ solution - Dissolve 25 g $SnCl_2.2H_2O$ in 100 ml of 2N HCl. Heat if necessary to dissolve, cool and make to 1 ℓ. Store in a bottle with a siphon or side opening near the bottom of the bottle. Protect



1. NaOH Tower
2. Mercury Valve
3. Reaction Flask
4. Dropping Funnel
5. Condenser
6. Sulphuric Acid Tube
7. Mercury Valve
8. NaOH Tower
9. Tube to Suction

Fig. 6. Apparatus for carbonate determination by method 3.45

the solution from air by a layer of white mineral oil 5 mm thick. Keep an atmosphere of H_2 gas above the liquid by means of a H_2 generator (Zn + HCl in a U-tube).

Procedure

(1) Weigh out 0.5 to 10 grams, depending on the amount of carbonate present, of 100 mesh soil into 500 ml wide-mouthed erlenmeyer flasks which will serve as reaction flasks. Moisten the soil with a few drops of water. Attach the flasks in their proper positions in the train.

(2) From a burette, run 40 ml of 0.5 N NaOH into two other 500 ml wide-mouthed flasks and connect them to the two absorption towers.

(3) Place 50 ml portions of the dilute HCl containing $SnCl_2$ in the dropping funnels leading into the reaction flasks.

(4) Proceed as follows:

- Turn on the water so that cold water flows through the condensers.

- Turn on the suction, adjusting the rate of flow by means of the screw clamps so that air is drawn through at a rate of about 4 bubbles per second.

- Allow the acid in the dropping funnels to drain into the reaction flasks slowly. When only a few drops of acid remain in the funnel, close the stopcock.

- Allow the reaction to proceed about 2 minutes.

- Apply heat to the reaction flasks by means of Meker burners. Adjust the flame so that the contents of the flasks boil gently.

- Boil for 20 minutes.

- During the 20 minutes, weigh out 3 more samples of soil and prepare 3 more flasks of base for the absorption towers.

- Remove the burners and continue aspiration for about a minute.

- Turn the suction off by means of the screw clamps.

- Release the pressure in the apparatus by opening the stopcocks on the dropping funnels.

- Disconnect the tops of the towers from the suction line.

- Disconnect the flask from one of the absorption towers, wash the tower with about 150 ml of water and rinse off the tip of the tower using a wash bottle. Set the flask down beneath the tower, so that any liquid dropping from the tower will fall into the flask.

- Wash down the other towers in the same way.

- Disconnect the reaction flasks and replace them with the flasks containing the new samples (previously moistened).

- Add the dilute HCl to the dropping funnels.

- Connect the flasks containing fresh portions of NaOH to the absorption towers.

- Connect the tops of the towers to the suction line.

- Adjust the suction to the proper rate of aspiration.

- Run the acid slowly into the reaction flasks as before.

- After 2 minutes, apply the heat and allow the reaction to proceed for 20 minutes.

- Add 10 ml of 10% $BaCl_2$ to the absorption flasks and add 2-3 drops of Phenolphthalein Indicator.

- Titrate using standard 0.5 N HCl to a colorless end-point.

- "Blanks" are run in the same way using only the reagents.

Calculations

$$\% \text{ inorganic carbon} = \frac{\text{Blank-titre (ml)} \times \text{N of acid} \times .006 \times 100}{\text{weight of soil used (g)}}$$

where Blank-titre = difference in ml between the titre for the Blank and the titre for the sample.

References

(1) Schroer, R.W. 1940. An Examination of several methods of determining organic carbon and organic matter in soils., M. Sc. Thesis, Univ. of Saskatchewan.

(2) Shaw, W.M. 1931. Determination of carbon dioxide in soil carbonates - a modification of the official method. J. Assoc. Off. Agric. Chem. 14, 283-292.

(3) Schollenberger, C.J. 1930. Determination of carbonates in soil. Soil Sci. 30, 307-324.

3.5 EXTRACTABLE Al, Fe AND Mn (AND Si IF DESIRED) - C. Wang

The three extraction procedures provide a basis for an approximate differentation of the forms of Fe, and to a lesser degree, of Al in soils. Dithionite-citrate-bicarbonate, 3.51, removes finely-divided hematite and goethite, amorphous inorganic Fe and Al oxides and organic-complexed Fe and Al. It extracts Fe and Al from most silicate minerals only slightly. The procedure is often used for removing the sesquioxide coatings from soils and clays prior to x-ray analysis. It provides an estimate of "free" (non-silicate) Fe in soils, but sand-sized goethite and hematite are not dissolved completely and magnetite is not dissolved.

Acid ammonium oxalate, 3.52, dissolves amorphous inorganic Fe and Al and organic-complexed Fe and Al from soils. It attacks most silicate minerals and goethite and hematite only slightly, but it dissolves magnetite and finely divided, easily-weathered silicates such as olivine to a considerable extent.

Pyrophosphate, 3.53, extracts organic-complexed Fe and Al from soils. It dissolves amorphous inorganic forms only slightly and silicate minerals and crystalline Fe and Al oxides are not attacked to a significant extent.

Thus an estimate of three forms of Fe in soil can be made as follows:

(a) Finely divided hematite and goethite: (dithionite Fe - oxalate Fe)

(b) Amorphous inorganic Fe: (oxalate Fe - pyrophosphate Fe)

(c) Organic complexed Fe: (pyrophosphate Fe)

Relationship b and c hold approximately for Al also. In the case of Mn, both dithionite and oxalate dissolve some crystalline oxide forms. The forms of Si extracted are not known and Si in these extracts is not usually determined. Silicon can be determined by atomic absorption or by colorimetric procedures (Weaver, Syers and Jackson, 1968).

3.51 Dithionite-Citrate-Bicarbonate Method (Mehra and Jackson, 1960)

Reagents

Citrate-bicarbonate solution - Mix 500 ml of 1 M sodium bicarbonate solution (42 g of $NaHCO_3$ in 500 ml) with 4 ℓ of 0.3 M sodium citrate (353 g of $Na_3C_6H_5O_7.2H_2O$ in 4 ℓ).

Sodium dithionite, $Na_2S_2O_4$.

Sodium chloride, saturated solution.

Extraction Procedure

(1) Weigh 0.500 g of soil that has been ground to pass a 100 mesh sieve into a 15 ml test tube marked at 5 ml (use a 0.2 g sample for clays and a 1 g sample for coarse soils).

(2) Add citrate-bicarbonate buffer to the mark (5 ml).

(3) Using a calibrated scoop, add about 0.2 g of $Na_2S_2O_4$, mix well and put the tube into a water bath at 80°C.

(4) Stir every 2 or 3 minutes throughout a 15 minute extraction period.

(5) Remove the tubes from the bath, add 1 ml of saturated NaCl solution and mix. Wash off stirring rod into tube.

(6) Centrifuge for about 5 minutes at about 1500 rpm. An International No. 2 centrifuge with a 16 place head and multiple carriers permits the centrifuging of 48 tubes at a time.

(7) Pour off the centrifugate into a 100 ml volumetric flask.

(8) Repeat the extraction (steps 2 to 7). A paint shaker with holders to carry the 15 ml test tubes facilitiates loosening the soil after centrifugation, or use a vortex mixer to loosen the soil cake.

(9) Wash the soil twice with 5 ml of citrate-bicarbonate buffer solution and 1 ml of saturated NaCl. Centrifuge after mixing and add the wash solutions to the volumetric flask.

(10) Make the extract to volume with distilled water and mix well.

3.511 Determination of Fe, Al and Mn (and Si) by atomic absorption

Standard atomic absorption procedures are used. A few details are listed.

(1) Extracts containing suspended material should be filtered.

(2) Standard solutions containing Fe, Al, Mn and Si are prepared in a matrix of the extracting solution.

Sodium dithionite is dissolved in citrate bicarbonate buffer solution with added NaCl solution on a steam bath and aliquots of stock solutions of standard Fe, Al, Mn and Si are added.

(3) An air-acetylene flame is suitable for the determination of Fe and Mn, and a nitrous oxide-acetylene flame is used for Al (Webber et al. 1974), and Si (Parker, 1972).

(4) If it is necessary to dilute the extracts, either dilute them with the extracting solution or prepare standards containing the same concentration of extracting solution as the diluted extract.

3.512 Determination of extracted Al and Fe by colorimetry

Digestion Procedure

(1) Pipette an aliquot of the extract prepared as in 3.51 into a 50 ml volumetric flask (use a 5 ml aliquot for most samples and 10 ml for soils low in extractable Fe).

(2) Add 5 ml of concentrated HNO_3 and exactly 1.0 ml of 16 N H_2SO_4 (222 ml of conc. H_2SO_4 added slowly to about 250 ml H_2O, cooled and made to 500 ml) and heat at about 120°C on a hotplate. Gradually increase the heat as the water evaporates until the white fumes of sulfuric acid rise to the necks of the flasks. If the residue in the flask is brown, cool to about 100°C, add a few drops of HNO_3 and reheat. If the residue is green, cool and add a few drops of hydrazine sulfate. Usually the residues are pale yellow.

(3) Cool the flasks to 50°C or so, add about 30 ml of distilled water and heat at about 80°C for an hour or until the residue is dissolved. Cool, make to volume and mix. The whole digestion procedure takes about 2 to 3 hours.

Reagents

Hydroxylamine hydrochloride, $NH_2OH.HCl$, 10% solution.

Ortho-phenanthroline, 0.1% solution.

Sodium citrate, 20% solution.

Thioglycollic acid, dilute 1 ml to 100 ml with water (prepare daily).

Aluminon buffer solution. Dilute 120 ml of glacial acetic acid to about 900 ml. Add 37 g of NaOH and 0.35 g of aluminon, mix, cool to room temperature,

dilute to 1 ℓ and mix. The solution is good for several months.

Sulfuric acid, 0.32 N (add 9 ml of concentrated H_2SO_4 to about 800 ml of water and dilute to 1 ℓ).

Hydrazine sulfate, 1% solution.

Fe Determination

(1) Pipette an aliquot of the digested solution into a 50 ml volumetric flask. Use a 10 ml aliquot if extractable Fe is less than 1.5% and a 5 ml aliquot if extractable Fe is estimated to be greater than 1.5%.

(2) Add 3 ml of 10% $NH_2OH.HCl$. Let stand 5 minutes or more.

(3) Add 4 ml of 0.1% o-phenanthroline.

(4) Add 5 ml of 20% sodium citrate.

(5) Make to volume, mix well and read in 1 cm tubes on a spectrophotometer at 510 mμ after 1 hour or more. Color is stable for days.

(6) Read μg Fe from a graph of μg Fe vs. absorbance. Reagent grade Fe wire can be used to prepare the Fe standard solutions. The standard curve should cover the range 0 to 200 μg of Fe in 50 ml.

Al Determination (Wang and Wood, 1973)

(1) Pipette a 10 ml aliquot of the digested solution (if a smaller aliquot is used, such as 3 or 5 ml instead of 10 ml, add 7 or 5 ml 0.32 N H_2SO_4 to give 3.2 m.e. of acid altogether) into a 50 ml volumetric flask.

(2) Add 1 ml of a 1% solution of thioglycollic acid from a pipette.

(3) Mix and add H_2O to about 30 ml.

(4) Add 10 ml of aluminon solution, make to volume and mix well. Read at 530 mμ after 1 hour (Absorbance increases slowly after 1 hour so read samples within 1 to 2 hours of making to volume). The final pH should be 4.2. Add 10 ml of 0.32 N H_2SO_4 to each standard. Run 3 or 4 standards with each set of samples as the standard curve will vary slightly from day to day. Read μg Al from a curve of absorbance vs. μg Al. The Al standards can be prepared from aluminum foil or from $KAl(SO_4)_2.12H_2O$. The standard curve should cover the range 0 to 120 μg Al in 50 ml.

Calculations

For a .500 g sample, a 5 ml aliquot digested and a 10 ml aliquot for analysis % Fe or Al =

$$\frac{\mu g \text{ in final solution}}{500 \times 1000} \times \frac{50}{5} \times \frac{50}{10} \times \frac{100}{1} = \frac{mg}{100}$$

NOTE, 1. The dithionite method used by the Soil Conservation Service (1972) is somewhat simpler and it gives closely similar results (Sheldrick and McKeague, 1975).

References

(1) Mehra, O.P and Jackson, M.L. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. 7th Natl. Conf. Clays and Clay Minerals. pp. 317-327.

(2) Parker, C.R. 1972. Water analysis by atomic absorption. Varian Techtron Ltd., Springvale, Australia.

(3) Sheldrick, B.H. and McKeague, J.A. 1975. A comparison of extractable Fe and Al data using methods followed in the U.S.A. and Canada. Can. J. Soil Sci. 55, 77-78.

(4) Soil Conservation Service, U.S.D.A. 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Investigations Report No. 1 (Revised), U.S. Govt. Printing Office, Washington, D.C.

(5) Wang, C. and Wood, F.A. 1973. A modified aluminon reagent for the determination of aluminum after HNO_3-H_2SO_4 digestion. Can. J. Soil Sci. 53, 237-239.

(6) Weaver, R.M., Syers, J.K. and Jackson, M.L. 1968. Determination of silica in citrate-bicarbonate-dithionite extracts of soil. Soil Sci. Soc. Am. Proc. 32, 497-501.

(7) Webber, M.D., McKeague, J.A., Raad, A.T., DeKimpe, C.R., Wang, C., Haluschak, P., Stonehouse, H.B., Pettapiece, W.W., Osborne, V.E. and Green, A.J. 1974. A comparison among nine Canadian laboratories of dithionite-, oxalate-, and pyrophosphate-extractable Fe and Al in soils. Can. J. Soil Sci. 54, 293-298.

3.52 Acid Ammonium Oxalate Extractable Fe and Al (and Mn and Si if Desired)

The oxalate procedure was used 50 years ago by Tamm to remove the sesquioxide weathering products from soils. It was revived by Schwertmann who showed that it could be used to estimate amorphous Fe in soils. It extracts the Fe and Al accumulated in Podzol B horizons and from 1965 to 1973, oxalate extraction served as a basis for distinguishing between Bf and Bm horizons in Canada.

Reagent

Acid oxalate solution

A. Prepare a 0.2 M solution of $(NH_4)_2C_2O_4.H_2O$ Ammonium oxalate) (28.3 g/1).

B. Prepare a 0.2 M solution of $H_2C_2O_4.2H_2O$ (Oxalic acid) (25.2 g/1).

Mix about 700 ml of A and 535 ml of B, check pH and adjust to 3.0 by adding either A or B.

Extraction Procedure

(1) Weigh out 0.250 g of soil ground to pass a 100 mesh sieve into a 15 ml test tube (weigh 0.125 g for soils with more than 2% extractable Fe or Al).

(2) Add 10 ml of the acid oxalate solution and stopper the tube tightly.

(3) Place the tubes horizontally in a covered box and shake for 4 hours (the extraction has to be done in the dark).

(4) Centrifuge the tubes and decant the clear centrifugate into a suitable container and store for analysis within a few days.

3.521 Determination of Fe and Al (and Mn and Si) by atomic absorption

Follow standard atomic absorption procedures and note the points mentioned in 3.511. In general dilute the extracts (about 1 ml extract and 4 ml NaCl solution) to give a convenient concentration. The solutions and standards should contain Na at about 2000 ppm to suppress interferences. Aspirating water and aerosol between samples prevents clogging of the burner.

3.522 Determination of extracted elements by colorimetry

Follow the procedures given in 3.512.

Calculations

For 0.250 g of soil, a 2 ml aliquot digested and a 10 ml aliquot determined,

$$\% \text{ Fe or Al} = \frac{\mu g \text{ in final solution}}{250 \times 1000} \times \frac{10}{2} \times \frac{50}{10} \times \frac{100}{1} = \frac{\mu g}{100}$$

References

(1) Baril, R. and Bitton, G. 1967. Anomalous values of free iron in some Quebec soils containing magnetite. Can. J. Soil. Sci. 47, 261.

(2) Blume, H.P. and Schwertmann, U. 1969. Genetic evaluation of profile distribution of aluminum, iron, and manganese oxides. Soil Sci. Soc. Am. Proc. 33, 438-444.

(3) McKeague, J.A. and Day, J.H. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46, 13-22.

(4) Schwertmann, W. 1964. The differentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate. Z. Pflanzenernahr. Dung. Bodenkunde, 105, 194-201.

(5) Schwertmann, U. 1973. Use of oxalate for Fe extraction from soils. Can. J. Soil Sci. 53, 244-246.

3.53 Sodium Pyrophosphate Extractable Fe and Al (and Mn and Si if Desired)

Since 1973 this procedure has been a basis in Canada of differentation of Podzolic B horizons from other horizons. It is more suitable for this purpose than oxalate because it avoids problems with some soils containing either volcanic ash or magnetite. Similar procedures are used widely in the world as a chemical basis of identification of podzolic B horizons.

Reagents

(1) Sodium pyrophosphate solution, 0.1 M - Dissolve 44.6 g of $Na_4P_2O_7.10H_2O$ in water and make to 1 ℓ.

(2) Superfloc (N-100), available from Cyanamid of Canada Ltd., P.O. Box 1038, Montreal, Que. H3C2X4.

Extraction Procedure

(1) Weigh 0.300 g of soil ground to pass a 100 mesh

sieve into a 50 ml plastic centrifuge tube (use 1 g for samples low in extractable Fe and Al).

(2) Add 30 ml of 0.1 M sodium pyrophosphate solution, stopper, shake overnight.

(3) Centrifuge at 20,000 x gravity or more for 10 minutes, or add 0.5 ml of 0.1% superfloc solution and centrifuge at 1500 rpm for 10 min. (Sheldrick and McKeague, 1975).

(4) Decant a portion of the clear centrifugate into a container and store for analysis.

3.531 Determination of Fe and Al (and Mn and Si) by atomic absorption

Standard atomic absorption procedures are used. Standards are made up in 0.1 M sodium pyrophosphate. Sufficient Na is present to suppress interferences. Note points mentioned in 3.511.

3.532 Determination of Fe and Al by colorimetry

(1) Digest a 5 ml aliquot of the extract with HNO_3-H_2SO_4 as specified in 3.512.

(2) Determine Fe and Al as specified in 3.512.

Calculations

For a .300 g sample, 5 ml digested and a 10 ml aliquot for analysis,

$$\% \text{ Fe or Al} = \frac{\mu g \text{ in final solution}}{300 \times 1000} \times \frac{30}{5} \times \frac{50}{10} \times \frac{100}{1} = \frac{\mu g}{100}$$

References

(1) Bascomb, C.L. 1968. Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19, 251-268.

(2) McKeague, J.A. 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in Podzols and some other soils. Can. J. Soil Sci. 47, 95-99.

(3) McKeague, J.A., Brydon, J.E. and Miles, N.M. 1971. Differentiation of forms of extractable iron and aluminum in soils. Soil Sci. Soc. Am. Proc. 35, 33-38.

(4) Sheldrick, B.H. and McKeague, J.A. 1975. A comparison of extractable Fe and Al data using methods followed in the U.S.A. and Canada. Can. J. Soil Sci. 55, 77-78.

3.54 Alkali-extractable Si and Al

A number of procedures are used for extracting "amorphous", alkali-soluble Si and Al from soils and clays. Such procedures are not used routinely in soils laboratories in Canada, but two are outlined.

Cold 5% sodium carbonate extracts the more readily soluble amorphous Si and Al material (Mitchell, Farmer and McHardy, 1964) and hot 0.5 M NaOH (Hashimoto, Jackson, 1960) extracts greater amounts of Si and Al.

3.541 Cold 5% Na_2CO_3 extractable Si and Al.

Reagents

(1) 5% Na_2CO_3 - make up about 3 ℓ.

(2) 1N H_2SO_4 - make up about 2 ℓ.

(3) 0.3M ammonium molybdate adjusted to pH7 with NaOH (54 g. of $(NH_4)_6Mo_7O_{24}.4H_2O$ per ℓ. = 0.3M with respect to MoO_4^{-2}).

(4) 10% tartaric acid

(5) Reducing solution - dissolve 0.7 g of sodium sulfite in 20 or so ml. of H_2O. Add 0.15 g. of 1-amino-2 naphthol-4-sulfonic acid and stir (magnetic stirrer) until dissolved. Dissolve 9 g. of sodium bisulfite in about 40 ml. of H_2O. Add this solution to the first, make to 100 mls. and mix. This solution deteriorates after about a week.

(6) 1% Thioglycollic acid solution - prepare daily.

(7) Aluminon buffer solution. Dilute 120 ml. of glacial acetic acid to about 900 mls. Add 24 g. of NaOH and mix. Dissolve 0.35 g of aluminon in the solution, dilute to 1 ℓ. and mix.

Procedure for extraction

Place 0.1 g of 100 mesh samples with 25 ml. of 5% Na_2CO_3 solution in 50 ml. plastic centrifuge tubes. Shake overnight, centrifuge and pour the extract into plastic containers.

NOTE: use only plastic as the Na_2CO_3 solution may extract Si from glass.

Si determination

(1) Place 8 ml. of 1N H_2SO_4 in 50 ml volumetric flasks. Pipette 5 ml of extract directly into the acid and mix

well (5 ml of acid are required to neutralize the Na_2CO_3). If a smaller aliquot is necessary add Na_2CO_3 solution so that all samples contain the same amount. Standards should range from 0-100 µg and contain the same amounts of acid and Na_2CO_3 as the samples.

(2) Heat samples and standards on a hot plate at 80C for 30 min. to drive off the CO_2.

(3) When cool, add 4 ml. of 0.3M ammonium molybdate, mix and allow to stand for 5 min.

(4) Add 4 ml. of 10% tartaric acid and mix.

(5) Add 1 ml. of reducing solution, mix, make to volume and read at 660 mµ after 1 hr.

Al determination

(1) Place 8.5 ml of 1N H_2SO_4 in 50 ml. volumetric flasks. Pipette 5 ml of extract directly into the acid and mix well (5 ml of acid are required to neutralize the Na_2CO_3 and 3.5 ml are for the procedure). If a smaller aliquot is necessary add Na_2CO_3 solution so that all samples contain the same amounts of acid and Na_2CO_3 as the samples.

(2) Heat samples and standards on a hot plate at 80-90°C. for 30 min. to drive off the CO_2.

(3) When cool, add 1 ml. of 1% thioglycollic acid solution.

(4) Add H_2O to about 30 ml and mix.

(5) Add 10 ml of aluminon solution, make to volume and mix well. Read at 530 mµ after 2 hrs. (absorbance increases slightly after 2 hrs. so read samples within 2 to 3 hrs. of making to volume.

NOTE: Atomic absorption might be used for the determination of Si and Al in the extracts.

References

(1) Follett, E.A.C., McHardy, W.J., Mitchell, B.D. and Smith, B.F.L. 1965. Chemical dissolution techniques in the study of clays. Pts. 1 and 2 Clay Miner. 6, 23-43.

(2) Mitchell, B.D., Farmer, V.C. and McHardy, W.J. 1964. Amorphous inorganic materials in soils. Adv. Agron. 16, 327-383.

3.542 Boiling 0.5 N NaOH Extractable Si and Al

Reagents

(1) 0.5N NaOH - make up about 3-4 ℓ.

(2) 1N H_2SO_4 - make up about 2 ℓ.

(3) Reagents 3 to 7 as for 3.541.

Procedure for extraction

Weigh 50 mg of 100 mesh sample and place in a 100 ml plastic tube. Heat the NaOH solution to boiling and then add 50 ml to the sample and stir (Vortex stirrer). Place the tube in a 1000 ml beaker containing boiling water for 2.5 min. Stir again and then filter into a plastic bottle.

NOTE: use only plastic as hot NaOH extracts Si from glass.

Si determination

(1) Place 5.5 ml of 1N H_2SO_4 in 50 ml volumetric flasks. Pipette 5 ml of extract directly into the acid and mix well (2.5 ml. of acid are required to neutralize the NaOH). If a smaller aliquot is necessary add NaOH so that all samples contain the same amount. Standards should range from 0-100 µg. and contain the same amounts of acid and NaOH as the samples.

(2) Follow steps 2,3 and 4 as in 3.541.

Al determination

(1) Place 6 ml of 1N H_2SO_4 in 50 ml volumetric flasks. Pipette 5 ml of extract directly into the acid and mix well (2.5 ml of acid are required to neutralize the NaOH). If a smaller aliquot is necessary add NaOH so that all samples contain the same amount. Standards should range from 0-80 µg and contain the same amount of acid and NaOH as the samples.

(2) Follow steps 2,3 and 4 as in 3.541.

References

(1) Hashimoto, J. and Jackson, M.L. 1960. Rapid dissolution of allophane and kaolinite-halloysite after dehydration. Clays and Clay Miner. 7, 102-113.

3.6 TOTAL C, N, S AND P - W.B. McGill

3.61 Total Carbon

Several quantitative methods are available for the determination of total C in soils and the choice of method depends on the equipment available. For samples containing carbonates, organic C can be determined by subtracting carbonate C (3.42 or 3.43) from total C. Method 3.612 is accurate and it uses simple equipment but 3.611 is faster and more convenient. The modified Walkley - Black method, 3.613, is not quantitative but it is adequate for some purposes and certainly preferable to "Loss on Ignition" as an estimate of organic matter.

3.611 Carbon by dry combustion, LECO induction furnace

Follow the procedures given in the instruction manual. These differ somewhat depending upon the age of the instrument and the CO_2 measuring system involved. The following procedure is suitable for the model 577-100 carbon analyzer. The procedure described requires 5 or 6 minutes per sample. Other kinds of CO_2 analyzers permit more rapid determinations of C.

(1) Plug in the furnace 15 minutes or so before analyzing a sample. This allows the catalyst furnace, which converts CO to CO_2, to warm up. Turn on the filament switch (green pilot light) 5 minutes before blanking the apparatus.

(2) Blanking the apparatus and testing for leaks. This should be done at the start of each day of operation.

(a) Turn on the O_2 tank to about 4 psi and close the needle valve on the purifying train. DO NOT apply too much force to the needle valve.

(b) Turn the buret stopcock to the exhaust position (down) and raise the levelling bottle to the upper cup until the red solution fills the buret and seats the float valve. Seat the valve SLOWLY BY PINCHING the tubing BEFORE the liquid reaches the valve. This keeps the solution out of the stopcock.

(c) Turn the buret stopcock to the furnace position (left) and place a crucible on the pedestal of the raising mechanism. The crucible should contain one scoop of tin accelerator, one scoop of iron chip accelerator, and one copper ring accelerator which is centered in the crucible.

(d) Open the needle valve and adjust the O_2 flow to 0.5 liters/minute. Close the raising mechanism on the furnace and set the levelling bottle on the base. Lay the tubing on the bench.

(e) When the red solution is about 2/3 of the way down the calibrated stem of the buret, open the raising mechanism. Turn off the needle valve and turn the stopcock to the exhaust position (down).

(f) Allow the buret to drain (about 30 seconds, use a stopwatch). Check the drainage time periodically by turning the stopcock to the lock position (right) and noting if the red fluid rises above zero. If the red liquid is not at zero after draining, add or remove some red solution from the levelling bottle.

(g) Turn the buret stopcock to the caustic position (up) BEFORE (to avoid loss of CO_2) raising the levelling bottle to the upper cup and above to remove all the gas from the buret.

(h) Lower the levelling bottle below the table level until the KOH solution in the absorption vessel rises and seats the float valve (this can be seen through the window).

(i) Turn the buret stopcock to the lock position (right) and then place the levelling bottle on the base and lay the tubing on the bench. Allow the buret to drain for 60 seconds and read. It should be 0. Frequently there is a blank reading of .04 or so after the first flushing with O_2. If this occurs, repeat the blanking procedure.

(j) Test for leaks by filling the buret with the red solution and letting O_2 enter until the red solution reaches some level on the calibrated stem of the buret. Turn off the needle valve. If the solution continues to fall, a leak is indicated. Progressively pinch off sections of tubing between the needle valve and the carbon determinator to find at what point the solution stops falling. The leak is then BEHIND the last pinched off point.

(3) Analyzing a sample

(a) Weigh samples ground to 0.5 mm or finer into crucibles. The maximum C that can be determined is 15 mg. For samples with less than 1% C weigh 500 mg

1 - 4% C weigh 250 mg

4 - 8% C weigh 125 mg

8 - 20% C weigh 50 mg

20 - 50% C weigh 25 mg

(b) Add one scoop of iron chip accelerator, one scoop of tin accelerator, and one copper ring accelerator. Center the Cu ring in the crucibles. Include standards and blanks with each set of samples. MAKE SURE THAT THE ACCELERATOR COVERS ALL OF THE SAMPLE. The amount of accelerator required may vary depending upon the furnace.

(c) Repeat steps 2(a) and 2(i). The O_2 flow rate should be 0.5 ℓ/m. The meter above the filament switch should read over 300 milliampers at the hottest stage of combustion and it should reach this level before the red solution is half way down the bulb of the buret. If this does not occur, the results will be low as combustion and sweeping will be incomplete. It is important to lower the raising mechanism before the red fluid reaches the bottom of the buret.

(d) Read the buret by raising the levelling bottle until the liquid in the side arm reading tube is at exactly the same level as the liquid in the buret. Read the right scale of the buret. The right scale is calibrated in % C for 0.250 g samples; the left scale for 1.00 g samples. By weighing the above recommended amounts, calculations of % C are simplified.

(e) Correct for T and P. Read thermometer in the buret and read a barometer (once a day is usually sufficient). The correction is made with the aid of the factor chart supplied. Suppose the sample weight was 0.200 g, correction factor was 0.950 and the reading was 2.40. Then % C is $\frac{.250}{.200} \times \frac{95}{100} \times \frac{2.40}{1} = 2.85$

(f) When the instrument is not in use, pull out the furnace plug. Fill the buret with red solution to just below the valve. DO NOT SEAT the valve. Turn the stopcock to the lock position (right) and place the levelling bottle on the base.

