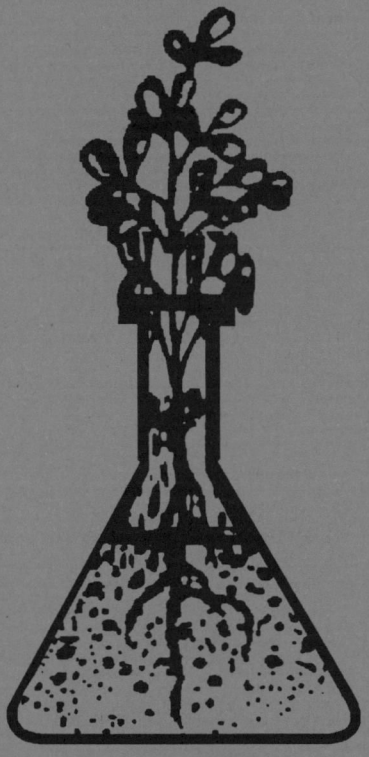
Methods of Soil Analysis Used in the Soil Testing Laboratory at Oregon State University



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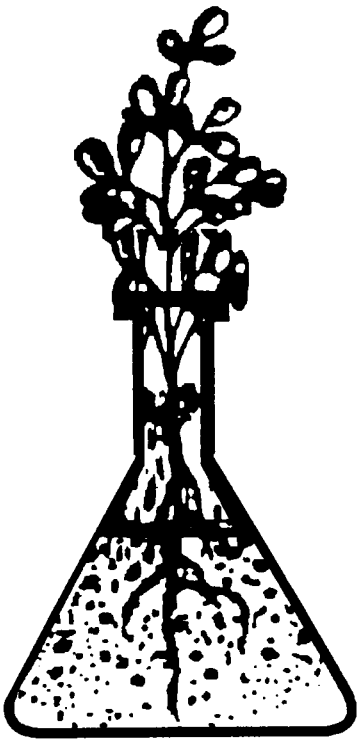
D. A. Horneck, J. M. Hart, K. Topper, B. Koepsell



CONTENTS

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INTRODUCTION

General

This manual describes and documents procedures used in the Oregon State University Soil Testing Laboratory (OSUSTL), and to supply information on the appropriate documentation of these methods. Of the numerous methods for soil analysis, research at Oregon State University indicates that the procedures outlined in this publication are suitable for Oregon conditions.

The Cascade Mountain Range is a natural boundary that separates Oregon into eastern and western sectors. Western Oregon soils tend to be acidic, while the soils in eastern Oregon tend to be slightly acidic or alkaline. In view of these differences, some testing procedures differ for eastern and western Oregon. For example, the phosphorus test for western Oregon requires a dilute acid-fluoride (Bray P1) extraction solution, while sodium bicarbonate is used for samples from eastern Oregon.

Although reference is made to specific scientific supplies and instruments used in the OSUSTL, similar equipment from other manufacturers can be substituted. Mention of a model or brand name is neither an endorsement nor a promotion for the product.

The appendix contains a combination of alternate procedures, seldom used procedures and instructions for standardization of an acid.

Future Considerations

Improving analytical procedures for fertilizer recommendation is an on-going project at the College of Agricultural Sciences, Ag. Experiment Station, Extension Service, Department of Soil Science and the OSUSTL. Consequently, after thorough research, soil testing procedures and methods of reporting are periodically updated. Comments from the farming and university communities, along with suggestions from the fertilizer industry, commercial laboratories, and agriculture consultants are considered. Future topics for research include:

1. Using a volume scoop for routine analyses versus weighing samples.
2. Evaluating a universal extractant, such as Melich III for analyses performed on an ICP.
3. Computerizing of data acquisition from laboratory equipment.

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4. Rewriting the computer program which prints and writes fertilizer recommendations.
5. Compile an annual report that includes data from other soil testing laboratories.

When major analytical changes are accepted, an updated edition of this publication would be made available.

Collection and Preparation of Soil Samples

Collecting soil samples from the field is an integral part of soil testing. Samples must represent the soil in the field from which it is taken. This involves obtaining 20-40 subsamples per sample submitted for analysis. Information on soil sampling is provided in Oregon State University Extension Circular 628, "How to Take a Soil Sample and Why." Sampling instructions are also available at county Extension offices or from OSUSTL.

Samples should be submitted in a standard soil sample bag or in a plastic container. Plastic containers are preferable to metal containers for collecting and mixing soil samples. Contamination may be a problem for boron (B) and zinc (Zn) when samples are collected and stored in certain kinds of paper bags. In the field, extreme care is necessary to avoid contaminating the soil sample with fertilizer or with extraneous materials from the sampling tools.

When the soil samples arrive at the OSUSTL, they are placed on trays and dried in a forced-air drying cabinet at 35 C or lower. Drying at higher temperatures may affect analytical results. Soil samples normally dry in 24 to 48 hours and are then pulverized and sieved with a Custom Laboratory Equipment Co. Dynacrush soil crusher.[1] Soil passing through the 14-mesh (2 mm) stainless steel sieve is returned to the original sample bag and stored for analysis. OSUSTL releases soil test results and fertilizer recommendations immediately after sample analysis has been completed. Soil samples are stored for future reference for 4 to 6 months, then discarded.

Accuracy and Precision

Laboratory instruments are calibrated using standard solutions that are either purchased commercially or mixed by the OSUSTL. Standard soil samples are also maintained as reference samples for evaluating

Documentation of Methods

The analytical methods used in the OSUSTL, including appropriate literature citations, are outlined in the following sections. Modifications of the published methods with respect to changes in reagents or in procedural detail is described under "Comments." Some procedures have been modified to facilitate the use of a continuous-flow analyzer. Since this equipment is not available in all laboratories, alternative procedures are also reported. A general reference for procedures used in analyzing soil is *Methods of Soil Analysis* published by the American Society of Agronomy in Madison, Wisconsin (1982).

Use of ppm

In this manual the use of parts per million (ppm) is meant to be equivalent to milligrams per liter (mg/L) or milligrams per kilogram (mg/kg), with the weight of 1 liter of water equal to 1000 g or 1 kg. General use of ppm follows:

ppm = mg/L = mg L^{-1}
for solids weighed in water

ppm = mg/kg = mg kg^{-1}
for results on a dry weight basis

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contribution made by M. D. Kauffman, S. Roberts, M. Berg, and R. V. Vodraska on the writing of previous editions of this publication. The authors also wish to express their appreciation to the Soil Testing Laboratory personnel for their suggestions and contributions to this manual.

ANALYTICAL METHODS

pH
1:2 soil to water ratio

A. Reagents
Buffer solutions for calibration of pH meter.
Note: The buffer solutions can be purchased if desired.

1. pH 4.005 - 0.05 M potassium biphthalate ($KHC_8H_4O_4$). Dry $KHC_8H_4O_4$ for two hours at 110 C. Dissolve 10.21 g $KHC_8H_4O_4$ in distilled water and dilute the solution to a volume of 1 L with distilled water. As a preservative, add 1.0 mL chloroform or a crystal (about 10 mm in diameter) of thymol per liter of the buffer solution.
2. pH 6.860 - 0.025 M KH_2PO_4 and 0.025 M Na_2HPO_4. Dry the two phosphate salts for two hours at 110 C. Dissolve 3.40 g of KH_2PO_4 and 3.55 g of Na_2HPO_4 in distilled water and dilute the solution to a volume of 1 L with distilled water. As a preservative, add 1.0 mL of chloroform or a crystal (about 10 mm in diameter) thymol per liter of the buffer solution.
3. pH 9.177 - 0.01 M $Na_2B_4O_7$-$10H_2O$. Dry the $Na_2B_4O_7$-$10H_20$ for two hours at 110C. Dissolve 3.81 g in distilled water and dilute the solution to 1 L.
4. Hydrochloric acid, 0.1 N HCl - Dilute 8.3 mL of concentrated HCl to 1 L volume with distilled water.

B. Procedure
1. Scoop 20 cc (g) of dry soil into a 3-oz paper cup or 100 mL beaker.
2. Add 40 mL of distilled water and stir thoroughly.
3. Let stand about 15 min, stir a second time, and allow suspended soil to settle for at least 15 min before reading pH.
4. Calibrate the pH meter according to instrument instructions using two of the prepared buffer solutions. After instrument calibration, rinse the electrodes with 0.1 N HCl and then distilled water to remove any trace of the buffer solutions.
5. Read the pH by placing the electrodes in the supernatant liquid and swirling gently. Record the pH to the nearest 0.1 unit.
6. Rinse the electrodes with distilled water and pat dry between pH determinations.
7. When the meter is not in use, immerse the electrodes in pH 6.860 buffer.
8. pH readings should be made routinely on known standard soil samples, every 15 samples in the OSUSTL.

C. Comments
This method is described by McLean (1982). The one used has a 1:2 soil-water ratio where the pH is measured in the supernatant instead of in the soil suspension, for convenience and to minimize the errors introduced by liquid junction potential.

Buffer solutions should be prepared fresh at least once a month. If solutions are purchased, expiration dates need to be noted. The pH meter needs to be calibrated periodically when making a series of determinations to check for drift. Check samples should also be incorporated into a series of analyses to ensure accurate readings. For pH measurements in soil a combination (single) or a dual electrode can be used. The OSUSTL uses a dual electrode.

Greweling and Peech (1968) indicate that pH may shift slightly with a change in the soil-to-water ratio used in sample preparation. Seasonal fluctuations in pH can also be expected. Soil pH will tend to be lower for samples collected after heavy fertilization. Conversely, pH may increase as the concentration of fertilizer salts decreases. Salt accumulation in soil tends to lower pH, and salt removal by leaching will have the opposite effect of raising pH. Fluctuations in pH due to seasonal or analytical effects may vary from 0.1 to 1.0 pH units.

Soil pH can also be determined using prepared salt solutions; this indicates the effect of salts in the sample. For example, the pH value obtained using 1 N KCl will normally be 1 to 1.5 units lower than the distilled water value. The soil pH measured in 0.01 M $CaCl_2$ will be about 0.4 to 0.8 units lower than in distilled water. Measuring soil pH in these salt solutions has the added advantage of maintaining flocculation which minimizes errors caused by liquid junction potentials.

D. Equipment
1. pH meter with suitable electrode
2. Paper cups

LIME REQUIREMENT
SMP Buffer Method

A. Reagents
1. SMP buffer solution - Using a 1-L volumetric flask, completely dissolve 1.8 g of ground para-nitrophenol in 500 mL distilled water. Add 2.5 mL or 2.8 g of triethanolamine (weigh rather than pipette this viscous liquid). Then dissolve 3.0 g potassium chromate (K_2CrO_4), 2.0 g calcium acetate ($Ca(OAc)_2$-H_2O) and 53.1 g calcium chloride dihydrate ($CaCl_2$-$2H_20$) in the solution. Bring to 975 mL volume with distilled water and stir overnight with magnetic stirrer. Adjust the solution to pH 7.5 with 0.1 N NaOH if necessary. Bring to 1 L volume with distilled water. This solution is usually made in 8 L quantities for convenience.

CAUTION: Trietanolamine and potassium chromate can be hazardous. Read label before use.

