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

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Agricultural Experiment Station
Oregon State University, Corvallis
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INTRODUCTION

General

The chemical analysis of soil, sometimes referred to as "soil testing," is a means for evaluating the potential of soil to supply some of the essential plant nutrients. Deficiencies of several plant nutrients essential for commercial crop production occur in Oregon soils. In the Soil Testing Laboratory at Oregon State University, major emphasis is placed on analyzing soil samples for some of the elements which are most likely to be deficient for the crops which are grown. Besides the diagnostic testing of soils in the laboratory, other analyses are conducted which provide useful data for soil characterization studies and other research projects.

The purpose of this publication is to outline the methods of chemical analysis which are used in the Soil Testing Laboratory, and to supply information on the appropriate documentation of these methods. Numerous other methods for the chemical analysis of soil, some of which are not suited to Oregon conditions, are not covered in this summary.

The Cascade Mountain Range is a natural boundary which separates Oregon into eastern and western sectors. Western Oregon has soil which tends to be well leached and acid in reaction, but much of the soil in eastern Oregon is either slightly acid or alkaline. In view of these and other major differences in soil chemical properties, not all of the soil testing methods included in this report are applicable or useful for the analysis of samples from all areas of the state. For example, two methods are used in analyzing soil for phosphorus. The phosphorus test for western Oregon involves the use of the dilute acid-fluoride (Bray P₁) method (2)\(^\text{1/}\), but the sodium bicarbonate method (13) is used for the analysis of samples from eastern Oregon.

Although reference is made to the specific scientific supplies and instruments used in the Oregon State University laboratory, similar equipment from other manufacturers can serve the same purpose.

Collection and Preparation of Soil Samples

Collecting soil samples from the field is an integral part of the diagnostic testing program. Samples must be taken in a prescribed manner to fulfill the basic requirement: the soil sample is representative of the soil in the field from which the sample is taken. Some suggestions on soil sampling are indicated on the soil sample bag.

\(^{1/}\) Underlined numbers in parentheses refer to Literature Cited, page 33.
which is supplied to the grower by the Extension Service and more detailed information is provided in Extension Circular 628, "How to Take a Soil Sample and Why" which is available on request.

The Soil Testing Laboratory provides a standard bag in which to submit soil samples to the laboratory. Other containers should not be used. For example, contamination may be a serious problem for boron (B) and zinc (Zn) when samples are collected and stored in certain kinds of paper bags. Extreme care in the field is also necessary to avoid contaminating the soil sample with fertilizer or with extraneous materials from the sampling tools.

When the soil samples arrive at the laboratory, they are placed on trays and dried in a forced-draft drying cabinet at a temperature not in excess of 50°C. The soil sample usually dries in about 24 hours. The sample is pulverized with a Custom Laboratory Equipment Co. soil crusher and sieved by a Nasco-Asplin soil grinder. The part of the sample which passes through the 14-mesh sieve is returned to the original sample bag and stored ready for analysis. The remainder of the sample is discarded. The samples usually are analyzed within one to two days after they are received at the laboratory. The soil test results are released immediately after sample analysis, and the soil samples are stored for future reference. Three months after analysis, the samples are discarded unless there is some reason for retaining them.

Accuracy and Precision

The instruments are calibrated by standard solutions of the nutrient elements, and the accuracy of the determinations is cross-checked by evaluating the quantitative recovery of measured amounts of the nutrients which are added to sample extracts. Selected soil samples also are maintained as reference samples in evaluating the day-to-day precision of the analytical results.

Documentation of Methods

The analytical methods used in the laboratory are outlined in the following section under the following subheadings: Reagents, Procedure Calculation (when required), and Comments. The appropriate literature citation for each method is indicated along with the title of the method. Any modification of the published method with respect to change in reagents or in procedural detail is indicated under the subheading of Comments. In view of the limited distribution and availability of this summary of soil testing methods, specific reference to this report is not recommended for use in scientific publications.

2/ Distributed by Custom Laboratory Equipment Company, Raleigh, N.C.
3/ Distributed by Nasco, Fort Atkinson, WI.
ANALYTICAL METHODS

pH - 1:2 Soil to Solution Ratio and Glass Electrode pH Meter (8)

A. Reagents

Buffer reagents may be purchased or prepared as described (7).

1. Potassium biphthalate, 0.05M, pH 4.005 at 25°C - Dry KH-
phthalate for two hours at 110°C. Dissolve 10.21 g of KH-
phthalate in distilled water, and dilute the solution to 1
liter with distilled water. As a preservative, add 1.0 ml of
chloroform or a crystal (about 10 mm in diameter) of thymol,
per liter of the buffer solution.

2. Phosphate, 0.025M KH$_2$PO$_4$ and 0.025M Na$_2$HPO$_4$, pH 6.860 at 25°C -
Dry the two phosphate salts for two hours at 110°C. Dissolve
3.40 g of KH$_2$PO$_4$ and 3.55 g of Na$_2$HPO$_4$ in distilled water, and
dilute the solution to 1 liter 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. Borax, 0.01M Na$_2$B$_4$O$_7$·10H$_2$O, pH 9.177 at 25°C - Dry the Na$_2$
B$_4$O$_7$·10H$_2$O for two hours at 110°C. Dissolve 3.81 g in distilled
water and dilute the solution to 1 liter.

B. Procedure

1. Weight or scoop 20 g of soil into a 3-ounce paper cup.
2. Add 40 ml of water and stir thoroughly.
3. Let stand at least 30 minutes, stirring two or three times.
4. Standardize the pH meter in accordance with instructions for
the instrument using two of the prepared buffer solutions.
After standardization of the instrument, rinse the electrodes
with distilled water to remove the film of buffer solution.
5. After the soil has settled to the bottom of cup (around 15
minutes after last stirring) read the pH by placing the pH
meter electrodes in the supernatant solution. Record the pH
to the nearest 0.1 unit. Rinse the electrodes with distilled
water prior to each pH determination, and when not in use
immerse the electrodes in distilled water.