NOTES:

(1) The combustion tube must be cleaned about four times each day. A brass brush is supplied and the vacuum cleaner is quite helpful. TURN OFF the filament switch before cleaning. A partly plugged tube will result in low temperature and incomplete combustion.

(2) Replace dust filter cloth periodically. Clean it with the vacuum at least twice each day.

(3) Replace MnO_2 periodically when samples high in S are being run.

(4) The temperature in the tube during combustion is directly related to the amount of accelerator added and the O_2 flow rate. If the previously mentioned values are used, one will seldom have any trouble using this instrument. If the meter above the filament switch should reach 500 milliamps and hold for more than three seconds, IMMEDIATELY lower the raising mechanism. Repeat the sample using less accelerator.

References

(1) Bremner, J.M. and Tabatabai, M.A. 1971. Use of automated combustion techniques for total carbon, total nitrogen and total sulfur analysis of soils. In Instrumental methods for analysis of soils and plant tissue. p. 1-16. L.M. Walsh, ed. Soil Sci. Soc. Am. Proc., Madison, Wisconsin.

(2) Tabatabai, M.A. and Bremner, J.M. 1970. Use of the Leco automatic 70-second carbon analyzer for total carbon analysis of soils. Soil Sci. Soc. Am. Proc. 34, 608-610.

3.612 Total C by wet oxidation (Allison, 1960)

Apparatus - see Fig. 7

The apparatus can also be used for determining inorganic C. (Allison, 1960).

A. Air supply and needle valve.

B. Soda-lime tower, 10 in high

C. Kjeldahl flasks, 100 ml, to fit a #2 stopper

D. Allihn 4-bulb condenser, fitted with a #2 stopper at the delivery end.

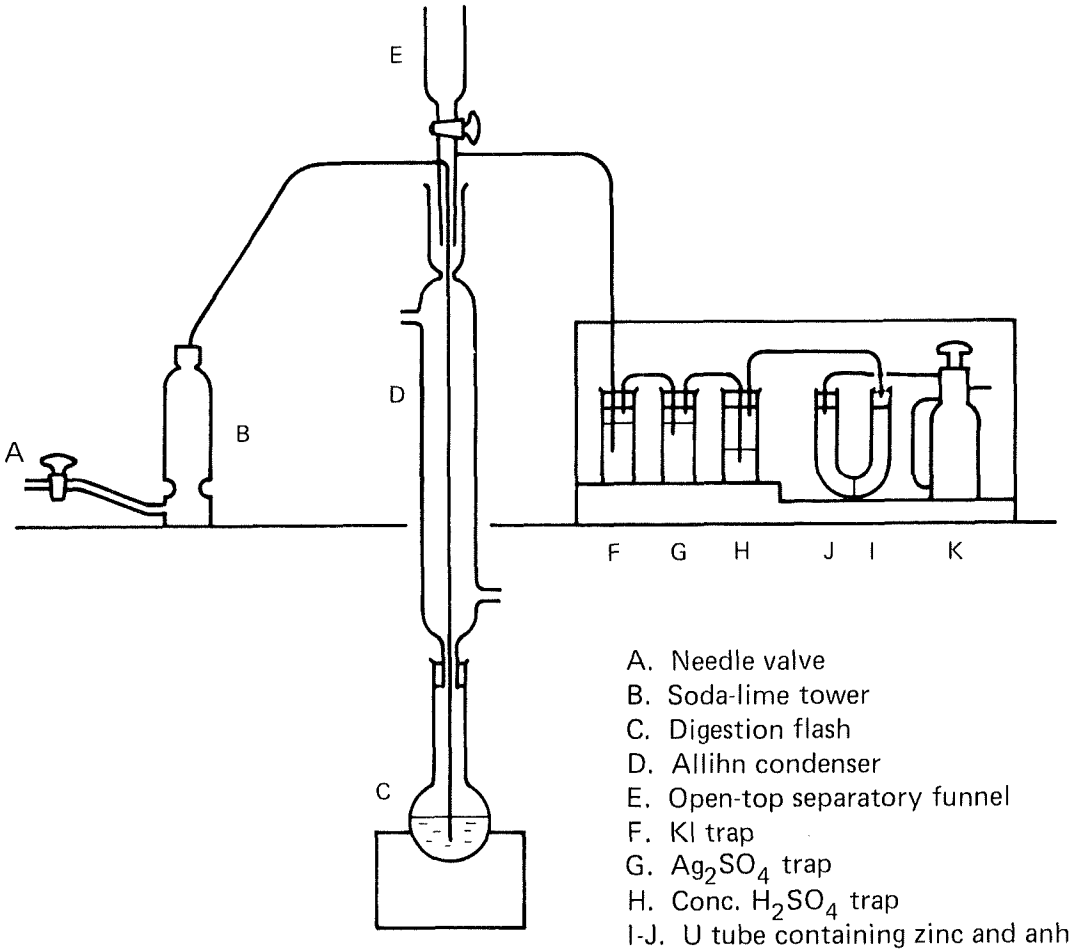
E. 60 ml open top separatory funnel

F, G, & H - Vials (25 x 90 mm) with #4 stopper

Vial F: filled to 2/3 full with 50% KI
Inlet tube 1-2 mm opening extending 4 cm below surface of KI

Vial G: 2/3 full, Ag_2SO_4
Inlet tube 1-2 mm opening and extending 2 cm into Ag_2SO_4

Vial H: 1/3 full, concentrated H_2SO_4
Inlet tube - barrel of 5 ml pipette with tip extending not more than 1 cm below surface of H_2SO_4



A. Needle valve
B. Soda-lime tower
C. Digestion flash
D. Allihn condenser
E. Open-top separatory funnel
F. KI trap
G. Ag_2SO_4 trap
H. Conc. H_2SO_4 trap
I-J. U tube containing zinc and anhydrone
K. Nesbitt absorption bulb

Fig. 7 Apparatus for determination of carbon
(by method 3.612)

I & J U-tube 15 cm long

Vial H attaches (4 mm O.D. tubing) to trap I (right side of U-tube)

Place a fiberglass disc in the bottom of the U-tube and fill the right side, trap I, with 30 mesh granular Zn

Fill the left side, trap J, with anhdrous $Mg(ClO_4)_2$

K Nesbitt absorption bulb or NaOH (0.2 N) bubble tower

Nesbitt tube filled with self-indicating CO_2 absorbent. The bulb is filled as follows, from bottom to top:

glass wool plug

3 cm layer of 8-14 mesh absorbent

2 cm layer of 14-20 mesh absorbent

1 cm overlayer of anhydrous $Mg(ClO_4)_2$

glass wool plug

Use neoprene stoppers, gum rubber tubing and silicone lubricant. Assemble as in Fig. 7.

Reagents

(1) Digestion acid: pour 600 ml concentrated H_2SO_4 into 400 ml of 85% H_3PO_4. Cool and store in a glass stoppered bottle.

(2) Potassium dichromate ($K_2Cr_2O_7$) reagent.

(3) Potassium iodide (KI) solution 50% Dissolve 100 g KI in 100 ml H_2O.

(4) Silver sulfate (Ag_2SO_4) saturated.

(5) CO_2 absorbent (self-indicating) 7-14 and 14-20 mesh. Several including ascarite, indicarb, caroxite and mikhobite are available.

(6) Soda-lime 8-14 mesh.

(7) Granular zinc (Zn) 30 mesh.

(8) Anhydrous magnesium perchlorate $Mg(ClO_4)_2$.

Procedure

(1) Grind soil sample to <0.5 mm.

(2) Place sample containing 20 to 40 mg of C (0.5-3 g of O.D. soil) into Kjeldahl flask.

(3) Add 1 g $K_2Cr_2O_7$, wash down neck with 3 ml distilled H_2O and connect flask to the condenser (D).

(4) Weigh the Nesbitt bulb (K), attach it to the system and open the valve at the top of the bulb.

(5) Pour 25 ml of digestion acid into the separatory funnel (E) and cover, open the stopcock on the funnel and allow the acid to flow through the condenser into the Kjeldahl flask, close the stopcock immediately.

(6) Turn on the cooling water and open the air inlet valve to allow an air flow of 2 bubbles per second.

(7) Heat the sample to bring it to a boil in 3-4 minutes. If high in Cl^- heat more slowly; bring it to a boil in 4-5 minutes, continue heating for a total of 10 minutes. If SO_2 fumes (white) appear above the second bulb of the condenser, reduce the rate of heating.

(8) Remove the heat, and aerate for an additional 10 minutes at 6-8 bubbles per second.

(9) Shut off the air stream, close the valve on the Nesbitt bulb, disconnect it from the train, brush it with a camel hair brush and weigh.

Calculations

$$\text{Total C \%} = \frac{(\text{g } CO_2 \text{ in sample}) - (\text{g } CO_2 \text{ in blank})}{\text{g dry soil}} \times 27.27$$

References

(1) Allison, L.E. 1960. Wet-combustion apparatus and procedure for organic and inorganic carbon in soil. Soil Sci. Soc. Am. Proc. 24, 36-40.

(2) Allison, L.E., Bollen, W.B., and Moodie, C.D. 1965. Total Carbon. In Methods of Soil Analysis, Part 2. p. 1346-1378. C.A. Black, ed-in-chief. No. 9 in Agronomy series, Am. Soc. Agron., Madison, Wisconsin.

3.613 Organic C by wet oxidation (modified Walkley-Black method)

A number of assumptions are made in this method, and some are not strictly correct. Two of these are:

(a) Organic C is the only substance present that reduces dichromate,

(b) 75% of the organic matter present is oxidized. Thus, the results are approximate, but adequate for some purposes.

Reagents

(1) Potassium dichromate solution - 1.000 N. Dissolve 49.04 g reagent grade K_2CrO_7 (dried for 1 hr at 150°C) in water and dilute to 1 ℓ. Mix thoroughly.

(2) Ferrous sulphate solution - 0.5 N. Dissolve 140 g reagent grade $FeSO_4.7H_2O$ in water, add 40 ml conc. H_2SO_4, cool and dilute to 1 ℓ. Mix thoroughly. Standardize daily by titrating against 10 ml N $K_2Cr_2O_7$ solution as directed in method below. Ferrous ammonium sulfate is preferred by some (196g/1 for approx. 0.5 N).

(3) Barium diphenylaminesulphonate indicator solution. Prepare 0.16% aqueous solution (Alternatively ferroin, ortho-phenanthroline-ferrous sulfate (0.025 M) may be used as indicator. If ferroin is used, no addition of phosphoric acid is required. The endpoint can also be measured potentiometrically using a calomel and a platinum electrode. The latter method is best for some highly colored soils.

(4) Sulphuric acid - H_2SO_4, conc., not less than 96%.

(5) Phosphoric acid - H_3PO_4, 85%, U.S.P. grade.

Procedure

(1) Weigh 0.100 to 2.00 g of soil (depending on organic matter content) ground to 0.5 mm or finer, place in a 1000 ml beaker and add 10 ml N $K_2Cr_2O_7$ solution. Then add rapidly 20 ml conc. H_2SO_4, directing stream into solution. Immediately swirl vigorously by hand for 1 minute and let beaker stand on a sheet of asbestos for 30 minutes. If the solution has a green colour, add more $K_2Cr_2O_7$ and H_2SO_4. Keep the same proportions 1:2.

(2) Add 500 ml water, 10 ml H_3PO_4 (for barium diphenylamine sulphonate) and 1.0 ml of indicator solution. Stir with a magnetic stirrer and from a burette, add $FeSO_4$ solution rapidly until liquid in beaker is purple or blue, then more slowly until color flashes to green (green to reddish brown with ferroin). If end point is passed, add a small volume (0.5 ml) of N $K_2Cr_2O_7$ solution and complete titration. If more than 8 of the available 10 ml of $K_2Cr_2O_7$ solution is reduced, repeat determination with less soil.

$$\% \text{ organic C in soil sample} = \frac{(\text{ml N } K_2Cr_2O_7 \text{ reduced}) \times 0.40}{\text{weight of sample (g)}}$$

References

(1) Allison, 1960, See 3.612.

(2) Grewling, T. and Peech, M. 1960. Chemical soil tests. Cornell Univ. Agr. Exp. Sta., Bull. 960, pp. 34-36.

(3) Walkley, A. and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci. 37, 29-38.

3.614 Total carbon by dry combustion, resistance furnace

Apparatus

(See Fig. 8)

The apparatus consists of four main sections:

(1) air purification train - acid dichromate tube to remove dust, sodium hydroxide tower to remove CO_2, sulphuric acid tube to remove water, and a mercury valve to prevent back pressure.

(2) electric furnace with the heating element at the centre so as to heat about a 5-inch length of the sillaminite combustion tube (24 inches long, 1 inch diameter). A plug of copper oxide wire placed in the heated portion of the combustion tube and near the outlet end serves to convert nitrogenous gases to elemental nitrogen and to remove chlorine compounds. A mercury valve placed immediately following the combustion chamber prevents any gases from backing up into the chamber.

(3) the gas purification train consists of a tube of sulfuric acid that serves as a drier and removes SO_3 and any oxides of nitrogen formed from the combustion of organic matter, separated by a trap from a tube of zinc which also removes oxides of nitrogen and sulfur.

(4) CO_2 absorption towers (20 mm by 50 cm) connected to the gas purification train by means of a two-way stopcock. The tops of the towers are connected to a suction line.

Reagents

(1) Approximately 0.5 N NaOH.

(2) Standard 0.5 N HCl.

(3) 15% $BaCl_2$.

(4) Phenolphthalein Indicator (1% in 95% alcohol).

(5) MnO_2 powder, reagent grade.

(6) CuO wire.

Procedure

(1) After assembling the apparatus as indicated, the furnace is heated to 925°C and the suction is turned on to free the apparatus of carbon dioxide.

(2) A sample of from 0.5 to 4.0 grams of 100 mesh soil is weighed out and placed in a porcelain boat on top of approximately 0.25 grams of manganese dioxide which has been evenly spread in the bottom of the boat (for soils high in organic matter, 0.5 grams are used, while for calcareous soils 2.0 grams are weighed out. For samples relatively low in organic matter and lime, generally 4.0 grams are used). A "Blank" determination is run using a porcelain boat containing only the manganese dioxide.

(3) A burette is used to measure out 40 ml of approximately 0.5 N NaOH into the flasks used with the absorption towers.

(4) After the furnace has reached the required temperature and the apparatus has been flushed free of carbon dioxide, proceed as follows:

- Turn off the suction, using the screw-clamp on the suction line.

- Connect a flask containing 40 ml of the base to one of the absorption towers.

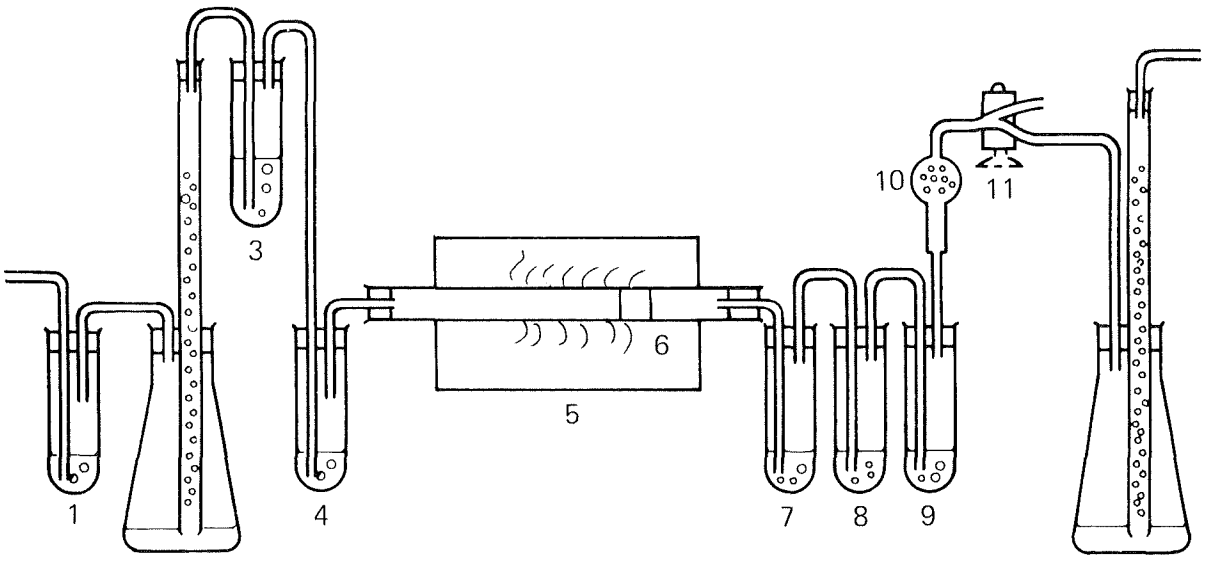
- Disconnect the train at the inlet end of the combustion tube.

- Switch the two-way stopcock to the proper absorption tower.

- Apply suction slowly to the line so that air bubbles slowly through the scrubbers and towers.

- Insert a boat into the combustion tube so that its forward end barely reaches the hottest part of the tube, and connect the tube quickly to the air purification train.

- Adjust the suction to the proper rate, so that air is drawn through at a rate of about 4 bubbles per second.



1. Acid dichromate tube
2. NaOH tower
3. Conc. H_2SO_4 tube
4. Mercury valve
5. Combustion tube
6. Copper oxide plug
7. Mercury valve
8. Conc. H_2SO_4 tube
9. Trap
10. Zinc (20 mesh) tube
11. Two-way stopcock
12. NaOH tower

Fig. 8. Apparatus for C determination by method 3.615

- After heating for 7 minutes, decrease the rate of aspiration.

- Loosen the stopper at the inlet end of the combustion tube, being careful that the scrubbers and NaOH in the towers do not bubble too violently and foam over.

- Quickly push the boat into the hottest portion of the tube and close the inlet end.

- Readjust the suction.

- After another 7-8 minutes, turn the stopcock off.

- Turn the suction off by means of the screw-clamp.

- Open the inlet end of the combustion tube slowly till the stopper is loose.

- Switch the stopcock over to the new tower.

- Readjust the suction slowly so as to have air bubbling through the line very slowly.

- Remove the spent boat, and insert the new sample as before.

- Close the inlet end of the tube.

- Readjust the suction to the proper rate of aspiration.

- Continue as before.

- Rinse the tower used for the previous sample with about 150 ml of water, rinsing the tip of the tower using a wash bottle.

- Rinse down the sides of the flask.

- Add 10 ml of 15% $BaCl_2$ (Note: make certain that sufficient Barium chloride is present to precipitate all the carbonate present).

- Add 2-3 drops of Phenolphthalein Indicator.

- Titrate using standard 0.5 N HCl to a colorless end-point.

Calculations

$$\text{Total carbon (\%)} = \frac{\text{(Blank - titre) x N of acid x .006 x 100}}{\text{weight of soil used}}$$

where: (Blank - titre) = difference in ml between the titre for the blank and the titre for the sample.

In order to determine the organic carbon content of the sample, it is necessary to know the amount of inorganic carbon present. Then:

% organic carbon = % total carbon - % inorganic carbon.

NOTES:

(1) Placing the sample directly in the hottest portion of the combustion tube usually results in loss of CO_2.

(2) Care must be taken to avoid leaks in any part of the apparatus.

References

(1) Schroer, F.W. 1940. "An examination of several methods of determining organic carbon and organic matter in soils". Master's Thesis. University of Saskatchewan Soils Department.

(2) Treadwell, F.P. and Hall, W.T. 1947. Analytical Chemistry. Vol. 2, 9th ed. John Wiley and Sons, Inc., New York. 364 pp.

(3) Piper, C.S. 1950. Soil and Plant Analysis. Interscience Publishers, Inc., New York. 216 pp.

3.615 Pyrophosphate-soluble organic matter index for organic soils - Schnitzer and Desjardins, 1965.

Apparatus

Shaking bottles, filter funnels, spectrophotometer.

Reagents

Sodium pyrophosphate 0.025 M. Dissolve 11.152 g $Na_4P_2O_7.10H_2O$ in 1 ℓ of distilled water.

Procedure

(1) Weigh 0.5 g air-dried soil into a shaking bottle and add 50 ml of 0.025 M $Na_4P_2O_7$.

(2) Shake for 18 hours.

(3) Filter and dilute filtrate to 250 ml with distilled water.

(4) Measure the absorbance of this solution at 550 mμ.

Calculation

Multiply absorbance by 100 to give an index of solubility.

Reference

Schnitzer, M. and Desjardins, J.G. 1965. Carboxyl and phenolic hydroxyl groups in some organic soils and their relation to degree of humification. Can. J. Soil Sci. 45, 257-264.

3.62 Total N

Both semi-micro- and macro-Kjeldahl procedures are given with and without steps to include nitrate and nitrite. In many soils N as NO_3^- and NO_2^- is a negligible component of total N, and procedures 3.622 or 3.624 are adequate. The semi-micro procedures are preferable as they save chemicals, space and capital expenditures. Even for the macro-Kjeldahl procedures, soil samples containing more than about 0.5% N should be ground to pass a 100 mesh sieve. During digestion, the Kjeldahl flasks should be rotated at intervals.

3.621 Semi-micro Kjeldahl method - NO_2^- and NO_3^- included

Apparatus

(1) Semi-micro Kjeldahl digestion rack:

A circular rack holding 12 flasks and complete with its own exhaust manifold can be obtained from Aminco (Silver Springs, Maryland). It takes less space than the straight, 6 place racks.

(2) Semi-micro Kjeldahl flasks:

100 ml capacity with ₹ 19/38 ground glass joint (as for the Quickfit distillation apparatus).

(3) Semi-micro Kjeldahl Steam Distillation Apparatus (Fig. 9).

This apparatus uses the above-mentioned digestion flasks for distillation, thus preventing errors that arise during transfer from digestion to distillation flasks.

Reagents

(1) $KMnO_4$ solution (50 g $KMnO_4$ in one liter of H_2O - stored in Amber bottle).

(2) Dilute H_2SO_4 (1:1 (V/V) H_2O - H_2SO_4).

(3) Fe finely ground to pass 100 mesh sieve (British Drug Houses or Ealing Corporation).

(4) N-octyl alcohol, concentrated H_2SO_4, K_2SO_4, $CuSO_4.5H_2O$.

(5) Hengar granules, both selenized and non-selenized.

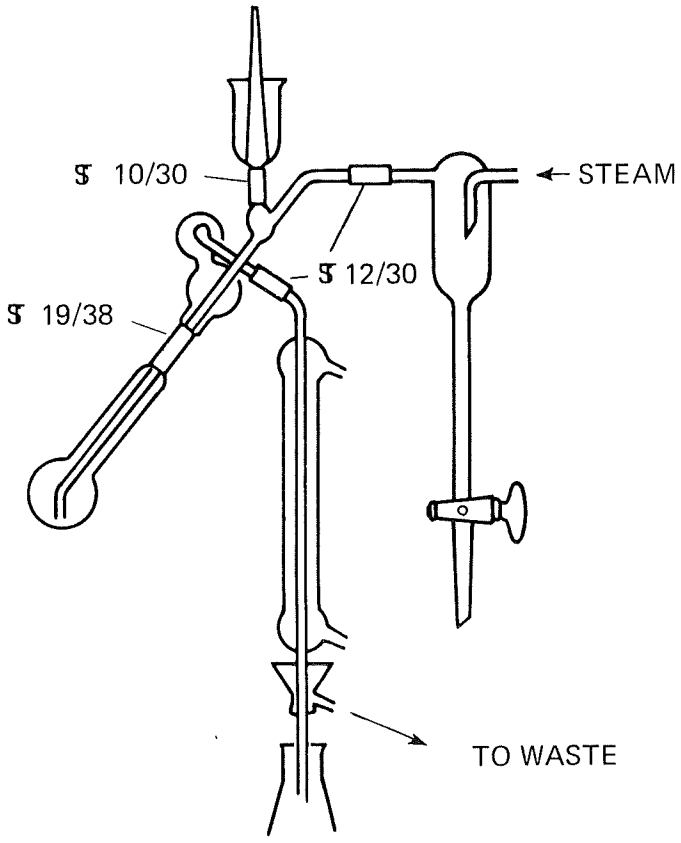


Fig. 9. Steam Distillation Apparatus (Bremner, 1965)

(6) Digestion mixtures prepared as follows:

To 1,000 ml hot concentrated H_2SO_4 add 450 g K_2SO_4 with vigorous stirring.

To 500 ml cold concentrated H_2SO_4 add 44 ml 25% $CuSO_4$ (25 g $CuSO_4$ in 75 ml H_2O).

After dissolution of K_2SO_4 (powder) add H_2SO_4 + $CuSO_4$ mixture and let cool. The K_2SO_4 may crystallize out upon cooling; if so, keep the digestion mixture at 40°C or reduce the amount of H_2O in the mixture.

Procedure, Digestion

(1) Place sample, ground to pass a 100 mesh sieve, containing up to 2 mg nitrogen in dry Kjeldahl flask, add 2 ml H_2O, swirl, and allow to stand 30 minutes.

(2) Add 1 ml $KMnO_4$ solution, swirl 30 seconds; hold at 45° and pipette in 2 ml dilute H_2SO_4. Add H_2SO_4 very slowly. Allow to stand 5 minutes.

(3) Add 1 drop octyl alcohol (prevents frothing), and add 0.5 g Fe powder through a dry thistle tube with a stem to reach down to the bulb.

(4) Immediately cover to prevent loss of H_2O and gases (15 mm test tube cut in half with expanded lip and filled with H_2O to form a condenser).

(5) Swirl to bring Fe into contact with acid and allow to stand until strong effervescence has ceased.

(6) Heat to a slow boil for 30 minutes, cool and remove cover.

(7) Add 7-10 ml of H_2SO_4-$CuSO_4$ mixture plus 1 selenized hengar granule and one non-selenized boiling chip, and heat cautiously on the digestion stand.

(8) When H_2O is removed and frothing ceases, increase the heat until the digest clears (H_2SO_4 should condense 2/3 way up the neck of the flask). Boil gently for 2-3 hours after clearing, cool.

Distillation

Reagents

(1) NaOH 10 N, and 0.1 N.

(2) Boric acid 2%. Place 80 g of pure boric acid (H_3BO_3) into a 5 liter flask marked to indicate a volume of 4 ℓ. Add approximately 3,800 ml of H_2O and heat gently while swirling or using a stirring hot plate until

the H_3BO_3 is dissolved. Cool the solution and add 80 ml of mixed indicator prepared as follows: 0.099 g bromocresol green and 0.066 g methyl red dissolved in 100 ml ethanol. Add 0.1 N NaOH cautiously until the solution turns reddish purple (pH ca 4.8-5.0). Make to 4 ℓ with distilled H_2O and mix thoroughly.

Procedure

(1) Slowly and with shaking, add 20 ml H_2O to the digested mixture. If all material does not enter into suspension, heat slowly until it does.

(2) Add about 30 ml of 10 N NaOH and distill (caution - bumping may occur). Collect the distillate in 10 ml H_3BO_3 (2%) with the end of the condenser below the surface of the H_3BO_3. Collect 30 ml of distillate.

(3) Titrate the distillate with 0.01 N H_2SO_4. The color change at the endpoint is from green to pink. Use a 10 ml burette graduated at 0.02 or 0.01 ml intervals. One ml of 0.01 N H_2SO_4 is equivalent to 0.14 mg of N (as NH_4^+).

Calculations

$$\text{Total N \%} = \frac{\text{ml } H_2SO_4 \times N \times 1.4}{\text{weight of sample in g}}$$

References

(1) Bremner, J.M. 1965. Total Nitrogen. In Methods of soil analysis, Part 2, p. 1149-1178. C.A. Black ed-in-chief. Number 9 in Agronomy Series, Am. Soc. Agron., Madison, Wisconsin.

(2) Bremner, J.M. and Tabatabai, M.A. 1971. Use of automated combustion techniques for total carbon, total nitrogen and total sulfur analysis of soils. In Instrumental methods for analysis of soils and plant tissue. p. 1-16. L.M. Walsh ed. Soil Sci. Soc. Am., Madison, Wisconsin.

(3) Heese, P.R. 1971. A textbook of soil chemical analysis. John Murray, London.

3.622 Semi-micro Kjeldahl method without precautions to include NO_3^- and NO_2^-

Follow the same procedure as 3.621 except that steps 2 to 6 are omitted.

3.623 Macro Kjeldahl method, NO_3^- and NO_2^- included

Apparatus

(1) Macro-Kjeldahl digestion flasks (350 or 500 ml).

(2) Macro-Kjeldahl digestion stand.

(3) Macro-Kjeldahl distillation apparatus.

Reagents

(1) Sulfuric acid (H_2SO_4), concentrated.

(2) Potassium sulfate (K_2SO_4).

(3) Copper sulfate ($CuSO_4.5H_2O$).

(4) Selenium.

(5) Sodium hydroxide (NaOH), approximately 10 N: Place 4.2 kg of NaOH in a heavy-walled 10-ℓ Pyrex flask, add 4 ℓ of water, and swirl the flask until the alkali is dissolved. Cool the solution with a rubber stopper in the neck of the flask to prevent absorption of atmospheric CO_2, and allow it to stand for several days to permit any Na_2CO_3 present to settle. Siphon the clear supernatant liquid into a large Pyrex bottle which contains about 1.5 ℓ of CO_2-free water and is marked to indicate a volume of 10 ℓ, and make the solution to 10 ℓ by addition of CO_2-free water. Then swirl the bottle vigorously to mix the contents, and fit the neck with some arrangement which permits the alkali to be stored and dispensed with protection from atmospheric CO_2 (see Piper, 1944; Jackson, 1958).