2. Sodium hydroxide, 0.1 N NaOH - Dissolve 4.0 g of NaOH pellets in about 500 mL distilled water. Allow to cool to room temperature and bring to 1 L volume.
3. Hydrochloric acid, 0.1 N HCl - Dilute 8.3 mL of concentrated HCl to 1 L volume with distilled water.
4. Phosphate buffer, pH 6.860 - See pH.

B. Procedure

1. Weigh 5.0 g of soil into paper cup or beaker. Generally samples are placed in rows of six to accommodate continuous stirring and reading of samples.
2. Add 5.0 mL of distilled water. Stir (leaving a stir rod in each sample) and allow to soak for 30 min.
3. Standardize the pH meter, described in B.4 of pH Procedure.
4. Add 10 mL of SMP buffer solution and stir every 5 min during the ensuing 20 minute period.
5. Immediately following the final stirring (20 min after addition of SMP buffer solution), insert the electrodes and observe the pH reading of the suspension, swirl gently and observe the subsequent reading. Continue until pH readings are constant, then record the pH reading to the nearest 0.1 unit.
6. Between readings, thoroughly rinse electrodes with distilled water and pat dry.

C. Comments

Reading the pH of the soil-buffer solution between 20 and 25 min after the addition of the SMP buffer is necessary because the pH of the suspension will continue to decrease over time. The electrodes should be rinsed with 0.1 N HCl and distilled water occasionally when making a series of determinations to eliminate increased pH readings caused by contamination of the electrodes.

The method outlined is a modification of the method described by McLean (1982).

D. Equipment

1. pH meter and suitable electrode
2. Paper cups

EXTRACTABLE PHOSPHORUS
Sodium Bicarbonate Method

Note: This method is used for all samples received from east of the Cascade Mountains.

A. Reagents

1. Sodium bicarbonate, 0.5 M $NaHCO_3$ - Using a 1-L volumetric flask, dissolve 42.01 g $NaHCO_3$ in 500 mL of distilled water and make up to volume. Cover and store overnight. Adjust the pH to 8.5 with 1 M NaOH. Cover the surface of the solution with an approximately 1 inch thick film of purified mineral (paraffin) oil to seal the solution from the air. When stored in a glass container, prepare a fresh solution monthly. A longer storage period is acceptable when the solution is stored in a polyethylene container. Check the pH of the solution each month, and adjust the pH if necessary. (See Section D, Comments.)
2. Ammonium paramolybdate - In a 1-L flask dissolve 15.0 g $(NH_4)_6Mo_7O_{24}$-$4H_2O$ in 300 mL of warm distilled water (60C). After cooling, filter the solution if turbidity is evident, adding 342 mL of concentrated HCl gradually while swirling; bring to volume. This solution contains enough concentrated HCl so that a 2 mL aliquot of ammonium paramolybdate solution has sufficient acid to neutralize the NaHCO in a 2 mL aliquot of soil extract.
3. Stannous chloride
   a. Stock solution - Dissolve 10.0 g $SnCl_2$-$2H_2O$ in 25 mL of concentrated HCl. Prepare fresh every two months or less. Use large reagent crystals for preparing the solution rather than fine powder, and store the stock solution in a refrigerator.
   b. Dilute solution - Add 0.5 mL aliquot of the stock solution to 66 mL of distilled water. Prepare this solution fresh daily.
4. Standard phosphate solutions
   a. Standard stock solution (50 ppm P) - Dissolve 0.2195g oven dried KH_2PO_4 in 500 mL distilled water and dilute to 1 L volume.
   b. Standard work solutions - Pipette the following aliquots of 50 ppm P stock solution into 100 mL volumetric flasks. Bring to volume with $NaHCO_3$ extracting solution.

mL stock solution	ppm P work solution
1	0.5
2	1.0
4	2.0
6	3.0
10	5.0

5. Sodium hydroxide, 1 M NaOH - Dissolve 40 g NaOH pellets in 500 mL distilled water and dilute to 1 L volume.

B. Procedure

1. Weigh or scoop 2.0 g of soil into a 50 mL extracting bottle and add 40 mL of $NaHCO_3$ extracting solution.
2. Shake the sample for 30 min, remove the sample from the shaker immediately after it stops. Decant the contents of the bottle into a filter funnel fitted with a Whatman No. 42 or equivalent filter paper. Refilter the extract if it is not clear.
3. Pipette 2.0 mL of the filtrate into a 25 mL colorimeter tube. Automatic pipettes are suitable for dispensing the small volumes used in all of the following steps of this procedure.
4. Add 2.0 mL of ammonium paramolybdate solution to each tube and mix well using a Vortex mixer. Remove all traces of the molybdate solution from the neck of the flask by washing with 5.0 mL of distilled water. Vortex for 5 s.
5. Add 0.5 mL of the dilute $SnCl_2$ solution, mix immediately.
6. Read color intensity in the colorimeter[3] set at a wavelength of 660 nm, at least 10 min but not more than 30 min after addition of the $SnCl_2$ solution.
7. Prepare a calibration curve using steps 3-6, but substitute 2.0 mL aliquots of the 0.5 to 5 ppm P standard solutions for the soil extract. Report the results in ppm P (mg kg^1) in the soil sample.

C. Calculations

ppm P in the soil sample = ppm P in the soil extract x 20

D. Comments

This method for extractable P follows a procedure outlined by Olsen and Sommers (1982) with the following exceptions:

1. The ammonium paramolybdate solution contains sufficient HCl to neutralize the NaHCOa 2 mL aliquot of extractant. This eliminates the step of acidifying the aliquot with H_2SO_4.
2. A colorimeter tube is used for the color development step rather than a volumetric flask.
3. Stannous chloride is used as the reducing agent instead of ascorbic acid.

When P is extracted from soil with a 0.5 M $NaHCO_3$ solution at an approximate pH of 8.5, the concentrations of calcium (Ca), aluminum (Al), and iron (Fe) in solution are maintained at low levels. A decrease in activity or concentration of soluble Ca, Al, and Fe allows extraction of more soluble phosphate.

An increase in shaker speed or temperature of the extractant may cause an increase in P extracted from the sample. Normally, for routine testing, the extraction is performed at room temperature, though it may vary seasonally. The OSUSTL uses a constant-speed reciprocating shaker, which has a 2-inch stroke and operates at 200 oscillations per minute.

When exposed to the atmosphere, $NaHCO_3$-extracting solution increases over time. When pH of the extractant exceeds 8.5, an increase in extractable soil P is anticipated. Spreading a layer of mineral oil spread over the surface of the extracting solution will decrease the rate pH will change. Prolonged storage of the $NaHCO_3$ extractant in glass may also allow a pH increase. When glass storage vessels are used, check the pH of the solution at least monthly; if pH of the solution exceeds 8.5, prepare a new solution.

E. Equipment

1. Spectrophotometer
2. Flow-through cell or cuvettes
3. Extraction bottles
4. Filtration vials
5. Vortex mixer
6. Reciprocating shaker

EXTRACTABLE PHOSPHORUS
Dilute Acid-Fluoride Method (Bray-P1)

Note: This method is used for all samples received from west of the Cascade Mountains, including Hood River County.

A. Reagents

1. Ammonium fluoride, 1 N NH_4F - Dissolve 74 g of NH_4F in distilled water and dilute the solution to 2 L. Store the solution in a polyethylene bottle.
2. Hydrochloric acid, 0.5N HCl - Dilute 103 mL of concentrated HCl to a volume of 2500 mL with distilled water.
3. Extracting solution - Add 1350 mL of 1.0 N NH_4F and 2250 mL of 0.5 N HCl to 45 L of distilled water. This produces a solution of 0.03 N NH4F and 0.025 N HCL. It will keep indefinitely.
4. Standard phosphate solutions

   a. Standard stock solution, 100 ppm P - Dissolve 0.4393 g of oven dry KH_2PO_4 in 500 mL of distilled water and dilute to a volume of 1 L.

   b. Standard work solution - Pipette the following aliquots of 100 ppm stock solution into 100 mL volumetric flasks. Bring to volume with NH_4F extracting solution.

Aliquot mL	ppm P of solution
5	5
10	10
15	15
20	20

B. Procedure

(i) Automated Colorimetric Analysis (OSU Procedure)

1. Weigh 2.9 g (or scoop 2 g) of soil into a 50 mL extracting bottle and add 20 mL of the extracting solution.

2. Shake for 60 sec. and filter immediately using Whatman No. 42 or equivalent filter paper.

3. The concentration of P in the extract solution is determined on a ALPKEM rapid flow analyzer No. RFA-300 which relies on molybdate and antimony in acid to form a complex with ortho phosphate to yield a blue color.

(ii) Manual Colorimetric Analysis

1. Use same procedure as for sodium bicarbonate method.

C. Calculations

ppm P in soil sample = ppm P in soil extract x 7

D. Comments

The dilute acid-fluoride method for P follows a method described by Olsen and Sommer (1982). OSUSTL modifications are a 2.9 g weight used with a 60 second shaking time.

The dilute acid-fluoride extractant tends to dissolve Al and Fe phosphates in soil. The dissolution of Al and Fe phosphates occurs very rapidly and probably results from the fluoride anion complexing these metal cations in the acid solution. Interference in the development of the color complex occurs if appreciable amounts of Al, Fe (excess of 100 ppm), and molybdate are present. The fluoride ion may also interfere with color development when present in excess of 50 ppm. To minimize interferences, standards are made using the extracting solution.

E. Equipment

1. Auto-analyzer or spectrophotometer
2. Reciprocating shaker
3. Filtration vials
4. Extraction bottles

EXTRACTABLE CALCIUM, MAGNESIUM, POTASSIUM, AND SODIUM
Ammonium Acetate Method

A. Reagents

1. Ammonium acetate extracting solution, neutral, 1 N - Commercial ammonium acetate is purchased for ease of handling and to reduce ammonia contamination in the lab. To mix add 77.1 g ammonium acetate per liter of solution, usually mixed in 45 L quantities. This solution does not have to be neutralized as it does when acetic acid and ammonium hydroxide are used.
2. Lithium - lanthanum chloride solution (reagent grade $LaCl_3$-$7H_2O$ and LiCl), dissolve 200 g $LaCl_3$-$7H_2O$ and 50 g LiCl in a 22 L container with 5 L distilled water. Fill to the 22-L mark and mix.
3. Standard solutions

   a. Standard stock solutions. These can be prepared from commercial standard solutions which are available through most chemical suppliers, or can be prepared as follows:
   (i) Calcium (500 ppm Ca) - Dissolve 1.249 g of $CaCO_3$ in 1:1 HCl and evaporate to dryness on a hot plate. Dissolve the residue and bring to exactly 1 L with distilled water.
   (ii) Magnesium (500 ppm Mg) - Dissolve 0.50 g pure Mg ribbon in 1:1 HCl and evaporate to dryness on a hot plate. Dissolve the residue and then dilute to 1L with distilled water.
   (iii) Potassium (500 ppm K) - Prepare a standard solution of K by dissolving 0.9535 g oven dried KCl in a small volume of distilled water and diluting to 1 L with distilled water.
   (iv) Sodium (500 ppm Na) - Prepare a standard solution of Na by dissolving 1.271 g NaCl in a small volume of distilled water and diluting to 1 L with distilled water.
   b. Standard work solutions4 K, Ca, Mg, and Na - Pipette the following aliquots of 500 ppm stock solutions into 100 mL volumetric flasks.