C. Comments

The method outlined here is a modification of method 3-26 described
by Jackson (8). The modifications are the following: (1) A 1:2 soil-
solution ratio is used instead of a 1:2.5 ratio. (2) The pH reading is
taken in the supernatant solution instead of in the soil suspension.
These modifications were made for convenience and to minimize the errors
introduced by liquid junction potential and the settling of the soil
particles during the time the pH measurement is being made.

It is advisable to prepare fresh buffer solutions at least once a
month, and to check the standardization of the pH meter periodically
when making a series of determinations.

Greweling and Peech (7) indicate that the measured pH value may
shift slightly with each change in the soil-to-water ratio used in
preparation of the soil sample and that seasonal fluctuations in pH may
also be anticipated. According to their results, the pH of the saturated
soil paste or of the aqueous soil suspension may tend to decrease for samples collected from a given field during extremely dry periods or after heavy fertilization. During the rainy season, the pH normally shifts back to the level previously observed for the soil when in the moist, well leached condition. Salt accumulation in soil tends to lower the soil pH determined in water, but salt removal from the same soil by leaching may have the opposite effect. In most instances, pH fluctuations resulting from the effects mentioned should be less than 0.2 to 0.3 pH units.
LIME REQUIREMENT - THE SMP BUFFER METHOD

A. Reagent - Buffer Mixture

Add 1.8 g of para-nitrophenol to a liter volumetric flask and dissolve it in 700 ml of distilled H₂O. Add 2.5 ml of triethanolamine (2.8 g since it's easier to weigh than pipette this viscous liquid accurately). Then dissolve 3.0 g K₂CrO₄, 2.0 g Ca (OAc)₂·H₂O, and 53 g CaCl₂·2H₂O in the solution. Bring to 975 volume with distilled water and adjust to pH 7.5 with 0.1 N NaOH. Bring to 1 liter volume with distilled H₂O.

B. Procedure

1. Transfer 5 g of air dried soil which has passed a 2 mm sieve to a beaker, add 5 ml of distilled H₂O. Stir and allow to soak for 30 minutes.

2. Add 10 ml of buffer mixture and stir 3 times over a 20 minute period.

3. Calibrate pH meter with standard buffer solutions.

4. Read the pH within 20 to 25 minutes after the buffer addition since the pH of the buffer continues to drop with time. The sample should be stirred immediately prior to inserting the electrodes.

5. When the meter ceases to drift, remove the electrodes, stir the mixture, reinsert the electrodes and record the pH.

C. Comments

The electrodes should be rinsed with 0.1N HCl and distilled water between each sample. This eliminates the problem of a constant increase in the pH measured because of contamination of the electrodes.
EXTRACTABLE PHOSPHORUS - Sodium Bicarbonate Method (13)
(Note. This method is used for all samples received from east of the Cascade Mountains.)

A. Reagents
1. Sodium bicarbonate, 0.5M - Dissolve 42.01 g NaHCO₃ in distilled water and make up to 1 liter. Adjust the pH to 8.5 with 1M NaOH. Completely cover the surface of the solution with a film of mineral oil (amount of oil needed will depend on shape and size of container) to seal off the solution from the air. Prepare a fresh solution before use if it has been standing more than one month in a glass container. Store the solution in a polyethylene container for a storage period longer than one month. Check the pH of the solution each month, and adjust the pH if necessary. (See Section D, Comments.)
2. Carbon black - Use carbon black "G" (Fisher Scientific Company Cat. No. C-179) or "Darco G 60" (Nurnberg Scientific Company, Cat. No. CX645) in the condition in which it is received from the supplier.
3. Ammonium molybdate - Dissolve 15.00g (NH₄)₂Mo₇O₂₄·4 H₂O in 300 ml of warm distilled water (60°C). After cooling, filter the solution if turbidity is evident, and then add 342 ml of concentrated HCl gradually with mixing. Dilute the contents to 1 liter with distilled water. This solution contains an extra 50 ml of concentrated HCl so that a 2-ml aliquot contains sufficient acid to neutralize the NaHCO₃ in a 2-ml aliquot of soil extract.
4. Stannous chloride
   a. Stock solution - Dissolve 10 g SnCl₂·2H₂O 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 for each set of determinations or at least once a day.
5. Standard phosphate solution - Dissolve 0.2195 g KH₂PO₄ in 50 ml of distilled water. Dilute to 1 liter with NaHCO₃ extracting solution. This solution contains 50 ppm of P and serves as the base stock solution. Prepare standard solutions which contain from 0.5 to 5 ppm P by diluting each one of a series of 1 to 10 ml aliquots of stock solution to a volume of 100 ml with NaHCO₃ extracting solution.

B. Procedure
1. Weigh 2 g of soil into a 70-ml extracting bottle, add 0.5 teaspoon of carbon black and 40 ml of NaHCO₃ extracting solution.
2. Place the extracting bottle containing the sample on the shaker for 30 minutes. Remove the sample from the shaker and then decant the contents of the bottle into a filter funnel fitted with a Whatman No. 5 or equivalent paper.
3. Place 2 ml of the filtrate in a 25-ml colorimeter tube. Automatic pipettes are suitable for dispensing the small volumes used in all steps of this procedure.

4. Add 2 ml of ammonium molybdate solution to each tube and shake well. Remove all traces of the molybdate solution from the neck of the flask by washing with 5 ml of distilled water.

5. Add 0.5 ml of the dilute SnCl₂ solution, mix well immediately.

6. Read color intensity in the colorimeter set at a wavelength of 660 µm, 10 minutes after addition of the SnCl₂ solution.

7. Obtain 2 calibration curve by following the color development steps (3-5) for the soil extracts but substituting a 2 ml aliquot of the 0.5 to 5 ppm P standard solutions instead of the soil extract. Report the results in ppm P in the soil sample which is equivalent to micrograms of P per gram of sample.