(6) Boric acid-indicator solution: Place 80 g of pure boric acid (H_3BO_3) in a 5-ℓ flask marked to indicate a volume of 4 ℓ, add about 3,800 ml of water, and heat and swirl the flask until the H_3BO_3 is dissolved. Cool the solution, and add 80 ml of mixed indicator solution prepared by dissolving 0.099 g of bromocresol green and 0.066 g of methyl red in 100 ml of ethanol. Then add 0.1 N NaOH cautiously until the solution assumes a reddish purple tint (pH ca 5.0), and make the solution to 4 ℓ by addition of water. Mix the solution thoroughly before use.

(7) Potassium permanganate ($KMnO_4$) solution: Dissolve 50 g of $KMnO_4$ in 1 ℓ of water, and store the solution in an amber bottle.

(8) Dilute sulfuric acid (H_2SO_4): To 1 ℓ of water in a 4-ℓ Pyrex flask add slowly, and with continuous shaking, 1 ℓ of concentrated H_2SO_4.

(9) Reduced iron: Use a finely divided product, and sieve it to remove any material which does not pass a 100 mesh sieve.

(10) n-octyl alcohol.

(11) Sulfuric (or hydrochloric) acid (H_2SO_4 or HCl); 0.01 N standard.

Procedure

(1) Place a sample, ground to 0.5 mm or finer, containing about 10 mg of N in a dry macro-Kjeldahl flask, add sufficient water to bring the total water content to around 10 ml; and, after swirling the flask for a few minutes, allow it to stand for a further 30 minutes.

(2) Add 10 ml of $KMnO_4$ solution; and, after swirling the flask for about 30 seconds, hold it at a 45^o angle, and pipette 20 ml of dilute H_2SO_4 down the neck using a pipette with a fine tip to ensure slow addition of the acid. Swirl the flask continuously during this operation; and when the addition of acid has been completed, allow the flask to stand for 5 minutes, and add 2 drops of octyl alcohol.

(3) Add 5 ± 0.1 g of reduced iron through a dry thistle funnel having a long stem that reaches down into the bulb of the Kjeldahl flask; and immediately place a 25 ml Erlenmeyer flask in inverted position in the neck of the Kjeldahl flask, and swirl the flask to bring the iron into contact with the acid. Allow the flask to stand until the initial strong effervescence has ceased (about 15 minutes), and then heat it gently on the digestion stand so that the mixture just boils.

Keep the Erlenmeyer flask in the neck of the Kjeldahl flask during this process to limit the loss of water; and, after heating the mixture for 45 minutes, turn off the heater, allow the Kjeldahl flask to cool, and remove the Erlenmeyer flask.

(4) Add 10 g of K_2SO_4, 1 g of $CuSO_4.5H_2O$, 0.1 g of Se, and 30 ml of concentrated H_2SO_4, and heat the flask cautiously on the digestion stand. When the water is removed and frothing ceases, increase the heat until the mixture assumes a yellowish-green color, and complete the digestion by boiling the mixture gently for 5 hours (2 hours is adequate for most soils).

(5) After completion of digestion, allow the Kjeldahl flask to cool, and add about 150 ml of water, slowly and with shaking. If the digest has solidified on cooling, and the solid cake of digest does not disintegrate during addition of water, heat the flask cautiously with vigorous swirling until the digest

is in a fluid condition. Then cool the flask under a cold-water tap, and transfer the diluted digest by means of a funnel to a 500 ml volumetric flask.

(6) Rinse the Kjeldhal flask 4 times with about 70 ml of water to complete the transfer, and rinse the stem of the funnel with water until the level of the liquid in the volumetric flask is about 2 cm below the graduation mark. Then allow the flask to stand; and, when it has reached room temperature, add water to make 500 ml, and mix the contents thoroughly.

(7) To determine ammonium in the digest, place a 250-ml Erlenmeyer flask containing 10 ml of H_3BO_3-indicator solution under the condenser of the distillation apparatus so that the end of the condenser is in contact with the H_3BO_3. Then mix the contents of the volumetric flask thoroughly by inverting the flask several times, and immediately transfer an aliquot (usually 50 or 100 ml) of the diluted digest to a 500-ml Kjeldahl flask containing two glass beads (to prevent bumping) and a few drops of liquid paraffin (to prevent frothing).

(8) Add sufficient water to give a total volume of about 200 ml, hold the Kjeldahl flask at a 45^{o} angle, and pour sufficient 10 N NaOH down the neck to ensure an excess of about 10 ml of 10 N NaOH. The amount of alkali required depends upon the amount of H_2SO_4 consumed during digestion and the volume of the aliquot taken for distillation. It is convenient to use 25 ml of 10 N NaOH for a 50 ml aliquot, and 50 ml for a 100-ml aliquot.

(9) Immediately after addition of the alkali, connect the flask to the distillation apparatus, swirl the flask to mix the contents, and commence distillation. Regulate the heating so that about 10 ml of distillate are collected per minute, and check that the flow of cold water through the condenser is sufficient to keep the temperature of the distillate below $35^{o}C$.

(10) When about 100 ml of distillate have been collected, lower the receiver flask so that the end of the condenser is above the surface of the distillate, rinse the end of the condenser with water, remove the receiver flask, and stop distillation.

(11) Determine ammonium-N in the distillate by titration with 0.01 N H_2SO_4 using a 25-ml burette graduated at 0.02-ml intervals (1 ml 0.01 N H_2SO_4 = 0.14 mg ammonium-N). The color change at the end-point is from green to pink.

Calculations

Total N % =

$$\text{ml acid used in titration} \times N \times 14 \times \frac{500}{\text{aliquot digested}} \times \frac{100}{\text{mg sample}}$$

References

(1) Bremner, J.M. 1965. Total nitrogen in Methods of Soil Analysis, Part 2, pp. 1149-1178. C.A. Black, ed., Agron. No. 9. Am. Soc. Agron., Madison, Wisconsin.

(2) Jackson, M.L. 1958. Soil chemical analysis. Prentice-Hall Inc. Englewood Cliffs, N.J.

(3) Piper, C.S. 1944. Soil and Plant Analysis. Interscience Publ. Inc., New York.

3.624 Macro-Kjeldahl, without steps to include NO_2^- and NO_3^-.

Apparatus

As for 3.623.

Reagents

(1) Reagents 1 to 6 as in 3.623.

(2) Sulfuric or hydrochloric acid, 0.05 N standard.

Procedure

(1) Place a sample containing about 10 mg of N in a dry macro-Kjeldahl flask, add 20 ml of water; and, after swirling the flask for a few minutes, allow it to stand for a further 30 minutes.

(2) Add 10 g of K_2SO_4, 1 g of $CuSO_4.5H_2O$, 0.1 g of Se and 30 ml of concentrated H_2SO_4, and heat the flask cautiously on the digestion stand. When the water has been removed and frothing has ceased, increase the heat until the digest clears, and thereafter boil the mixture gently for 5 hours (2 hours is usually adequate). Regulate the heating during this boiling so that the H_2SO_4 condenses about one-third of the way up the neck of the flask.

(3) After completion of digestion, allow the flask to cool, and add about 100 ml of water (slowly, and with shaking). Then cool the flask under a cold-water tap, and transfer the contents to a 1-ℓ conical (or 800-ml Kjeldahl) flask for distillation. As far as is practicable, retain any sandy residue in the digestion

flask during this transfer, because sand can cause severe bumping during Kjeldahl distillation. Four washings of the sandy residue with 50 ml of water are usually adequate for quantitative transfer of the ammonium in the digest.

(4) To determine the ammonium-N liberated by digestion, place a 500 ml Erlenmeyer flask containing 50 ml of H_3BO_3-indicator solution under the condenser of the distillation apparatus so that the end of the condenser is below the surface of the H_3BO_3. Then hold the distillation flask at a 45° angle, add a teaspoonful of pumice, and pour about 150 ml of 10 N NaOH down the neck so that the alkali reaches the bottom of the flask without mixing appreciably with the digest. Attach the flask as quickly as possible to the distillation apparatus, mix the contents thoroughly by swirling, and immediately commence distillation. Regulate the heating to prevent suck-back of H_3BO_3 and to minimize frothing or bumping during distillation, and check that the flow of cold water through the condenser is sufficient to keep the temperature of the distillate <35°C.

(5) When about 150 ml of distillate have been collected, lower the receiver flask so that the end of the condenser is above the surface of the distillate; and, after rinsing the end of the condenser with water, remove the flask and stop distillation. Determine ammonium-N in the distillate by titration with 0.05 N H_2SO_4 using a 25-ml burette graduated at 0.1-ml intervals (1 ml 0.05 N H_2SO_4 = 0.7 mg ammonium-N). The color change at the end-point is from green to pink.

Calculations

$$\text{Total N \%} = \frac{\text{ml acid} \times \text{N} \times 14 \times 100}{\text{weight sample in mg}}$$

3.63 Total Sulfur

Total soil S may be determined by spectrophotometric procedures after dissolving the sample in either acid or alkali. Acid digestion is more convenient than alkali fusion but some samples may not dissolve completely in acid. Perchloric acid must be used with care in a laboratory equipped with a perchloric acid fumehood. Technicians using this acid should know its properties and the hazards if proper equipment and procedures are not used.

High temperatures induction furnaces (LECO) with S analyzers are available. They are rapid and have been reported to produce results consistent with more tedious methods such as the Parr oxygen bomb (Lowe, 1965). Considerable art is involved in their use, however, and several laboratories have had difficulty getting reasonable results with them (Bremner and Watanabe, 1971).

The best method currently is probably the alkaline hypobromite oxidation method of Tabatabai and Bremner (1970), method 3.633.

3.631 Na_2CO_3 - $NaNO_3$ (Bardsley and Lancaster, 1965)

Fusion Procedure

(1) Mix 1 g of soil (80 mesh or finer) with 5 g Na_2CO_3 (reagent grade) and 0.2 g $NaNO_3$ (reagent grade) in a 25 ml platinum crucible.

(2) Preheat at 400°C for 1 hour in a muffle furnace.

(3) Fuse at 950°C (electric furnace is best since there is no contamination from S that may be present in gas), fusion should be complete in 10-20 minutes for most soils.

(4) Manipulate the crucible using Pt-tipped tongs until most of the melt is spread in a thin sheet over the lower two-thirds of the inside of the crucible.

(5) Allow crucible to cool and place it on its side in a 100 ml beaker. Add enough H_2O to cover the contents and heat in a steam bath to disintegrate the melt. If the melt does not disintegrate, add a few drops of ethanol and 20 ml of 6 N HCl.

(6) After disintegration, scrub the crucible with a policeman (S-free) and wash it with distilled H_2O. If HCl was not required to disintegrate the melt, add 20 ml HCl to the beaker and mix the contents.

(7) Transfer to a 100 ml volumetric and after cooling, make to volume with distilled water.

Determination of S in solution

Reagents

(1) Reducing agent (stable for about 5 days)

Mix 300 ml of hydriodic acid (57% and 1% preservative) with 75 ml of 50% hypophosphorous acid and 150 ml of 90% formic acid. Boil gently with a stream of N_2 flowing through the solution for 10 minutes after the temperature reaches 115°C. Cool with the N_2 still flowing.

(2) Sodium hydroxide (1 N), dissolve 80 g of NaOH in 2,000 ml H_2O.

(3) Bismuth reagent, heat 3.4 g of bismuth nitrate pentahydrate in 230 ml of acetic acid until dissolved. Filter if necessary through No. 50 filter and cool. Add 30 g gelatin to 500 ml H_2O and dissolve by warming. Add the bismuth solution to the gelatin solution and dilute to 1,000 ml.

(4) Standard sulfate solution (1,000 µg S/ml), dissolve 2.717 g K_2SO_4 in 500 ml of H_2O. Make up standards containing 1-20 µg S/ml.

(5) N_2 purification solution, add 5 to 10 g of $HgCl_2$ per 100 ml of 2% $KMnO_4$ solution.

Procedure (see Fig. 10)

(1) Add up to 40 µg S in an aliquot (usually 2 ml) to the boiling flask, add 4 ml of reducing agent, adjust the N_2 flow to 75 ml/minute per flask.

(2) Heat to just barely boiling (heat gradually so that bubbles are evolved for 4 to 5 minutes before boiling starts) and distill for 20 minutes with the evolved H_2S trapped in 5 ml of 1 N NaOH held in a 20 ml test tube. The gas flow rate and the tip size of the inlet tube should be such as to minimize the size of the bubbles.

(3) After distillation, add 2.5 ml of bismuth reagent and mix, read immediately at 400 or 480 mµ and compare against standard treated as the sample solutions. The standard SO_4^{2-} solution is prepared as follows: Dissolve 0.5434 g of oven-dry, reagent grade K_2SO_4 in sulfur-free distilled water and dilute to 1 ℓ (S, 100 ppm). Dilute aliquots with S-free distilled water to give standards at concentrations of S of 0 to 20 ppm.

Calculations

$$\text{Total S \%} = \frac{\text{µg S in aliquot} \times 10}{\text{aliquot (ml)} \times \text{mg sample}}$$

NOTES:

(1) A 2.0 ml volume is preferable and if larger volumes are necessary, the sample should be evaporated or the amount of reductant increased. Samples high in iron may also require extra reducing agent. The presence of excessive amounts of oxidizing agents is indicated by the formation and persistence of considerable brown iodine color in solution.

(2) Reduction of $SO_4^{=}$ to $S^{=}$ using bismuth nitrate pentahydrate has been found by some workers to be superior to the methylene blue procedure.

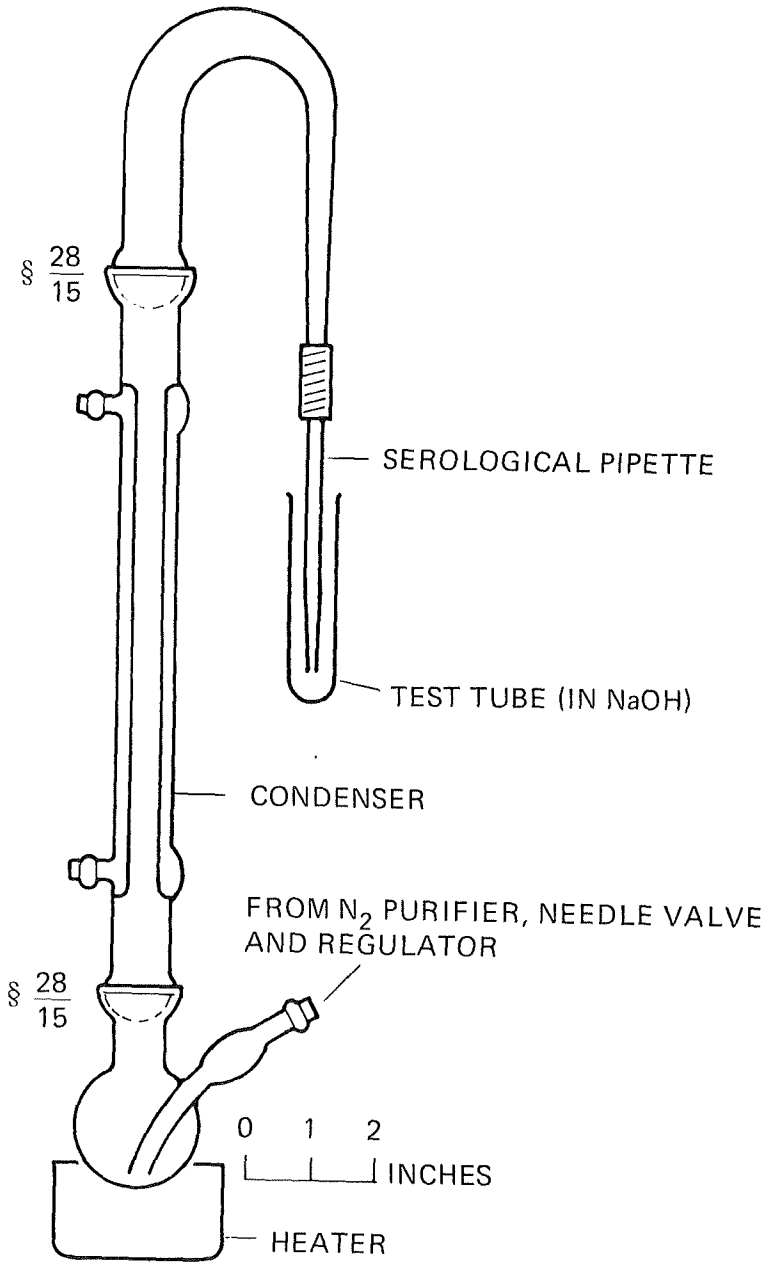


Fig. 10. Apparatus for $SO_4^=$ reduction to $S^=$

(3) All tubing should be tygon to prevent S contamination. Only silicone-based lubricants should be used.

3.632 Acid digestion

(1) Weigh 2.0 g of 80 mesh or finer soil into a 125 ml tall-form beaker (micro-Kjeldahl flasks are also suitable).

(2) Add 3.0 ml 69% HNO_3, swirl and cover, heat on a steam bath for 1 hour.

(3) Add 3.0 ml 60% $HClO_4$ and 7.0 ml 85% H_3PO_4 (these may be premixed for ease of handling), heat on a sand bath at 190-210°C until heavy white fumes of $HClO_4$ are visible, continue heating for 30 minutes. (This step must be carried out in a perchloric acid fume-hood).

(4) Cool, add 30 ml HCl (37%) and heat again until $HClO_4$ fumes are visible, cool, transfer to a 100 ml volumetric flask and make to volume with dilute HCl. The total acidity of the diluted sample should be at least one molar.

(5) Determine S as in 3.631.

3.633 Alkaline hypobromite oxidation (Tabatabai & Bremner, 1970)

Apparatus

Digestion-distillation unit, see Tabatabai and Bremner (1970).

Reagents

(1) Sodium hypobromite solution - Prepare immediately before use by adding 3 ml of bromine slowly (ca. 0.5 ml/min), and with constant stirring, to 100 ml of 2N NaOH.

(2) Formic acid - 90%

(3) Reducing mixture - Mix 300 ml of hydriodic acid (specific gravity 1.7, methoxyl grade), 75 ml hypophosphorus acid (50%) and 150 ml formic acid (90%). Boil gently with a stream of N_2 flowing through this solution for about 10 min. after the temperature has reached 115C. Do not let the temperature of the solution exceed 117C. Do not attempt to recover spent reagent by distillation.

Caution: Extremely poisonous fumes of phosphine (PH_3) may be liberated from the reagent if heated above 120C or if the reagent is spilled on a hot surface.

(4) Pyrogallol-sodium phosphate wash solution. Dissolve 10 g of sodium dihydrogen phosphate and 10 g of pyrogallol in 100 ml of sulfur-free distilled water with the aid of a stream of N_2 bubbling through the solution. Prepare fresh daily.

(5) Zinc acetate-sodium acetate sulfide absorbing solution. Dissolve in sulfur-free water, 50 g of zinc acetate dihydrate and 12.5 g of sodium acetate trihydrate. Make to 1 ℓ volume and filter.

(6) p-dimethylaniline solution. Dissolve 2 g of Eastman Kodak Co. No. 1333 p-aminodimethylaniline sulfate in 1500 ml of distilled water. Add 400 ml of conc. reagent grade H_2SO_4. Cool and make to 2 ℓ.

(7) Ferric ammonium sulfate solution. To 25 g of ferric ammonium sulfate add 5 ml conc. reagent grade H_2SO_4 and 195 ml of distilled water.

(8) Nitrogen purification solution. Add an excess of mercuric chloride, 5 to 10 g per 100 ml, to 2% $KMnO_4$ solution.

(9) Standard sulfate solution. Prepare a stock solution containing 5.434 g of reagent grade K_2SO_4 per ℓ. One ml of this solution contains 1 mg of S. Dilute the stock solution with water to give working solutions of the desired concentrations.

(10) Water -- All water used in preparing reagents and washing glassware should be free of copper and sulfur.

Procedure

(1) Place a sample of air-dried, finely ground (100 mesh) soil containing 10 to 50 µg of S (usually 0.1 to 0.2 g) in a dry digestion-distillation flask and add 3 ml of sodium hypobromite solution.

(2) Swirl the flask for a few seconds and allow it to stand for 5 min., swirl it again and place the flask upright in a sand bath situated in a hood. Maintain the temperature of the sand at 250-260 C.

(3) Heat the flask until its contents are evaporated to dryness and continue heating for 30 min.

(4) Remove the flask from the sand bath, allow it to cool for about 5 min., add 1 ml of water, and heat the flask on the sand bath for a few seconds to bring the residue into suspension.

(5) Remove the flask from the sand bath, swirl it for a few seconds and allow it to cool to room temperature.

(6) Prepare the digestion-distillation apparatus: place 10 ml of pyrogallol-sodium phosphate solution in the gas washing column, add 10 ml of zinc acetate-sodium acetate solution to 70 ml water in a 100 ml glass stoppered volumetric flask and attach the connecting tube to the side arm of the gas washing column (see fig. in Tabatabai and Bremner, 1970).

(7) Add 1 ml of formic acid and 4 ml of reducing mixture to the cooled flask from (5), moisten the joint of the flask with a drop of water, quickly connect the flask to the digestion-distillation apparatus and attach the spiral steel joint springs.

(8) Quickly connect the tube from the nitrogen wash bottle to the side arm of the flask, and put the receiving flask in place.

(9) Start the flow of cooling water in the condenser and adjust the nitrogen flow rate to 100 to 200 ml/min (the N_2 has passed the nitrogen purification solution).

(10) Heat the digestion flask and maintain at a low boil for 1 hour. Remove the receiving flask, leaving the connecting tube in the flask.

(11) Using a rapid delivery pipet, quickly add 10 ml of p-dimethylaniline solution to the receiving flask.

(12) Stopper the flask, mix, add 2 ml of ferric ammonium sulfate solution, stopper and mix again, make to volume and mix thoroughly.

(13) Read absorbance after 10 min. and within 24 hours at 670 nm.

Calculations

$$S \text{ ppm} = \frac{\mu g \text{ S}}{\text{wt of sample, g}}$$

References

(1) Arkley, T.H. 1961. Sulfur compounds of soil systems. Ph.D. Dissertation, University of California, Berkeley.

(2) Bardsley, C.E. and Lancaster, J.D. 1965. Sulfur. In Methods of Soil Analysis. Part 2, p. 1102-1116. C.A. Black, ed.-in-chief. Number 9 in Agronomy Series, Am. Soc. Agron., Madison, Wisconsin.

(3) Beaton, J.D., Burns, G.R. and Platou, J. 1968. Determination of sulfur in soils and plant material. Technical bulletin number 14, The Sulfur Institute, Washington, D.C.

(4) Bremner, J.M. and Tabatabai, M.A. 1971. Use of automated combustion techniques for total carbon, total nitrogen, and total sulfur analysis of soils. In Instrumental methods for analysis of soils and plant tissue, pp. 1-16. L.M. Walsh, ed. Soil Sci. Soc. Am., Madison, Wisconsin.

(5) Carson, J.A., Crepin, J.M. and Nemunis-Siugzdinis, P. 1972. A sulfate-sulfur method used to delineate the sulfur status of soils. Can. J. Soil Sci., 52, 278-281.

(6) Dean, G.A. 1966. A simple colorimetric finish for the Johnson-Nishita microdistillation of sulfur. Analyst, 9/(1085): 530-532.

(7) Johnson, C.M. and Nishita, H. 1952. Microestimation of sulfur in plant materials, soils and irrigation waters. Anal. Chem. 24, 736-742.

(8) Johnson, C.M. and Ulrich, A. 1959. Analytical methods for use in plant analysis. California Agr. Exp. Sta. Bull. 766.

(9) Lowe, L.E. 1965. Sulphur fractions of selected Alberta soil profiles of the Chernozemic and Podzolic orders. Can. J. Soil Sci., 45, 297-303.

(10) Tabatabai, M.A. and Bremner, J.N. 1970. An alkaline oxidation method for determination of total sulfur in soils. Soil Sci. Soc. Am. Proc. 34, 62-65.

3.64 Total Phosphorus

Total phosphorus is determined spectrophotometrically in solutions obtained by dissolving the soil sample with acid or alkali. For some soils, acid digestion is reported to result in slightly low P values, due perhaps to undissolved mineral grains containing P (Syers et al, 1969). However, for most soils, acid digestion is suitable and it is more convenient than alkali fusion.

3.641 Acid digestion procedure (Hesse, 1971)

Digestion

(1) Accurately weigh 1.00 g of soil (80 mesh or finer) into a 100 ml tall-form beaker.

(2) Add 20 ml concentrated HNO_3, cover with a watch glass and heat (130°C) to oxidize organic matter.

(3) Add 10 ml of 60% $HClO_4$ and digest at 200°C until dense white fumes appear, use a little extra $HClO_4$ to wash down the sides of the beaker as necessary, continue heating for a further 10-15 minutes, cool the solution and dilute to about 25 ml with warm water. (This step must be done in a perchloric acid fumehood).

(4) Filter through a Whatman No. 41 paper into a 100 ml volumetric flask. Wash the residue with 0.5 N HCl (the residue may be discarded or saved for further analyses).

(5) Make to volume (100 ml) with dilute HCl (0.5 N).

Determination of P

Reagents

A. Dissolve 12 g of ammonium molybdate in 250 ml of distilled water. In 100 ml of distilled water dissolve 0.2908 g antimony potassium tartrate. Add both of these solutions to 1000 ml of 5N H_2SO_4 (140 ml concentrated H_2SO_4 per ℓ). Make to 2,000 ml and store in a dark pyrex bottle in a cool compartment.

B. Dissolve 1.056 g ascorbic acid in 200 ml of reagent A and mix. Prepare reagent B as needed, it is stable for only 24 hours.

Procedure

(1) Pipette aliquots containing up to 50 µg of P into 50 ml volumetric flasks, add distilled H_2O to make 35 ml.

(2) If necessary acidify (5 N H_2SO_4) to pH 5 with p-nitrophenol (colorless in acidic, yellow in alkaline solution). This will generally not be necessary for soil extracts since the P is dissolved in 0.5 N HCl.

(3) Add 10 ml of reagent B and add distilled H_2O to bring to volume (50 ml), mix, allow 10 minutes for color development and read at 690 or 880 mµ (there are two absorption maxima, the one at 880 is a little more intense).

(4) Prepare a blank with all reagents except P. The blank should be run through the digestion process.

(5) Calibrate using standard P solutions in the same manner as above (0-1 µg P/ml). The P standard may be prepared as follows: Dilute 0.4393 g of oven-dry KH_2PO_4 to 1 ℓ in a volumtric flask. The concentration of P is 100 ppm.

Calculations

$$\text{Total P \%} = \frac{\mu g \text{ P in aliquot} \times 10}{\text{aliquot (ml)} \times \text{mg sample}}$$

NOTES:

(1) Ascorbic acid is preferable to $SnCl_2$ as a reductant as the molybdenum blue color developed is more stable.

References

(1) Alexander, T.G. and Robertson, J.A. 1968. Ascorbic acid as a reductant for total phosphorus determination in soils. Can. J. Soil Sci., 48, 217-218.

(2) Hesse, P.R. 1971. A textbook of soil chemical analysis. John Murray, London. pp. 520.

(3) Olsen, S.R. and Dean, L.D. 1965. Phosphorus. In Methods of soil analysis, Part 2, p. 1035-1049. C.A. Black, ed-in-chief. Number 9 in Agronomy series, Am. Soc. Agron., Madison, Wisconsin.

(4) Syers, J.K., Williams, J.D.H., Tyner, E.H. and Walker, T.W. 1969. Primary and secondary origin of "non-extractable" soil inorganic phosphorus. Soil Sci. Soc. Am. Proc. 35, 635-636.

(5) Watanabe, F.S. and Olsen, S.R. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Sci. Soc. Am. Proc., 29, 677-678.

3.642 Sodium carbonate fusion (Atkinson et al., 1958)

(1) Weigh 0.5 g of 80 mesh or finer soil into a platinum crucible. Add 2 to 4 g anhydrous reagent grade Na_2CO_3 and mix thoroughly. Cover the mixture with a thin layer of Na_2CO_3.

(2) Put the lid on the crucible and heat it with a Meker burner. Heat slowly at first to drive off water. Then increase the heat gradually to fuse the sample. Do not let the reducing part of the flame come in contact with the crucible and do not let the flame envelop the crucible. Cautiously lift the cover slightly to let air in after spattering has ceased.

(3) Continue heating at full blast for about 10 minutes. The bottom of the crucible should be red. If there are any patches of fused material sticking to the sides of the crucibles, heat these places to cause all of the material to run together.

(4) Remove the cover and continue heating for a few minutes. Remove the flame and after a few seconds, grasp the crucible with Pt tipped tongs and rotate it as it cools so as to distribute the fused mass as a thin layer on the bottom and sides of the crucible.

(5) When the crucible is cool enough to touch, roll it gently between the hands to facilitate removal of the melt, then place in a 200 ml beaker containing 80 ml hot water. Heat beaker at 100°C for 2 hours.

(6) Remove melt from crucible and rinse crucible and lid into beaker. Continue heating for 30 minutes.

(7) Acidify with 6 N H_2SO_4 to about pH 5 (use p-nitrophenol indicator, colorless in acidic and yellow in alkaline solution). Silica will precipitate. Cool and allow time for silica to coagulate.

(8) Filter through Whatman No. 42 filter paper into a 100 ml volumetric and wash the residue on the paper. Make to volume.

(9) Determine P as in 3.641.

References

(1) Atkinson, H.J., Giles, G.R., MacLean, A.J. and Wright, J.R. 1958. Chemical methods of soil analysis. Contrib. No. 169 (Revised) Chemistry Division, Science Service, C.D.A., Ottawa.

(2) Jackson, M.L. 1958. Soil Chemical Analyses. Prentice-Hall Inc., Englewood Cliffs, New Jersey.