Dilutions of stock solutions for standard preparation.

Flask or	Ca		Mg	
Standard	Aliquot	ppm in	Aliquot	ppm in
No.	mL	solution	mL	solution
1	5	25	1.0	5.0
2	15	75	1.5	7.5
3	25	125	2.0	10.0
4	35	175	2.5	12.5
5	70	350	7.5	37.5

Flask or	Na		K	
Standard	Aliquot	ppm in	Aliquot	ppm in
No.	mL	solution	mL	solution
1	1	5	2	10
2	2	10	3	15
3	4	20	4	20
4	5	25	6	30
5	10	50	12	60

Bring to 100 mL volume with ammonium acetate. Mix thoroughly and store in plastic bottles.

B. Procedure

1. Weigh or scoop 2.0 g of soil into a 50-mL extracting vessel. Add 40 mL of the ammonium acetate extracting solution and place the extracting vessel containing the sample on the shaker for 30 min.
2. Filter through a Whatman No. 40 or equivalent filter paper.
3. K, Ca, Mg and Na. Using a Custom Lab Equipment diluter dispenser or the equivalent, dilute a 0.5 mL aliquot of the sample filtrate with 12 mL of $LaCl_3$-LiCl solution (a 25-fold dilution). Prepare standards by substituting 0.5 mL of standard K, Na, Ca or Mg work solutions for the sample filtrate. The blank is made by diluting the ammonium acetate extracting solution.
4. Calibrate the atomic absorption spectrophotometer[5] with the standard work solutions according to instrument instructions.
5. Report Ca, Mg, K and Na in millequivalents per 100 g, ppm or mg/kg of soil.

C. Calculations

ppm in the soil sample = ppm in the soil extract solution x 20

meq per 100g of sample = ppm in the soil sample divided by equivalent weight (K=390, Ca=200, Mg=120, Na=230)

D. Comments

The procedure for determining extractable cations with neutral 1 N ammonium acetate is a modification of the procedure outlined by Knudsen et al. (1982) for exchangeable K. The modification is the equilibration of a sample with one extracting solution (1:20 ratio of soil to extractant) rather than three different extractions, as specified in the original procedure. A further modification is the dilution of the soil extract with a joint lanthanum chloride and lithium chloride solution.

The single extraction technique for cations in non-calcareous soil results in values which are equivalent to at least 95% of the values obtained by the process of multiple extraction. For samples which contain carbonates of Ca or Mg, the multiple extraction with ammonium acetate may dissolve these carbonates and result in higher values for Ca and Mg than are obtained with a single extraction. However, for purposes of routine soil testing, there is usually no interest in determining the extractable Ca and Mg in alkaline samples which contain free lime.

Interferences caused by refractory compound formation and ionization are minimized by the dilution of the soil extract with lanthanum chloride and lithium chloride, respectively. The addition of lanthanum chloride minimizes the formation of Ca and Mg refractory compounds. Lithium chloride is added for Na and K determinations to minimize ionization interferences. In the past, these have been two separate solutions but it was determined that they could be mixed without sacrificing analytical accuracy. For some samples, the use of this mixture tends to stabilize readings and improve precision.

E. Equipment

1. Atomic absorption instrument
2. Filtration vials
3. Extraction bottles
4. Reciprocating shaker
5. Diluter-dispenser

HOT-WATER EXTRACTABLE BORON
Azomethine H Method

A. Reagents

1. Buffer masking agent - Completely dissolve 250 g ammonium acetate (reagent grade $NH_4C_2H_3O_2$), 25 g tetrasodium salt of ethylene-dinitrillotetraacetic acid (Na_4-EDTA), and 10 g disodium salt of nitrilotriacetic acid (Na_2-NTA) in 400 mL distilled water in a 1-L beaker using a magnetic stirrer. Add 125 mL glacial acetic acid very slowly, while stirring. The temporary acidic conditions may cause a slight precipitation of the EDTA salts. Continue to stir the solution until all the EDTA redissolves. Do not heat the solution. Adjust the buffer to a pH of 5.4 to 5.6 with acetic acid or ammonium hydroxide as necessary. If the spectrophotometer is equipped with an aspirating flow-cell, add six drops of Brij-35 surfactant (ALPKEM) to 250 mL buffer masking agent. Prepare this solution every two months.
2. Azomethine-H solution - Dissolve 0.9 g azomethine-H reagent (Pierce Chemical Co., Rockford, IL) and 2.0 g ascorbic acid ($C_6H_8O_6$) in about 50 mL of distilled water. A hot tap water bath facilitates dissolution. Bring to 100 mL volume with distilled water. Prepare this solution fresh daily.
   Note: Azomethine-H reagent may also be prepared in the laboratory.
3. Calcium chloride extracting solution, 0.02 M - Dissolve 2.84 g calcium chloride dihydrate ($CaCl_2$-$2H_2O$) in about 700 mL distilled water, then bring to one liter volume. Store in plastic container.
4. Boron standard solutions - All standard solutions should be stored in plastic bottles.
   a. Standard solution I, 500 ppm B - Pipette 5.0 mL of 5000 ppm aqueous boron standard solution (available commercially) into a 50 mL volumetric flask. Bring to volume with distilled water. A 500 ppm B standard solution can also be prepared by dissolving 0.8820 g oven-dry re-crystallized sodium tetraborate (reagent $Na_2B_4O_7$-$10H_2O$) in distilled water and diluting to 200 mL.
   b. Standard solution II, 5 ppm B - Pipette 5.0 mL of standard solution I (500 ppm B) into a 500 mL volumetric flask. Bring to volume with distilled water.
   c. Standard work solution - Prepare work solutions by pipetting the following aliquots of standard solution II (5 ppm B) into 100 mL volumetric flasks. Bring to volume with $CaCl_2$ extracting solution.

mLs Stock II (5 ppm B)	Standard Work Solution (ppm B)
4	0.20
8	0.40
12	0.60
20	1.00
28	1.40
40	2.00

B. Procedure

1. Weigh or scoop 15 g of soil into a sealable plastic bag (heat sealed boilable bags or ziplock freezer bags work). Add 30 mL of $CaCl_2$ extracting solution.
2. Place plastic bags into boiling water and leave for 10 min. The OSUSTL uses a porcelain canning pot with cover.
3. Remove plastic bags, let cool to room temperature and filter the contents through a Whatman No. 42 or equivalent filter paper.
4. Pipette 4.0 mL of soil extract into a 12 mL polyethylene sample vial.
5. Add 1 mL of buffer masking agent and vortex.
6. Add 1 mL of azomethine-H solution and vortex. Allow color to develop for at least 1 hour but no longer than 3 hours.
7. Prepare standard curve following steps 4-6, substituting 4.0 mL of standard work solution for soil extract. A blank is prepared in the same manner using 4.0 mL $CaCl_2$ extracting solution instead of the soil extract.
8. For samples with a yellow extract: Prepare a second sample solution and blank following steps 4 and 5. Add 1.0 mL of distilled water in place of azomethine-H solution and vortex well. The blank for this determination consists of 5.0 mL $CaCl_2$ extracting solution and 1.0 mL buffer masking agent.
9. Read all color intensities on a spectrophotometer set at 420 nm. Read immediately after vortexing.

C. Calculations

ppm B in soil = (ppm B extract - ppm B in yellow extract) x2

D. Comments

A method described by Bingham (1982) is used here with adaptation to the use of plastic bags as described by Mahler et al. (1983). It was determined that plastic bags are more suitable and less expensive than boron free glassware, which is no longer obtainable. The pH of the buffer was originally prescribed as 5.2, but 5.4 to 5.6 is adequate. Further reductions in pH only increases the difficulty of keeping the EDTA in solution.

The EDTA and NTA chelates eliminate interferences from Al, Fe, and Cu. The concentration of these chelates should be effective for levels of these elements commonly found in soil extracts.

The azomethine-H should be added quickly so that time for color development is equal for all tubes. A constant check must be maintained on linearity and drift of the standard curve when analyzing a large batch of samples. Correction for a yellow extract as described here is probably legitimate for only

a mild yellow color and is insufficient for some of the deep brown or yellow extracts occasionally obtained. For these ICP analysis is preferable. Acid washing of all glassware is recommended to minimize the potentials for boron contamination.

D. Equipment

1. Spectrophotometer
2. Flow through cell or cuvettes
3. Filtration vials
4. Hot plate and boiling container with cover
5. Vortex stirrer

ORGANIC MATTER
Walkley-Black Method

A. Reagents

1. Potassium dichromate, 1 N $K_2Cr_2O_7$ - Dissolve 49.04 g of reagent grade $K_2Cr_20_7$ in 500 mL distilled water and dilute the solution to a volume of 1 L.
2. Ferrous ammonium sulfate, 0.4 N $Fe(NH_4)_2(SO_4)_2$-$6H_2O$ - Dilute 40 mL concentrated H_2SO_4 in 500 mL distilled water. Dissolve 159.6 g $Fe(NH_4)_2(SO_4)_26$-H_2O in the acid solution; cool the solution and dilute it to a volume of 1 L. Determine the normality periodically by titrating against the $K_2Cr_2O_7$ solution. Store in opaque bottle as light affects this solution.
3. O-phenanthroline ferrous sulfate complex indicator, 0.025 M-This solution is also referred to as 1,10 phenanthroline iron (II) sulfate and is commercially available under the trade name "Ferroin."
4. Phosphoric acid, 85 percent, H_3PO_4.
5. Sulfuric acid, concentrated, not less than 96 percent H_2SO_4.

B. Procedure

1. Pass the soil sample through a 0.5 mm sieve and weigh out 0.50 g of soil into a 500-mL Erlenmeyer flask.
2. Add 10 mL of 1 N $K_2Cr_2O_7$ solution and swirl the flask to gently disperse the soil in the solution. Take care not to throw sample onto sides of flask.
3. Rapidly add 20 mL of concentrated H_2SO_4. Swirl for 10 seconds. Let cool uniformly to room temperature, at least 20 min. 4. Dilute to approximately 150 mL with distilled water and add 10 mL of concentrated H_3PO_4. The addition of H_3PO_4 is optional and the OSUSTL omits this step for routine analysis.
5. Add 6 drops of O-phenanthroline indicator to the solution. Titrate with the ferrous ammonium sulfate solution (FAS) until the color changes from yellow or yellow-green to blue to finally a reddish brown endpoint. Record the volume (mLs) of FAS used to reach the endpoint.
6. Analyze a blank simultaneously following steps 2-5.

C. Calculation

Calculate the percent organic matter as follows:

$$\%OM = (\text{Blank-reading}) \times \frac{13.6}{\text{blank}}$$

Calculate the percent organic carbon as follows:

$$\%OC = \%OM \times 0.58$$

D. Comments

The wet oxidation method for determining organic matter in soil is the same method as described by Nelson and Sommers (1982). The only modification involves the use of the O-phenanthroline in place of the diphenylamine indicator.