C. Calculation

\[
\text{ppm P in the soil sample} = \text{ppm P in the soil extract} \times 20 \text{ ml of extract per gram of soil sample.}
\]

D. Comments

In principle, the test for NaHCO₃ extractable P is conducted precisely as outlined by Olsen and Dean (13), which follows the procedure published earlier by Olsen and others (12). The aforementioned reference covers all of the procedural steps from the extraction of soil P to the determination of P in the soil extract. The mechanics of conducting the test are modified slightly so that a colorimeter tube is used for the color development step rather than a volumetric flask. This modification is not likely to affect the analytical result.

According to Olsen and Dean (13), P is extracted from soil with a 0.5M NaHCO₃ solution at nearly a constant pH of 8.5. At this pH, the concentrations of calcium (Ca), aluminum (Al), and iron (Fe) in solution are maintained at a low level, most likely by various precipitation reactions. Chemical reactions which tend to decrease the activity or concentration of soluble Ca, Al, and Fe allow for a potential increase in soluble phosphate.

In discussing the extraction of soil P with 0.5M NaHCO₃, Olsen and Dean (13) suggest that an increase either in shaker speed or in temperature of the extractant usually causes a corresponding increase in the amount of P extracted from the sample. Normally, for routine testing, the extraction is carried out at the temperature of the laboratory without further regard for the temperature effect. This laboratory uses a constant-speed reciprocating shaker which has a 2-inch stroke and operates at 200 oscillations per minute. The same constant-speed shaker is used in all instances where extraction on the shaker is specified.

The pH of the NaHCO₃ extracting solution increases over time when exposed to the atmosphere. When the reaction of the extractant greatly exceeds pH 8.5, a notable increase in extractable soil P is anticipated. A thin layer of mineral oil spread over the surface of the extracting solution effectively decreases the rate at which the pH will change. Prolonged storage of the NaHCO₃ extractant in glass also may cause a pH

4/ The Bausch and Lomb "Spectronic 88 spectrophotometer used in this laboratory.
increase. When glass storage vessels are used, the pH of the solution should be checked at least monthly so the solution may be adjusted to the proper pH prior to use. Considerable effort involving a source of CO$_2$ or H$_2$CO$_3$, would need to be expanded if the pH is to be adjusted downward unless ions such as Cl$^-$ or SO$_4^{2-}$ are introduced. The most likely thing to do if the pH is too high is to discard the unused portion of the solution and make up a new solution.
EXTRACTABLE PHOSPHORUS - Dilute Acid-Fluoride Method (Bray) (2, 8)

(Note. This method is used for all samples received from west of the Cascade Mountains.)

A. Reagents

1. Ammonium fluoride, 1N - Dissolve 74 g of NH₄F in distilled water and dilute the solution to 2 liters. Store the solution in a polyethylene bottle.

2. Hydrochloric acid, 0.5N - Dilute 103 ml of concentrated HCl to a volume of 2500 ml with distilled water.

3. Extracting solution - Add 1350 ml of 1.0N NH₄F and 2250 ml of 0.5N HCl to 45 liters of distilled water. This gives a solution 0.03N in NH₄F and 0.025N in HCl. It will keep in glass more than 1 year.

4. Ammonium vanadate-molybdate reagent

   a. Stock solutions

      (1) Ammonium vanadate (0.25%)

         Dissolve 5.0 g of NH₄VO₃ (meta-powder) in about 100 ml of boiling distilled water. In a separate beaker, add 340 ml of concentrated H₂SO₄ to about 600 ml of distilled water. Combine the two solutions when cool and then dilute to 2 liters.

      (2) Ammonium molybdate (5.0%)

         Dissolve 100 g of (NH₄)₆Mo₇O₂₄·4H₂O in about 1000 ml of warm distilled water. Cool the solution and dilute to 2 liters.

   b. Work Solution

      Mix 0.8 ml of ammonium vanadate (0.25%) solution, 0.8 ml of ammonium molybdate (5.0%) solution and 1.4 ml of distilled water together for each determination to be run. Prepare this work solution fresh each time samples are run.

5. Standard phosphate solution - Dilute 0.4393 g of oven-dry KH₂PO₄ to 1 liter in a volumetric flask with extracting solution. One ml of this solution contains 100 µg of P.

B. Procedure

1. Weigh 2.9 g of soil into an extracting bottle. Add 1/4 teaspoon of activated charcoal to each sample. Add 20 ml of the acid fluoride extracting solution for a 1:7 soil to solution ratio.

2. Shake for 1 minute and filter immediately. It is very important that the final extract be clear. A yellow-colored solution will introduce an error.

3. Using Custom Lab Equip. diluter dispenser, take 5 ml aliquot of each standard solution and soil sample. Dispense this aliquot and 3 ml vanadate-molybdate work solution into a test tube. Make blank solution using 3:5 ratio of reagent work solution to ammonium fluoride extracting solution.
5. Use standards from 2-25 ppm.

C. Calculations

\[
\text{ppm P in soil sample} = \frac{\text{ppm P in soil extract} \times 7 \text{ ml of soil extract/g of soil}}{	ext{ppm P in standard solution}} \times \frac{\text{O.D. for soil extract solution}}{\text{O.D. reading for standard solution}}
\]

D. Comments

The dilute acid-fluoride method for P follows Method la of Bray and Kurtz (2). The method has been modified to use an ammonium vanadate-ammonium molybdate color forming reagent. This modification was introduced because: (1) the larger concentration of P which could be analyzed, (2) the steps involved in developing the color are less involved, and (3) the color complex is more stable (24 hours and over). The analytical results obtained are comparable to those obtained by means of the original method.

The dilute acid-fluoride extractant tends to dissolve Ca, Al, and Fe phosphates in soil. The dissolution of Al and Fe phosphates occurs very rapidly and it probably results from the fluoride anion complexing these metal cations (12). For this procedure, initiation of the filtration step is advisable immediately after the brief period of extraction on the shaker. Interference in the development of the color complex occurs if appreciable amounts of As, Fe (excess of 100 ppm), and molybdate are present. The fluoride ion also interferes in excess of 50 ppm (8). In this method, the effect of this interference is minimized by making up the standards in the extracting solution.
EXTRACTABLE POTASSIUM, SODIUM, CALCIUM, AND MAGNESIUM - Ammonium Acetate Method (15)

A. Reagents

1. Ammonium acetate, 1N - Add 68 ml of ammonium hydroxide (C.P. reagent 28-30% NH₃) to about 800 ml of distilled water. Then add 57 ml of glacial acetic acid (99.8%) and dilute to 1 liter. Adjust the solution to pH 7.0 by adding either ammonium hydroxide or glacial acetic acid.