3.7 DETERMINATION OF TOTAL MAJOR AND MINOR ELEMENTS (OTHER THAN C, N, P AND S)

There are many adequate methods for both dissolving soil samples and determining the elements in solution and for non-destructive total analysis of soils. The choice of methods depends to a large degree upon the equipment available. Total contents of elements are absolutes and thus the adequacy of data can and should be checked by analysis of standard soil samples and comparisons with the best data available. For many laboratories, atomic absorption spectroscopy is the simplest and most efficient way of determining elements in solution. Procedures required are usually given in manuals supplied with the instrument. Thus details of total analysis of soils are not given.

Dissolving the soil sample

3.71 Acid dissolution - J.G. Desjardins

(1) Weigh 1.000 g oven-dry, 300 mesh sample (mineral soil) into a 100 ml Teflon beaker.

(2) Add 20 ml conc. HNO_3, cover, boil gently for $\frac{1}{2}$ h on a hot plate at 100-150°C, and cool.

(3) In a perchloric acid fumehood, add 20 ml conc. $HClO_4$, cover, boil gently for $\frac{1}{2}$ hour on a hot plate at 200-250°C, cool and remove covers.

(4) Add 20 ml conc. HF, cover and heat in a perchloric acid fumehood for 1 h at 80°C. Remove covers and gradually increase heat as the HF evaporates and take nearly to dryness at 250°C but do not dry completely.

(5) Cool and wash down walls of beaker with 25 ml 1 N HCl or 1 N HNO_3.

(6) Cover and bring to a boil to dissolve residue, cool. Add slowly 10 ml 30% H_2O_2 (to ensure Cr^{+++}). Boil off excess H_2O_2. Make up to 50.0 ml in a volumetric flask. (Not necessary if Cr is not determined).

(7) Determine elements by atomic absorption or other method. Run reagent blank and standard soil with each batch of samples.

Notes

(1) Low values for Cr may result from volatilization of CrO_2Cl_2 (Sulcek, Povondra and Dolezal, 1977).

(2) Longer periods of digestion in $HClO_4$ and HF are necessary for some refractory samples. Fine grinding is critical to complete dissolution.

(3) For organic samples, weigh 1.000 to 5.000 g of dry sample, moisten with water and heat with 20 to 50 ml of conc. HNO_3 for an hour or more. The $HClO_4$ treatment is the same as for mineral soils except that digestion time is increased to 1 h. Only 10 ml of HF is used.

(4) For some elements, a correction was made for non-atomic absorption. The wavelengths used for the corrections are: Ni - 237.1 nm, Pb - 220.1 nm, Cd - 226.4 nm.

Other procedures to improve results are:

a. For Ca at 422.7 nm, increase lamp current to 100 mA to overcome shot noise caused by the high emission intensity of Ca.
b. For K, add Na at 1000 ppm to standards and sample solutions.
c. For Na, add K at 1000 ppm to standards and sample solutions.

3.72 Lithium metaborate fusion (Ingamells, C.O. 1966)

The sample is fused with $LiBO_2$ in a graphite crucible at 950°C and the melt is dissolved in dilute HNO_3.

3.73 Sodium carbonate fusion (Kanehiro and Sherman, in Black, 1965)

References

(1) Black, C.A. ed-in-chief. 1965. Methods of Soil Analysis, Part 2. Am. Soc. Agron., Madison, Wisconsin.

(2) Ingamells, C.O. 1966. Absorptiometric methods in rapid silicate analysis. Anal. Chem. 38, 1228-1234.

(3) Shapiro, L. and Brannock, W. 1956. Rapid analysis of silicate rocks. Bull. 1036-C. U.S. Geol. Survey, Washington, D.C.

(4) Sulcek, Z., Povondra, P., and Dolezal, J. 1977. Decomposition procedures in inorganic analysis. CRC Crit. Rev. Anal. Chem. 6, 255-323.

3.74 Total Mercury in Soils (B. Stone & L. Dowser)

The determination of Hg in soils in the p.p.b. range became feasible with the development of flameless atomic absorbtion spectrophotometry techniques. The procedure outlined was adapted from that of Malaiyandi and Barrette (1970) for biological materials. It is also suitable for the determination of Hg in plant materials.

Digestion

Reagents

(1) Concentrated sulphuric acid
(2) Concentrated nitric acid
(3) Vanadium pentoxide
(4) Hydrogen peroxide, 50%
(5) Dry ice.

Apparatus

Cold finger digestion apparatus as shown in Fig. 11.

Procedure

(1) Prepare sample suitably for the analysis. (for most soils the <2 mm material is adequate).

(2) Weigh 2-5 grams of sample into a modified 200 ml Erlenmeyer flask.

(3) Add 0.1 gm of vanadium pentoxide (Do not weigh vanadium pentoxide on paper).

(4) Add 3-4 glass beads to sample, assemble glassware and add powdered dry ice to cold finger.

(5) Turn on condenser cooling water and add 5 ml of conc. HNO_3 dropwise from dropping funnel.

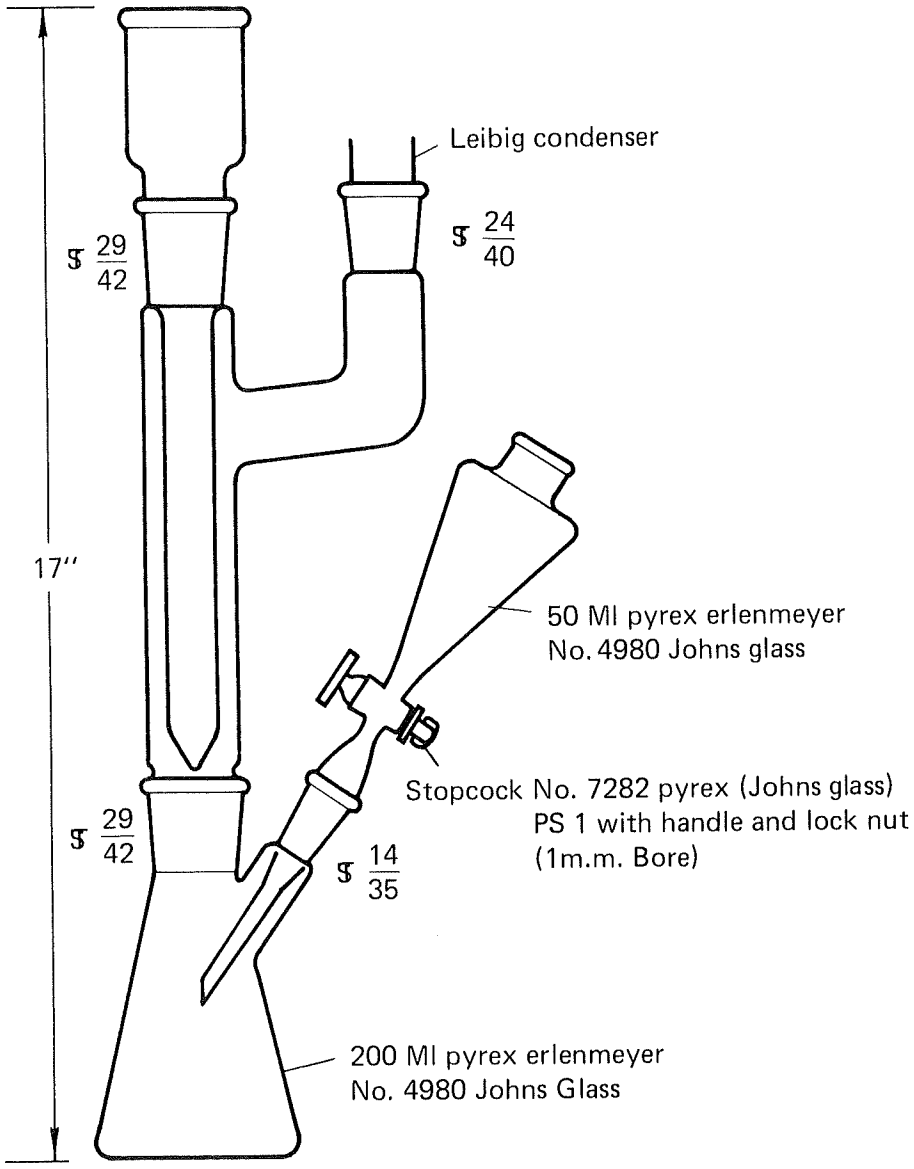


Fig. 11 Digestion assembly for Hg determination (3.74)

(6) Lower apparatus to preheated hot plates, 125°C for soils.

(7) Heat samples gently for five minutes and add 5 cc of conc. H_2SO_4 dropwise from dropping funnel lifting from hot plate and swirling while exothermic reaction occurs.

Keep the brown fumes (NO_2) and the bluish green nitrous anhydride (N_2O_3) at least one third below the top of the cold finger. Always maintain the dry ice level.

(8) Resume heating and reflux digest for about 30 minutes, maintaining dry ice level.

(9) Cool digest and add 3-4 drops of hydrogen peroxide (50%) while swirling.

(10) When room temperature is reached remove the dry ice from the cold finger and wash the apparatus parts with a minimum of 2% aqueous sulphuric acid (30-40 ml), catching washings in the digestion flask.

(11) Filter digest through prewashed glass wool into 100 ml volumetric flask and make to volume with 1.0 N sulphuric acid

Determinations

Reagents

(1) Hydroxylamine Sulphate-sodium chloride: 15 g hydroxylamine sulphate and 15 g of sodium chloride in 500 ml of distilled water. (make daily)

(2) Stannous sulphate - 25 g of stannous sulphate and 5 g of sodium chloride in 250 ml of 2 N sulphuric acid. Add 1 g of mossy tin (stable 2 weeks).

(3) Wash solution: 800 ml of distilled water, 120 ml of conc. sulphuric acid and 80 ml of conc. nitric acid. Add acids slowly while cooling. (make fresh daily)

(4) Standards. Dissolve 1.3535 g of mercuric chloride in 1 litre of 1N sulphuric acid (1000 ug/ml)

(5) Make standards daily of 2.5, 5 and 10 ppb.

Apparatus

(1) An atomic absorption spectrophotometer, a recorder and mercury lamp.

(2) A gas absorption cell 210 mm long, 3 mm. inside diameter made of pyrex with quartz end windows cemented in place with epoxy (Fig. 12).

(3) Technicon auto analyzer proportional pump.

Procedure

(1) Mercury wavelength 253.7 mu, 5 mAmps.

(2) Maximize signal from mercury lamp.

(3) Align gas cell where the flame would normally be.

(4) Start the proportional pump with reagent lines in place (Fig.12)

(5) Manually input samples and standards for up to one minute.

Calculations

(1) Prepare standard curve from readings of standards.

(2) Convert peaks for samples to ppb Hg using standard graphs.

(3) ppb Hg in soil = ppb in solution $\times \frac{100}{\text{wt of sample in g}}$

Notes

(1) Clean glassware with tap water followed by rinsing in 10% nitric acid and 5-6 rinses with distilled water.

(2) Hydrochloric acid and hydrofluoric acid contain small amounts of mercury.

References

Malaiyandi, M. and Barrette, J. 1970. Determination of submicro quantitiies of mercury in biological materials. Anal. Lett. 3, 579-584.

3.75 Total Se in soils (modified from Levesque and Vendette, 1971).

Reagents

(1) Concentrated nitric acid

(2) Perchloric acid, 72%

(3) Stabilizing solution - 0.04 M disodium EDTA ($Na_2C_{10}H_{14}O_8N_x.2H_2O$) containing 10% hydroxylamine hydrochloride (14.9 g of EDTA and 100 g of $NH_2OH.HCl$ per 1ℓ of solution). Filter the solution using Whatman 42 paper and store in a brown bottle.

(4) Formic acid solution, dilute formic acid 1:1 with H_2O.

(5) Reducing solution, 1.0N HCl (83 ml concl HCl per ℓ of solution).

(6) DAN solution (2,3-diaminonaphthalene). Prepare a 0.1% DAN solution immediately before use (prepare daily) by dissolving 0.1 g of DAN in 100 ml of 0.1N HCl containing 0.5g of $NH_2OH.HCl$.

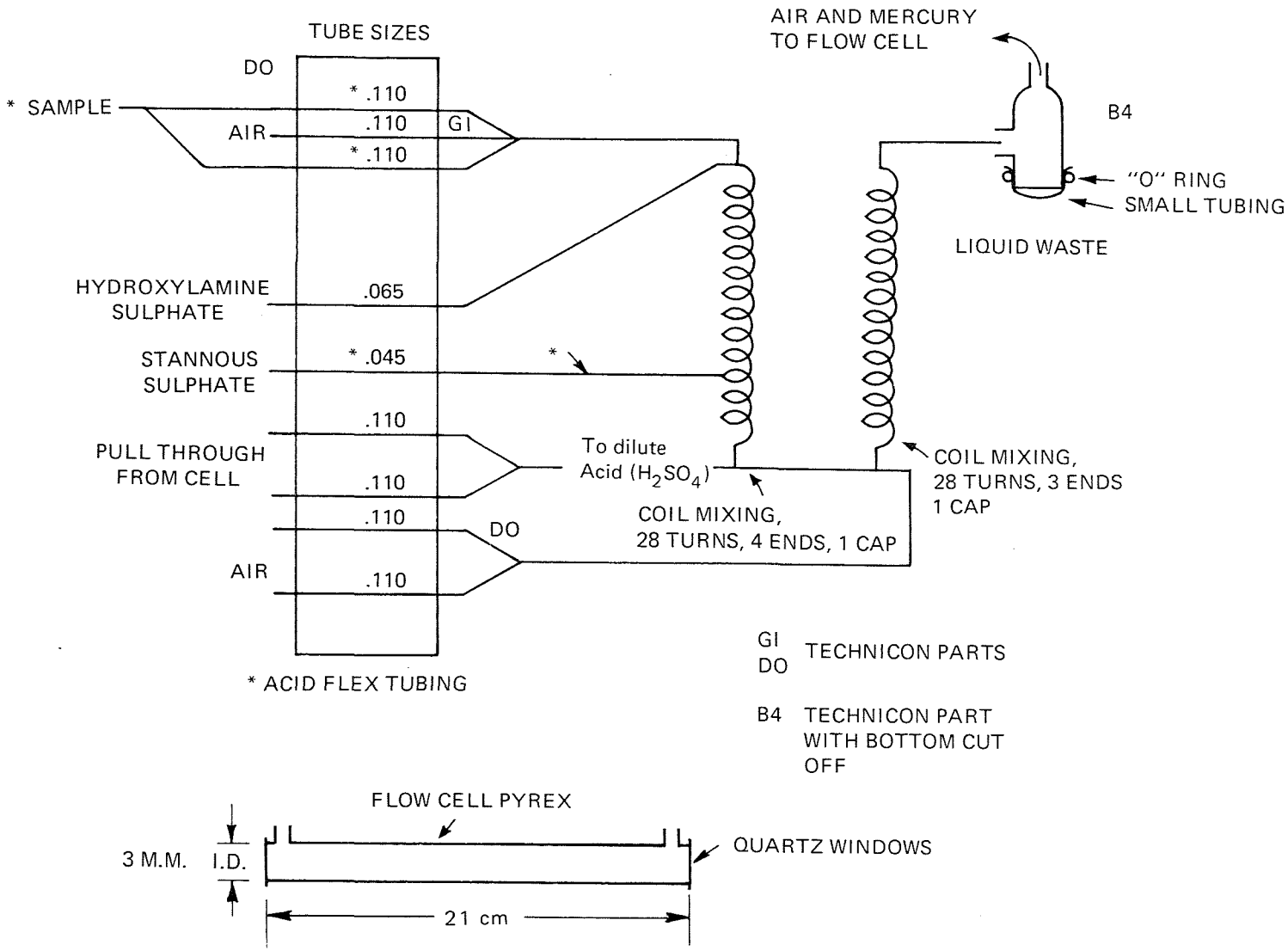


Fig. 12 Flow diagram and flow cell for the determination of Hg(3.74)

Heat the solution at 50°C for 30 min. with occasional shaking, cool and extract with 20 ml of cyclohexane. Centrifuge, remove the cyclohexane and store the DAN solution in a brown bottle. All operations with the DAN solution should be done under low, diffused lighting.

(7) Cyclohexane (Fisher certified). Store in a dark brown bottle.

(8) Se standard: Prepare a stock solution of 100 µg/ml by dissolving 0.1742 g of selenious acid in a minimum amount of HNO_3, heating in a water bath until complete disappearance of NO_2 fumes, and diluting to 1 ℓ with 1.0N HCl. Dilute the stock solution with 0.1N HCl to obtain a final concentration of 0.01 µg Se/ml (10 ml of stock to 1 ℓ gives 1 µg/ml, and 10 ml of the latter solution to 1 ℓ gives 0.01 µg/ml).

Apparatus

(1) Microkjeldahl digestion unit in which the 100 ml digestion flasks sit in a cup such that the heating element encases about 1/3 of the bulb of the flask. Alternatively, if the heating element is at the surface of the digestion apparatus, put asbestos sleeves around the bulb of the digestion flask except where it touches the heating element.

(2) Perchloric acid fumehood.

(3) Fluorometer (Turner 110 or other appropriate model), with filters to permit irradiation of sample at 360 nm and detection of a narrow band of fluorescent light at 520 nm.

(4) Water bath and perforated aluminum plates to hold reaction flasks during reduction step.

Digestion Procedure

(1) Weigh 0.200 g soil ground to 60 mesh or finer into a 100 ml microkjeldahl flask, add 10 ml conc. HNO_3 and let stand overnight.

(2) Add 3 to 4 glass beads and 2 ml of perchloric acid, place flasks on digestion apparatus in a perchloric acid fumehood and heat gradually. Raise temperature when brown fumes appear and heat until HNO_3 has boiled off (no more brown NO_2 fumes).

(3) Continue heating at high temperature until white perchloric acid fumes appear and continue heating for about 1 min. About 1 ml of solution should remain in the flask.

Determination of Se

(1) Cool the digestion flasks to room temperature, add 2 ml of 1.0N HCl and place flasks in a water bath at 100°C for 15 min. to reduce selenate (SeO_4^{-2}) to selenite (SeO_3^{-2}).

(2) Transfer the digest to pointed, graduated, 50 ml brown or red tubes fitted with teflon stoppers. Wash flasks with 0.1N HCl and add washings to tubes, bring volume to 25 ml.

(3) Add 5 ml of 1:1 formic acid and 5 ml of stabilizing solution, and titrate the solution to pH 1.8 with 4N NH_4OH.

(4) Place tubes in a water bath at 50°C.

(5) After 10 min., add 5 ml of 0.1% DAN solution, stopper and shake the tubes (20 sec.) and put back in the water bath for 30 min.

(6) Remove tubes, allow them to cool, add 5 ml cyclohexane, stopper and shake on a reciprocating shaker for 5 min.

(7) Draw off the water phase using a medicine pipette.

(8) Wash the cyclohexane with 25 ml of 0.1N HCl, and transfer the cyclohexane phase to a cuvette.

(9) Measure fluorescence of standards and samples at 520 nm (irradiation at 360 nm) after zeroing the instrument with a blank solution. The range of standards is 0 to 0.100 µg of Se.

Calculations

Se (ppm) = µg Se x 5 (0.2 g sample).

Notes

(1) Quality of reagents is important. New bottles of DAN should be checked before use. If the blank value is higher than usual, reject the batch of DAN. Deionized water seems to be adequate but double distilled water may be preferable.

(2) Plastic containers should not be used as some plastics contaminate solutions with fluorescent substances. The nitric acid may contain fluorescent contaminants from the plastic bottle cap.

(3) It is important that very little of the perchloric acid is evaporated. Thus, the flasks must be watched closely to detect the start of perchloric acid fumes. Loss of perchloric acid could be avoided by using a condenser around the necks of the flasks.

References

(1) Lévesque, M and Vendette, E.D. 1971. Selenium determination in soil and plant materials. Can. J. Soil Sci. 51, 85-93.

3.8 Loss on Ignition - Atkinson et al (1958)

The loss in weight resulting from igniting a soil in contact with air includes that due to combined water in soil colloids, to combustion of organic

matter and to decomposition of carbonates. The temperature recommended for determining loss on ignition varies depending upon the information desired. Weight loss between 105 and about 420 C is approximately equal to the amount of organic matter in the sample, although the result obtained is usually somewhat higher than that determined from the amount of carbon present. Weight loss resulting from ignition at 850°C includes structural water and carbonates as well as organic matter. The latter temperature may be used in procedures for total analysis of a soil sample.

3.81 Loss on Ignition (L01) at 420 C

This provides an estimate of organic matter but calculation of organic matter from organic carbon values determined by any of procedures 3.611 to 3.614 is preferable.

Procedure

(1) Weigh about 20 g of soil (2 mm) into a tared porcelain or vycor crucible, heat the sample overnight at 105C and reweigh to determine the oven dry weight of the sample. Alternatively use the already oven dried sample from the determination of hygroscopic water (2.412).

(2) Place the crucible containing the oven dried sample in a muffle furnace, heat slowly to 420 C and continue heating at that temperature for 45 min. in the case of mineral soils and $1\frac{1}{2}$ hr. in the case of organic soils.

(3) Remove the crucible from the furnace, place it in a desiccator, cool and weigh.

(4) Calculate loss on ignition at 420 C as follows:

$$L01\% = \left(\frac{\text{Weight of oven dry sample - weight of sample after ignition}}{\text{weight of oven dry sample}}\right) \times 100$$

Note A different temperature and time of ignition is specified in the Soil testing section of this Manual (4.23). Information is inadequate to permit a recommendation of one of these procedures.

3.82 Loss on Ignition (L01) at 850C

This procedure is used in some methods of total elemental analysis of soils (3.7).

Procedure

(1) Determine the weight of an oven dry soil sample as in step 1 of 3.81.

(2) Place the sample, in a heat stable crucible, in a muffle furnace, gradually increase the temperature for $\frac{1}{2}$ hr.

(3) Remove the crucible from the furnace, place it in a desiccator after it has cooled somewhat, cool and weigh.

(4) Calculate LOI at 850 C as follows

$$LOI\% = \left(\frac{\text{Weight of oven dry sample - weight of sample after ignition}}{\text{weight of oven dry sample}}\right) \times 100$$

References

(1) Atkinson, H.J., Giles, G.R., MacLean, A.J. and Wright, J.R. 1958 Chemical methods of soil analysis. Contrib. No. 169 (Revised), Chem. Div., Sci. Serv., CDA, Ottawa.

(2) Ball, D.F. 1964. Loss on ignition as an estimate of organic matter and organic carbon in noncalcareous soils. J. Soil Sci. 15, 84-92.

4. - SOIL TESTING LABORATORY METHODS - G.E. Byers

Each province of Canada has at least one government-supported soil testing service laboratory (Table 9). Each laboratory has specific procedures (stepwise instructions) for various methods used in testing the fertility status of soils. These procedures have been developed or adapted independently by each laboratory, and each province has decided unilaterally what is to be included in its soil testing program. Thus it is not surprising that a great variety of methods and procedures within methods are used in soil testing laboratories in Canada. Indeed, it is probably not desirable that there be national unity on soil testing methodology since soils and climates differ greatly from region to region in Canada.

Thus the methods given in this section of the Manual are not standard national methods, but are examples of common provincial procedures and methods used. This material was brought together to give a national picture of soil testing in Canada.

It is noteworthy that a high degree of uniformity exists for some soil test methods (note exchangeable K, Ca, and Mg in Table 10). On the other hand, there is a great diversity of methodology for extractable P. No doubt, there is room for some unification of methods on at least a regional scale. It is hoped that this manual will stimulate increased cooperation among Soil Testing Laboratories.

Many laboratories are modifying existing routine procedures with the advent of instrumentation advances such as auto-analyzer, atomic absorption, and specific ion electrodes. This is resulting in greater volume capabilities as well as expanded services for "on request" soil analyses in addition to fertilizer, livestock feed, foliar and animal tissue, water, and agricultural by-product analyses. Therefore, many of the following procedures will be undergoing modifications as advances continue in chemistry and especially instrumentation.

It should be noted that Soil Testing Laboratories are performing a public service. They are required to analyze and report on large numbers of samples with an average turn-around time of two weeks. Thus procedures must be capable of permitting high output while maintaining accuracy and precision. Note, for example, the use of weight-calibrated volumes rather than absolute weights. This keeps to a minimum the initial handling of the soil. Note also the use of automated gadgetry and instrumentation for the handling and analysis of soil samples in large numbers.

Some soil testing methods are identical to those outlined in previous sections. Such methods are not repeated here, unless there are some modifications.

Table 9. Canadian Soil Testing Laboratories[1]

Mr. J.W. Neufeld, Lab Supervisor
Soils, Feed and Tissue Testing Lab
Field Crops Branch
Department of Agriculture
Court House
Kelowna, British Columbia
V1X 1J2

Mr. D.H. Laverty
Soil and Feed Testing Lab
Plant Industry Division, Soils Branch
801 O.S. Longman Building
P.O. Box 8070
Edmonton, Alberta
T6H 4P2

Mr. J.W. Hamm
Provincial Soil Testing Laboratory
Department of Soil Science
University of Saskatchewan
Saskatoon, Saskatchewan
S7N OWO

Mr. K.S. McGill, Director
Provincial Soil Testing Laboratory
Department of Soil Science
University of Manitoba
Winnipeg, Manitoba
R3T 2N2

Dr. Tom Bates
Soil Testing Laboratory
Department of Land Resource Science
Ontario Agricultural College
University of Guelph
Guelph, Ontario
N1G 2W1

Mr. Roland St. Laurent
Directeur du Laboratoire des Sols et Végétaux
Gouvernement du Québec
St. Hyacinthe, Québec

[1] Some provinces, especially Quebec, have more than one Soil Testing Laboratory. The laboratories listed here are those involved in supplying information for this manual.

Dr. Ib Ghanem, Lab Supervisor
Soil and Feed Testing Laboratory
Plant Industry Branch
N.B. Department of Agriculture
and Rural Development
Fredericton, New Brunswick

Mr. Richard Veinot, Lab Supervisor
Soil and Feed Testing Laboratory
P.E.I. Department of Agriculture
and Forestry
P.O. Box 1600
Charlottetown, Prince Edward Island

Mr. Gerald E. Byers, Lab Supervisor
Provincial Agricultural Chemistry Laboratory
Soils and Crops Branch
N.S. Department of Agriculture
and Marketing
Truro, Nova Scotia
B2N 5E3

Mr. Peter Heringa
Research Station
P.O. Box 7098
St. John's West
Newfoundland

Table 10. Soil Testing Laboratory Methods by Province[1]

	pH	Cond.	O.M.	NO_3	P	S	K	Ca	Mg	B	Lime Req.	Texture
B.C.	4.11	4.13	4.22	4.32	4.45	4.47	4.51	4.51	4.51	4.61	-	4.8
Alta.	4.12	4.13	-	4.32	4.44	4.47	4.51	4.51	-	4.62	-	4.8
Sask.	4.13[2]	4.13	-	4.33	4.42	4.48	4.52	4.51[2]	4.51[2]	-	-	-
Man.	4.11	4.11	-	4.33	4.41	-	4.51	-	-	-	-	4.8
Ont.	4.13	4.12[2]	-	4.31[2]	4.41	-	4.51	4.51[2]	4.51	-	-	4.8[2]
Que.	4.12	-	4.22	4.34	4.43	-	4.51	4.51	4.51	4.63	-	-
NB	4.11	4.12	-	-	4.45	-	4.51	4.51	4.51	-	-	-
NS	4.11	4.12	4.23	4.34	4.46	-	4.51	4.51	4.51	4.61	4.71	-
PEI	4.11	4.12	4.21	-	4.43	-	4.51	4.51	4.51	4.61	4.71	-
Nfld.	4.11	4.13	4.23	HAc[3]	HAc[3]	-	HAc[3]	HAc[3]	HAc[2]	-	-	4.8

1. The methods are those outlined in this section of the Manual: 4.11 - 1:1 soil:water; 4.12 - 1:2 soil:water; 4.13 - soil paste; 4.21 - wet oxidation, colorimetric; 4.22 - wet oxidation, titration; 4.23 - Loss-on-Ignition; 4.31 - incubated, water extract; 4.32 - 0.02 N $CuSO_4$ + 0.007 N Ag_2SO_4; 4.33 - 0.5 M $NaHCO_3$; 4.34 - 1:1 soil: water, nitrate electrode; 4.41 - 0.5 M $NaHCO_3$; 4.42 - 0.5 M $NaHCO_3$, autoanalyzer; 4.43 - 0.03 N NH_4F + 0.1 HCℓ; 4.44 - 0.03 N NH_4F + 0.03 NH_2SO_4; 4.45 - 0.03 N NH_4F + 0.025 N HCℓ; 4.46 - 0.05 N NH_4F + 0.1 N HCℓ; 4.47 - 0.1 M $CaCl_2$, colorimetric; 4.48 - 0.01 M $CaCl_2$, turbidimetric; 4.51 - 1.0 N NH_4OAc; 4.52 - 0.5 M $NaHCO_3$; 4.61 - Hot water, azomethine-H; 4.62 - Hot water, curcumin; 4.63 - Dianthrimide; 4.71 - Buffer method; 4.8 - Hand texturing.

2 Non-routine methods

3 Extractable with 0.025 N Acetic acid (Spurway extractant).

4.1 pH and CONDUCTIVITY

4.11 1:1 soil:water ratio

(1) Weigh 25 g of soil into an Erlenmeyer flask, add 25 ml of distilled water and shake the mixture for 30 minutes on a reciprocating shaker.

(2) Measure the pH of the suspension using a combination electrode or a glass-calomel electrode pair and a pH meter.

(3) Measure the conductivity of the suspension using a conductivity meter and a conductivity cell with cell constant 1.0 (see 3.21).

(4) If the conductivity exceeds 3.0 mmhos/cm, filter the suspension and measure the conductivity of the clear filtrate.