Grinding of the soil sample to pass a 0.5 mm sieve facilitates obtaining a representative subsample, increasing surface area and ridding the sample of ground plant material. If more than 75% to 80% of the total dichromate reagent is reduced by the oxidizable material in the sample, the entire analysis must be repeated using a smaller soil sample.

The soil is digested with the dichromate and sulfuric acid mixture by the heat of dilution. For precise results the sulfuric acid should be added rapidly and the flasks should be cooled uniformly. Once these steps are accomplished, variations in reaction time from 20 to 40 min do not appreciably affect the results.

For soils or other materials high in organic matter, the organic matter content may be more accurately determined using the Ignition method presented in the Appendix.

E. Equipment

1. Titration apparatus
2. Lighted stirring plate

SOLUBLE SALTS
Electrical Conductivity Method

A. Reagent

1. Potassium chloride reference solution, 0.01 N KCl - Dissolve 0.7456 g of KCl in distilled water and dilute the solution to a volume of 1 L at 25 C. This solution has a conductivity of 1.4118 mmhos per cm (ds/m).

B. Procedure

1. Place 30 to 50 mL of soil in a 10 oz paper cup; add distilled water while stirring to prepare a saturated soil paste. (At saturation, the soil paste glistens as it reflects light and it flows slightly when the container is tipped. The paste slides freely and cleanly off the spatula unless the soil has a high clay content.)
2. Allow the saturated soil to stand at least 30 min. Then ascertain that the above criteria for saturation are still evident. Free water should not collect on the soil surface, nor should the paste stiffen markedly or lose its glisten. Remix the sample, if necessary, by adding either additional water or soil to obtain a saturated paste.
3. Transfer the saturated soil paste to a Buchner funnel fitted with a Whatman No. 42 filter. By vacuum filtration[6], collect an aliquot of the saturation extract in a 25 mL receiving flask.
4. Using the reference solution, calibrate the conductivity meter[7] according to instrument instructions.
5. Record the electrical conductivity (EC) reading for the saturation extract when it has reached the same temperature as the reference solution.

C. Comments

The procedure for determining total soluble salts follows closely a method described by Rhoades (1982b). For an appraisal of soil salinity, the extraction can usually be made a few minutes after the saturated paste is prepared. The recommended time lapse between preparation of the soil paste and extraction is several hours for gypsiferous samples and from 4 to 16 hr in all cases where the chemical constituents are to be determined in the extract. Determination of chemical constituents in the extract requires a larger soil sample (200-400 g soil) than for soluble salts alone. If the initial filtrate is turbid, it can be discarded or refiltered through a clean sheet of filter paper.

The Solu-Bridge used in the OSUSTL is designed specifically for determining the conductivity of saturation extracts. When the compensator dial is set on the temperature of the solution, the conductivity dial at balance indicates directly the electrical conductivity at 25 C. A calculation to obtain the result is unnecessary.

E. Equipment

1. Conductivity meter
2. Suction filtration apparatus

CATION EXCHANGE CAPACITY (CEC)
Ammonium Acetate Method

A. Reagents

1. Ammonium acetate extracting solution, neutral, 1 N - Prepare according to the specifications outlined in the ammonium acetate method for extractable cations.
2. Ethanol, 95%
3. Hydrochloric acid, 0.1 N HCl - Dilute 8.3 mL of concentrated HCl reagent to 1 L with distilled water.

B. Procedure

1. Weigh 10 g of soil into a 125 mL Erlenmeyer flask; add 50 mL of ammonium acetate solution and place the flask containing the sample on the shaker for 30 min.
2. Connect a 1-L vacuum extraction flask to a Buchner funnel fitted with a Whatman No. 5 or equivalent filter paper. Moisten the filter paper with distilled water.
3. Transfer the soil suspension into the Buchner funnel and leach the sample with 175 mL of 1 N ammonium acetate. This soil extract may be analyzed for extractable K, Ca, Mg, and Na.
4. Rinse the excess ammonium acetate from the soil sample in the Buchner funnel by leaching with a total volume of ethanol and discard the leachate. Note: Be sure to gently fill funnel to remove all excess ammonium and allow it to drain until only damp soil remains. Continue adding alcohol in this manner until 200 mL of ethanol has been used.
5. Change to a clean 500-mL suction flask and leach the soil sample with 225 mL of 0.1 N HCl to replace the exchangeable ammonium. Bring leachate to volume in a 250 mL volumetric flask using distilled water.
6. The concentration of ammonium-N in the final leachate is determined with an ALPKEM rapid flow analyzer (RF-300), which relies on ammonium to complex with salicylate to form indophenol blue (Technicon Method No. 334-74A/A). This color is intensified with sodium nitroprusside and measured at 660 nm. This determination can also be made using the Kjeldahl distillation method (see Appendix).

C. Calculation

$$\text{CEC in meq per 100 g of soil} = (\text{ppm } NH_4\text{-N in leachate}) \times \frac{0.25}{14} \times \frac{100}{\text{sample size (g)}}$$

ppm NH_4-N in leachate is determined using a standard curve.

D. Comments

The procedure used is essentially the same as that of Schollenberger (1945) except that determination of NH_4-N is done spectrophotometrically rather than by Kjeldahl distillation and titration. To determine the NH_4-N content using the Kjeldahl distillation method, follow steps 1-5 above, then proceed to Appendix. Care must be taken not to allow soil to dry and

crack between alcohol leachings, as this could result in incomplete removal of excess NH_4-N. A similar procedure is described by Rhoades (1982a).

E. Equipment

1. Buchner funnels and source of vacuum
2. Auto analyzer or Kjeldahl distillation equipment
3. Vacuum flasks

TOTAL NITROGEN (TN)
Kjeldahl Method

A. Reagents

1. Sulfuric acid, concentrated H_2SO_4 - reagent grade
2. Digestion catalyst - Mix together 1000 g of ground sodium sulfate (reagent anhydrous Na_2SO_4) or potassium sulfate, 25 g cupric sulfate (reagent anhydrous $CuSO_4$), and 10 g of reagent selenium (Se) powder. Packets of prepared catalyst can be purchased.

CAUTION: DO NOT BREATHE $CuSO_4$ and Se dust..

B. Procedure

1. Weigh 3.0 g of soil into a 75 mL volumetric digestion tube. Use 1.0 g of soil if sample is greater than approximately 20% in organic matter.
2. Add a 3 g scoop of digestion catalyst and mix thoroughly with the dry soil.
3. Add 10 mL of concentrated H_2SO_4 to the soil-catalyst mixture. ***Note: It is essential that all dry material be completely moistened and well mixed with the acid to insure complete digestion.***
4. Prepare a blank with each set of samples analyzed by following steps 2-3 above using no soil. Allow the samples and blank to stand overnight.
5. Place tubes on a digestion block[8] at 150 C. Check samples every 20 min for foaming. After one hour (or more if foaming persists), raise temperature to 250 C, and continue digestion for one hour. After one hour at 250 C raise temperature to 350 C and heat until samples are completely digested, usually about two additional hours. At completion, mineral soils will be greyish-white while organic soils will be blue-green in color.
6. Remove samples from block and leave under a fume hood until cool. Then add 10-20 mL distilled water to each tube to keep samples from hardening.
7. The ammonium-N content of the digest solution is determined with an ALPKEM rapid flow analyzer (RF-300) which relies on ammonium to complex with salicylate to form indophenol blue (Technicon Method No.334-74A/A). This color is intensified with sodium nitroprusside and measured at 660 nm. This determination can also be made using the Kjeldahl distillation method (see Appendix). For samples to be analyzed on an auto analyzer, continue with steps 8-9 and determine total N using calculation in Part C.
8. Bring samples to volume with deionized water in 75 mL digestion tubes and mix.
9. Obtain a clear digest solution for analysis either by allowing samples to settle overnight and pipetting an aliquot or by filtering through an acid washed filtering apparatus fitted with Whatman No. 042 or equivalent filter paper. Digest solutions may be refrigerated prior to analysis.

C. Calculation

$$\%\ \text{Total Nitrogen} = (\text{ppm } NH_4^+\text{-N in digest solution}) \times \frac{75\ \text{mL}}{\text{sample size (g)}} \times \frac{1}{10{,}000}$$

D. Comments

The Kjeldahl method outlined by Bremner and Mulvaney (1982) is modified by eliminating the water from the digestion step. One further modification is the determination of NH_4-N spectrophotometrically rather than by Kjeldahl distillation and titration. To determine the NH_4-N concentration using the Kjeldahl distillation method, follow steps 1-6 and then proceed to Appendix.

E. Equipment

1. Digestion block
2. Digestion tubes
3. Autoanalyzer or Kjeldahl distillation unit

AMMONIUM AND NITRATE NITROGEN
KCl Extraction Method

A. Reagents

1. Potassium chloride extracting solution, approximately 2 N KCl - Dissolve 150 g of reagent KCl in 500 mL distilled water and dilute to a volume of 1 L.

B. Procedure

1. Place 20 g of soil into a 250 mL extracting bottle and add 75 mL of 2 N KCl extracting solution. ***Note: If using the Kjeldahl distillation method, add 150 mL of extracting solution.*** Shake the vessel on a mechanical shaker for one hour. Remove from shaker and allow the soil-KCl suspension to settle (about 30 min).
2. Filter the extract solution through Whatman No. 42 or equivalent filter paper. To minimize contamination by filter paper, it is first leached with 20-50 mL of KCl solution. If the extract cannot be analyzed on the same day as prepared, store in a refrigerator or freezer until analysis can be performed.
3. The ammonium-N content of the extract is determined with an ALPKEM rapid flow analyzer (RF-300) which relies on ammonium to complex with salicylate to form indophenol blue (Technicon Method No. 334-74A/A). This color is intensified with sodium nitroprusside measured at 660 nm. This determination can also be made using the Kjeldahl distillation method (see Appendix).

4. The nitrate-N content of the extract is determined with an ALPKEM rapid flow analyzer (RF-300) which reduces nitrate to nitrite via a cadmium reactor then complexes nitrite with sulfanilamide and N-(1-Napthyl)-ethylenediamine dihydrochloride to form a red-purple color that is measured at 540 nm (Technicon Method No. 329-74W/A). This determination can also be made using the Kjeldahl distillation method (see Appendix).

C. Calculation

ppm NH_4-N or NO_3-N in soil sample =
(ppm NH_4-N or NO_3-N in filtrate x 3.75)

D. Comments

The method outlined by Keeney and Nelson (1982) for determining ammonium and nitrate-N is used with a modification in which 75 mL of KCl and 20 g of soil are used instead of 100 mL and 10 g soil. To determine NH_4-N or NO_3-N concentration using the Kjeldahl method, follow steps 1-2 and then proceed to Appendix.

The extended period of shaking the soil sample with 2 N KCl according to the specifications of Bremner's original procedure permits the simultaneous extraction of ammonium and nitrate.