2. Standard solutions

   a. Standard stock solutions

      (i). calcium (500 ppm Cu) - Dissolve 1.249 g of CaCO₃ in 1:1 HCl and evaporate to dryness on a hot plate. Dissolve the residue and make to 1 liter with distilled water.

      (ii) Magnesium (500 ppm Mg) - Dissolve 500 g pure Mg ribbon in 1:1 HCl and evaporate to dryness on a hot plate. Dissolve the residue and then dilute to 1 liter 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 liter 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 liter with distilled water.

   b. Standard Work Solutions

      (i) Calcium (Ca), Magnesium (Mg) and Sodium (Na)

      Standard solutions

      Pipette the following aliquots of 500 ppm stock solutions into 100 ml volumetric flasks.

<table>
<thead>
<tr>
<th>Flask or Standard No.</th>
<th>Ca Aliquot ml</th>
<th>ppm of solution</th>
<th>Mg Aliquot ml</th>
<th>ppm of solution</th>
<th>Na Aliquot ml</th>
<th>ppm of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>25</td>
<td>1</td>
<td>5</td>
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<td>5</td>
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<tr>
<td>2</td>
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<td>75</td>
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<td>4</td>
<td>35</td>
<td>175</td>
<td>8</td>
<td>40</td>
<td>5</td>
<td>25</td>
</tr>
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   Bring to volume with ammonium acetate. Mix thoroughly and store in plastic bottles.

   (ii) Potassium (K) standard solution

   Pipette 1, 2, 3, 4, and 5 ml aliquots of 500 ppm stock solution into 100 ml volumetric flasks. Bring to volume with ammonium acetate. Mix thoroughly and store in plastic bottles. The final concentration of the standards are 5, 10, 15, 20, and 30 ppm K.

B. Procedure

1. Weigh 2 g of soil into a 70-ml extracting vessel, add 40 ml of the ammonium acetate extractant, and place the extracting vessel containing the sample on the shaker for 30 minutes.
2. Filter through a Whatman No. 42 or equivalent paper if Na is to be determined; when determining the other elements only, use the Whatman No. 5 or equivalent paper for sample filtration.

3. Ca, Mg, and Na
   Using Custom Lab Equip. diluter dispenser pick up a .75 ml aliquot of each sample extract or standard solution. Dispense these aliquots and 17 mls H₂O into 30 ml plastic vials making approximately a 25 fold dilution. Repeat the above step another time placing the aliquot and dilutent in the same vial.

4. Adjust the dilutor mentioned above to make a 10 fold dilution and to use 0.1 N NaCl on the dilutent. Repeat the same two step procedure described above using a different set of vials.

5. Calibrate the atomic absorption spectrophotometer with the diluted standard work solutions. Use distilled water for the zero setting when analyzing for Ca, Mg and Na and the 0.1 NaCl for K. Determine all the elements by atomic adsorption.

6. Report K, Na, Ca, and Mg in milliequivalents per 100 g of soil, and also report K in parts per million on a soil basis.

C. Calculation
   ppm of cation in the soil sample = ppm of cation in the soil extract solution x 20 ml of extract per gram of soil.
   meq of cation per 100 g of sample = meq of cation per liter of soil extract solution x 2 liters of extract per 100 g of sample.

D. Comments
   The procedure for determining extractable cations with neutral 1N ammonium acetate is a modification of the procedure outlined by Pratt (16) for exchangeable K. The modification concerns the single equilibration of the sample with the extracting solution (1:20 ratio of soil to extractant) rather than three successive extractions specified in the original procedure. A further modification is the dilution of the soil extract with H₂O or a 0.1 N NaCl solution.
   The four cations are determined on the same soil extract but with different dilutions. The single extraction technique for cations in non-calcareous soil gives 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 give higher values for Ca and Mg than are obtained with a single extraction. For purposes of routine testing there is usually no interest in determining the extractable Ca and Mg in alkaline samples which contain free lime.
WATER SOLUBLE BORON – Curcumin Method (6)

A. Reagents
1. Curcumin-oxalic acid solution – Dissolve 0.4 g finely ground curcumin in about 500 ml 95% ethyl alcohol by warming slightly in a warm water bath. Dissolve 50 g oxalic acid in the curcumin solution and cool. Bring to a volume of 1 liter with 95% ethyl alcohol and store in a brown bottle in a refrigerator for at least two days before using. When stored in a refrigerator, the reagent should keep up to two weeks.
2. Ethyl alcohol – 95%.
3. Standard boron stock solution, 100 ppm – Dissolve 0.5716 g of C.P. boric acid in distilled water and dilute to 1-liter. Prepare a standard solution which contains 5 ppm boron by diluting 5 ml aliquot of the 100 ppm stock solution to 100 ml. Starting with the diluted stock solution, prepare a series of standard solutions ranging in concentration from 0.2 to 2 ppm.

B. Procedure
1. Weigh 10 g of soil into a 100-ml boron-free boiling flask, and add 20 ml of distilled water.
2. Connect the boiling flask to the condenser of the refluxing unit and reflux for 5 minutes after sample comes to a full boil. Condensers should be made of boron-free glass. (Note: The aluminum block should be heated to a maximum temperature before samples are placed on it.)
3. Place the suspension in a 50-ml centrifuge tube, add 0.02 g calcium chloride as a floculant, and centrifuge for 20 to 30 minutes at 2000 RPM.
4. If extract is colored, add small amount of decolorizing charcoal and filter.
5. Place 1 ml of the clear solution in a Coors No.000 evaporating dish.
6. Add 4 ml curcumin-oxalic acid solution and mix thoroughly by rotating the evaporating dish.
7. Evaporate to dryness on a water bath at 55° ± 3° C, and then continue to bake the residue at this temperature for a minimum of 15 minutes to insure complete dryness (approximately 3 hours).
8. After the residue has cooled, dissolve it with 25 ml of 95% ethyl alcohol.
9. Filter through a Whatman No. 1 (or equivalent) filter paper within 20 min of adding the alcohol.