4.12 1:2 soil:water ratio

(1) Weigh 15 g of soil, add 30 ml of water and proceed as in 4.11. Table 11 shows the relationships among conductivity, salt content and plant response.

NOTE:

(1) Weights of soil may be chosen according to convenience but the ratios of soil:water should be maintained at either 1:1 or 1:2.

4.13 Saturated soil paste

(1) Prepare a saturated soil paste as outlined in 3.21 and measure its pH.

(2) Extract the paste under vacuum as outlined in 3.21 and transfer a portion of the fitrate to a vial. The saturation extracts can be stored for short periods (1 week) under refrigeration before measuring the conductivity.

(3) Measure the conductivity as outlined in 3.21.

4.2 ORGANIC MATTER

The wet oxidation procedures are modifications of 3.613 to permit rapid analysis. Some loss of accuracy is involved. Loss-on-ignition provides only a rough estimate of organic matter in many soils.

4.21 Wet Combustion, Colorimetric Method

Reagents

(1) Potassium dichromate solution - 1.0 N. Dissolve 49.04 g of dried $K_2Cr_2O_7$ in distilled water and make the volume to 1 litre.

(2) Concentrated H_2SO_4.

Table 11. Soluble Salts in Soils (1:2 Soil:Water Ratio)

Conductivity	Approximate Salt Content	Plant Response
mhos x 10^{-5}	parts per million	
25	150	
30	210	Suitable for
35	310	most plants.
40	400	
45	500	
50	600	
55	650	May result in
60	750	a slightly
65	850	stunted condition
70	940	in most plants
75	1050	
80	1120	Slight to severe
85	1225	burning of most
90	1300	plants.
95	1400	
100	1500	
125	1950	
150	2400	
175	2850	Excessive salts.
200	3300	Prevents normal
250	4200	growth of most
300	5100	plants.
400	7150	
500	9200	
600	11200	

Procedure

(1) Place $\frac{1}{4}$ level teaspoon of air-dried soil ground to 0.5 mm or finer in a 125 ml Erlenmeyer flask. Add (under a fume hood) 10 ml of 1.0 N $K_2Cr_2O_7$ followed by 10 ml of concentrated H_2SO_4. Allow the mixture to stand for at least 20 minutes with occasional stirring.

(2) Add distilled water to the 100 ml mark on the flask. Mix and filter a portion of the suspension through Whatman no. 2 paper.

(3) Measure the percent transmittance of the filtered solution using an Autoanalyzer at 610 nm, using 2X scale expansion (Fig. 13). (Alternatively the measurement can be done manually with a colorimeter). The analysis should be done the same day that the samples are treated.

(4) The % T is read directly from the autoanalyzer chart and converted to % OM by the use of Table 12.

NOTE: A check sample must be run with each batch as there are no standards in this method.

Reference

Sims, J.R. and Haley, V.A. 1971. Simplified colorimetric determination of soil organic matter. Soil Sci. 112, 137-141.

4.22 Wet Combustion, Titration Method

Reagents

(1) Chromic Acid solution - 0.4 N. Dissolve 19.616 g of dried $K_2Cr_2O_7$ in 1 litre of a 1:1 mixture of concentrated H_2SO_4 and 85% H_3PO_4 by heating the mixture on a water bath at 95-100°C for about 2 hours with occasional stirring. The solution is stable for at least two months.

(2) Ferrous Ammonium Sulfate solution - approx. 2 N. Dissolve 80 g of $Fe(NH_4SO_4)_2.6H_2O$ in about 500 ml of distilled water containing 5 ml of conc. H_2SO_4. Dilute to 1 litre and store in a tightly stoppered bottle away from the light.

(3) Diphenylamine Indicator - Dissolve 0.20 g of diphenylamine in 100 ml of conc. H_2SO_4. Store in an amber glass bottle. (The Ba-sulfonate salt can be used).

Procedure

(1) Weigh a sample of <0.5 mm air-dried soil (usually 0.3 to 0.5 g) and place it in a dry 25 X 200 mm test tube.

(2) Add 10 ml of chromic acid and place the test tube in a sand bath at approximately 175°C for 3 minutes.

Table 12. Organic matter estimation from percent transmittance (method 4.21)

% T	% OM	% T	% OM
71.5	1.5	40.5	4.1
70.0	1.6	39.5	4.2
68.5	1.7	38.5	4.3
67.0	1.8	37.5	4.4
65.5	1.9	37.0	4.5
64.2	2.0	36.0	4.6
63.0	2.1	35.5	4.7
61.5	2.2	34.5	4.8
60.0	2.3	34.0	4.9
58.5	2.4	33.0	5.0
57.5	2.5	32.5	5.1
56.0	2.6	31.5	5.2
55.0	2.7	31.0	5.3
54.0	2.8	30.0	5.4
52.5	2.9	29.5	5.5
51.5	3.0	29.0	5.6
50.5	3.1	28.5	5.7
49.0	3.2	27.5	5.8
48.0	3.3	27.0	5.9
47.0	3.4	26.5	6.0
46.0	3.5	26.0	6.1
45.0	3.6	25.5	6.2
44.0	3.7	24.5	6.3
43.0	3.8	24.0	6.4
42.0	3.9	23.5	6.5
41.0	4.0		

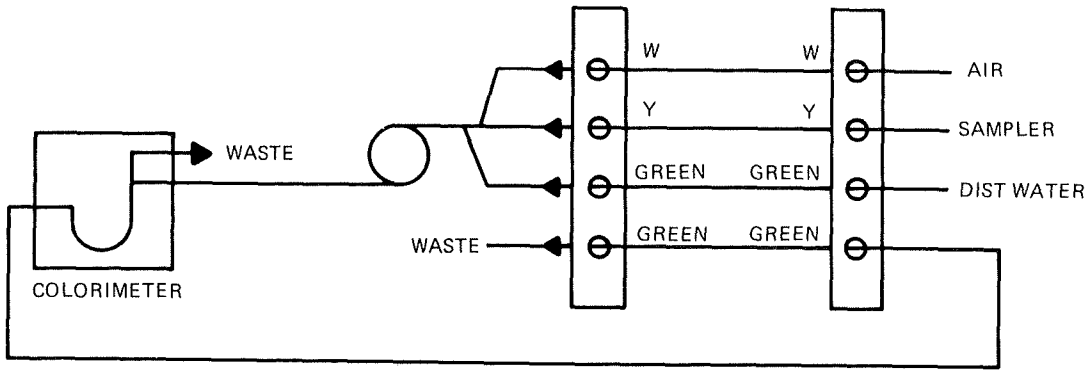


Fig. 13 Flow diagram for organic matter determination by autoanalyzer (Method 4.21).

(3) Remove the tubes, allow them to cool, and transfer the contents to 250 ml Erlenmeyer flasks with enough distilled water to make a final volume of about 100 ml.

(4) Allow the solution to cool, add 5 drops of indicator and titrate with ferrous ammonium sulfate to a green end point. Run a blank containing chromic acid but no soil with the samples.

Calculation

$$\% \text{ OM} = \frac{2.16 \text{ (Blank titer - Sample titer)}}{\text{Blank titer x sample weight}}$$

NOTE: % C may be calculated as % OM/1.8

4.23 Loss-on-Ignition

(1) Weigh approximately 2.0 g of soil into a Vycor or other suitable crucible of known weight.

(2) Dry the sample at 105°C for a minimum of 6 hours, cool, and reweigh. This weight of soil is the value to use in calculating % organic matter.

(3) Place the crucible and soil in a muffle furnace at 375°C ± 5°C for 16 hours.

(4) Remove the crucibles from the furnace, cool, and weigh.

Calculation

Loss-on-ignition (approximate OM%) =

$$\frac{\text{(Weight after drying at 105°C)-(Weight after heating to 375°C)}}{\text{Weight of soil after heating to 105°C}} \times \frac{100}{1}$$

Reference

Ball, D.F. 1964. Loss on ignition as an estimate of organic matter and organic carbon in non-calcareous soils. J. Soil Sci. 15, 84-92.

4.3 NITRATE AND AMMONIA

4.31 Incubated Nitrate-N Determination

Sample Preparation and Leaching

The samples must be maintained in a moist condition. The moist soil samples are screened through a 2 mm sieve the day they are received. If the water content is estimated to exceed about 20%, the sample is spread and dried at room temperature with frequent mixing to a water content slightly below 20%. The moist samples are placed in ½ pint containers, the containers are sealed in plastic bags and placed in a freezer at -5°C. The

samples should be frozen the day they are received; if this is impossible, store them overnight in a refrigerator. When the samples are to be analyzed, they are removed from the freezer and placed in a refrigerator overnight to thaw.

(1) Oven dry a portion of the sample for soil moisture determination (105°C).

(2) Take 10.0 g sample and mix with 10.0 g of acid-washed sand. Place the mixture in a No. 4 gooch crucible fitted with a 2.4 cm glass fiber filter.

(3) Place the gooch crucible on a filtering flask and leach the sample immediately (do not allow the soil to dry) with 80 ml of distilled water under suction. Place a piece of filter paper on the surface of the soil to prevent "puddling" of the soil when pouring in the water.

(4) After all the free water has been sucked from the sample, remove the crucible from the flask and add 10 ml of distilled water. Remove the piece of filter paper from the surface and place the crucible on the pressure manifold at 3.5 p.s.i. pressure for 1 hour.

(5) After 1 hour of pressure, but before releasing the air pressure, wipe the bottom of each crucible with an absorbent tissue. Then release the air pressure and remove the crucible from the manifold.

(6) Place the sample in a desiccator which has previously been fitted with a lead weight and water in the bottom. When all samples are placed in the desiccator, seal it carefully and submerge it in a constant temperature water bath at 30 ± 0.1°C. It is vitally important that the desiccator be held at this temperature and that the water level in the bath be kept constant, completely covering the desiccator (except for the vent opening) during the entire incubation.

(7) Incubate the samples for exactly two weeks.

(8) Remove the desiccator from the water bath and remove the crucibles from the desiccator. Fit them in a suction flask and leach with 80 ml of distilled water.

(9) Make the leachate up to 80 ml with distilled water (in the calibrated receiving tubes) and analyze it for nitrate-N by either 4.311, 4.312.

4.311 Cadmium Reduction Method for Nitrate

Reagents

(1) EDTA Reagent Dissolve 10.5 g of disodium EDTA in 450 ml distilled water and then adjust the pH to 6.5 - 7.0 with dilute NaOH. The final volume is adjusted to 500 ml with distilled water.

(2) Sulphanilamide Reagent Dissolve 1.0 g of sulphanilamide in a mixture of 90 ml distilled water and 10 ml conc. HCl.

(3) Naphthylethylenediamine Reagent Dissolve 0.10 g of N-1, Naphthylethylenediamine dihydrochloride in 100 ml of distilled water and store in an amber glass bottle. This solution is stable for only a few weeks and should then be discarded.

(4) Cadmium Reduction Column Cadmium filings are prepared by filing Cd sticks with an open rasp file. Approximately 20 mesh material is packed in a short mixing autoanalyzer column.

(5) Ammonium Hydroxide (Approximately 1 N) Mix 72 ml of conc. NH_4OH with water to make 1 liter.

Standards

(1) Stock Standard Dissolve 0.7200 g of KNO_3 (dried overnight at 105°C) in distilled water and make up to 1 liter. This solution is 100 ppm in Nitrate-N.

(2) Standards Dilute the stock standard to standards of 1,2,3,4, and 5 ppm NO_3-N.

Procedure

Prior to placing samples or standards on the autoanalyzer, the leads to the Cd reduction column are disconnected from the manifold and 30% HCl is passed through the column for 1 rapid wash cycle of the autoanalyzer pump. The column is then washed with distilled water and then reconnected to the manifold. Samples are then run directly on the autoanalyzer using the manifold and optics as shown in Figure 14.

Calculations

$$\text{ppm } NO_3\text{-N (soil)} = \frac{\text{ppm } NO_3\text{-N (extract)} \times 80}{\text{wt. dry soil sample (g)}}$$

4.312 Phenoldisulphonic Acid Method for Nitrate

Reagents

(1) Phenoldisulphonic acid (Commerical preparation)

(2) Calcium hydroxide (saturated solution) Thoroughly mix together 4 g of $Ca(OH)_2$ and 1 liter of distilled water. Allow the suspension to settle overnight and filter the supernatant through Whatman #1 filter paper.

Standards

The same as for the Cd reduction procedure (4.311).

Procedure

(1) Pipet a 10 ml aliquot of the leachate (4.31) into an evaporating dish and add 2 ml of saturated calcium hydroxide. Evaporate the sample to dryness on a steambath and allow it to cool.

(2) Add 2 ml of phenoldisulfonic acid and rotate the dish to ensure that the acid comes in contact with all the residue.

(3) After 10 minutes, transfer the sample from the evaporating dish to a 50 ml volumetric flask. Rinse the dish with distilled water, and add rinsings to flask to a volume of about 35 ml.

(4) Add 10 ml conc. NH_4OH to the solution in the flask, mix, allow to cool, make to 50 ml and mix.

(5) Read the absorbance at 420 nm against a blank and standards prepared like the samples.

(6) Read ppm of NO_3-N in solution from a standard curve.

(7) Calculate ppm NO_3-N as in 4.311

4.313 Specific Ion Electrode for Nitrate Determination

(1) Prepare nitrate standards containing 0, 5, 10, 20, 30, 50, 75, 100 ppm NO_3 (as nitrate).

(2) Remove the desiccator (4.31, step 8) from the water bath and remove crucibles from the desiccator.

(3) Remove soil from crucibles by reversing the crucible and blowing the soil into 4 oz Dixie cups.

(4) Rinse each crucible with 20 mls of distilled water (to remove what soil remains) into the sample cup.

(5) Stir intermittently for 30 minutes.

(6) Read nitrate in sample solutions and standards in millivolts on the nitrate specific ion electrode assembly.

(7) Calculations:

$$\text{ppm N in dry soil} = \text{ppm } NO_3 \text{ in extract} \times 2 \times 0.225 \times \frac{\text{weight of moist soil}}{\text{weight of oven dry soil}}$$

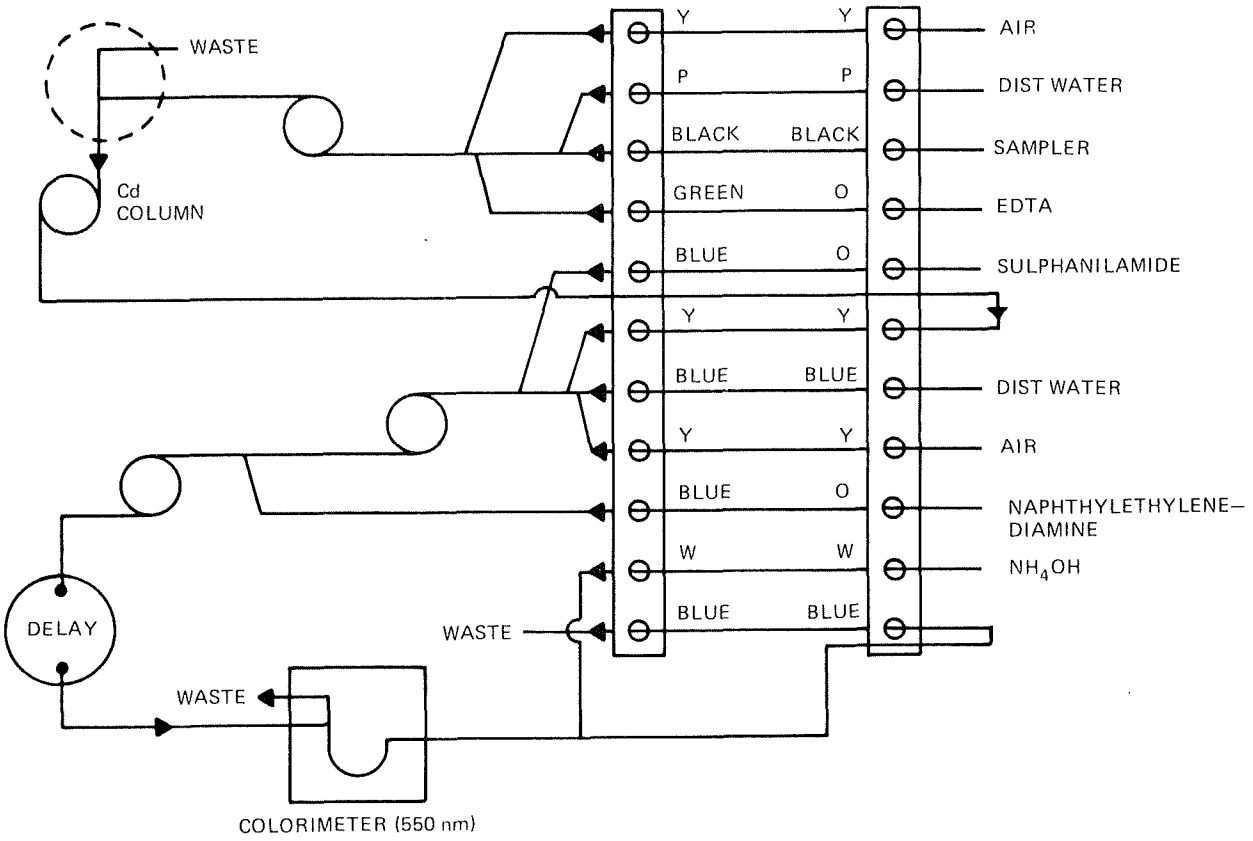


Fig. 14 Flow diagram for the determination of nitrate by autonanalyzer (Method 4.311)

4.32 Nitrate Extractable by 0.02 N $CuSO_4$ + .007 N Ag_2SO_4

Reagents

(1) Extracting solution 0.02 N $CuSO_4$ and 0.007 N Ag_2SO_4 - Dissolve 125 g Cupric Sulfate $CuSO_4.5H_2O$ in 4 litres of distilled water. Dissolve 60 g Silver Sulfate Ag_2SO_4 in 8 litres of distilled water (silver sulfate dissolves very slowly). Mix both solutions and make the volume up to 50 litres.

(2) Calcium Hydroxide - Must be dried at 800°C for 2 hours before using and should then be kept in a desiccator.

(3) Magnesium Carbonate - Light powder

(4) Phenoldisulphonic Acid - Dissolve 150 g phenol in 900 ml of concentrated H_2SO_4. Add 450 ml fuming sulfuric acid (30% SO_3). Mix and heat the flask in boiling water for 2 hours.

(5) Ammonium Hydroxide (7.5 N) - Mix one part NH_4OH to one part distilled water.

(6) Standard Solution (1000 ppm N) - Dissolve 7.2170 g of dry potassium nitrate in 1000 ml extracting solution.

Extraction Procedure

(1) Dispense a 5 g scoop of soil into a 50 ml Erlenmeyer flask.

(2) Add 25 ml extracting solution (50 ml for Greenhouse) and shake for 10 minutes.

(3) Add about 0.2 g Calcium Hydroxide ($Ca(OH)_2$) to each flask and shake for 10 minutes.

(4) Add half a teaspoon (about 0.5 g) of magnesium carbonate to each flask, shake for 2 minutes, and filter through Whatman #30 filter paper into 30 ml test tubes.

(5) Reduce volume in test tube to 10 ml and transfer to 50 ml Erlenmeyer flask (transfer 2 ml for Greenhouse).

(6) Place flask on hot plate. Bring the sample to dryness at low heat and cool the residue.

(7) Add 2 ml phenoldisulphonic acid, rotate the flask and let stand for 10 minutes.

(8) Add 28 ml of distilled water and 20 ml of ammonium hydroxide.

(9) Read absorbance on Spectrophotometer at 420 nm against standards diluted from the 1000 ppm stock solution. Determine NO_3-N in solution from a standard curve.

Calculations

NO_3-N (ppm in soil) = ppm N in solution X 10

4.33 Nitrate Extractable by 0.5 M $NaHCO_3$

Sample Preparation and Extraction

(1) Dry soil samples and grind to pass a 2 mm sieve. Extract by shaking 2.5 g soil with 50 ml 0.5 M $NaHCO_3$ (pH 8.5) in 125 ml Erlenmeyer flask for 30 minutes on Eberbach reciprocating shaker on slow speed. Add one teaspoon of activated charcoal (Darco G-60, CX 650 L1026 for soil analysis) prior to shaking to remove color. Filter the extract through Whatman #30 paper into 125 ml beakers. Transfer a portion of the filtrate to an Auto Analyzer cup. A reagent blank should be included with each set of 48 samples.

(2) Place the cups in a receiving tray of a Sampler 11 on a Technicon Auto Analyzer system. Nitrate plus nitrite-nitrogen is determined on one portion of the stream by an automated colorimetric method. Nitrate is reduced to nitrite with copper and hydrazine in alkaline solution at 53°C. The nitrite is then treated with sulfanilimide under acid conditions to yield a diazonium salt. This salt is reacted with a coupling reagent, N-1 naphthylethylenediamine dihydrochloride, to form a colored azo compound. The absorbance is measured at 520 nm.

4.34 Nitrate in 1:1 Soil:Water Suspensions (Nitrate electrode)

(1) Prepare 1:1 soil:water suspensions by adding 20 ml of distilled water to 20 g of air dry soil in a suitable container, stir intermittently for 30 minutes.

(2) Prepare standard nitrate solution as in 4.313.

(3) Read standards and samples with a pH meter with nitrate-calomel electrode assembly. Rinse electrode tips carefully after each reading.

(4) Prepare a graph of millivolts vs ppm N and read ppm NO_3-N in soil directly from the graph.

4.35 Nitrate and Ammonium Extractable by 2 N KCl and Determined by Steam Distillation

Reagents

(1) MgO - Heat heavy MgO at 700°C for 2 hours. Cool in a desiccator containing KOH pellets and store in a tightly stoppered bottle.

(2) Devarda's alloy - ground to pass a 100 mesh sieve.

(3) Sulphuric acid 0.0050 N.

(4) Boric acid - indicator solution. Dissolve 20 g of pure H_3BO_3 in about 700 ml of hot water. Transfer the cooled solution to a 1 litre volumetric containing 200 ml ethanol and 20 ml of mixed

indicator prepared by dissolving 0.33 g of bromocresol green and 0.165 g of methyl red in 500 ml ethanol. Mix contents of flask and add 0.05 N NaOH until a color change from pink to pale green is just detectable when 1 ml of the solution is treated with 1 ml of water. Dilute to volume with water and mix.

(5) Standard NH_4NO_3 solution.

A. Stock solution containing 500 ppm N as NH_4 and 500 ppm N as NO_3. Dissolve 5.7143 g of NH_4NO_3 dried at 100°C and make to 2 litres with distilled water. Store in a refrigerator.

B. 10 ppm standard solution. Make 20 ml of solution A to 1 litre.

(6) Extracting solution (2 N KCl) - 149.2 g KCl per litre.

(7) Sulfamic acid - 2 g in 100 ml of water.

Procedure

(1) Weigh 10 g of air-dry soil into a 100 ml flask, add 50 ml of extracting solution and shake for 1 hour.

(2) Transfer the suspension to a centrifuge tube and centrifuge for 5 minutes. Filter the supernatant solution through Whatman #1 paper.

(3) Determination of KCl-extractable NH_4:

Add 5 ml of boric acid-indicator solution to a 50 ml Erlenmeyer flask and place the flask under the condenser of a steam distillation apparatus so that the end of the condenser is about 4 cm above the surface of the boric acid solution. Pipet an aliquot (10 to 20 ml) of the soil extract into a steam distillation flask, add 0.2 g of MgO through a dry powder funnel having a long stem that reaches down into the bulb of the flask. Attach the flask to the steam distillation apparatus (see Fig. 9) and commence steam distillation. When the volume of distillate reaches about 30 ml, stop the distillation by opening the stopcock on the steam-bypass tube and rinse the end of the condenser. Determine NH_4 by titrating the distillate with 0.005N H_2SO_4 (green to faint pink endpoint). Also titrate a water blank and a nitrate standard.

Calculations

ppm NH_4-N (in soil) =

$$\frac{(\text{sample titre (ml)} - \text{blank titre (ml)}) \times (\text{N of } H_2SO_4) \times 14{,}000 \times 50}{\text{aliquot (ml)} \times 10}$$

$$= \frac{\text{net sample titre (ml)} \times \text{N of } H_2SO_4 \times 70{,}000}{\text{aliquot (ml)}}$$

(4) Determination of KCl-extractable NO_3

Add 1 ml of sulfamic acid to the distillation flask after distillation of ammonia (step 3). Add 0.2 g of Devarda's alloy rapidly through a dry powder funnel that reaches the bulb of the flask and immediately replace the stopper in the side arm. Steam distill as in step 3 and determine the reduced nitrate as ammonia as in step 3. The calculation for nitrate is the same as that for ammonium.

NOTES

(1) Add about 1 ml concentrated H_3PO_4 per litre of water in steam generator, maintain water level above 1/3 and replace water - H_3PO_4 solution every few days. Use boiling chips (charcoal or pumice) in the steam generator.

(2) Check by distilling blank and standard NH_4NO_3 solution (20 ml of standard should give a net titre of 2.998 ml for NH_4 plus NO_3).

Reference

(1) Bremner, J.M. 1965. Inorganic forms of nitrogen In Methods of Soil Analysis. C.A. Black, ed. Agron. No. 9, Part 2, pp. 1179-1237.

4.4 EXTRACTABLE PHOSPHORUS AND SULFUR

4.41 Sodium bicarbonate soluble P (Olsen and Dean, 1965)

Reagent

(1) Sodium bicarbonate ($NaHCO_3$) solution, 0.5 M.

Dissolve 42 g $NaHCO_3$ and make to one litre. Adjust the pH of this solution to 8.5 with 1 M NaOH. Add mineral oil to avoid exposure of the solution to the air. Prepare a fresh solution before use if it has been standing over 1 month in a glass container. Store the solution in a polyethylene container if for periods longer than 1 month, but check the pH of the solution each month.

(2) Carbon black: Use carbon black G as received.

(3) Ammonium molybdate-ascorbic acid. Dissolve 12 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in 250 ml of distilled water. In 100 ml of distilled water dissolve 0.2908 g of antimony potassium tartrate. Add both of these solutions to 1,000 ml of 5 N H_2SO_4 (140 ml concentrated H_2SO_4 per liter). Make to 2 litres and store in a dark pyrex bottle in a cool compartment (solution A). Prepare reagent B daily as required by dissolving 1.056 g ascorbic acid in 200 ml of solution A. Reagent B is stable for 24 hours at room temperature.

(4) Standard phosphorus solution: Weigh 0.4393 g of monobasic potassium phosphate (KH_2PO_4) into a 1 litre volumetric flask. Add 500 ml of distilled water, and shake the contents until the salt dissolves. Dilute the solution to 1 litre with distilled water. Add 5 drops of toluene to diminish microbial activity. This solution contains 0.1 mg of P per ml.

(5) Dilute phosphorus solution: Dilute 20 ml of the standard phosphorus solution to 1 litre with distilled water. This solution contains 2 µg of P per ml.

Procedure

(1) Add 5 g of soil, 1 teaspoon of carbon black, and 100 ml of the extracting solution to a 250-ml Erlenmeyer flask. Shake the flask for 30 minutes on a suitable shaker.

(2) Filter the suspension through the Whatman No. 40 paper. Add more carbon black if necessary to obtain a clear filtrate. Shake the flask immediately before pouring the suspension into the funnel.

(3) Pipet an aliquot of the extract containing 1 to 20 µg of P into a 25 ml volumetric flask (usually 5 ml).

(4) Add 0.5 ml of 5 N H_2SO_4 to reduce the pH to 5.

(5) Add distilled water to bring the volume to about 20 ml, then add 4 ml of reagent B. Make to volume and mix.

(6) Read absorbance at 880 nm after 10 minutes. The color is stable for 24 hours.

NOTES:

(1) The determination of P can be done conveniently by auto-analyzer.

(2) The results obtained depend to a degree upon temperature and shaking speed (Stone, 1971).

References

(1) Olsen, S.R. and Dean, L.A. 1965. Phosphorus In Methods of Soil Analysis. Part 2, pp. 1035-1049, C.A. Black ed. Agron. No. 9, Am. Soc. Agon., Madison, Wisconsin.

(2) Stone, B. 1971. Effect of temperature and shaking rate on sodium bicarbonate soluble phosphorus. Can. J. Soil Sci. 51, 312-313.

(3) Watanabe, F.S. and Olsen, S.R. 1965 (see 3.641).

4.42 Sodium Bicarbonate Soluble P (autoanalyzer)

This method is similar to 4.41 but it does not involve the use of carbon black and details are given for the determination by autoanalyzer.

Reagents

(1) $NaHCO_3$ Extracting Solution (0.5 M adjusted to pH 8.5) - Dissolve 42 g of sodium bicarbonate in distilled water and make up to one litre. Adjust to pH 8.5 with 0.5 N NaOH (usually about 25 ml per litre required).

(2) Ammonium Molybdate Reagent (2.0% in 3.56 N H_2SO_4) - Dissolve 20 g of $(NH_4)_2MoO_4.4H_2O$ in about 200 ml of distilled water heated to 50-60°C. Cool. Add 100 ml of conc. H_2SO_4 to about 200 ml of distilled water slowly and with constant stirring. Cool. When both solutions have cooled, add the molybdate solution slowly to the H_2SO_4 solution with stirring. Dilute to one litre and store in a dark bottle.

(3) Ascorbic Acid Reagent - Dissolve 0.88 g of ascorbic acid in each 100 ml of distilled water. Make up fresh daily.

(4) HCl and SN Diluent - 141.7 ml of conc. HCl and 10 drops of SN detergent per litre of solution. Add the acid slowly to water with stirring, cool, and dilute to volume.