E. Equipment

1. Autoanalyzer or Kjeldahl distillation apparatus
2. Reciprocating shaker
3. Filtration Vials
4. Extraction Bottles

EXTRACTABLE ZINC, COPPER, AND MANGANESE
DTPA Method

A. Reagents

1. Diethylenetriaminepentaacetic acid, 0.025 M DTPA - Mix 9.83 g DTPA in glass-distilled water and dilute to a volume of 1 L.
2. Triethanolamine, 0.5 M TEA - Mix 74.60 g TEA in glass-distilled water and dilute to a volume of 1 L.
3. Calcium chloride, 0.05 M $CaCl_2$ - Dissolve 5.55 g anhydrous $CaCl_2$ in glass-distilled water and dilute to 1 L.
4. DTPA extracting solution, 0.05 M DTPA, 0.1 M TEA, and 0.01 M $CaCl_2$ - Combine reagents from steps 1, 2, and 3, and dilute to 5 L with glass-distilled water. Adjust the resulting solution after it has set for 12 hr to pH 7.3 with concentrated HCl. Two mL of concentrated HCl is needed to change the pH of the DTPA solution 0.1 units. Store the solution in the refrigerator.
5. **Standard solutions**

a. Standard stock solutions - These are easily made from commercial standard solutions which are available through most chemical suppliers, or can be prepared as follows:
(i) Zinc (100 ppm Zn) - Weigh 0.1000 g of pure Zn metal (30-mesh, analytical reagent) into a 1-L volumetric flask. Add 50 mL of Zn-free water and 1 mL of concentrated H_2SO_4. When the Zn has dissolved, make to volume with DTPA extracting solution.
(ii) Copper (100 ppm Cu) - Dissolve exactly 0.1000 g of pure metallic Cu in 15 mL of 3 N HNO_3 at room temperature in a covered 125-mL Erlenmeyer flask. When the solution has cooled, add 1 mL of concentrated H_2SO_4 and evaporate the solution cautiously until SO_4 fumes are evolved. Cool the solution again; dilute it cautiously with 10 to 15 mL of glass distilled water and again evaporate until it fumes SO_4. Finally, when the solution has cooled, dilute it cautiously with water, transfer it quantitatively to a 1-L flask and dilute the solution to volume with DTPA extracting solution.
(iii) Manganese (100 ppm Mn) - Dissolve 0.2880 g of dry, pure $KMnO_4$ in about 250 mL of H_2O in a 1-L beaker. Add 20 mL of 18 N H_2SO_4; heat the solution to boiling. Add solid Na_2SO_4 until the color of permanganate disappears (avoid a large excess of Na_2SO_4) and boil off the SO_2. Cool the solution, transfer to a 1-L volumetric flask, and bring to volume with DTPA extracting solution.

b. Standard work solutions - Prepare standard work solutions by pipetting the following amounts of 100 ppm standard stock solutions into 100 mL volumetric flasks and diluting to volume with DTPA extracting solution:

Dilutions of stock solutions for metal standard preparation.

Zn		Cu		Mn	
mL 100 ppm Zn	ppm Zn in solution	mL 100 ppm Cu	ppm Cu in solution	mL 100 ppm Mn	ppm Mn in solution
0.5	0.50	1.0	1.00	1.0	1.00
1.0	1.00	2.0	2.00	3.0	3.00
3.0	3.00	5.0	5.00	9.0	9.00

B. Procedure

1. Weigh 10 g of soil into a 125 mL Erlenmeyer flask.
2. Add 20 mL of DTPA extracting solution.
3. Shake on mechanical shaker for two hours at a speed fast enough to keep soil in suspension.
4. Immediately filter through a Whatman No. 42 or equivalent filter paper. Refilter if filtrate is cloudy.
5. Calibrate the atomic absorption spectrophotometer in accordance with instrument instructions using the prepared standard work solutions. The blank is DTPA extracting solution.
6. Determine the concentration of Zn, Cu, and Mn in the filtrate and report as ppm metal in the soil on a dry weight basis.

C. Calculations

ppm Zn in soil sample = ppm Zn in soil extract x 2

D. Comments

The following precautions are essential to avoid problems of contamination in conducting analyses: (1) All solutions should be prepared with glass-distilled water; (2) All glassware is rinsed with .5 N HCl and then rinsed with glass-distilled water; (3) The filter paper should be checked continuously for presence of zinc, copper, and manganese by analyzing a blank that has been filtered.

The DTPA soil test was developed to measure the availability of zinc, copper, manganese, and iron for plant uptake (Lindsay and Norvell, 1978). Since there have been few reported iron deficiencies in Oregon, the OSU soil testing lab does not routinely measure this nutrient in the extract.

E. Equipment

1. Filtration vials
2. Extraction bottles
3. Reciprocating shaker
4. Atomic absorption spectrophotometer

SULFATE SULFUR (SO_4-S)
Ion Chromatograph Method

A. Reagents

1. Standard sulfate-S solutions

   a. Standard stock solution, 100 ppm SO_4-S - Dissolve 0.5434 g of oven dry potassium sulfate (K_2SO_4) in 500 mL distilled water and dilute to a volume of 1 L.

   b. Standard working solutions - Prepare work solutions by pipetting the following aliquots of 100 ppm SO_4-S stock solution into 100 mL volumetric flasks. Bring to volume with calcium phosphate extracting solution. The standards are adjusted to suspected concentration of the samples being analyzed. For example, if a sample has a concentration of 3 ppm (.3 ppm in extract) then a standard curve may be developed at .1, .3, .7, and 2 ppm SO_4.

mL 100 ppm stock solution	ppm SO_4-S in work solution
1	1
3	3
7	7
10	10
20	20

2. Calcium phosphate extracting solution, 500 ppm PO_4 - Dissolve 2.17 g calcium phosphate ($Ca(H_2PO_4)_2$) in 500 mL distilled water and dilute to 1 L volume.

B. Procedure

1. Extraction of SO_4-S

   a. Weigh 5 g of soil into a 100 mL glass or plastic bottle.

   b. Add 50 mL of extracting solution and shake vigorously enough to keep soil suspended for 1 hr.

   c. Filter through Whatman No. 42 filter paper (or equivalent).

2. Determination of SO_4-S Inject 50 uL of extract into ion chromatograph (dionex 2000i) equipped with AS4A anion exchange column with flow rate set at 2 mL per min. The sulfate peak elutes between 6 and 8 minutes.

C. Calculations

Peak height is integrated by computer and compared to known standards to yield concentration of SO_4 in the extraction solution.

Soil concentration in ppm SO_4 is then calculated by multiplying solution concentration by ten.

D. Comments

The use of an ion chromatograph for sulfate analysis has been shown to be comparable to the methylene blue method (Dick and Tabatabai, 1979). The use of an ion chromatograph also yields greater precision and accuracy than other procedures, especially at low concentrations. The methylene blue method, recommended if access to an ion chromatograph is not available, is described in the Appendix.

EXCHANGEABLE SODIUM
Ammonium Acetate Displacement Method[9]

A. Reagents

1. Ammonium acetate extracting solution, neutral, 1 N - Use the same solution prepared for determining ammonium acetate extractable cations.
2. Standard solution, 500 ppm sodium (Na) - Use the same solution which was prepared for determining ammonium acetate extractable Na in the extractable cations section.

B. Procedure

1. Weigh 5 g of soil into a 50-mL plastic centrifuge tube.
2. Add 10 mL of distilled water.
3. Shake by hand three or four times during a 5 to 10-min period to mix.
4. Centrifuge to clarify. Decant supernatant liquid into a paper cup. Test conductivity of supernatant liquid. If over 1.1 mmhos/cm, add 10 mL of distilled water and repeat dilutions until conductivity is below 1.1.
5. Using a stainless steel spatula to loosen the soil in the tube, quantitatively transfer the soil into a 125-mL Erlenmeyer flask using exactly 100 mL of ammonium acetate extracting solution.
6. Swirl every five minutes during a half-hour period.
7. Filter through a Whatman No. 40 or equivalent filter paper.
8. Determine the concentration of Na in the soil extract by the same atomic absorption procedure used to determine ammonium acetate extractable Na.
9. Report the results as exchangeable Na in milliequivalents (meq) per 100 g of soil.

C. Calculations

meq of exchangeable Na per 100 g of soil sample =
ppm of Na in extract x 0.087 (x additional dilution if necessary)

D. Comments

All soil samples should be washed at least once with distilled water to remove any soluble Na. After most of the soluble Na is removed by washing, the conductivity of the wash water should be reduced to approximately 0.9 to 1.1 mmhos/cm (ds/m). The ammonium acetate extractable Na is determined and regarded as an estimate of exchangeable Na. An estimate of exchangeable Na in conjunction with the value for cation exchange capacity serves as a basis for predicting the quantity of soil amendments needed to reclaim sodic soils.

EXCHANGEABLE HYDROGEN
Barium Chloride-Triethanolamine Method

A. Reagents

1. Buffer solution, approximately 0.5 N barium chloride ($BaCl_2$-$2H_2O$) and 0.2 N triethanolamine (TEA) - Prepare the following solutions (a and b) and mix together. Protect the buffer solution from CO_2 contamination by storing in a tightly closed plastic container or attaching a tube containing soda lime to the air intake.
   a. TEA, 0.4 N - Mix 50 mL (56.3 g) of TEA (specific gravity 1.125, about 8N) in 500 mL of distilled water. Partially neutralize the pH to 8.1-8.3 using approximately 150 mL of 1.0 N HCl. Dilute this solution to a volume of 1 L with distilled water.
   b. BaCl2, 1.0 N - Dissolve 125 g $BaCl_2$-$2H_2O$ in 500 mL distilled water and then dilute to a volume of 1 L.
2. Replacement solution, 0.5 N $BaCl_2 2H_2O$ in dilute buffer solution - Dissolve 250 g of $BaCl_2$-$2H_20$ in 2 L of distilled water and dilute to a 4 L volume. Then mix with 20 mL of buffer solution (Reagent 1).
3. Hydrochloric acid, 0.3 N HCl, standardized - Dilute 24.9 mL of reagent concentrated HCl to 1 L with distilled water. Standardize against 0.1000 N sodium carbonate (Na_2CO_3) or 0.1000 N sodium hydroxide (NaOH). These standard base solutions are available through most chemical suppliers, or can be prepared from pure, dry reagent Na_2CO_3 or NaOH. See Appendix for general standardization procedure.
4. Mixed indicator - Dissolve 0.1 g of bromocresol green and 0.02 g of methyl red indicators in 75 mL of 95% ethyl alcohol, then bring to 100 mL volume.

B. Procedure

1. Place at least 10 g of soil in a 125-mL Erlenmeyer flask. *Note: With soils having very high acidity, use 5 g and adjust calculation accordingly.*
2. Add 25 mL of buffer solution and swirl the flask occasionally during a 30-minute period to mix the sample suspension.
3. Fit a Buchner funnel which contains a Whatman No. 42 or equivalent paper to a 500-mL vacuum extraction flask. Moisten filter paper with a small amount of buffer solution.
4. Transfer the sample suspension to the Buchner funnel using an additional 25 mL of buffer solution to completely remove sample from the original 125-mL Erlenmeyer flask. Adjust the filtration rate so that this filtration step requires at least 30 min.
5. When the buffer solution has leached through and only damp soil remains, leach the soil sample with an additional 100 mL of the replacement solution (Reagent 2) by repeatedly adding small increments of the solution to the sample in the funnel.
6. When leaching is completed, remove suction flask and add 10 drops of mixed indicator to the filtrate. Titrate with standardized 0.3 N HCl to a faint pink endpoint. Record the mLs of acid used to reach the endpoint.
7. Titrate a blank solution which contains 50 mL of buffer solution to the same endpoint selected for the sample. The blank determination serves as a reference for the calculation.