\(^5\) A 6-unit electrical heater, Cat. No. 500-2, a product of Labline, Inc., Chicago, Illinois with an aluminum block which covers all six heaters to assure uniform heat.
10. Read the absorbence of the filtrate with a colorimeter or spectrophotometer at 540 μμ within two hours after dissolving the residue in alcohol.

11. Determine the amount of B from a standard curve prepared by running a series of standard solution which contains 0.2 to 2.0 ppm of B. Report the results as parts per million in the soil sample, which is equivalent to micrograms of B per gram of sample.

C. Calculation

\[
\text{ppm B in the soil sample} = \text{ppm B in the soil extract} \times \frac{2 \text{ ml of extract}}{\text{g of soil sample}}.
\]

D. Comments

The method of Dibble and others (6) is followed in detail for the determination of B. For convenience, the 100-ml boiling flask is used in place of the larger Florence flask originally prescribed.

Several important points must be observed in the B procedure (21). It is essential to use low boron, square label glassware for storing reagents and samples at all stages up to the point of color development. Other potential sources of contamination include chemicals, filter paper, dust, boron-containing fumes, and the operator's hands. Deterioration at room temperature is a problem with the prepared curcumin reagent and with the boron-curcumin complex which is formed in sample analysis. For this reason, the curcumin reagent should be refrigerated. The colorimetric step in the analysis should be completed immediately after adding the alcohol to the sample; otherwise, some fading of the developed color is inevitable.
ORGANIC MATTER - Walkley-Black Titration Method (22)

A. Reagents
1. Potassium dichromate, 1N - Dissolve 49.04 g K₂Cr₂O₇ in distilled water and make up to 1 liter. If this solution is carefully prepared, it will be exactly 1N.
2. Ferrous ammonium sulfate, 0.4N - Dissolve 159.6 g Fe(NH₄)₂(SO₄)₉·6H₂O in distilled water containing 40 ml concentrated H₂SO₄ and make up to 1 liter. Determine the exact normality periodically by titrating against the potassium dichromate solution.
3. O-phenanthroline ferrous sulfate complex - 0.025M solution - Obtain the prepared solution under the trade name of "Ferroin."
4. Phosphoric acid, 85 percent.
5. Sulfuric acid, concentrated not less than 96 percent.

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 potassium dichromate solution and 20 ml of concentrated H₂SO₄. Mix rapidly and thoroughly for one minute. Let stand on a sheet of asbestos for at least 20 minutes or until cool.
3. Dilute to 150 ml with water and add 10 ml of concentrated H₃PO₄. The addition of H₃PO₄ may be omitted for most routine analyses.
4. Titrate with the standardized solution of ferrous ammonium sulfate. Use six drops of the O-phenanthroline indicator. At the endpoint, the color flashes from green to reddish brown. If the endpoint is overrun, add 0.5 ml of dichromate and titrate again with ferrous ammonium sulfate.
5. Run a blank simultaneously using the same procedure.

C. Calculation
Calculate the normality of the ferrous ammonium sulfate as follows:

\[ \frac{\text{ml of dichromate} \times 1.0N}{\text{ml of ferrous ammonium sulfate}} \]

The equivalents of dichromate that react with the soil sample are equal to the difference in equivalents of ferrous ammonium sulfate used to titrate the blank and the sample, respectively. The factor 1.36 is derived as follows:

\[ \frac{12}{4000} \times \frac{1.72}{0.76} \times \frac{100}{0.5} = 1.36 \]

in which 12/4000 is the milliequivalent weight of carbon, 1.72 is the factor used based on the assumption that organic matter is 58% carbon, 0.76 is the percent recovery factor, and 0.5 is the weight of the sample in grams.
Calculate the result as follows from the volume and normality of $\text{Fe(NH}_4\text{)}_2\text{(SO}_4\text{)}_2$ used: \( \frac{\text{Blank - sample titration in ml} \times N_{\text{Fe solution}}}{1.36} \approx \% \text{O.M.} \)

D. Comments

The wet oxidation method for determining organic matter in soil is precisely that of Walkley and Black (22). The only modification involves the use of the O-phenanthroline in place of the diphenylamine indicator. This modification should not affect the value of the final result.

Grinding of the soil sample to pass a 0.5 mm sieve facilitates obtaining a representative subsample. In some cases, this method requires the use of a fractional gram sample so that obtaining representative subsamples may be a problem. 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 sample.

The soil is digested with the dichromate and sulfuric acid mixture under the effect of the heat of dilution. According to Greweling and Peech (7), for precise results the sulfuric acid should be added rapidly and the flasks should be cooled uniformly on a sheet of asbestos. Once these steps are accomplished, variations in reaction time from 20 to 40 minutes do not appreciably affect the results.
TOTAL SOLUBLE SALTS - Electrical Conductivity Method (1)

A. Reagent
1. Potassium chloride solution, 0.01N - Dissolve 0.7456 g of KCl in distilled water, and add water to make 1 liter at 25°C. This solution has a conductivity of 1.4118 mmhos per cm.

B. Procedure
1. Place 30 to 50 g of soil in a 10 oz paper cup, add distilled water with 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 minutes, and ascertain that the criteria for saturation are still evident. Remix the sample, if necessary, by adding either additional water or soil to obtain the saturated paste.
3. Transfer the saturated soil paste to a Buchner funnel fitted with a Whatman No. 42 filter. By vacuum filtration collect an aliquot of the saturation extract (filtrate) in a 25 ml receiving flask.
4. Calibrate the RD-26, Solu-Bridge by adjusting the temperature when the conductivity cell is filled with 0.01N KCl reference solution and the reading is set at 1.41 mmhos/cm.
5. In a similar manner, record the electrical conductivity (EC) reading for the saturation extract, which should have reached the same temperature as the reference solution.