(5) Phosphorus standard - Stock solution (1000 ppm P) - Dissolve 4.3930 g of KH_2PO_4, which has been dried for 24 hours at 80°C, in 1 litre of distilled water. Sub-Stock Solution - (25 ppm P in 0.5 M $NaHCO_3$ solution) - dilute 25 ml of the 1000 ppm P solution to 1 litre with 0.5 N $NaHCO_3$ solution.

Working Standards

Conc. of P (ppm or ug/ml)	Aliquot of 25 ppm sub-stock
0.1	2 ml
0.25	5 ml
0.5	10 ml
1.0	20 ml
2.0	40 ml
3.0	60 ml

Pipette the aliquot of 25 ppm P sub-stock solution into a 500 ml volumetric flask and dilute to volume with 0.5 N $NaHCO_3$ solution.

Extraction of Soil

(1) Add 50 ml 0.5 M $NaHCO_3$ solution to one-half teaspoon (Level - full) or 2.5 g soil.

(2) Shake for 30 minutes.

(3) Filter through a #5 Whatman Filter 11 cm diam.

(4) Approximately 5 ml of the filtered solution for the autoanalyzer is placed in a sample cup from which a 1.2 ml aliquot is pumped out for use in the determination.

Determination of P by Autoanalyzer (Fig. 15)

(1) Check that the correct filters and aperture are in the colorimeter: 815 mu filters and No. 2 aperture (reference side).

(2) Turn on colorimeter lamp. Allow at least 30 min warm-up before running baseline as in 10. below.

(3) Place proper manifold on pump and attach all connections:

(a) manifold to heating bath (95°C)

(b) heating bath to colorimeter

(c) colorimeter to manifold return

(d) manifold to sampler wash receptacle

(e) manifold, colorimeter, and wash receptacle overflow to waste sink

(f) turn on slow flow of cold water to cooling coil

(4) Place all reagent lines in distilled water.

(5) Stretch manifold pump-tubes, lower pump rollers and start pump. Run for at least 5 minutes with lines in the water.

(6) Arrange standards and samples on sampler, starting at position No. 1 on the inner rim. Insert u-shaped pin in appropriately numbered hole on the outer rim to stop sampler at the last sample.

(7) Insert reagent lines in full reagent bottles. Check with diagram for correct connections. Put sample line and probe into the $NaHCO_3$ reagent bottle. Run for about 5 minutes. Order of solutions is: sample, molybdate, ascorbic acid, HCl and SN.

(8) Turn on pen drive of recorder (bottom switch). Top switch must never be turned off.

(9) Check zero adjustment with zero aperture on sample side of colorimeter. Adjust pen to 0% T by means of the zero control on the colorimeter. Remove the zero aperture.

(10) With reagents running and sample line in $NaHCO_3$ solution, establish baseline at 100% T by means of the 100% T control on the colorimeter.

(11) Check gain on recorder and adjust if necessary.

(12) When reagent baseline is satisfactory, switch on sampler.

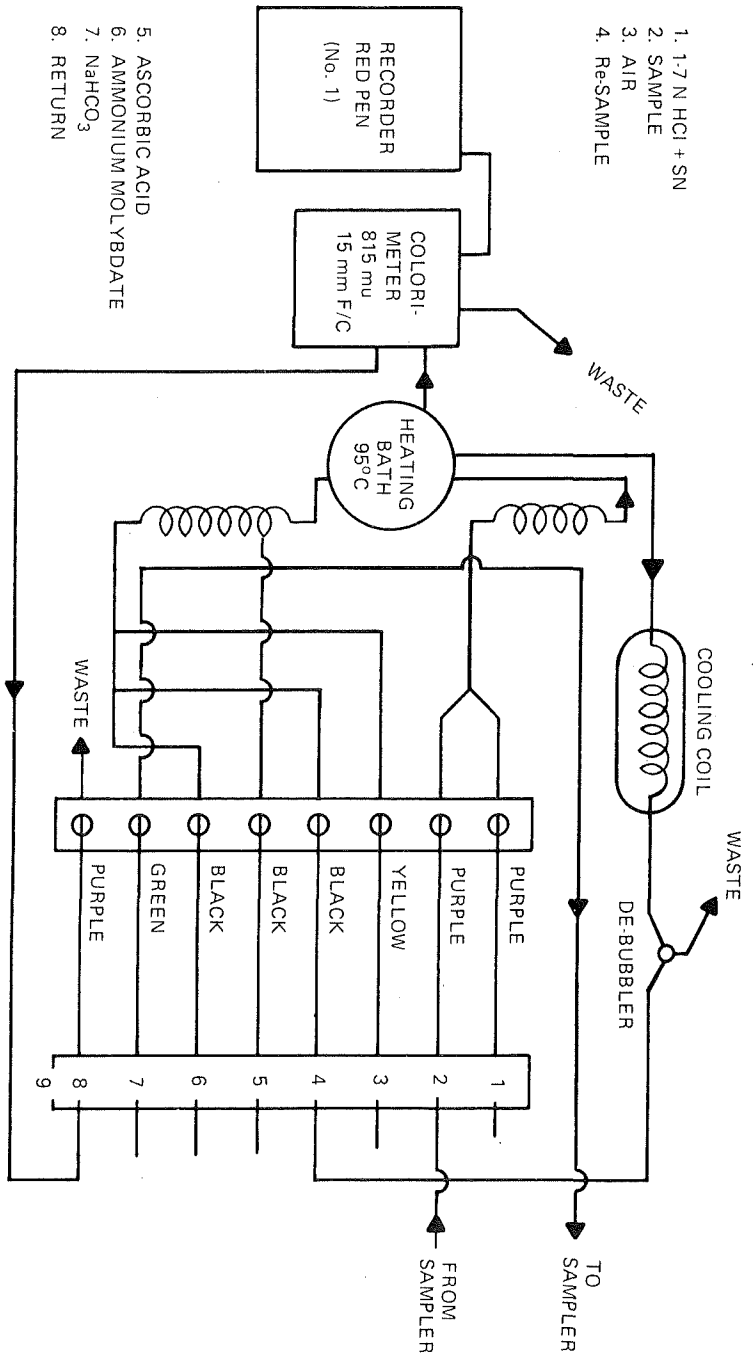


Fig. 15 Flow diagram for the determination of phosphorus by autoanalyzer (Method 4.42)

(13) Shut off sampler after last sample has been taken, stopping the probe in the wash receptacle (or transfer the sample probe to the $NaHCO_3$ reagent bottle).

(14) When last sample has been recorded, shut off the pen drive (bottom switch) and, if work has been completed for the day, the colorimeter lamp.

(15) Place sample and reagent lines in detergent solution and run for 15 minutes, or one fast wash and 5 minutes of slow running.

CAUTION: After a fast wash, the pump must run at standard speed for 5 min. before another fast wash is attempted.

NEVER HOLD SWITCH ON FAST SPEED

(16) Place sample and reagent lines in distilled water and run as in 3 above. Observe CAUTION above.

(17) Stop pump by raising the roller assembly.

(18) Release tension of pump tubes on manifold.

(19) Cap all reagent bottles and return to shelf. Remove all samples from sampler. Clean up any spillage.

(20) Prepare standard curve from recorded readings of standards and calculate P in samples.

4.43 Phosphorous Extractable by "Medium-Strength" Bray Extract (0.03 N NH_4F + 0.1N HCl)

Reagents

(1) Ammonium fluoride stock (1.0 N solution). Dissolve 37.0 g of NH_4F in distilled water and make up to 1 litre.

(2) Hydrochloric acid (approximately 0.5 N solution). Dilute 40.4 ml of conc HCl with distilled water to make to 1 litre.

(3) Extracting solution (0.03 N in NH_4F and 0.1 N in HCl). Add 30 ml of NH_4F stock and 200 ml of 0.5 N HCl to distilled water and make to 1 litre. This solution is stable for approximately 1 year.

(4) Ammonium molybdate. Dissolve 20.0 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 225 ml of conc H_2SO_4. Dilute to 2 liters with distilled water.

(5) Ascorbic acid. Dissolve 1.76 g of ascorbic acid in 200 ml of distilled water. This solution must be made up fresh each day before use.

(6) Detergent. Add 10 drops of SN solution to 1 litre of distilled water. The SN solution is prepared by mixing 50 ml of SN paste with 25 ml ethanol and 25 ml of water. The amount of ethanol can be varied slightly to achieve a clear solution.

Standards

(1) Stock Standard. Dissolve 0.8786 g of KH_2PO_4 which has been dried for 24 hours at 80°C in distilled water to make up 1 litre. This stock contains 200 ppm of P.

(2) Standards

P_2O_5/acre	ppm P	ml of Stock Standard
160	5.0	6.2
320	9.9	12.4
480	14.9	18.6
640	19.9	24.8
800	24.8	31.0
960	29.9	37.2
1500	46.6	57.0

All standards are made up to 250 ml with extracting solution.

Procedure

(1) Measure approximately 1.0 g of air-dry <0.5 mm soil into a 50 ml Erlenmeyer flask.

(2) Add 7.0 ml of extracting solution and shake for 40 seconds on a mechanical shaker.

(3) Allow to settle for several minutes or filter.

(4) Determine P either as outlined in 4.41 or 4.42 (see Fig. 16 for determination by autoanalyzer).

4.44 Phosphorus Extractable by 0.03N NH_4F + 0.03N H_2SO_4 (Medium-strength Bray, modified)

Reagents

(1) Extracting solution - 0.03 N NH_4F in 0.03 N H_2SO_4. Dissolve 55.4 g of NH_4F and 77 g of H_2SO_4 in 50 litres of H_2O.

(2) Color development reagent.

Solution A - dissolve 100 g ammonium molybdate in 1 litre of water.

Solution B - dissolve 5.0 g ammonium meta vanadate in 1 litre of boiling water, cool, add 1 litre of HNO_3 and cool again.

Add solution A to solution B and make the volume to 4 litres with distilled water.

Procedure

(1) Dispense about 5 g of soil (calibrated scoop) into a 50 ml Erlenmeyer and add 1 teaspoon of carbon black.

(2) Add 25 ml of extracting solution, shake for 2 minutes, and filter through Whatman 30 paper.

(3) Add 3 ml of color development reagent to 3 ml of extract and let stand for 15 to 20 minutes.

(4) Read absorbance at 400 nm and compare with standards.

Calculations

P in soil (ppm) = 5 x ppm in extract.

4.45 Phosphorus Extractable by 0.03 N NH_4F + 0.025N HCl Reagents

Reagents

(1) Extracting solution - Dissolve 55.4 g of NH_4F and 105 ml of conc. HCl in distilled water and make the volume to 50 litres.

(2) Other reagents as in 4.43 or 4.44.

Procedure

(1) Dispense 2.5 g of soil (calibrated scoop if desired) into a 50 ml Erlenmeyer flask. Add 25 ml of extracting solution, shake for 1 min. and filter.

(2) Determine P as in 4.43 or 4.44.

4.46 Phosphorus Extractable by "strong" Bray Extract 0.05 N NH_4F + 0.1 N HCl

Reagents

(1) Ammonium fluoride stock (2N) - Dissolve 74 g of ammonium fluoride in distilled water and dilute to 1 litre. Keep in polyethylene bottle.

(2) Phosphorus extracting solution (0.05N NH_4F + 0.1N HCl) - Dilute 450 ml of 2 N NH_4F and 150 ml of conc. HCl to 18 litres. Keep in polyethylene containers. (A 5 gal. polyethylene bottle will hold 18 litres).

(3) Ammonium Molybdate - Dissolve 20 g $(NH_4)_6MoO_{24}.4H_2O$ in 225 ml conc. H_2SO_4. Dilute to two litres with distilled water.

(4) Asorbic Acid - Weigh 0.88 g ascorbic acid into a 150 ml beaker placed on a top load 3-place balance. Remove and add 100 ml water and dissolve crystals on a magnetic stirrer.

(5) Detergent - SN paste at 10 drops per litre of distilled water (a substitute detergent is Levor IV).

Procedure

Measure a level calibrated (2.5g) spoonful of soil into a 50 ml Erlenmeyer flask (12 flasks per rack). Add 25 ml of

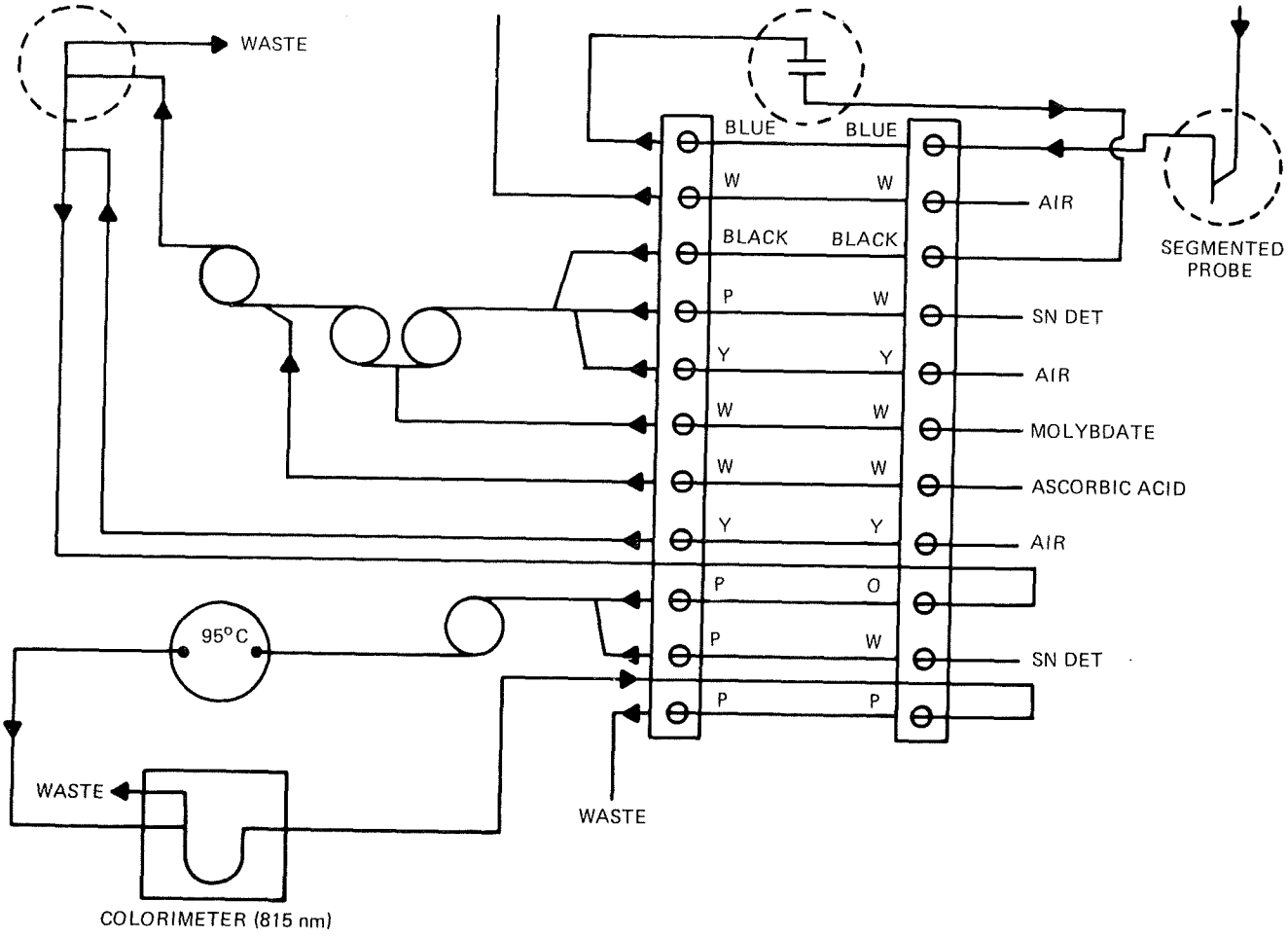


Fig. 16 Flow diagram for the determination of phosphorus by autoanalyzer (Method 4.43).

phosphorus extracting solution by an automatic Brewer Pipetting Machine. Shake for one minute on a mechanical shaker at 200 rpm. (4 racks per shaker). Filter (#5 Whatman) through a funnel on stand (48 funnel capacity) into a filter tube (48 tubes/tray). Remove tray. Suction off all but 10 ml of filtrate by use of calibrated suction probes (12 probe unit). Add 10 ml of distilled water by a 10 ml automatic pipettor. Note: Run one check sample with each set of 48 soil samples.

Transfer to disposable polystyrene sample cups and load Auto-Analyzer trays. (40 samples/tray). Run standards concurrently at a rate of 70 samples per hour.

P standards: similar to 4.43

4.47 Sulfate Extractable by 0.1 M $CaCl_2$

Reagents

(1) Reducing Agent - Mix 300 ml of hydriotic acid (57%) and 1% preservative, 75 ml of hypophosphorus acid (50%), and 150 ml of formic acid (90%). Boil with a stream of nitrogen flowing through the solution for 10 minutes (gently) after the temperature reaches 115°C. After use do not regenerate this reagent. It is usually not stable more than five or six days.

(2) Nitrogen Purification Solution - Add 5 to 10 g of mercuric chloride per 100 ml of 2% potassium permangante solution.

(3) Sodium Hydroxide Solution (1N) - Dissolve 80 g of NaOH in two litres of water.

(4) Bismuth Reagent - Heat 3.4 g of bismuth nitrate pentahydrate in 230 ml of acetic acid until dissolved, filter if needed through No. 50 filter paper and cool. Add 30 g gelatin to 500 ml of water and dissolve by warming. Add the gelatin solution to the bismuth solution and dilute to 1000 ml.

(5) Standard Sulfate Solution - 1000 ppm S. Dissolve 5.43 g K_2SO_4 in one litre of water. Make up standards of 1-2-3-5-10-15-20 ppm S.

(6) Extracting solution - Dissolve 29.4 g of $CaCl_2.2H_2O$ in distilled water and make the volume to 2 litres.

Procedure

(1) Weigh 20 g of soil and put it into 125 ml Erlenmeyer flasks, Add 40 ml of 0.1 M $CaCl_2.2H_2O$ and shake 30 minutes.

(2) Centrifuge 20 minutes (at 2500 rpm) and filter through Whatman #42 filter paper. Analyze within 8 hours.

(3) Add 2 ml of extract (or standard solution) to a boiling flask, and add 4 ml of reducing agent.

(4) Adjust the nitrogen flow to a total of 500 ml/minute for 6 flasks (read on flowmeter).

(5) Adjust electric heater to low heat (2-3). Distill for 30 minutes with the evolved H_2S trapped in 5 ml of 1 N NaOH held in a test tube.

(6) Dispense 2.5 ml of bismuth reagent into a clean test tube.

(7) After distillation drain NaOH into bismuth, mix, and read immediately at 400 or 480 nm.

(8) Calculate ppm S by comparisons of extracts with standards.

NOTES:

(1) Use of neoprene tubing (sulfur free) was not satisfactory and released what is believed to be a sulfur compound. Tygon gave good results.

(2) Regulate heat so the sample will bubble without boiling for about 4-5 minutes before starting to boil.

(3) The bubbles passing through NaOH should be as small as possible.

(4) Modifications were suggested by Kowalenko and Lowe, see reference 3.

References

(1) Johnson, C.M. and Nishita, H. 1952. Microestimation of sulfur in plant materials, soils and irrigation waters. Anal. Chem. 24, 736-742.

(2) Dean, G.A. 1966. A simple colorimetric finish for the Johnson-Nishita microdistillation of sulfur. Analyst 9/(1085) 530-532.

(3) Kowalenko, C.G. and Lowe, L.E. 1972. Observations on the bismuth sulfide colorimetric procedure for sulfate analysis in soil. Comm. Soil Sci. Plant Anal. 3, 79-86.

4.48 Sulfate Extractable by 0.01 M $CaCl_2$ (Turbidimetric)

Reagents

(1) Calcium Chloride (0.01 M). Dissolve 2.94 g of $CaCl_2.2H_2O$ in distilled H_2O to make 2 litres of solution.

(2) Sodium Peroxide (2%). Dissolve 10 g of Na_2O_2 in distilled water and make to 500 ml of solution.

(3) Acid "Seed" Solution. Mix 40 ml of 100 ppm S solution with 100 ml conc HCl and make to 200 ml with distilled H_2O.

(4) Sulfur Stock Standard - Dissolve 0.5434 g of dry K_2SO_4 in distilled H_2O and make up to 1 litre. This solution is 100 ppm in S.

(5) Working Sulfur Standards.

ppm S	ml Stock Solution	ml 0.01 M $CaCl_2$	Final Vol.
0	0	100	200
1	2	100	200
2	4	100	200
3	6	100	200
4	8	100	200
5	10	100	200

Procedure

(1) Weigh 25 g air-dry soil into a 125 ml Erlenmeyer flask, add 50 ml 0.01 M $CaCl_2$ and shake for 30 minutes.

(2) Filter through Whatman #30 paper and pipet 25 ml of filtrate into a 50 ml beaker.

(3) Add slowly by pipette 2 ml of 2% Na_2O_2, and let stand for 5 minutes.

(4) Filter off the gelatinous precipitate by gravity through Whatman #42 paper.

(5) Adjust the pH of the clear filtrate to 3.0 by adding dilute HCl and make the volume to 50 ml.

(6) Pipette 10 ml of the clarified extract into a 50 ml Erlenmeyer flask, add 1 ml of acid "seed" solution, swirl, and add 0.5 g of $BaCl_2 \cdot 2H_2O$. Let the solution stand 1 minute and then swirl the solution in the flask frequently until the crystals are dissolved.

(7) Within the time interval of 2-8 minutes after the crystals are completely dissolved, read the absorbance at a wave-length of 420 nm.

To prepare a standard curve, treat 10 ml portions of the standards in exactly the same manner as described above.

Calculations

ppm S (soil) = ppm S (acidified extract) x 4.

NOTES:

(1) Any change of chemicals or operators requires a new calibration curve.

(2) An automated procedure for this determination is outlined in:

Hamm, J.W., Bettany, J.R. and Halstead, E.H. 1973. A soil test for sulphur and interpretive criteria for Saskatchewan. Comm. Soil Sci. and Plant Anal. 4, 219-231.

4.5 EXTRACTABLE K, Ca and Mg

4.51 Ammonium Acetate Extractable Cations

Exchangeable cations (i.e. Ca, Mg, Na and K) may be determined by displacing these ions from soil colloids with NH_4. This is done by shaking the soil with 1 N NH_4OAc adjusted to pH 7.0. Analysis of the filtered extract involves emission spectrophotometry for Na and K and atomic absorption for Ca and Mg.

This method does not correct for Ca and Mg extracted from free carbonates; thus acetate-extractable Ca and Mg are not usually measured in calcareous soils. Also, water soluble Ca, Mg, Na, and K should be subtracted to get a true measure of concentration for the respective exchangeable cations. However, the concentration of water-soluble cations in many acid soils is almost negligible. In the case of saline soils, or soils containing gypsum, the procedure does not determine exchangeable cations.

The procedure outlined here is essentially the same as 3.32, but details of analysis are given.

Reagents

(1) 1.0N NH_4OAc Extracting Solution - Dissolve 77.1 g NH_4OAc in water and dilute to 1000 ml. Adjust pH to 7.0 with NH_4OH or HAc as required.

(2) 16.67 meq/l Li Solution - Dilute 22.23 ml of 1500 meq/l Li stock solution to 2000 ml with demineralized water.

(3) 15 meq/l Li Solution - Dilute 10 ml of 1500 meq/l Li stock solution to 1000 ml with demineralized water.

(4) 1% La and 5% HCl Solution - Dissolve 11.77 g La_2O_3 in 500 ml of demineralized water. Add 50 ml conc. HCl and dilute to 1000 ml.

(5) Na and K Standards - Prepare a series of solutions containing 20, 40, 80, and 160 and 240 ug/ml Na and K in 1.0 N NH_4OAc extracting solution.

(6) Ca Stock Standards - Prepare a series of solutions containing 160, 320, 480 and 640 ug/ml Ca in 1.0 N NH_4OAc extracting solution.

(7) Mg Stock Standards - Prepare a series of solutions containing 100, 200, 300 and 400 ug/ml Mg in 1.0 N NH_4OAc extracting solution.

Procedure

(1) Weigh 2.5 g air-dry, <2 mm soil into 125 ml Erlenmeyer flasks and add 25 ml of NH_4OAc extracting solution using an automatic pipettor.

(2) Shake for 30 min on a reciprocating shaker and filter through Whatman No. 30 filter paper into beakers.

Determination of Ca and Mg

Calcium

1. Prepare standards and 1% La solution as described under Reagents.

2. Dilute standards and extracts 40x with 1% La solution using an auto-dilutor. This results in a working range of 0-16 ug/ml. Save unused portion of diluted sample for Mg determination.

3. Prepare I.L. Model 153 Atomic Absorption Spectrophotometer as outlined in I.L. Procedure Manual Sec. 2-15-1 (or other AA according to the appropriate manual).

4. Aspirate blank and zero servo. Aspirate 8 ug/ml Ca standard and set servo to read 800. Remaining standards should read 400, 1200 and 1600. If not, use curve correct, and analyze samples.

5. Samples which read higher than 1600 should be diluted a further 2x with 1% La solution. Use this for Mg determination as well.

6. Calculation: $\frac{\text{Servo}}{100} \times 400 = \text{ug Ca/g soil}$

Magnesium

1. Prepare standards and 1% La solution as described under Reagents.

2. Dilute standards 40x with 1% La solution and a further 10x with distilled water using auto-dilutors. This results in a working range of 0.25 to 1.00 ug/ml Mg.

3. Dilute the unused portion of the diluted calcium sample a further 10x with distilled water.

4. Prepare I.L. Model 153 Atomic Absorption Spectrophotometer as outlined in I.L. Procedure Manual Sec. 2-49-1 (or other AA according to the appropriate manual).

5. Aspirate blank and zero servo. Aspirate 0.5 ug/ml Mg standard and set servo to read 1000. Remaining standards should read 500, 1500, and 2000. If not, use curve correct, and analyze samples.

6. Calculation: $\frac{\text{Servo}}{2000} \times 4000 = \text{ug Mg/g soil}$

OR

$\frac{\text{Servo}}{1000} \times 2000 = \text{ug Mg/g soil}$

Determination of Na and K

These cations are determined simultaneously using an I.L. Model 143 Flame Photometer as follows (or other Flame Photometer with appropriate procedure):

1. Prepare stock standards and Li solutions as described under Reagents.

2. Dilute stock standards 10x with 16.67 meq/l Li solution resulting in a working range of 0-24 ug/ml Na and K.

3. Dilute original soil extracts in the same manner.

4. Prepare I.L. Model 143 Flame Photometer as outlined in the Owner's Manual (or other Flame Photometer according to the appropriate manual).

5. Aspirate blank and standards, setting the servo to read 800 for the 8 ug/ml standard. The others should read 200, 400, 1600, and 2400 to permit direct servo reading. If not, prepare a standard curve and use.

6. Samples which read higher than 2400 should receive a further dilution with 15 meq/litre Li solution.

7. Calculation: Servo Reading = ug/g soil.

Report results as ug/g soil or meq/100 g soil when requested.

4.52 Bicarbonate Extractable K

K is determined in 0.5 M $NaHCO_3$ extracts (see method 4.41) by flame photometry.

4.6 EXTRACTABLE TRACE ELEMENTS

4.61 Hot Water Soluble Boron - Azomethine-H Method

Distilled water that is redistilled in a boron-free glass still and stored in polyethylene container should be used for rinsing glassware, preparation of reagents and dilutions. All glassware should be weathered in HCl and rinsed thoroughly.

Reagents

(1) Buffer-masking agent - Add 560 g ammonium acetate, 40 g potassium acetate, 40 g of the tetrasodium salt (ethylenedinitrilo) tetra-acetic acid and 16 g of nitrilotriacetic acid to 480 ml of charcoal treated water in a

2000 ml plastic beaker. The contents are partially dissolved by placing the beaker in a warm water bath. To the partially dissolved contents, add 140 ml of acetic acid slowly with stirring. The beaker is kept in the warm bath and the contents are stirred until dissolved. The solution is allowed to stand overnight and filtered through a Whatman #1 filter paper if any precipitate is apparent.

(2) Azomethine-H: (Pierce Chemical Co., Box 117, Rockford, Ill., 61125). Dissolve 0.9 g of azomethine-H and 2 g of ascorbic acid in 10 ml of water with gentle heating in a water bath. Make to 100 ml with water. If turbid, reheat in the water bath, making up to the original volume after cooling. This reagent will keep for about 14 days if refrigerated.

(3) Standard Boron Solution (100 ppm B) - Dissolve 0.5716 g boric acid (dried overnight in a desiccator) in water and make up to 1 liter. Dilute 20 ml to 200 ml = 100 ppm B. Prepare daily standards of 0.25, 0.50, 0.75, 1.0, 2.0 and 3.0 ppm using the 10 ppm stock in 100 ml volumetric flasks.

(4) Activated Charcoal - Darco G60.

Procedure

(1) Weigh 15 gram sample of air-dry soil that passed through a 2 mm sieve into a 150 ml beaker. Add 30 ml of redistilled water and $\frac{1}{2}$ level teaspoon of charcoal. A beaker containing 30 ml water serves as a blank. Weigh the sample plus beaker, stir gently but well with a glass rod and place on a preheated hot plate. After boiling commences leave on the hot plate for exactly 5 minutes.

(2) Cool for 5 to 10 minutes and reweigh, the loss in weight being adjusted to the original by the addition of redistilled water. Stir the contents well and filter through two Whatman No. 42 filter papers into a 125 ml Erlenmeyer flask. The resulting extract should be very clear. If the extract is not clear, add $\frac{1}{2}$ teaspoon of charcoal, stir well and filter again.

(3) Place 3 ml of clear extract in a 5 ml photometric tube. Add 0.5 ml buffer masking agent and 0.5 ml azomethine-H. Stopper and mix well. Let stand for one hour. Read on a spectronic-70 spectrophotometer at 430 nm.