C. Calculation

Calculate the result as follows from the volume of standardized HCl used:

Exchangeable hydrogen in meq per 100 g of soil sample =

$$\frac{(\text{mL HCl}_{\text{blank}} - \text{mL HCl}_{\text{sample}}) \times \text{N HCl} \times 100}{10\ (\text{g of sample})}$$

D. Comments

The $BaCl_2$-TEA method for determination of exchangeable H as described by Thomas (1982) is followed except for the following modifications:

1. 0.3 N HCl is used instead of 0.2 N HCl.
2. After addition of 25 mL buffer solution into 10 g of soil, the flask is occasionally swirled over a 30 minute period rather than allowing the mixture to stand for 1 hour.
3. Only 25 mL of additional buffer solution is added to remove sample from the original 125-mL Erlenmeyer flask instead of 75 mL of buffer solution.
4. The mixed indicator is slightly different.

This procedure is used as a research tool and is not performed on a routine basis in the OSUSTL.

At the endpoint of the titration, the mixed indicator changes from blue-green through violet and finally to pink. Any stage of the progressive color change may be selected as the endpoint; but the blank and the samples must be titrated to the same endpoint.

The $BaCl_2$-TEA extraction estimates the total "potential" acidity which may be related to a potential liming level and a potential CEC. Thomas suggested the use of a KCl extraction method which estimates the neutral and salt-exchangeable acidity. The KCl method is thought to be related to the immediate need for lime and an existing CEC.

E. Equipment

1. Extraction flasks
2. Buchner funnels
3. Vacuum source
4. Titration equipment

CARBONATE
Titrimetric Method

A. Reagents

1. Hydrochloric acid, 2 N HCl - Add 167 mL of concentrated HCl to about 700 mL of distilled water and then dilute to a volume of 1 L.
2. HCl, 1 N - Add 83 mL of concentrated HCl to about 700 mL of distilled water and then dilute to a volume of 1 L.
3. HCl, 0.1 N standardized - Dilute 8.3 mL of concentrated HCl to a volume of 1 L with distilled water. See Appendix for general standardizing instructions.
4. Potassium hydroxide, 2 N KOH - Dissolve 132 g of KOH (85%) in about 700 mL of distilled water and dilute to a volume of 1 L. Protect the solution from atmospheric CO_2 by storing in a tightly stoppered bottle.
5. Bromocresol green indicator - Dissolve 0.1 g of bromocresol green in 100 mL of 95% ethanol.
6. Phenolphthalein indicator - Dissolve 0.05 g of phenolphthalein in 50 mL of ethanol. Add 50 mL of distilled water and mix well.

B. Procedure

1. Weigh 3.0 g of soil into a 250-mL Erlenmeyer flask (or 8 oz French square bottle). If the needle-puncture stopper pops off the glass tube following the addition of the 2 N HCl (Step 4), use 2.0 g of soil. The amount of soil can be further reduced if needed, to as little as 0.5 g. If the stopper pops when using 0.5 g of soil, use the $CaCO_4$ equivalent procedure used for liming materials, in Appendix.
2. Connect a 5.0 mL beaker to the glass tube below the stopper about 5 mm above the lower end of the tube. Pipette 4.0 mL of 2 M KOH into the 5.0 mL beaker.
3. After stoppering the flask, remove 50 mL of air from the flask via the needle-puncture stopper using a 50-mL gas syringe. Be sure the stopper has been resealed.
4. Inject 20 mL of 2 N HCl into the flask via the needle-puncture stopper with a 20 mL syringe. Be sure stopper has resealed. Swirl the flask gently to mix contents, being careful not to spill the KOH.
5. Allow the flask to stand at room temperature (20-25 C) for 16 to 24 hrs. Then quantitatively transfer the contents of the 5.0 mL beaker into a 125-mL Erlenmeyer flask using 50 mL of distilled water.
6. Add 6 drops of phenolphthalein indicator to the flask and titrate with 1 N HCl until the pink color begins to fade. At this point, titrate with 0.1 N HCl until the solution turns colorless. It is advisable to do one sample at a time, as the pink color of the phenolphthalein tends to fade with time.
7. Add 8 drops of bromocresol green indicator and titrate with the standardized 0.1 N HCl to a pale-yellow endpoint.
8. Determine a blank by following the procedures in the above analysis except do not add soil.

C. Calculations

Inorganic carbonate expressed as percent $CaCO_3$ =

$$\frac{[(\text{mL HCl}_{\text{sample}} - \text{mL HCl}_{\text{blank}}) \times \text{N} \times 0.100]}{\text{wt. of soil sample}} \times 100$$

where mL HCl refers to the amount of acid titrated following the addition of the mixed bromocresol green indicator.

D. Comments

This method follows the same procedure as presented by Bundy and Bremner (1972), except 4 mL of KOH is used instead of 3 mL KOH; N-octyl alcohol is not used and the bromocresol green indicator is made up with ethanol rather than NaOH. These changes should not significantly affect the results.

This procedure determines total carbonate which may be present in compounds such as calcium carbonate, magnesium carbonate and various bicarbonates.

MINERALIZABLE NITROGEN
Anaerobic Incubation

A. Reagents

1. Potassium chloride, 2 N KCl - Dissolve 150.0 g of KCl in about 500 mL distilled water and dilute to a volume of 1L.

B. Procedure

1. Using a sample splitter, obtain a soil sample of at least 20 g. Weigh 20.0 g of sample into a 125-mL extraction bottle.
2. Add 25.0 mL of distilled water and stir well with a glass rod to insure that the soil is completely wet. Add another 25.0 mL of distilled water to rinse glass rod and side of jar.
3. Place a sheet of parafilm, then a layer of plastic wrap over the mouth of the bottle and tightly secure the lid. Place in an incubator set at 40 plus or minus 0.5 C for 7 days (168 hr).
4. Remove samples from incubator and carefully add 50.0 mL of 2 N KCl. Replace the plastic covers and tighten lid securely.
5. Shake briskly to disperse the soil and place on a mechanical shaker for 1 hour. Filter through a Whatman No. 42 or equivalent filter paper into acid-rinsed filter vials.
6. Determine the NH_4-N content of the extract solution from the incubated sample on an automated colorimetric analyzer. This determination can also be made using the Kjeldahl distillation-titration method, described in Appendix.
7. Determine the initial NH_4-N (reference) content in the soil by following steps 1-2 and 4-6 above.

C. Calculations

ppm mineralizable NH_4-N = (ppm NH_4-N in incubated extract - ppm NH_4-N in reference extract) x 5

D. Comments

This procedure is a modification of the anaerobic incubation described by Keeney (1982). Sample size has been increased from 5 to 20 g. A 125-mL screw-top extracting bottle is used here to accommodate the larger sample size and volume of solutions.

Because of the biological nature of this procedure, there is a higher level of variability in the results than in many other soil testing procedures. Therefore, all attempts to reduce variation are critical. To reduce experimental error, the following are recommended: thorough sample mixing, complete sealing of bottles during incubation, avoidance of floating particles during incubation, and strict temperature control. Preliminary results showed no advantage in excluding oxygen from the headspace by introducing a N_2 atmosphere immediately prior to sealing of the incubation vessel. Keeney and Bremner (1966) reported the erratic results whenever the smell of H_2S was detected during analysis.

The mineralizable NH_4-N content of some soils has been found to vary with time in dry storage. The OSUSTL currently recommends holding samples in dry storage for a minimum of three weeks before analysis. It is also recommended that samples be rapidly air-dried at ambient temperature immediately after sampling.

WATER ANALYSIS METHODS
Irrigation Water Quality

CALCIUM, MAGNESIUM, AND SODIUM

A. Reagents

Same as used for Extractable Bases.

B. Procedure

1 Filter through Whatman No. 42 or equivalent filter paper.
2. Dilute and analyze sample filtrate following steps 3-5 of the Extractable Bases procedure.

C. Calculations

$$\text{meq of cation/liter} = \frac{\text{ppm (mg/L) of cation in sample}}{\text{meq weight of cation}}$$

BORON

A. Reagents

Same as used for soil boron test.

B. Procedure

1. Add 2 drops of $CaCl_2$ extracting solution to about 30 mL of the water sample. Allow to stand for 5-10 min.
2. Filter through Whatman No. 42 or equivalent filter paper.
3. Follow steps 4-9 of the Hot-Water Soluble Boron procedure for soils, substituting the water sample for the soil extract.

C. Calculations

ppm B in water sample = ppm B in water - ppm B in yellow colored sample (if any)

SALINITY

A. Reagent

1. Potassium chloride solution 0.01 N. See Soluble Salts for soils.

B. Procedure

1. Calibrate the solu-bridge with .01 N KCl by placing instrument indicator on 1.41 and turning the temperature indicator until red and green lights are of equal intensity (same as step B.4, in Soluable Salts).
2. Record the electrical conductivity reading for each sample.

pH

A. Reagents

Same as used for soil pH test.

B. Procedure

Same as used for soil pH test except use 40 mL of water sample and omit steps 1-3.

CARBONATES AND BICARBONATES

A. Reagent

1. Hydrochloric acid, 0.1 N standardized HCl - Dilute 8.3 mL of concentrated HCl to a volume of 1 L using distilled water.
2. Phenolphthalein indicator: Dissolve 0.05 g of phenolphthalein in 50 mL of 95% ethanol and dilute to a volume of 100 mL using distilled water. Mix well.
3. Mixed indicator: Dissolve 0.1 g bromocresol green and 0.02 g of methyl red indicators in 100 mL of 95% ethanol.

B. Procedure

1. Pipette 50 mL of water sample into a 125 mL Erlenmeyer flask.
2. Add 6 drops of phenolphthalein indicator.
3. Titrate with 0.1 N standardized HCl until the indicator changes from a pink color to a clear end point. If solution remains clear after addition of phenolphthalein then proceed directly to the second titration (step 4).
4. Add 6 drops mixed indicator and titrate with 0.1 N standardized HCl to a pale pink end point.

C. Calculations

1. First titration (step 3)
   meq carbonate/liter = mL of HCl x 2 x N of HCl x 20
2. Second titration (step 4)
   meq carbonate + bicarbonate/liter = mL of HCl x N of HCl x 20

SULFATE SULFUR

A. Reagents

Reagents will be the same as for the soil SO4-S test except that calcium phosphate solution is not required.

B. Procedure

Follow steps of the soil SO_4-S test.

C. Calculations

Determine the amount of SO_4-S from a standard curve prepared from a series of standard solutions.

TOTAL NITROGEN
Kjeldahl Procedure

A. Reagents

Same used for soil TN.

B. Procedure

1. Pipette a 10.0 mL aliquot of the water sample into a 75 mL volumetric digestion flask.
2. Follow steps 2-8 of the soil Total Nitrogen procedure. The samples will be a clear blue-green color when digested. A blank should be run using 10 mL of distilled water.

C. Calculation

$$\text{ppm total nitrogen} = \text{ppm NH4-N in filtrate} \times \frac{75}{\text{sample size (mL)}}$$

AMMONIUM AND NITRATE NITROGEN
KCl Extraction Method

A. Reagents

None.