C. Comments
The procedural outline for determining total soluble salts (1) follows closely Method 3a of Richards (17). Richards indicates that for the usual appraisal of soil salinity, the extraction can be made a few minutes after the saturated paste is prepared. The recommended time lapse between preparation of the soil paste and extraction is on the order of several hours for gypsiferous samples and from 4 to 16 hours in all cases where the chemical constituents are to be determined in the extract. If the initial filtrate is turbid, it can be discarded or refiltered through the soil sample.

The Solu-Bridge 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 and a calculation to obtain the result is unnecessary. The standard KCl solution is still used as a check on the instrument. Important details on the care and cleaning of the pipette-type conductivity cell are covered by Bower and Wilcox (1).

6/ The five-unit vacuum filtering rack used in this laboratory is supplied by Soil Test, Inc., Evanston, Illinois
7/ A product of Industrial Instruments, Inc., Cedar Grove, New Jersey.
EXCHANGEABLE SODIUM - Ammonium Acetate Displacement Method

A. Reagents
1. Ammonium acetate, neutral, 1N - Use the same solution which was prepared for determining ammonium acetate extractable cations.
2. Standard solution, 1000 ppm sodium (Na) - Use the same solution which was prepared for determining ammonium acetate extractable Na.

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 minute period.
4. Centrifuge to clarify. Decant supernatant liquid into a paper cup. Test conductivity of supernatant liquid. If over 1.1 but not over 2.0 mmhos/cm, add another 5 ml H₂O and repeat steps 3 and 4 until conductivity of supernatant liquid reads between .9 and 1.1.
5. When conductivity is between .9 and 1.1, add 10 to 15 ml of 1N ammonium acetate to the soil in the tube.
6. Use a stainless steel spatula to loosen the soil in the tube. Pour the suspension into a 200-ml Erlenmeyer flask.
7. Repeat the addition of small portions of ammonium acetate, each time washing soil into the Erlenmeyer flask until exactly 100 ml of 1N ammonium acetate is used. All soil should then be in the Erlenmeyer flask.
8. Stir or swirl every five minutes during a half-hour period.
9. Filter about 25 ml into a filtering vial.
10. Determine the concentration of Na in the soil extract by the same process of flame emission used to determine ammonium acetate extractable Na.
11. Report the results as exchangeable Na in the milliequivalents per 100 g of soil sample.

C. Calculation
meq of exchangeable Na per 100 g of soil sample = meq of Na per liter of extract x 2 liters of extract per 100 g of sample x dilution factor.

D. Comments
All soil samples should be washed at least once with distilled water to remove any soluble Na which may be present. After most of the soluble Na is removed by washing, as indicated when the conductivity of the wash water is reduced to 0.9 to 1.1 mmhos/cm, 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 partial basis for predicting the amount of amendment which may be needed in the process of reclamation.

8/From an unpublished procedure entitled, "A Gypsum Requirement Test, Determination of Sodium in Equilibrium Ammonium Acetate Solution," which was supplied by Dr. A.R. Halvorson, Extension Soils Specialist, Washington State University, Pullman.
CATION EXCHANGE CAPACITY - Ammonium Acetate Method (20)

A. Reagents
1. Ammonium acetate, 1N - Prepare according to the specifications outlined in the ammonium acetate method for extractable cations.
2. Ethyl alcohol, 95%.
3. Hydrochloric acid, 0.1N - Dilute 8.3 ml of concentrated HCl reagent to 1 liter with distilled water. Use a portion of the 0.1N HCl (unstandardized) as leaching solution (See step 4 under Section B, Procedure), and standardize another portion as follows for titration purposes. Standardize against 5 ml of 0.100N sodium carbonate (Na₂CO₃) solution made by dissolving 5.300 g of oven-dried Na₂CO₃ in distilled water in a 1-liter volumetric flask and diluting to volume. Use the mixed indicator.
4. Boric acid-indicator solution - Dissolve 0.5 g bromocresol green and 0.1 g methyl red in 100 ml of 95% ethanol. Add 5 ml of this indicator and 0.1 g P-nitrophenol to 1 liter of 4% boric acid indicator solution and adjust to pH 4.6. The color changes from bright green to orange red at the end point.
5. Sodium hydroxide (40% solution) - Add 10 kg NaOH flakes to 15 liters of distilled water. Add the flakes slowly with constant stirring.
6. Mixed indicator - Dissolve 0.1 g bromcresol green and 0.02 g methyl red indicators in 100 ml of 95% ethyl alcohol.

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 minutes.
2. Transfer the soil suspension to a Buchner funnel fitted with a Whatman No. 42 filter and leach the sample with 150 to 200 ml of ammonium acetate. Collect the filtrate in a 1-liter flask; if desired, this soil extract may be analyzed for exchangeable K, Ca, Mg, and Na.
3. Wash the excess ammonium acetate from the soil samples with 150 to 200 ml ethyl alcohol (95%) and discard the filtrate. (Note, be sure to fill funnel completely to wash NH₄⁺ from its sides.)
4. Change to a clean 1-liter receiving flask and leach the soil sample with about 250 ml of 0.1N HCl to replace the exchangeable ammonium. Bring leachate to volume in a 250 ml volumetric flask.
5. Transfer a 50 ml aliquot of filtrate from step 4 to a 300-ml Kjeldahl flask, add 3 g NaCl, and 20 ml 40% NaOH.
6. Place the flask on the distillation unit and distill approximately 75 ml into a 125 ml Erlenmeyer flask containing 10 ml of boric acid indicator solution.
7. Lower the Erlenmeyer receiving flask and remove plug to prevent back suction of the distillate and turn off the burner.