Calculations

ppm B in soil = ppm B (extract) x 2

4.62 Hot-water Soluble Boron - Curcumin Method

Reagents

(1) Curcumin - Dissolve 0.125 g curcumin in 100 ml glacial acetic acid.

(2) Acid reagent - Mix 1:1 of 96% H_2SO_4 and glacial acetic acid.

(3) Ammonium acetate and acetic acid - Add 200 g ammonium acetate to 300 ml glacial acetic acid and make to 1 litre.

Procedure

(1) Weigh 20 g soil into a 125 ml flask and add 40 ml redistilled water.

(2) Attach reflux condenser and reflux for 5 min.

(3) Centrifuge and filter through no. 42 Whatman paper.

(4) Pipet a 0.50 ml aliquot into a 60 ml polyethylene bottle add 3.0 ml curcumin reagent and 3.0 ml acid reagent, swirl and allow to stand for 2 hr.

(5) Add 15 ml ammonium acetate-acetic acid reagent and read the absorbance at 555 nm in 1 cm cells against a water blank that was carried through the procedure. Read ug B from a standard curve prepared from standards run with the samples.

Calculations

ppm B in soil = ug B x 4

NOTE:

(1) A modified method suggested by Uppstrom seems to be preferable but it has not been tested in this laboratory. See reference 1.

References

(1) Kowalenko, C.G. and Lavkulich, L.M. 1976. A modified curcumin method for boron analysis of soil extracts. Can. J. Soil Sci. 56, 537-539.

4.63 Hot-water Soluble Boron-Dianthrimide Method

As in the other methods for B, glassware should be boron-free and water should be redistilled.

Reagents

(1) Calcium chloride, $CaCl_2.2H_2O$

(2) Calcium hydroxide, $Ca(OH)_2$, saturated solution (protect from CO_2 with a trap to absorb CO_2).

(3) Sulfuric acid, 0.36 N - 10 ml conc. H_2SO_4 to 1000 ml.

(4) Hydrogen peroxide, 30%

(5) Dianthrimide solution - Add 400 mg of 1,1-dianthrimide (1-1'-iminodianthraquinone) to 100 ml of conc. H_2SO_4 (containing very little B). Keep the stock solution refrigerated.

Each day prepare a working solution - 1 ml of the above dianthrimide solution and 40 ml conc H_2SO_4.

(6) Boric acid standard - Solution A - Dissolve 0.5716 g orthoboric acid (dried in desiccator) in 1 litre of water. Solution B - Dilute 10 ml of solution A to 1 litre (1 ug B/ml).

Procedure

(1) Weigh 20 g of air-dry, <2 mm soil (10 g of organic soils) into a 125 ml Erlenmeyer, add 40 ml of H_2O, attach a condenser and boil for 5 min.

(2) Add about 0.05 g of $CaCl_2.2H_2O$ to speed coagulation and filter.

(3) Pipet 20 ml of filtrate into a porcelain dish, add 2 ml of saturated $Ca(OH)_2$ and evaporate to dryness on a steam bath.

(4) Add a few drops of H_2O_2 to the residue and heat to destroy organic matter. Then add 4 ml of H_2SO_4 solution, stir and filter.

(5) Pipet 1 ml of the filtrate into a boron free test tube, add 10 ml of diluted dianthrimide solution, and put into the oven at 90°C for 3 hr.

(6) Read the transmittance on a colorimetric (orange filter), against a blank adjusted to read 100% T.

(7) Read ug B from a standard curve prepared by adding 1 to 10 ml of standard solution B to evaporating dishes and following through steps 3 to 6 as with the samples.

ppm B in soil = ug x 0.4

4.64 Al and Mn Extractable in 0.02 M $CaCl_2$

(1) Weigh 20 g soil, add 40 ml of 0.02 M $CaCl_2$ (2.94 g $CaCl_2.2H_2O$/litre) and shake for 1 hour.

(2) Centrifuge for 5 minutes at 1250 x g, and filter supernatant through Whatman #40 paper (avoid transferring any soil to the filter).

(3) Determine Al and Mn by atomic absorption. Use standards made up in 0.02 M $CaCl_2$.

NOTES:

(1) Extractable Al and Mn by this method provide a useful index of plant available Al and Mn.

(2) Al can also be determined colorimetrically.

Reference

(1) Hoyt, P.B. and Nyborg, M. 1971. Toxic Metals in Soil: I. Estimation of plant available aluminum, II. Estimation of plant available manganese. Soil Sci. Soc. Am. Proc. 35, 236-244.

4.65 DTPA-TEA Extractable Elements

Reagents

(1) Extracting solution - DTPA (0.005 M diethylenetriamine pentacetic acid, pentasodium salt, M.W. 503.26),TEA (0.1 M triethanolamine) in 0.01 M $CaCl_2$. Adjust pH to 7.30 with HCl.

For 20 l of solution: DTPA aqueous solution (41%, S.G. 1.29) - 95 ml. Triethanolamine - 268 ml. $CaCl_2$ - 29.4 g of $CaCl_2.2H_2O$

(2) Standard solutions of the trace elements to be determined should contain the extracting solution.

Procedure

(1) To 10 g soil, add 20 ml extractant, shake continuously for 2 hours and filter.

(2) Measure Zn, Fe and other trace metals if desired (Cu, Pb, Mn, Ni, etc.) by atomic absorption.

Reference

(1) Lindsay, W.L. and Norvell, W.A. 1969. Equilibrium relationships of Zn^{2+}, Fe^{3+}, Ca^{2+} and H^{+} with EDTA and DTPA in soils. Soil Sci. Soc. Am. Proc. 33, 62-68.

4.66 EDTA Extractable Elements

Reagents

Extracting solution - 0.05 M disodium EDTA, 0.01 M $CaCl_2$, 0.1 M triethanolamine (TEA). Dissolve 372.2 g disodium EDTA, 29.4 g $CaCl_2.2H_2O$ and 268 ml of TEA in water and make the volume to 20 litres. Adjust pH to 7.0 with NaOH or HCl. Prepare standards in extracting solution.

Procedure

(1) Weigh 20 g soil, add 40.0 ml of extracting solution, shake for 30 minutes, centrifuge at 15,000 rpm, filter through Whatman #42 paper.

(2) Determine Cu, Mn, Zn, Pb, Fe, Ni, Co, Cd, Cr by atomic absorption.

4.67 0.1 N HCl Extractable Elements

(1) Weigh 2.5 g soil into a 50 ml Erlenmeyer flask, add 25 ml 0.1 N HCl (8.3 ml conc HCl per litre) and shake for 30 min.

(2) Filter (Whatman #42) into test tubes.

(3) Determine Fe, Mn, Zn, Cu, etc by atomic absorption. Standards are made up in the extracting solution.

(4) Calculations

ppm element in soil = ppm in extract x 10

4.7 LIME REQUIREMENT

4.71 Buffer Method

Reagents

(1) Para-nitrophenol - reagent grade, crystal

(2) Boric acid - powder, Reagent grade

(3) Potassium hydroxide - pellets, reagent grade

(4) Potassium chloride - crystal, reagent grade

(5) Buffer solution. Dissolve separately 360 g of p-nitrophenol and 270 g of H_3BO_3 in 3 litres each of hot distilled water. Allow to cool. (The p-nitrophenol should be allowed to cool slowly on the hot plate). Dissolve separately 189 g of KOH in approximately 200 ml distilled water. Dissolve separately 1332 g of KCl in two 4-litre beakers of distilled water. It is very important to have the KCl completely dissolved and well-mixed. Pour the contents of the two beakers of KCl into a 20 litre carboy with spigot. Add in order with thorough mixing between each addition: the KOH, the H_3BO_3, and the p-nitrophenol solutions. Make to 18 litres with distilled water. Adjust the pH to 8.00 with either KOH or HCl. Note: If the above procedure is followed with deliberation, there will be a minimum of residue formed.

Procedure

To the soil from the pH and nitrate determination (4.11 or 20 ml soil:20 ml H_2O), add 20 ml of the buffer solution and stir thoroughly. Let stand for a minimum of 10 minutes. Standardize the pH meter to read 8.00 with a 1:1 buffer-water mixture. Stir thoroughly and measure the pH of the soil-buffer suspension immediately with a glass electrode to the nearest 0.05 unit on expanded scale.

To raise the soil pH values to 6.4, add the pounds of limestone per acre in the table at the intersection of the soil pH and buffer pH values (Table 11).

NOTE:

(1) The T/A limestone table (Table 13) has a built-in factor of 1.65 from 60% immediately available $CaCO_3$ in the marketed product.

(2) A method outlined by Shoemaker et al. (1961) gives similar results. See references 1 and 2.

References

(1) Shoemaker, H.E., McLean, E.O. and Pratt, P.F. 1961. Buffer method for determining lime requirement of soils with appreciable amounts of extractable aluminum. Soil Sci. Soc. Am. Proc. 25, 274-277.

(2) Webber, M.D., Hoyt, P.B., Nyborg, M., and Corneau, D. 1977. A comparison of lime requirement methods for acid Canadian soils. Can. J. Soil Sci. 57, 361-370.

4.72 Reaction with $Ca(OH)_2$

(1) Weigh five 20 g samples of soil into 10 ml bottles, add $Ca(OH)_2$ at rates of 7.5, 15, 22.5, 30, 37.5 mg to bottle 1 to 5 respectively, and add 50 ml distilled H_2O.

(2) Stopper and shake the bottles twice a day for 3 days.

(3) Measure the pH of each soil suspension and plot pH against mg $Ca(OH)_2$ added for each soil.

(4) Calculate the lime required to raise the pH to the desired level. (7.5 mg $Ca(OH)_2$ per 20 g of soil = 0.5 tons of pure $CaCO_3$ per acre).

4.8 SOIL TEXTURE, HAND METHOD

Soil texture could be measured by the methods given under 2.1, but soil testing laboratories in Canada use these methods on request only. Texture is measured in some laboratories by the "feel" or "hand" method. A sample of soil (about 10 g) is moistened and rubbed in the hand. Water is added to about the plastic or the liquid limit. An estimate is made of texture as follows:
Sand feelsgritty, silt feels smooth, clay is sticky. With experience and checks against samples of known texture from the region, good estimates of texture can be made. For many purposes, a rating of coarse, medium or fine texture is adequate.

Table 13 - Quantity of limestone in tons per acre required to raise soil pH to 6.5 to a 6 in. depth[1]

pH of Soil-Buffer \ soil pH	6.0	5.9	5.8	5.7	5.6	5.5	5.4	5.3	5.2	5.1	5.0	4.9	4.8	4.7	4.6	4.5
7.85	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
7.80	0.5	0.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5
7.75	1.0	1.0	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	2.0
7.70	1.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.5
7.65	1.0	1.0	1.5	1.5	1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.5	2.5	2.5
7.60	1.0	1.5	1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.5	2.5	2.5	2.5	2.5	3.0	3.0
7.55	1.5	1.5	2.0	2.0	2.0	2.0	2.5	2.5	2.5	2.5	3.0	3.0	3.0	3.0	3.0	3.5
7.50	1.5	2.0	2.0	2.0	2.5	2.5	2.5	3.0	3.0	3.0	3.0	3.0	3.5	3.5	3.5	3.5
7.45	1.5	2.0	2.0	2.5	2.5	2.5	3.0	3.0	3.0	3.5	3.5	3.5	3.5	4.0	4.0	4.0
7.40	2.0	2.0	2.5	2.5	3.0	3.0	3.0	3.5	3.5	3.5	4.0	4.0	4.0	4.0	4.5	4.5
7.35	2.0	2.5	2.5	3.0	3.0	3.0	3.5	3.5	4.0	4.0	4.0	4.0	4.5	4.5	4.5	5.0
7.30	2.0	2.5	3.0	3.5	3.5	3.5	4.0	4.0	4.5	4.5	4.5	5.0	5.0	5.0	5.5	5.5
7.25	2.0	2.5	3.0	3.5	3.5	3.5	4.0	4.0	4.5	4.5	4.5	5.0	5.0	5.0	5.5	5.5
7.20	2.5	3.0	3.0	3.5	3.5	4.0	4.0	4.5	4.5	5.0	5.0	5.0	5.5	5.5	5.5	6.0
7.15	2.5	3.0	3.5	3.5	4.0	4.0	4.5	4.5	4.5	5.0	5.0	5.5	5.5	6.0	6.0	6.5
7.10	3.0	3.0	3.5	4.0	4.0	4.5	5.0	5.0	5.0	5.5	5.5	6.0	6.0	6.0	6.5	6.5
7.05	3.0	3.5	4.0	4.0	4.5	5.0	5.0	5.5	5.5	5.5	6.0	6.0	6.5	6.5	7.0	7.0
7.00	3.0	3.5	4.0	4.5	4.5	5.0	5.5	5.5	6.0	6.0	6.5	6.5	6.5	7.0	7.0	7.5

[1]To change these quantities to tonnes/ha (15 cm depth) multiply the values by 2.24.

5. - MINERALOGICAL ANALYSES - C.R. De Kimpe

The task of compiling methods of mineralogical analysis of soils in Canada was approached by preparing a questionnaire on methodology and sending it to all Canadian scientists known to be doing mineralogical analyses. Replies to this questionnaire from some 30 scientists were used in preparing an initial draft on mineralogical methods. This draft was criticized by several mineralogists and revisions were formulated with the aid of Kodama, Miles and Ross of the Soil Research Institute. We appreciate the cooperation of the many scientists who contributed to the preparation of this section of the Manual and invite their criticism of this version.

The mineralogy of certain particle-size fractions rather than of the whole soil is determined. The fractions considered may be any of those mentioned in section 2.1, namely: various sand fractions (2000 to 50 µm); total silt (50 to 2 µm) or coarse (50 to 20 µm), medium (20 to 5 µm), and fine (5 to 2 µm) silt fractions; total clay (<2 µm) or various clay fractions such as: either, coarse (2 to 0.2 µm) and fine (<0.2 µm) or coarse (2 to 0.2 µm), medium (0.2 to 0.08 µm) and fine (<0.08 µm). The reason for separating the various fractions is that mineralogy may differ according to particle size.

Various pretreatments are used to aid in fractionating soil samples according to particle size. These pretreatments may alter the phyllosilicate minerals and they should be kept to a minimum. However, with some soils, pretreatments are essential to achieve fractionation.

The determination of the clay mineralogy of soils involves comparisons of soil clays with reference clay standards such as Wyoming bentonite, Georgia kaolin etc. This procedure is fraught with problems as soil clay minerals are commonly quite unlike the reference clay minerals in degree of crystallinity, degree of homogeneity and in chemical composition. Ideally, the standards should be soil clays but monomineralic soil clays are rare. Thus caution must be used in comparing X-ray or infrared data for soil clays with those for reference clay minerals. Generally several methods must be used to permit a semi-quantitative estimate of soil clay mineralogy.

5.1 FRACTIONATION OF SAMPLES

Details of fractionation procedures are given in section 2.1. These procedures are referred to here.

5.11 Water dispersion

5.111 Shaking in water: see 2.114

5.112 Ultrasonic dispersion: see 2.115

5.12 Dispersion involving chemical pretreatments

5.121 Removal of soluble salts (if any) and organic matter: see 2.113

5.122 Removal of soluble salts, carbonates and organic matter: see 2.112 C

5.123 Removal of iron oxides: see 2.111

5.124 Removal of salts, carbonates, organic matter and iron oxides: see 2.111

NOTES:

(1). Peroxide may alter some phyllosilicates (Douglas and Flessinger, 1971).

(2). Other methods for the removal of iron oxides are not widely used in Canada (Dudas and Harward, 1969; Segalen, 1968).

5.13 Clay Collection and Flocculation

Clay may be sampled and fractionated as outlined in 2.111 G and H. See also Tanner and Jackson (1947) for separation of various size fractions by centrifugation.

A portion of the clay suspension is flocculated by adding either slightly acidified 1N $CaCl_2$ or 1N $MgCl_2$ and another portion is flocculated by adding 1N KCl. The flocculated clay may be kept for analysis as:

a) freeze-dried clay
b) clay suspension
c) air-dried
d) oven-dried below $65^{o}C$.

NOTES

(1). Some mineralogists prefer Ca-saturated clay for analysis by X-ray diffraction, other prefer Mg-clay. Advantages stated for Ca are that it is commonly the major exchangeable cation in soils and it is not a lattice cation. The advantage of Mg as a saturating cation is that it facilitates a clear distinction between some vermiculites and smectite.

(2). Air-drying and oven-drying the clay prior to analysis are less desirable than either freeze-drying or maintaining the clay in suspension. The dried clay must often be ground and this may alter the clay.

5.14 Silt collection

It is often useful to determine the mineralogy of the silt fractions, especially when the clay content of the soil is low. Analysis of the silt aids in determining the mineralogy of mica and chlorite and the provenance of the soil material.

Silt fractions are collected as indicated in 2.111 E.

5.15 Sand collection

A qualitative and quantitative analysis of the heavy minerals in the sand fractions may be useful to assess the origin of a deposit or the homogeneity of a soil profile. Analysis may be done by microscopy or by X-ray.

5.151 Separation with high density liquids.

Various liquids can be used:

Bromoform	2.89 g/cc
S-tetrabromoethane	2.96
Methylene Iodide	3.3
Clerici solution	4.2
Molten lead salts	5.8

The most widely used liquid is the S-tetrabromoethane. A better separation is obtained with separatory funnels and the centrifuge.

5.152 Separation by magnetic susceptibility

A Frantz isodynamic electromagnetic separator is used to separate the minerals in the sand fraction according to their magnetic susceptibilities. (Parfenoff, Pomerol and Toureng, 1970).

NOTE

(1). A combination of density and magnetic susceptibility separation is useful in fractionating sands.

References

(1) Douglas, L.A. and Fiesinger, F. 1971. Degradation of clay minerals by H_2O_2 treatments to oxidize organic matter. Clays and Clay Min. 19: 67-68.

(2) Dudas, M.J. and Harward, M.E. 1969. Effect of dissolution treatment on standard and soil clays. Soil Sci. Soc. Am. Proc. 35: 134-140.

(3) Muller, L.P. 1967. Mineral separation in Physical Methods in Determinative Mineralogy. Academic Press 514 pp.

(4) Parfenoff, A., Pomerol, C. et Toureng, J. 1970. Les minéraux en grains. Masson et Cie, pp. 69-86.

(5) Schultz, Leonard, G. 1964. Quantitative Interpretation of Mineralogical Composition from X-ray and chemical data for the Pierre Shale. Geol. Survey Professional paper 391-C. U.S. Gov't. Printin. Office Washington.

(6) Ségalen, P. 1968. Note sur une méthode de détermination des produits minéraux amorphes dans certains sols à hydroxydes tropicaux. Cah. ORSTOM, sér. Pédol. 6, no 1, 105-126.

(7) Tanner, C.B. and Jackson, M.L. 1947. Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. Soil Sci. Soc. Am. Proc. 12: 60-65.

5.2 X-RAY ANALYSIS

X-ray diffraction is the major method used in the determination of soil clay mineralogy. For unambiguous identification, the clay must be homoionic and preferably at a controlled relative humidity. Identification of minerals is done by interpretation of diffraction patterns of the clay sample treated in various ways. The kinds and number of treatments required depend upon the complexity of the mixture of clay minerals in the sample and on the degree of crystallinity of the minerals. The treatments done should be adequate to permit a clear identification of the minerals. In the material that follows, essential treatments and additional treatments for some purposes are outlined for both Ca-K saturated clays and Mg-K saturated clays.

5.21 Ca-K Sequence for Clay-size Fraction Analysis

5.211 Sample Preparation

(1) Two subsamples of the clay fraction are prepared, one Ca saturated and the other K saturated. This is done by treating the clay 3 times, including one overnight treatment with either 1N $CaCl_2$ solution or 1N KCl solution (clay to solution ratio 1:20 or less). After each treatment, the suspension is centrifuged and the centrifugate is discarded.

(2) Excess salts are removed by 3 washings with H_2O or ethanol-water mixture (excess Cl- can be checked with $AgNO_3$).

NOTE:

It has been suggested that K treatment can be avoided by heating the Ca-clay to 700 C but K-treatment is the most widely used method for distinguishing chlorite from vermuculite.

5.212 Specimen Preparation

Both random and oriented specimens are desirable for unambiguous identification of minerals, but oriented specimens only are used in many analyses. The random powder technique gives valuable information on 060 spacings that characterize dioctahedral and trioctahedral layer silicates. Oriented specimens are useful for the characterization of basal spacings and swelling properties.

A. Random orientation

Unoriented specimens may be desired for quantitative work on the hk reflections of coarse particles and clay minerals. In this case, an adequate fraction of the Ca-clay is freeze-dried and prepared in such a way as to prevent crystal orientations. This is better achieved with cameras such as the Guinier or Debye-Scherrer types. Preparation of random specimens for diffractometers is more difficult. Various techniques have been suggested (side-filling, filling from the back, atomization) but the major problem seems to be reproducibility (Brindley, 1961; Schoen, Foord and Wagner, 1973).

B. Oriented Specimen

Several methods are used to obtain specimens in which the basal plane of the phyllosilicates is oriented parallel to the surface of the specimen holder. The criterion of good orientation is strong basal reflections and weak 020 reflections.

1. Glass slide technique

(1) Prepare a few milliliters of a suspension containing between 20 and 40 mg of clay/ml (known concentration) using the freeze-dried sample, or dilute the suspended clay (5.13b) to an equivalent concentration. If the concentration is too high, the clay film may peel off.

(2) Allow 1 ml of the suspension to dry on a petrographic slide (3.7 x 2.5 cm) at room temperature and at a relative humidity of 40-50%.

2. Ceramic plate method

(1) A ceramic plate of an appropriate size is fitted on a suction pump or in a centrifuge tube with a special adapter.

(2) The clay suspension is then poured on the plate and water evacuated with the appropriate technique (vacuum or centrifugation). Film density will depend on the concentration of the clay suspension.

3. Paste method

(1) After the last washing and decantation (5.21, step 2), a small amount of sediment sufficient to give a thin layer, is removed from the centrifuge tube with a microspatula and smeared on a petrographic slide so as to provide a smooth surface.

An easy way to prepare uniform slides is to attach two strips of masking tape to a slide and fill the area between them by drawing a spatula with sample sideways over the slide.

(2) The sample is dried at room temperature and then in an oven at 65°C, for one hour to insure uniform conditions of dryness (Theisen and Harward, 1962).

NOTES:

(1) Due to differences in the densities of minerals in a sample, mineral segregation may occur through differential sedimentation during drying of a clay suspension on a slide (Stokke and Carson, 1973). However, no problem of mineral segregation of clays prepared on glass slides has been encountered in the Soil Research Institute mineralogy laboratory (Miles, pers. comm.).

(2) An advantage of the glass slide technique is the easy control of the amount of clay.

(3) The ceramic plate technique has some advantages for washing or treating the clay to form an organic complex.

5.213 Treatments

Clay minerals are identified by determining the effects of various treatments on the basal spacings of the phyllosilicates. The treatments required depend, to a degree, on the nature of the sample.

A. Swelling properties

The major basis of identification of smectites is the increase in the basal spacing after treatment with glycerol or glycol.

(1) Glycerol adsorption

(a) Mixing in the suspension: 20 mg of clay are shaken in 1 ml of a 1:1 glycerol:water mixture and the suspension is then allowed to stand until the free liquid evaporates.

(b) Spraying: a 1:1 glycerol:water mixture is sprayed onto the slide.

(2) Ethylene glycol adsorption.

(a) Spraying: see 1 b, above.

(b) Vapor adsorption: a 1-hour treatment of the clay sample in the vapor from an ethylene glycol bath at 60°C is said to be satisfactory (Kunze, 1955).

B. Heat treatments

These are usually applied to the K-clay. Successive treatments as follows are recommended:

(1) Room temperature

(2) 100 C

(3) 300 C

(4) 550 C

For distinguishing vermiculite from montmorillonite an additional treatment is recommended: Heat the K-clay to 300 C and treat with glycerol.

If the heat treatments are applied to the Ca-clay, the following temperatures are recommended:

(1) Room temperature (preferably at 0, 50% and 100% relative humidity)

(2) 100 C

(3) 300 C

(4) 550 C

(5) 700 C

NOTES:

(1) Heating the slides for an hour is adequate.

(2) Heating to 700 C is useful for distinguishing some chlorites from vermiculite. However, Fe chlorite peaks may disappear if the sample is heated to 700 C.

(3) The presence of hydroxide interlayers in clays will be recognized by the collapse to intermediate basal spacings as a result of heating. Identification of the minerals may require the removal of these interlayers. See 5.23.

C. Relative humidity treatments

Ideally, X-ray diffraction analysis should be done at controlled relative humidity. Useful information on expanding minerals and on mixed layer minerals with an expanding component is obtained by running the samples at room temperature and the following relative humidities:

(1) 0%

(2) 50%

(3) 100%

NOTE:

(1) Clays that collapse on heating to 300C may re-expand if the sample is left in a humid room.

5.214 Criteria for Identification

The criteria for identification of clay minerals by X-ray diffraction are summarized. Further details can be found in the references cited (Brown, 1961; Harward and Brindley, 1965; Sayegh et al., 1965; Harward et al., 1969).

Approximate 001 spacings (Å) obtained with the characterization treatments:

Smectites

Montmorillonite	Ca - saturation 54% R.H.	15.4 Å
	Ca - " and glycerol	17.7 and higher orders
	Ca - " and eth. glycol	16.9-17.1 and higher orders
	K - " 54% R.H.	12.1-12.4
	K - " 105°C; dry air	10.3
	K - " 300°C; dry air	9.9-10.4
	K - " 300°C; glycerol	17.7
	K - " 500°C; dry air	9.8-10.2

Beidellite has essentially the same behavior as Montmorillonite. See also note 1.

Vermiculite	Ca - saturation	54% R.H. at 25C	14.8
	Ca - "	glycerol	14.3 (see note)
	Ca - "	Eth. glycol	15.3
	K - "	54% R.H.	10.4
	K - "	105°C; dry air	10.3
	K - "	300°C, glycerol	10.4
	K - "	500°C, dry air	10

See also notes 2 and 3.

Chlorite

Most of the chlorites are trioctahedral chlorites. They have a 001 spacing around 14 Å which does not vary with solvation or K saturation and heating. At room temperature the 002 spacing is normally more intense than the 001 spacing, while after heating at 550°C, the contrary is observed.

In the presence of kaolinite, there may be some confusion between the various lines, but the 4.73 Å reflection is typical for chlorites.

In dioctahedral chlorite (Brydon et al., 1961, Sudo and Sato, 1966) the 001 spacing is more intense than the 002 spacing at room temperature. See also note 4.

Micaceous minerals

They are recognized by the presence of a 9.9-10.4 Å spacing regardless of saturating cation, humidity or solvation.

In the case of illite, K-saturation may contribute to a better organization of the layers and result in sharper reflections.

Kaolin minerals

Kaolinite is characterized by the presence of a 7.2-7.3 Å reflection regardless of saturation cation, humidity or solvation. Well crystallized kaolinite has a 001 spacing of 7.15 Å with sharp peaks. Some natural halloysites, prior to drying at 110°C, have a higher water content than kaolinite and show a strong reflection at 10.1 Å that collapses irreversibly to about 7.2 Å on drying. Reflections are also broader than for kaolinite. In the presence of chlorite and chloritized intergrades possible confusion may arise between the second order chlorite line and the first order kaolinite. However, since kaolinite is transformed into metakaolin below 550°C, heat treatment at this temperature will indicate whether kaolinite was present. With poorly crystallized chlorites, heat treatments at temperatures lower than that for the dehydration of kaolinite may decompose these chlorites. Treatment with HCl is also useful in differentiating chlorites from kaolinites due to the more rapid dissolution of chlorites (Grim, 1953; Ross, 1967, 1969).

Randomly Interstratified clay minerals

Many examples of interstratified minerals have been described. They can be divided into two groups, regularly and randomly interstratified minerals. The randomly interstratified minerals are discussed here.

Weaver (1956) documented the mixed layer mica-montmorillonite minerals. Various spacings can be observed which are not necessarily either the sum or the arithmetic mean of the sum of the original spacings. It must be considered that when interstratification involves swelling minerals, the different treatments (solvation or heat) will influence one of the constituents and thus modify the spacings of the interstratified minerals.

Most complexes involve mica (illite), montmorillonite, vermiculite and chlorite, either as binary or ternary mixtures.

Let us consider the case of randomly interstratified clay minerals commonly found in soil clays, which belong to a binary system. The identification of the two layer components may be made from a cross-examination of results of diagnostic tests. Some examples for cross-examination are tabulated below (Kodama and Brydon, 1968). When two spacings are given, they indicate the range within which a peak may be expected.

Type of Interstratification*	Glycerol	Humid 100% RH	Air-dry 50% RH	Dry 0% RH	550°C
Mica-vermiculite	x	x	10-14	10-11.5	10
Mica-chlorite	x	x	10-14	x	10-14
Mica-smectite	10 or 18	Expansion	10-15.5	10-11.5	10
Vermiculite-chlorite	x	x	14	11.5-14	10-14
Vermiculite-smectite	14-18	Expansion	14-15.4	11.5	10
Chlorite-smectite	14-18	Expansion	14-15.4	11.5-14	10-14

* As Ca-saturated specimen.
x Indicates that the basal spacing is unchanged from air-dry.