B. Procedures

1. Follow steps 2-3 of the Extractable Ammonium and Nitrate Nitrogen procedure substituting an aliquot of water sample for the KCl extract solution. The Kjeldahl distillation method requires a 50-mL aliquot of water.
2. If determinations are to be made by Kjeldahl distillation, follow the procedural steps outlined for ammonium and nitrate nitrogen in steps 3a-i.

C. Calculation

For samples analyzed with an automatic analyzer, ppm ammonium-N or nitrate-N in solution is determined directly.

NOTES

1. Distributed by Custom Laboratory Equipment, Inc., Orange City, FL.

2. The Bausch and Lomb "Spectronic 88 spectrophotometer is used in OSUSTL.

3. Some changes in the concentrations of the standard work solutions may be required to insure operation within the linear range of the spectrophotometer being used.

4. A Perkin-Elmer model 372 atomic absorption spectrophotometer is used in the OSUSTL.

5. The five-unit vacuum filtering rack used in the OSUSTL is supplied by Soil Test, Inc., Evanston, IL.

6. RD-26 Solu-Bridge, Industrial Instruments, Cedar Grove, NJ, is used in the OSUSTL.

7. A Technicon 40-position digestion unit is used in the OSUSTL (Technicon, Inc.).

8. From an unpublished procedure entitled, "A Gypsum Requirement Test, Determination of Sodium in Equilibrium Ammonium Acetate Solution," supplied by Dr. A. R. Halvorson, Extension Soils Specialist, Washington State University, Pullman.

9. In this laboratory, heating mantels and rheostat set at 90.

10. From an unpublished procedure entitled, "Procedure for Purifying Activated Charcoal," which was supplied by Dr. A. R. Halvorson, Extension Soils Specialist, Washington State University, Pullman, WA.

11. Distributed by Custom Laboratory Equipment, Inc., Orange City, FL.

12. Some changes in the concentrations of the standard work solutions may be required to insure operation within the linear range of the spectrophotometer.

13. The five-unit vacuum filtering rack used in the OSUSTL is supplied by Soil Test, Inc., Evanston, IL.

14. RD-26 Solu Bridge, Industrial Instruments, Cedar Grove, NJ, is used in the OSUSTL.

15. From an unpublished procedure entitled, "A Gypsum Requirement Test, Determination of Sodium in Equilibrium Ammonium Acetate Solution," supplied by Dr. A. R. Halvorson, Extension Soils Specialist, Washington State University, Pullman, WA.

16. All glassware should be acid washed and rinsed with glass-distilled water.

17. OSUSTL heating mantels and rheostats are set at 90.

18. From an unpublished procedure entitled, "Procedure for Purifying Activated Charcoal," which was supplied by Dr. A. R. Halvorson, Extension Soils Specialist, Washington State University, Pullman, WA.

APPENDIX*

ORGANIC MATTER
Ignition Method

A. Reagents

None

B. Procedure

1. Tare a 50-mL beaker or crucible by igniting it in a muffle furnace set at 550 C, cooling it in a desiccator, and weighing it to plus or minus 1 mg (tare).
2. Place 10-20 g of air-dried soil into the tared container and place in a drying oven set at 100 C for 2-3 hr. Cool container in a desiccator and weigh (soil).
3. Place the container plus sample in a muffle furnace set at 550 C for 4-5 hr. Cool container in a desiccator and weigh (burn).

C. Calculation

$$\% \text{ O.M.} = \frac{\text{soil - burn}}{\text{soil - tare}} \times 100$$

D. Comments

This method appears to be superior to the Walkley-Black method for samples high in organic matter. However, hydrated aluminosilicates, loose structural water, and carbonate minerals are decomposed upon heating which may result in weight losses in excess of the actual organic matter content. The method outlined by Nelson and Sommers (1982) in Section 29-4.3 suggests pretreatment of the soil with a mixture of HCl and HF to remove the hydrated mineral matter. Samples containing carbonate minerals should be pretreated with HCl to dissolve all of the carbonates. To test for the presence of carbonates follow the procedure below:

> Place small amount of finely ground soil on a sheet of wax paper and moisten with a few drops of water. Add approximately 4 N HCl drop-wise to the moist sample, and note any evidence of effervescence. Allow sufficient time to react.

KJELDAHL DISTILLATION
CEC, TN, NH_4-N, NO_3-N and Mineralizable-N

A. Reagents

1. Mixed Indicator - Dissolve 0.3 g of bromocresol green and 0.165 g of methyl red indicators in 400 mL of 95% ethanol, and bring to 500 mL volume.
2. Boric acid indicator, 4% H_3BO_3 - Dissolve 20 g of reagent grade H_3BO_3 in about 900 mL distilled water; heat and swirl until dissolved. Add 20 mL of mixed indicator (reagent 1). Adjust to reddish-purple color or until 1 mL water added to 1 mL solution turns indicator a light green. Adjust indicator solution with 0.1 N sodium hydroxide (NaOH) (pH around 5.0) and dilute to 1 L.
3. Sodium hydroxide, 40% NaOH - Dissolve 400 g of NaOH pellets in about 500 mL distilled water. Cool and bring to 1 L volume.
4. Sodium chloride (NaCl) - Reagent grade, granular.
5. Devarda's alloy - Grind reagent grade alloy in a ball mill until it will pass a 100-mesh sieve and 75% will pass a 200-mesh sieve.
6. Magnesium oxide - Oven dry heavy magnesium oxide (MgO) in a muffle furnace at 650 C for 2 hr. Cool and store in a desiccator.
7. Hydrochloric acid, 0.1 N, standardized - Add 8.3 mL of concentrated HCl to 500 mL distilled water, then bring to 1 L volume. Standardize following the general procedure outlined in Appendix. This is used for titrations in the determination of cation exchange capacity and total nitrogen.
8. Hydrochloric acid, 0.01 N, standardized - Dilute 100 mL of 0.1 N HCl with distilled water to a volume of 1 L. Standardize following the procedure outlined in Appendix. This is used for titrations in the determination of ammonium and nitrate nitrogen.

B. Procedure

1. Turn on heating unit to boiling flask and condensers.
2. Pipette 10 mL of boric acid indicator solution into a 125 mL Erlenmeyer flask. Place the Erlenmeyer flask under the condenser tip of the Kjeldahl unit. The end of the condenser should be in the boric acid indicator. Make sure the system is boiling before attaching the Kjeldahl flask to the distillation system in Step 3.

(Note: Steps 1 and 2 precede all succeeding steps.)

* The appendix contains a combination of alternate procedures, seldom used procedures and instructions for standardization of an acid.

CEC

3. Transfer a 50 mL aliquot of leachate from CEC step 5 into a 300-mL Kjeldahl flask. Add 3 g of NaCl to leachate in flask. Place flask on system.
4. Add 20 mL of 40% NaOH to the leachate through the stopcock; rinse with a small amount of distilled water, and close the stopcock.

Note: It is advisable to turn the steam off before adding reagents through the stopcock to avoid spitting. Be sure to turn the system back on before plugging the stopcock.

5. Distill approximately 75 mL into the 125-mL Erlenmeyer flask containing the boric acid indicator. Remove the steam bypass plug and then remove the Erlenmeyer flask.
6. Titrate with 0.100 N HCl to a pink endpoint.
7. Make a blank determination following the same procedure as the samples using 50 mL of 0.1 N HCl in place of the leachate.

TN

3. Quantitatively transfer the contents of the 75-mL volumetric digestion tube into a 300-mL Kjeldahl flask and attach to distillation system.
4. Add 30 mL of 40% NaOH to the digested solution through the stop cock, rinse with a small amount of distilled water and close the stop cock. *(See Note in CEC.)*
5. Follow Step 5 in CEC distillation.
6. Titrate with 0.1 N HCl to a pink endpoint.
7. Make a blank determination on sample that was digested with each set of samples following the same procedure only without adding soil.

Extractable NH_4-N and NO_3-N

3. Transfer a 50-mL aliquot of the filtered KCl extract solution into a 300-mL Kjeldahl flask.

NH_4-N Determination

4. Add 0.8 g MgO directly to the Kjeldahl flask and immediately attach to the distillation unit.
5. Follow Step 5 in CEC distillation.
6. Titrate with 0.01 N HCl to a pink endpoint.
7. Make a blank determination following the same procedure, using 50 mL of 1 N KCl in place of the sample filtrate.

NO_3-N Determination (Nitrite is also analyzed)

4. After removal of NH_4-N from the sample as described in the previous section, replace the Erlenmeyer flask with one containing fresh boric acid indicator (Step 2). Then add 0.8 g of Devarda alloy through the stopcock; rinse with a small amount of distilled water and close the stopcock.
5. Follow Step 5 in CEC distillation.
6. Make a blank determination following the same procedure, using 50 mL of 1 N KCl in place of the sample filtrate.

NO_3-N and NH_4-N Determination

4. Follow the same procedure described for determination of NH_4-N, but add 0.8 g of Devarda alloy to the distillation chamber immediately after addition of MgO.

Washing of Kjeldahl distillation unit.

a. Fill a Kjeldahl flask with 1 N HCl. Attach to the Kjeldahl distillation unit, insert the steam bypass stopcock, and turn on the steam generator unit.
b. Allow the acid to boil over through the condenser until thoroughly flushed. Remove the plug, then remove the Kjeldahl flask.
c. Repeat steps a and b above using distilled water.

Note: Washing is necessary to remove any traces of Devarda's alloy which may accumulate. The presence of the alloy will cause a negative error in the NO_3-N determination.

D. Calculations

1. Cation Exchange Capacity in meq/100 g soil =

$$\frac{(\text{mL HCl sample} - \text{mL HCl blank}) \times \text{N of HCl} \times 5 \times 100}{\text{soil sample size (g)}}$$

2. % Total Nitrogen in soil =

$$\frac{(\text{mL HCl sample} - \text{mL blank}) \times \text{N of HCl} \times 0.014\text{g N/meq}}{\text{soil sample size (g)}}$$

3. ppm NH_4-N or NO_3-N is soil =

$$\frac{(\text{mL HCl sample} - \text{mL blank}) \times \text{N of HCl} \times 0.014\text{ g N/meq}}{\text{soil sample size (g)} \times \left(\frac{\text{mL of aliquot}}{\text{mL of extract}}\right)}$$

E. Comments

Some of the reagents used in the Kjeldahl distillation determinations have been modified from the method presented by Bremner and Mulvaney (1982). These modifications have been developed so that the procedure can be used for routine soil analysis.

SULFATE SULFUR (SO_4-S) Distillation Method

A. Reagents[10]

1. Reducing agent - Under a fume hood, mix 400 mL of hydriodic acid (56%), 100 mL hypophosphorus acid (50%), and 200 mL formic acid (88%) in a sturdy 1000 mL beaker. Boil gently with a stream of nitrogen flowing through this solution for about 10 min after the temperature has reached 115 C. The nitrogen gas should be bubbled through the solution by passing N_2 through a glass tube placed near the bottom of the beaker. Do not let the temperature of the solution exceed 117 C. Do not attempt to recover spent reagent by distillation. Remove beaker from hot plate and maintain N_2 flow through the solution until cool. Store in glass container. Reagent is stable for two months.