8. Titrate the NH₃ with 0.1000N HCl, and report the cation exchange capacity (CEC) in meq per 100 g of soil.

C. Calculation

CEC in meq per 100 g of soil = ml of HCl \times \frac{N \text{ of HCl} \times 100}{10 \text{ g of sample}}
TOTAL NITROGEN - Micro-Kjeldahl Method (3)

A. Reagents
1. **Sulfuric acid, concentrated, low in N.**
2. **Sodium hydroxide, 40% solution** - Add 10 kg sodium hydroxide flakes to 15 liters of water. Add the flakes slowly with constant stirring.
3. **Hydrochloric acid, 0.1N** - Dilute 8.3 ml of reagent concentrated HC1 to 1 liter with distilled water. Standardize against 5 ml of 0.1000N sodium carbonate (Na2CO3) solution prepared by dissolving 5.300 g of oven-dried Na2CO3 in distilled water in a 1-liter volumetric flask and diluting to volume.
4. **Catalyst** - Prepare a mixture which contains 1000 g Na2SO4, 25 g CuSO4, and 10 g selenium powder.
5. **Boric acid-indicator solution** - Dissolve 0.5 g bromocresol green and 0.1 g methyl red in 100 ml of 95% ethanol. Add 5 ml of this indicator and 0.1 g P-nitrophenol to 1 liter of 4% boric acid indicator solution and adjust to pH 4.6. The color changes from bright green to orange red at the end point.

B. Procedure
1. Weigh 3 g of soil into a digestion tube.
2. Add one 3 g scoop of catalyst and 10 ml of concentrated H2SO4. (Note: mix the soil and the catalyst together before the H2SO4 is added, mix acid immediately.)
3. Digest until clear. Allow the digest to cool. Add 20 ml of H2O and stir.
4. Place a 125 ml Erlenmeyer flask containing 10 ml of boric acid indication solution under the condenser so that the tip of the condenser tube dips below the surface of the solution.
5. Transfer digest to a 300 ml Kjeldahl flask, washing out digesting flask with water and adding this to the digest.
6. Connect flask to distillation unit and add 30 ml 40% NaOH through opening at the top.
7. When water in the steam generator is boiling, place plug in steam tube and allow steam to bubble through unit.
8. Allow sample to boil until approximately 75 ml of distillate has been collected, lower Erlenmeyer flask, pull plug, and turn unit off. Remove Kjeldahl flask.
9. Remove the flask and determine ammonium-N in the distillate by titration with 0.100N HCl. The color change at the endpoint is from green to orange-red.
10. Run a blank whenever there is a change in reagents or at least once a day. Report the result as a percentage of N in the sample.
C. Calculation

Calculate the result as follows from the volume of HCl used in the titration:

\[
\text{Percentage N} = \frac{(\text{Sample} - \text{blank in mls}) \times N \text{ of HCl} \times 100 \times 0.014 \text{ g N/meq}}{3 \text{ g sample}}
\]

D. Comments

The Kjeldahl method outlined by Bremner (3) is modified by eliminating the water from the digestion step. The length of time the sample digests is controlled by the "Technicon" block digester which is used.
EXTRACTABLE AMMONIUM AND NITRATE NITROGEN - Steam-Distillation Method

A. Reagents
1. Potassium chloride solution, approximately 2M - Dissolve 1500 g of KCl reagent in 8 liters of water and dilute the solution to 10 liters.
2. Magnesium oxide - Heat heavy magnesium oxide (U.S.P.) in an electric muffle furnace at 600 to 700°C for two hours. Cool the product in a desiccator containing KOH pellets and store it in a tightly stoppered bottle.
3. Boric acid-indicator solution - Dissolve 0.5 g bromocresol green and 0.1 g methyl red in 100 ml of 95% ethanol. Add 5 ml of this indicator and 0.1 g P-nitrophenol to 1 liter at 4% boric acid indicator solution and adjust to pH 4.6. The color changes from bright green to orange red at the end point.
4. Devarda alloy - Grind reagent-grade alloy in a ball mill until the product will pass a 100-mesh sieve and at least 75% of it will pass a 200-mesh sieve.
5. Sulfuric acid or Hydrochloric acid - 0.02 N. Standardize with the appropriate amount of 0.1 N Na₂CO₃ using the mixed indicator (See Total Nitrogen Procedure).
6. Standard (ammonium + nitrate)-N solution - Dissolve 0.236 g of ammonium sulfate and 0.361 g of potassium nitrate in water, dilute the solution to 1000 ml in a volumetric flask, and mix thoroughly. If pure, dry reagents are used, this solution contains 50 ppm of ammonium-N and 50 ppm of nitrate-N. Store the solution in a refrigerator.

B. Procedure
1. Preparation of soil extract
   a. Place 40 g of soil in a 250 ml extracting bottle and add 150 ml of 2M KCl. Shake the vessel on a mechanical shaker for one hour.
   b. Allow the soil-KCl suspension to settle until the supernatant liquid is clear (usually about 30 minutes) and perform the analyses described on aliquots of this liquid. (If the KCl extract cannot be analyzed within 24 hours after its preparation, filter the soil-KCl suspension using a Whatman No. 42 or equivalent filter paper and store the filtrate in a refrigerator until analyses can be performed.)
2. Determination of ammonium-nitrogen
   a. Add 10 ml of boric acid-indicator solution to a 125 ml Erlenmeyer flask marked to indicate a volume of 75 ml and place the flask under the condenser of the steam-distillation apparatus so that the end of the condenser is in the boric acid.
b. Pipette an aliquot (usually 100 ml) of the soil extract into a distillation unit and add 0.8 g of MgO.

c. Commence distillation by placing plug in the steam bypass tube of the distillation apparatus and collect 75 ml of distillate.

d. Rinse the end of the condenser, and determine ammonium-N in the distillate by titration with .02N HCl using a microburette graduated at 0.02-ml intervals. The color change at the endpoint is from green or blue to a permanent faint pink.

3. Determination of nitrate-nitrogen (Nitrite is also analyzed)
   a. After removal of ammonium-N from the sample as described in the previous section, add 0.8 g of Devarda alloy to the distillation chamber.
   b. Determine the nitrate-N by following steps a, c, and d described in the previous section.