An approximate estimation of mixing ratio of the two component layers may be made by an inspection of the positions of basal reflections, since diffraction theory indicates that the basal reflections of an interstratification migrate according to interference phenomena between layers of two similar types. One should, however, realize that the movements of peak positions are not always linearly proportional to the mixing ratios. The direct Fourier transform method proposed by MacEwan may be applied not only to the binary system, but also to tertiary or more complicated system. The method requires that structure factors of component layers are similar. With this so-called "simulation method" (Sato et al., 1965), successful applications can provide useful information concerning types of component layers and modes of layer stacking sequence. If types of component layers are known and a large electronic computer is available, calculations for theoretical diffraction patterns of many types can be made according to a complete x-ray diffraction theory (Brown, 1961). Thus answers may be sought by a comparison between calculated and experimental diffraction patterns (Reynolds and Howes, 1970; Sato, Oinuma, and Kobayashi, 1965).

Other minerals

In soil specimens, quartz is a common constituent which gives a strong diffraction pattern with sharp reflections. The strongest reflection at 3.34 Å can be seen with less than 1 percent of quartz. As this line is confounded with the mica reflection at 3.33 Å, the presence of

quartz should also be verified by the presence of the 4.26 Å reflection.

Feldspars may be common in the clay fraction and may be a major part of some samples. All feldspars appear to have two or three strong reflections in the region 3.28-3.16 Å.

Amphiboles are often present in soils. Typical reflections occur in the 8.5-8.4 Å area, and they persist through the 700C heat treatment.

Among the iron oxides, four may be found in soil clays. When present, they may give sharp reflections, the most intense of which are indicated here for the various forms:

goethite:	4.18 - 2.69 - 2.45 Å
hematite:	2.69 - 2.51 - 1.69
magnetite:	2.53 - 1.48 - 2.97
lepidocrocite:	6.27 - 3.29 - 2.47

See Norrish and Taylor (1962) for further information.

Gypsum has the most intensive reflection at 7.56 Å, and less intense at 3.06 and 4.27 Å.

Among the carbonates, the most frequent ones are calcite and dolomite.

Calcite:	3.035 - 2.285 - 2.095 Å
Dolomite:	2.886 - 2.192 - 1.786 Å

NOTES:

(1) An additional test for beidellite is based on the irreversible collapse of Li-saturated smectite when heated to 200-300°C.

The Li-saturated specimen is heated overnight at 200-300°C. It is then saturated with glycerol. A 001 spacing of 17.7 Å will indicate beidellite and a 9.5 Å spacing will indicate montmorillonite.

(2) Low charge Ca vermiculite may expand with ethylene glycol.

(3) With K-saturation and 50% R.H., a line at 14 Å may still be present with vermiculite, particularly when these are low-charge vermiculites, derived from non-micaceous minerals (Weaver, 1958).

(4) In the soil, mainly under strong weathering conditions, montmorillonite and vermiculite may form chloritic intergrades with aluminum hydroxide between the layers. The properties will be intermediate between chlorite and vermiculite or montmorillonite. The predominant feature is the resistance to collapse upon K-saturation and heating, especially when

the amount and stability of hydroxy-interlayers increase. Samples toward the chlorite end of the spectrum (complete and well organized hydroxy-layers) may also exhibit resistance to expansion.

5.215 Semi-quantitative estimation of clay minerals

Quantitative analysis of the components in a clay mineral mixture may be desirable and useful in geochemical and pedological studies. The principle of the following method is similar to that of Johns et al. (1954) and of Sudo, Oinuma and Kobayashi (1961). The intensities of basal reflections are directly compared to the intensity ratios established from artificial mixtures of standard clay minerals. See also a more detailed treatment of quantitative clay mineral analysis by Kodama, Scott and Miles (1977).

Procedure

1. Determine working conditions for instruments

   a) Radiation, filter, operational high-voltage and X-ray tube current,
   b) Slit system, scanning speed of the goniometer,
   c) Electronic instrument for detector system,
   d) Electronic instrument for recording system.

2. Establish the intensity ratio of basal reflections of clay mineral components:

   a) Choose standard clay minerals with the same particle-size range (probably in many cases, <2μ)
   b) Prepare quartz powder for sample dilution and of calcite or fluorite powder for an internal standard (powder size should be same as that of clay minerals)
   c) Prepare binary mixtures of clay minerals with equal weights of each mineral
   d) Dilute the prepared binary mixtures with quartz powder in various proportions (for example, 5 mg kaolinite and 5 mg mica and 15 mg quartz equals 25 mg; 10 mg kaolinite and 10 mg mica and 5 mg quartz equals 25 mg; etc.)
   e) Add internal standard (add 5 mg to 25 mg mixture and make up 30 mg, for example)
   f) Prepare oriented aggregates on glass slides (37.5 mm x 25 mm) using a fixed amount of mixture (usually 20, 30 or 40 mg)
   g) Collect intensity data by measuring diffraction peak heights or areas for the standard and normalize by the internal standard
   h) Construct a calibration curve for each binary system to obtain intensity ratio (for example, S (smectite 15 Å): M (mica 10 Å): K (kaolinite 7 Å) equals 2.6:1.0:1.2) after comparison of results for various binary systems.

i) If standard minerals with various crystallinities are available, mean intensity ratios may be obtained.

3. Collect intensity data for unknown samples.

a) Carry out X-ray analysis of the samples under the same conditions used for the standards.
b) Divide the intensity of basal reflection attributable to a component by the corresponding intensity ratio (for example, I (kaolinite)/1.2).
c) Estimate "relative amounts" of clay minerals in the system from the corrected intensity data (b).
d) In the case where a basal reflection belongs to more than one component, apply appropriate diagnostic tests and try to isolate the basal reflection of a single component. Depending upon complications met, standards should be subjected to the same diagnostic tests and subsequently analyzed.

NOTE:

Other semiquantitative methods (Klug and Alexander, 1954) are:
1. The spike method
2. Direct method from mass absorption coefficient

5.22 Mg-K Sequence for Clay-Size Fraction Analysis

The procedure is similar to 5.21 except for the following:

(1) A 1N $MgCl_2$ solution is used instead of a 1N $CaCl_2$ solution (5.211) for saturating one of the clay subsamples.

(2) The normal treatments required are the same as in 5.213 except that the 300C glycerol treated specimen is not required.

(3) Spacings for the swelling minerals are as follows:

Montmorillonite

Mg - saturation	50% R.H.	15.3
Mg - "	+glycerol	17.4
Mg - "	+eth.glycol	16.9

Vermiculite

Mg - saturation	50% R.H.	14.3
Mg - "	+glycerol	14.1
Mg - "	+eth.glycol	14.1

5.23 Ca-K sequence with removal of sesquioxides interlayers for clay-size fraction analysis

5.231 Pretreatment for the removal of the interlayer

A commonly used method is the technique described by Tamura (1958):

Procedure:

(1) Weigh 50 mg of clay in a centrifuge tube

(2) Add 10 ml of N sodium citrate (pH 7.3) solution

(3) Heat in a water bath (100°C) for 1 hour

(4) Centrifuge and decant the supernatant

(5) Repeat (2) to (4) 2 times

(6) Wash with water

5.232 Sample preparation and analysis

Proceed as in 5.21

5.24 Mg-K sequence with removal of sesquioxides interlayers for clay-size fraction analysis.

Follow procedure 5.231 for removal of the interlayer material and procedure 5.22 for clay preparation and analysis.

5.25 Silt Analysis by X-ray Diffraction

The silt fraction generally contains high percentages of primary minerals and low percentages of secondary minerals. It is therefore necessary to run both random and oriented specimens. For random and oriented specimen preparation see 5.212.

If time does not permit analysis of all of the silt fractions, the 2 to 5 micron fraction is preferred. Coarser fractions may require grinding for X-ray analysis.

Treatments

(1) Treatments to determine swelling properties are the same as those outlined in 5.213.

(2) A single heat treatment at 500C for 2 hours may be adequate to enhance the peaks for some minerals. This treatment may destroy some other minerals such as goethite and Fe-rich chlorite.

References

(1) Brindley, G.W. 1961. Experimental methods. Chapt 1 in Brown's The X-ray identification and crystal structures of Clay Minerals. Ed. by Mineralogical Society, London.

(2) Brown, G. 1961. The X-ray identification and crystal structures of clay minerals. Mineralogical Society, London.

(3) Brydon, J.E., Clark, J.S. and Osborne, V. 1961. Dioctahedral chlorite. Can. Mineral. 6, 595-609.

(4) Foscolos, A.E. and Kodama, H. 1974. Diagenesis of clay minerals from Lower Cretaceous Shales of north eastern British Columbia. Clays and Clay Min. 22, 319-335.

(5) Grim, R.E. 1953. Clay Mineralogy, McGraw-Hill, Toronto

(6) Harward, M.E. and Brindley, G.W. 1965. Swelling properties of synthetic smectites in relation to lattice substitutions. Clays and Clay Min. 13th Conf. 209-222.

(7) Harward, M.E., Carstea, D.D. and Sayegh, A.H. 1969. Properties of Vermiculite and Smectites: expansion and collapse. Clays and Clay Min. 16, 437-447.

(8) Johns, W.D., Grim, R.E. and Bradley, W.F. 1954. Quantitative estimations of clay minerals by diffraction methods. J. Sed. Petrol. 24, 242-251.

(9) Klug, H.P. and Alexander, L.E. 1954. X-ray Diffraction Procedures, Wiley, New York.

(10) Kodama, H. and Brydon, J.E. 1965. Interstratified montmorillonite-mica clays from subsoils of the prairie provinces, western Canada. pp. 151-173 in Clays and Clay Minerals. Proc. 13th Natl. Conf., Madison, Wisconsin, 1964. Pergamon Press.

(11) Kodama, H. and Brydon, J.E. 1968. A study of clay minerals in podzol soils in New Brunswick. Clay Min. 7, 295-309.

(12) Kodama, H., Scott, G.C. and Miles, N.M. 1977. X-ray quantitative analysis of minerals in soils. Soil Research Institute, Ottawa. 49 pp.

(13) Kunze, G.W. 1955. Anomalies in ethylene glycol solvation technique. Clays and Clay Min. Publ 395 Nat. Acad. Sci. Wash. 88-93.

(14) Norrish, K. and Taylor, R.M. 1962. Quantitative analysis by x-ray diffraction. Clay Min. Bull. 5, 98-102.

(15) Reynolds, R.C., Jr. and Howes, J. 1970. The nature of interlayering in mixed-layer illite-montmorillonite. Clays and Clay Min. 18, 25-36.

(16) Ross, G.J. 1967. Kinetics of acid dissolution of an orthochlorite mineral. Can. J. Chem. 45, 3031-3034.

(17) Ross, G.J. 1969. Acid dissolution of chlorites: Release of magnesium iron and aluminum and mode of acid attack. Clays and Clay Min. 17, 347-354.

(18) Sato, M., Oinuma, K. and Kobayashi, K. 1965. Interstratified mineral of illite and montmorillonite. Nature 208, 179-180.

(19) Sayegh, A.H., Harward, M.E. and Knox, E.G. 1965. Humidity and temperature interaction with respect to K-saturated expanding clay minerals. Am. Min. 50, 490-495.

(20) Schoen, R., Foord, E. and Wagner, D. 1973. Quantitative analysis of clays. Problems, achievements and outlook. Proc. Int. Clay Conf. 1972, Madrid pp. 787-796.

(21) Stokke, P.R. and Carson B. 1973. Variation in clay mineral x-ray diffraction results with the quantity of sample mounted J. Sed. Pet. 43, (4), 957-964.

(22) Sudo, T. and Sato, M. 1966. Dioctahedral chlorite. Proc. Int. Clay Conf. 1966. Jerusalem, pp. 33-39.

(23) Sudo, T., Oinuma, K. and Kobayashi, K. 1961. Mineralogical problems concerning rapid clay mineral analysis of sedimentary rocks. Acta Universitatis Carolinae Geologica, Suppl. 1, 189-219.

(24) Tamura, T. 1958. Identification of clay minerals from acid soils. J. Soil Sci. 9, 141-147.

(25) Theisen, A.A. and Harward, M.E. 1962. A paste method for preparation of slides for clay mineral identification by x-ray diffraction. S.S.S.A. Proc. 26, 90-91.

(26) Walker, G.F. 1958. Reactions of Expanding-lattice clay minerals with Glycerol and ethylene glycol. Clay Miner. 3, 302-313.

(27) Weaver, C.E. 1956. Mixed layer clays in sedimentary rocks. Am. Min. 41, 202-221.

(28) Weaver, C.E. 1958. Potassium fixation by expandable clay minerals. Am. Min. 43, 839-861.

5.3 CHEMICAL ANALYSIS RELATED TO MINERALOGY

Chemical analysis is useful in support of X-ray and other physical methods in determining the mineralogy of soil clay fractions. Many of the chemical methods involved are outlined in section 3. of this Manual.

5.31 Exchange Properties

5.311 Exchange capacity by chemical methods

Any of the methods outlined in section 3.3 can be used for the determination of the cation exchange capacity of clays. Commonly the neutral ammonium acetate method, 3.32, is used but it is subject to the disadvantage that some clays fix NH_4.

Saturation of the clay with Ca, Mg or Na (3.31) by repeatedly equilibrating a clay sample with the appropriate chloride salt (2N), washing the sample with water to remove

free salts, displacing the exchangeable Ca, Mg or Na with 2N calcium or magnesium chloride and determining the exchangeable cation by atomic absorption is a preferable procedure.

5.312 Adsorption of dyes

See Brindley and Pham Thi Hang (1970).

5.313 Exchange with heavy atoms and subsequent determination of CEC by X-ray fluorescence.

5.314 A semi-quantitative determination of clays based on chemical analysis and exchange properties has been described by Alexiades and Jackson (1966). It rests upon the selective fixation of cations by clays.

5.32 Total Elemental Analysis

Total elemental analysis of the clay fraction is useful for some purposes, such as the determination of the chemical structure of a reasonably monomineralic clay sample. The determination of some elements (such as K) may be useful in evaluating the mica or illite content of the clay. See section 3.7 for methods.

5.33 Selective Dissolution of Non-clay Minerals

The clay-size fraction of many soils contains non-phyllosilicate minerals. Selective dissolution of these minerals may be useful in semi-quantitative analysis. Methods have proposed by Kiely and Jackson (1965).

References

(1) Alexiades, C.A. and Jackson, M.L. 1966. Quantitative clay mineralogical analysis of soils and sediments. 14th Nat. Conf. Clays and Clay Min. 35-52.

(2) Brindley, G.W. and Pham Thi Hang. 1970. Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities. Clays and Clay Min. 18, 203.

(3) Kiely, P.V. and Jackson, M.L. 1965. Quartz, feldspar and mica determination for soils by sodium pyrosulfate fusion. Soil Sci. Soc. Am. Proc. 29, 159-163.

5.4 THERMAL METHODS

5.41 Nomenclature in thermal analysis

The International Confederation for thermal analysis (ICTA) made recommendations for an uniform nomenclature in thermal analysis (MackKenzie et al., 1969, 1972, 1974). It has been generally well accepted and it should be more widely accepted by Canadian scientists. Certain arbitrary choices have had to be made, - e.g. between specimen and sample - but the only term in fairly common use that is rejected is inert material.

5.42 Differential Thermal analysis

This technique provides supplementary information to X-ray diffraction analysis.

As clays are very sensitive to environmental conditions, it is desirable that all samples be saturated with the same cation, which is usually either Ca^{2+}, or Mg^{2+}. Relative humidity control is also essential. It has been suggested by MacKenzie and Mitchell (MacKenzie, 1957) that equilibration for at least 4 days in vacuo over a saturated solution of $Mg(NO_3)_2.6H_2O$ be adopted as standard. This gives approximately 55% R.H. at 18°C and about 52% R.H. at 30°C. A further requirement is standardization of instruments and operating conditions.

5.43 Thermogravimetric analysis

TGA may be useful as it provides information on the thermal stability of sorbed and constitution water.

Pretreatments should be similar to those for DTA.

5.44 Characterization

The main features of the thermogravimetric and differential thermal curves are outlined. However, many factors, such as the crystallinity of the material, the particle size, the heating rate (generally 5 or 10°C/min) may induce changes. The following characteristics are thus a guideline and relevant textbooks should be examined.

allophane

TGA there is a continuous loss of water with 10 to 15% weight loss below 110°C and a roughly similar amount between 110°C and 1000°C.

DTA an endothermic peak occurs below 110°C and a possible exothermic peak at about 950°C.

kaolin

TGA there is no water loss below 400°C for kaolinite but a gradual loss of interlayer water for halloysite. Most of the dehydration occurs between 400 and 525°C, with a small amount (2-3%) gradually lost between 525 and 750°C.

DTA the endothermic peak between 400 and 600°C corresponds to dehydroxylation. Structural changes and the corresponding exothermic reaction occur in the temperature range of 900-1000°C.

smectite

TGA there is a considerable water loss at low temperatures (100 to 200°C) depending on the nature of the cation. As the dehydration curves are S-shaped, there is no sharp boundary between the interlayer water loss and the (OH) structural water loss; 300°C seems to be an acceptable break point.

DTA the endothermic peak between 100-200°C corresponds to the loss of interlayer water.

The main and broad endothermic peak starts at about 400 (nontronite) or 500°C (montmorillonite) and extends to 800°C.

Above 800°C: an endothermic plus an exothermic peak may be present but show considerable variations because of the various phases that can be formed.

vermiculite

TGA there is an important water loss below 100°C or thereabouts and then a gradual loss to about 850°C, although the water loss could be more stepwise: a) below 100°C, b) small peak between 250 to 400°C, c) above 600°C.

DTA there is a large endothermic peak at about 150-200°C, associated with a smaller one at about 250-275°C. The high temperature change (endo and exo thermic peaks) occurs at about 800°C.

illite

TGA there is a considerable water loss below 100°C, a gradual loss from 100 to 350°C, an abrupt loss from 350 to 600°C and a gradual loss above 600°C.

The curve is more gradual in micas, which also lack the water loss below 100°C (interstitial water).

DTA a first endothermic reaction (below 100°C) corresponds to the loss of interlayer water, the main endothermic peak starts at about 450-500°C and is observed at about 550-650°C, a third slight endo occurs between 900-1000°C. From the results obtained with "abnormal" illite, it seems that illite could be considered as an interstratified mineral with mica and montmorillonite layers (see MacKenzie, 1957, pp. 260-262).

chlorite

TGA the main water loss occurs between 500 and 550°C. Above that temperature, it may be either gradual from 600 to 850°C or gradual from 600 to 750°C and then abrupt from 750 to 850°C.

DTA the endothermic reaction occurs between 500 and 700°C with a second peak at about 800°C, immediately followed by a sharp exothermic peak.

quartz

the presence of quartz in many natural samples is very often a useful reference for the analysis of the curves. Natural quartz presents an inversion, $\alpha \rightleftharpoons \beta$ quartz at or near 573°C.

iron oxides

The most common naturally-occurring ferric oxide hydrate is goethite. The DTA curve is characterized by a single endothermic peak around 380°C.

Hematite, the most common naturally-occurring anhydrous ferric oxide does not show any feature in the range 0-1000°C. Similarly magnetite cannot be defined by any DTA peak. There is a small exothermic peak at about 350-400°C and a broad exothermic peak in the 600-1000°C range.

Naturally-occurring amorphous and hydrous gels generally give a sharp exothermic peak at about 350-400°C.

aluminum oxides — Gibbsite is the most common one found in nature. It gives a strong endothermic peak between 320 and 330°C and smaller ones between 250-300°C and at about 525°C.

References

(1) MacKenzie, R.C. 1957. The differential thermal investigation of clays. Publ. by the Mineralogical Society, London.

(2) MacKenzie, R.C. et al. Nomenclature in Thermal Analysis. I. Talanta, 1969, 16, 1227. J. of Pure and Applied Chem. 1974, 37, No. 4.

(3) MacKenzie, R.C. et al. Nomenclature in Thermal Analysis. II. Talanta, 1972, 19, 1079-1081.

NOTE:

Copies of the third reference are available, upon request, from C.R. De Kimpe (Research Station, 2560 Chemin Gomin, Ste Foy, Quebec).

5.5 INFRARED SPECTROSCOPY

Infrared spectroscopy appears to be the most useful diagnostic technique for amorphous materials such as allophanes and also for characterizing kaolinite in the presence of chlorite.

5.51 Methods

5.511 KBr pellets method

A fraction of the clay sample is diluted to about 0.5-1% (depending on the instrument) in infrared grade KBr. A pellet is subsequently pressed and analyzed.

5.512 Nujol Method

A paste is prepared by mixing the clay with Nujol, and the paste is spread on the window.

5.513 Film technique

A diluted suspension of the clay is allowed to settle and dry on a water-insoluble window, such as CaF_2, AgCl, IRTRAN.

5.52 Analysis of the Spectra and Identification

Spectroscopy allows the measurement of energy exchange between electromagnetic radiation and matter. In the infrared range, the photon energy corresponds to the energy of intramolecular vibrations of atoms or groups of atoms. When there is a change in the permanent dipole moment, energy absorption occurs. Several modes of vibration may occur for one molecule, and each one will occur at a characteristic frequency, normally independent of other modes. Therefore an analysis of the electromagnetic spectrum of a sample makes it possible to distinguish the various types of absorption. Hence characterization of the sample and identification of the minerals may be achieved. Small particle size such as that of phyllosilicates is very suitable for this technique.

The range considered for clay mineral analysis falls between 2 and 25 um in wavelength or 5,000 to 400 cm^{-1} in frequency.

Attempts (Stubican and Roy, 1961, Stubican, 1963, Farmer, 1973) were made to correlate particular absorption bands with specific modes of atomic or molecular vibrations in phyllosilicates.

The following ranges were recognized:

a) 3750-3500 cm^{-1} : Hydroxyl groups stretching vibrations

b) 1700-1600 cm^{-1} : water molecule deformation

c) 1150- 400 cm^{-1} : lattice vibrations and deformations

The schematic summary (Fig. 17) after Stubican (1963) illustrates the assignment of various infrared absorption bands.

The figure shows only the ranges of wavelengths where various types of absorption bands are observed. However, each band may consist of more than one component and in some cases, therefore, more defined absorption patterns may be observed in each range depending upon the geometry of crystal structure in question. When a mineral is extremely pure, the bands may be very sharp. However, a "bathochromic effect" is associated with the substitution of a cation by a heavier atom and this will induce a shift in the frequencies. In the infrared spectrum, this most often results in a broadening of the bands.

Particle size affects the position and shape of certain absorption bands (Farmer and Russell, 1966), this phenomena is known as the "Christiansen effect". It has to be borne in mind in interpreting spectra of samples having a wide range of particle sizes.

Typical spectra of minerals have been tabulated (Farmer, 1974) and for identification purposes, it is advisable to consult such references.

References

(1) Farmer, V.C., Ed. 1974. The Infra-red Spectra of Minerals. Monograph 4, Min. Soc. Britain.

(2) Farmer, V.C., and Russell, J.D., 1966. Effects of particle size and structure of the vibrational frequencies of layer-silicates. Spectrochim. Acta 22, 389-398.

(3) Grim, R.E. 1968. Clay Mineralogy. McGraw Hill, Miscellaneous properties, pp. 448-463.

(4) Hayaski, H. and Oinuma, K. 1965. Relationship between infrared absorption spectra in the region of 450-900 cm^{-1} and chemical composition of chlorite. Am. Mineral. 50, 476-483.

(5) Loh, E. Optical vibrations in sheets silicates. J. Phys. C. Solid State Phys. 6, 1091-1104 (1973) (includes far infrared region).

(6) Russell, J.D. and Farmer, V.C. 1970. Replacement of OH by OD in layer silicates, and identification of the vibrations of these groups in infra-red spectra. Min. Mag. 37, 869-879.

(7) Stubican, V. and Roy, R. 1961. Isomorphous substitution and infrared spectra of the layer lattice silicates. Am. Mineral. 46, 32-51.

(8) Stubican, V.S. 1963. The interaction of ions in complex crystals as shown by infrared spectroscopy. Penn. State Univ., Mineral Ind. Proc. 33 (2), 1-7.

(9) Tuddenham, W.M. and Lyon, R.F.P. 1959. Relation of infrared spectra and chemical analysis for some chlorites and related minerals. Anal. Chem. 31, 377-380.

(10) Vedder, W. 1964. Correlations between infrared spectrum and chemical composition of mica. Am. Mineral. 49, 736-768.

(11) Wilkins, R.W.T. and Ito, J. 1967. Infrared spectra of some synthetic talcs. Am. Mineral. 52, 1649-1661.

5.6 SURFACE AREA DETERMINATION

This technique may be useful in the identification of amorphous components which generally have a high surface area, in the determination of the amount of montmorillonite in a mixture by measuring of the internal surface area, or in determining the charge density.

5.61 Low temperature gas adsorption

A gas such as N_2 is adsorbed at the temperature of liquid nitrogen in a static or dynamic system and the surface area can be calculated from the results. For very small surface areas, Kr is generally preferred (Brunauer, 1943; Nelsen & Eggerstsen, 1958).

5.62 Ethylene glycol retention

A differential glycol retention between calcined and non-calcined samples allows the calculation of the internal surface of clays and thus the amount of montmorillonite (Dyal and Hendricks, 1950; Diamond & Kinter, 1958).

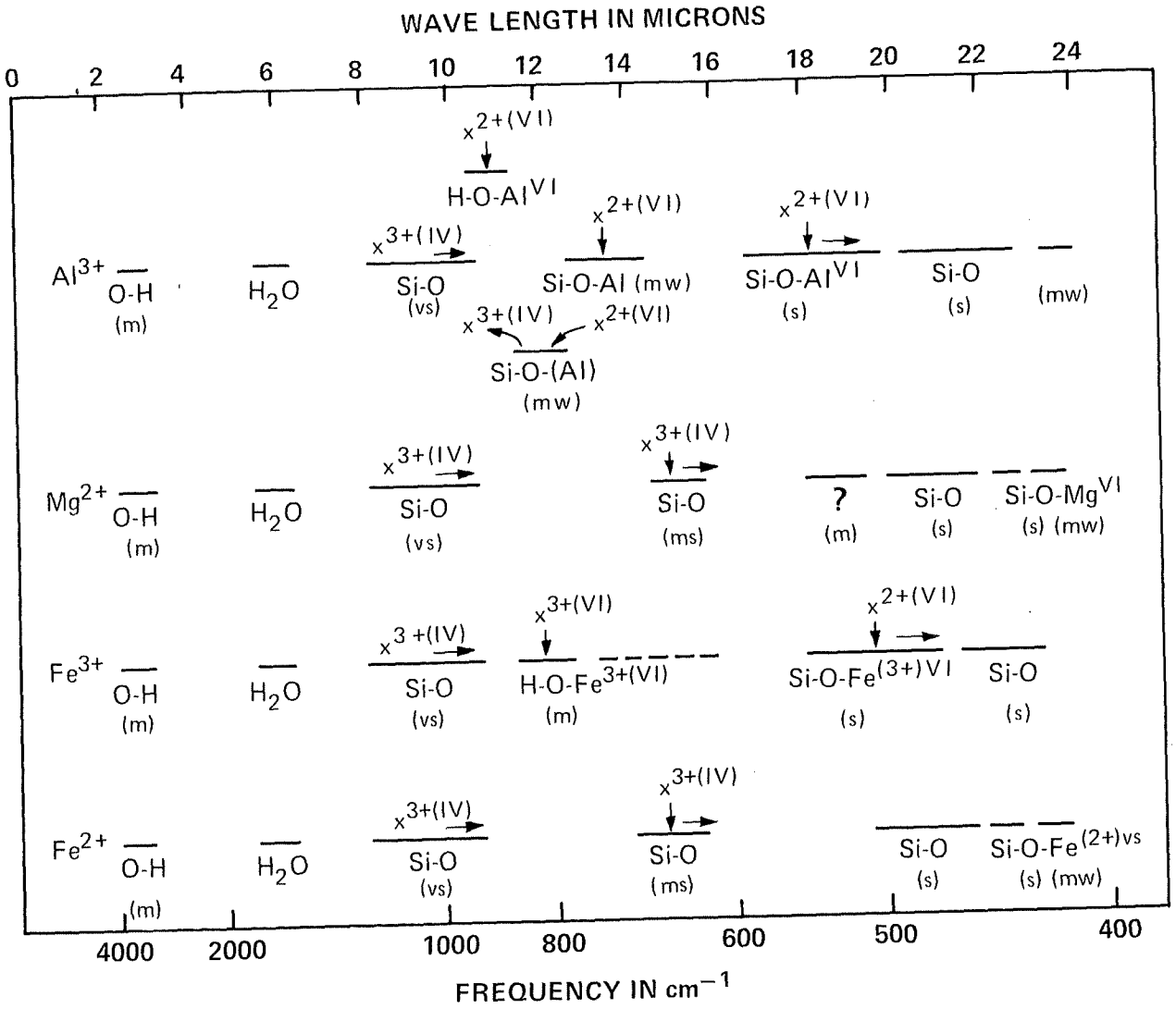


Fig. 17 Schematic summary of the assignments of the infrared-absorption bands in layer-lattice silicates containing basically Al^{3+}, Mg^{++}, Fe^{3+}, or Fe^{++} in the octahedral sites. Relative intensities of the bands are described as vs = very strong, s = strong, m = medium, and w = weak (Stubican, 1963).

5.63 Dye absorption

Methylene blue has been used to determine the total, external plus internal surface area of clay (Brindley and Hang, 1970).

References

(1) Brindley, G.W. and Pham Thi Hang. 1970. Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities. Clays and Clay Min. 18, 203.

(2) Brunauer, S. 1943. The adsorption of gases and vapors. Vol. 1. Princeton University Press.

(3) Diamond, S. and Kinter, E.B. 1958. Surface area of clay minerals as derived from measurements of glycol retention. Clays Clay Min. 5, 334-347.

(4) Dyal, R.S. and Hendricks, S.B., 1950. Total surface of clays in polar liquids as a characteristic index. Soil Sci. 69, 421-432.

(5) Nelsen, F.M. and F.T. Eggertsen. 1958. Determination of surface area adsorption measurements by a continuous flow method. Anal. Chem. 30, 1387-1388.