CAUTION! EXTREMELY POISONOUS FUMES OF PHOSPHINE (PH_3) may be liberated from the reagent if heated above 120 C or if the reagent is spilled on a hot surface.

2. **Pyrogallol - sodium phosphate wash solution** (Not used unless solution contains high levels of NO_3)
   a. Stock reagents
      (i) Dissolve 100 g of sodium phosphate monobasic (NaH_2PO_4-H_2O) in 500 mL glass-distilled water and dilute to 1 L volume.
      (ii) Crush about 100 g of crystalline pyrogallol [pyrogallic acid, $C_6H_3(OH)_3$] using a mortar and pestle. Store in a tightly closed container.
   b. Working wash solution
      (i) Weigh 1+ g of crushed pyrogallol into a 150 mL beaker for each distillation unit to be used (e.g., 6 g for a 5-unit system).
      (ii) Saturate the atmosphere in the beaker with N_2 gas. This can be accomplished by holding the end of a tygon tube from which an audible stream of N_2 gas is flowing near the bottom of the beaker for about 1 minute.
      (iii) Add 12 mL of sodium phosphate monobasic solution per distillation unit to the beaker and stir with a magnetic stirrer until the pyrogallol is dissolved. An atmosphere of N_2 gas needs to be maintained above the solution to prevent the pyrogallol from being oxidized and turning yellow.
3. **Zinc acetate-sodium acetate**(sulfide absorbing solution) - Dissolve 50 g of zinc acetate dihydrate ($Zn(CH_3COO)_2$-$2H_2O$) and 12.5 g of sodium acetate trihydrate (CH_3COONa-$3H_2O$) in 500 mL glass-distilled water then dilute to 1 L volume. A bulk supply of a dilute zinc acetate-sodium acetate can be made by diluting the above solution to a 7 L volume with glass-distilled water.
4. **Amino dimethylaniline solution** - Dissolve 2.0 g of p-amino dimethylaniline sulfate in 1500 mL of glass-distilled water. Slowly add 400 mL of concentrated reagent grade sulfuric acid (H_2SO_4) inside cold, running water bath to cool and avoid evaporation. Dilute the cooled solution to 2 L with glass-distilled water.
5. **Ferric ammonium sulfate solution** - Add 15 mL of concentrated H_2SO_4 to 75 g of ferric ammonium sulfate crystals [$FeNH_4(SO_4)_2$- $12H_2O$]. Add 585 mL of glass-distilled water slowly without mixing to keep H_2SO_4 on bottom and to allow dissolution of ferric ammonium sulfate. The crystals dissolve in around 10 days.
6. **Standard sulfate-S solutions**
   a. Standard stock solution, 100 ppm SO_4-S - Dissolve 0.5434 g of oven dry potassium sulfate (K_2SO_4) in 500 mL glass-distilled water and dilute to a volume of 1 L.
   b. Standard working solutions - Prepare work solutions by pipetting the following aliquots of 100 ppm SO_4-S stock solution into 100 mL volumetric flasks (bring to volume with the appropriate potassium chloride extracting solution):

mL 100 ppm stock solution	ppm SO_4-S in work solution
1	1
3	3
7	7
10	10
15	15

7. **Potassium chloride extracting solutions** -
   a. Eastern Oregon: 1 N KCl - Dissolve 74.56 g potassium chloride (KCl) in 500 mL of glass-distilled water and dilute to 1 L volume.
   b. Western Oregon: 1 N KCl + KH_2PO_4 - Dissolve 4.39 g KH_2PO_4 and 74.56 g KCl and bring up to 2 L with glass-distilled water.
8. **Nitrogen gas** (prepure)
9. **Sulfur-free ground joint lubricant** - Most ground joint lubricants contain appreciable sulfur that must be removed before use. Many lubricants deteriorate quickly when exposed to the hot reducing agent. Dow-Corning silicone stopcock lubricant has been found suitable if freed from sulfur contaminant. Place about 5 g of the silicone lubricant in a 100-mL beaker, add 5 mL of hydriodic acid and 5 mL of hypophosphorous acid. Place a watch glass filled with distilled water on top of the beaker to act as a condenser. Boil the mixture gently with frequent stirrings for about 45 min. Allow to cool, pour off the acid mixture, and wash the lubricant thoroughly with glass-distilled water.

B. Procedure

1. Extraction of SO^4-S
   a. Weigh 10 g of soil into a 50 mL plastic bottle.
   b. Add 20 mL of the appropriate KCl extracting solution and shake for one hour. The shaking action should be sufficiently vigorous to keep the soil suspended in solution.
   c. Filter through Whatman No. 42 filter paper (or equivalent).
2. Preparation of digestion-distillation apparatus
   a. Rinse washing columns with 0.5 N NaOH and then glass-distilled water.
   b. Lubricate all spherical joints with a minimal amount of S-free lubricant.
   c. Saturate the column with N_2 gas to reduce the possibility of oxidizing the pyrogallol. Place 10 mL of the pyrogallol-sodium phosphate wash solution in the gas washing column, then resaturate the column and solution with N_2 gas. Plain water may be used in gas traps unless solutions contain high levels of nitrate. Reattach the columns to the apparatus.
   d. Saturate the system (digestion-distillation apparatus and washing solution) with H_2S by using a 15 ppm SO_4-S standard solution. Follow sulphur determinate described below with the following exception: Vent H_2S-N_2 into the hood when the system is being saturated.

Note: Saturation should be done prior to analyzing samples each day or when new solution is introduced. The solution should be changed when yellow color appears or when the system has been used 25-30 times.

3. **Determination of SO_4-S**

a. Place 50 mL of the dilute zinc acetate-sodium acetate solution into a 100-mL volumetric receiving flask. Connect the glass delivery tube to the side arm of the gas washing column. Place the receiving flask with the delivery tube inside and near the bottom of the receiving flask, but not touching it.

b. Pipette a 2.0 mL aliquot of standard solution or sample extract into a 50 mL digestion-distillation flask and add 4 mL of reducing reagent. It is recommended that this and all succeeding steps (3b through 3h) be conducted under a suitable fume hood.

c. After moistening joint with a drop of water to insure a complete seal, immediately attach the digestion-distillation flask to the condenser and connect the nitrogen supply tube. Adjust the N_2 flow rate to about 2 bubbles per second. Make certain cool water is passing through the condenser.

d. After 5 min of N_2 flow to obtain a reduced atmosphere, apply heat to the digestion-distillation flasks by either lighting suitable microburners or positioning preheated heating mantels around the base of the flask. With N_2 still flowing, heat the contents of the flask and maintain at a low boil[11] for one hour.

e. Remove the receiving flask, leaving the glass delivery tube in the zinc acetate solution. Immediately add 10 mL of the amino dimethylaniline solution. Quickly stopper the receiving flask and mix thoroughly.

f. Add 2 mL of ferric ammonium sulfate solution and shake. Allow blue color to develop for at least 1/2 hr but no longer than 10 hr. Dilute to a 100 mL volume with glass-distilled water and mix thoroughly, leaving glass tube inside.

g. The blue color developed will be quite stable after 30 min. and should be read within 24 hr on a suitable spec trophotometer set at 670 nm.

h. Prepare standards following steps 3a-g, substituting 2.0 mL of the standard work solutions for the soil extract. A blank is prepared in the same manner using 2.0 mL of the appropriate extracting solution instead of soil extract.

i. If the color is more intense than that obtained for the highest standard work solution, make an appropriate dilution. For best results, dilute the soil extract to a concentration within the linear range of standard work solutions using the appropriate KCl extracting solution and following steps 3a-g.

C. Calculations

ppm SO_4-S in soil sample = ppm SO_4-S in soil extract x 2

D. Comments

The methylene blue method for the determination of sulfur as described by Tabatabai (1982) is followed except for the following modifications:

1. A special technique is used to make up the pyrogallol-sodium phosphate wash solution. When the wash solution is prepared in the manner described above, up to 25 determinations can be made before the solution becomes discolored.
2. The zinc acetate-sodium acetate is made up in the dilute form.

The methylene blue method used here yields more accurate values than the turbidimetric procedure of Tabatabai and Bremner (1970). A modified turbidimetric method has also been used for sulfur analysis but is not described here.

CALCIUM CARBONATE EQUIVALENT FOR LIMING MATERIALS AND HIGHLY BASIC SOILS

A. Reagents

1. Hydrochloric acid, 0.500 N HCl, standardized - Dilute 46.5 mL concentrated HCl to a volume of 1 L with distilled water. Standardize against 25 mL of 0.500 N sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH). These standard base solutions are available through most chemical suppliers, or can be prepared from pure, dry reagent Na_2CO_3 or NaOH.
2. Sodium hydroxide, 0.500 N NaOH, standardized - Dissolve 20.00 g NaOH pellets in about 500 mL distilled water. Cool and dilute to a volume of 1 L. Standardize against the 0.500 N standard HCl (reagent 1).
3. Phenolphthalein indicator - Dissolve 0.05 g phenolphthalein in 50 mL of 95% ethanol. Bring to 100 mL volume with distilled water.

B. Procedure

1. Place 1.0 g of ground liming material or 5 to 10 g of soil in a 150-mL Erlenmeyer flask. To initially determine how much soil to use, add a drop of 0.5 N HCl to some of the soil. If the soil effervesces, 5 g should be used.
2. Add 50.0 mL of the standardized 0.5 N HCl to the Erlenmeyer flask and boil gently for 5 min. A watch glass filled with cool distilled water placed on top of the flask will act as a condenser.
3. Allow the solution to cool. Rinse any condensation on the watch glass into the solution with distilled water. For soil, filter through a Whatman No. 42 or equivalent filter paper into a 250-mL flask, washing all soil from the Erlenmeyer flask with distilled water.
4. Titrate the excess acid with the standardized 0.5 N NaOH, using 4 drops of phenolphthalein indicator. The end point will be pink.

C. Calculations

$$\% \text{ calcium carbonate equivalent} = \frac{(\text{mL of HCL} \times \text{N of HCl}) - (\text{mL of NaOH} \times \text{N of Na OH}) \times 0.05}{\text{sample size (g)}}$$

D. Comments

The above test should be used for materials with percent calcium carbonate greater than 20. If percent calcium carbonate is less than 20, use the carbonate method found on p. 12. The above method does not differentiate between calcium and magnesium carbonates.

STANDARDIZATION OF ACID

A. Reagents

1. Sodium carbonate, 0.1 N (Na_2CO_3)
2. Acid - Acid of unknown normality to be standardized.
3. Mixed indicator - Dissolve 0.1 g of bromocresol green and 0.02 g of methyl red indicators in 75 mL of 95% ethyl alcohol, then bring to 100 mL volume.

B. Procedure

1. Pipette a known amount of 0.1 N Na_2CO_3 into a 100-mL beaker.
   Note: Use 10 mL for acid around 1.0 N, and 1.0 mL for acid around 0.1N.
2. Add 5 drops of mixed indicator.
3. Titrate with the unknown acid to a pink endpoint.
4. Calculate the normality of the acid.

C. Calculation

$$\text{Normality of acid} = \frac{(\text{N of } Na_2CO_3)\ (\text{mL } Na_2CO_3)}{\text{mL of acid used to titrate}}$$

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