4. Determination of ammonium + nitrate-N
   a. Follow the procedure described for determination of ammonium-N, but add 0.8 g of Devarda alloy to the distillation chamber immediately after addition of MgO.

5. Control and check analyses
   a. Controls should be performed in each series of analyses to allow for ammonium-N derived from the reagents used.
   b. Check the steam-distillation procedure at intervals by analyzing 5-ml aliquots of the standard (ammonium + nitrate-N) solutions. (This solution is stable for several months if stored in a refrigerator.)

6. Washing of equipment
   The distillation unit should be washed periodically with a 1:1 HCl and then flushed with water to remove any Devarda alloy which may accumulate. The presence of Devarda alloy will cause a negative error in the nitrate-N determination.

C. Calculation
   Calculate the analytical result from the volume of titrant as follows: ppm of ammonium or nitrate-N in the soil sample =
   \[(\text{Sample} - \text{blank titration in mls}) \times N \text{ of HCl} \times 14,000 \mu g \text{ N/meq}\]
   Weight of soil sample represented by aliquot

D. Comments
   The method of Bremner (5) for determining ammonium and nitrate-N is used without modification except that 150 ml of KCl is used instead of 100 ml. The standard equipment used for steam distillation is comparable to the set-up of Bremner and Edwards (4).
   Nitrate-N may be extracted from soil with a short 5 to 10-minute period of shaking with water or dilute, N-free salt solution (5). If there is no interest in determining sulfur (5) in addition to nitrate in the aqueous soil extract, a saturated calcium sulfate solution may serve as extractant. A dilute aqueous solution prepared from one of a number of chloride salts may be suitable for extracting both nitrate and sulfate.
Some improvement in the analytical precision is obtained for determining nitrate in the range of 1 to 5 ppm by using a 1 to 2.5 ratio of soil sample to extractant, which is a modification of the standard procedure. The extended period of shaking the soil sample with 2N KCl according to the specifications of Bremner's original procedure permits the extraction of exchangeable ammonium in addition to nitrate.

The MgO reagent used for distillation should be ignited for removal of carbonate. The purified product should be stored in an airtight container to protect it from the atmospheric CO₂. The liberation of CO₂ from the MgO may interfere with the determination of ammonia by the titration method (5).
A. Reagents

1. Extracting solution
   a. Diethylenetriamine pentaacetic acid, 0.025M - Dissolve 9.83 g DTPA in glass-distilled water and dilute to 1 liter.
   b. Triethanolamine, 0.5M - Dissolve 74.60 g TEA in glass-distilled water and dilute to 1 liter.
   c. Calcium chloride, 0.05M - Dissolve 5.55 g CaCl₂ in glass-distilled water and dilute to 1 liter. Combine reagents a, b, and c, and dilute to 5 liters. Adjust the resulting solution to pH 7.3 with HCl. (The concentrations in this solution are 0.005M DTPA, 0.1M TEA, and 0.01M CaCl₂.)

2. Standard Zinc solution, 100 µg Zn/ml - Weigh 0.1000 g of pure Zn metal (30-mesh, analytical reagent) into a 1-liter volumetric flask. Add 50 ml of Zn-free water and 1 ml of concentrated H₂SO₄. When the Zn has dissolved, make to volume with the extracting solution.

B. Procedure

1. Weigh 10 g of soil into an extraction flask.
2. Add 20 ml of DTPA-TEA extracting solution.
3. Shake on mechanical shaker for two hours at a speed fast enough to keep soil in suspension.
4. Filter through a Whatman No. 50 or equivalent paper using an assembly which was rinsed with acid and glass-distilled water.
5. Determine the concentration of zinc in the filtrate using the atomic adsorption instrument.
6. Calibrate the instrument using a set of standard solutions which cover the range from 0 to 5 µg Zn/ml.
7. Report the results in ppm Zn in the soil sample, which is equivalent to µg of Zn per gram of soil sample.

C. Calculation

   ppm Zn in soil sample = µg Zn/ml of soil extract x 2 ml soil extract/g of soil sample.

D. Comments

   Certain precautions are essential to avoid problems of contamination in conducting the analysis for zinc. All solutions are prepared with glass-distilled water. All glassware is rinsed with 3N HCl and then rinsed with glass-distilled water. The filter paper used should be checked continuously for presence of zinc.

   Theoretically, the use of the DTPA solution for extracting zinc from soil was developed for use on alkaline or calcareous samples, but the DTPA solution may be used on acidic samples also. Soil Test values for manganese, iron, and copper can also be obtained for the DPTA extract solution.
EXCHANGEABLE HYDROGEN - Triethanolamine Method (14)

A. Reagents
   1. Buffer solution, 0.5N barium chloride and 0.2N triethanolamine (TEA) - Dilute 100 ml (112.6 g) of commercial TEA (specific gravity 1.125, about 8N) to 1 liter with distilled water. Partially neutralize to pH 8.1 to 8.3, which requires approximately 360 ml of 1.0 N HCl. Dilute this solution to 2 liters with distilled water, and mix with 2 liters of a second solution which contains 250 g of BaCl₂·2H₂O. Protect the reagent solution from the CO₂ of the air.
   2. Replacement solution, 0.5 N barium chloride in dilute buffer solution - Dissolve 250 g of BaCl₂·2H₂O in 4 liters of distilled water, and mix with 20 ml of buffer solution (Reagent 1).
   3. Hydrochloric acid, 0.1N, standardized - Dissolve 8.3 ml of reagent concentrated HCl to 1 liter with distilled water. Standardize against 25 ml of 0.1000N sodium carbonate (Na₂CO₃) solution prepared by dissolving 5.300 g of oven-dried Na₂CO₃ in distilled water in a 1-liter volumetric flask and diluting to volume.
   4. Mixed indicator - Dissolve 0.1 g of bromcresol green and 0.02 g of methyl red indicators in 100 ml of 95% ethyl alcohol.

B. Procedure
   1. Place 10 g of soil in a 125-ml Erlenmeyer flask, and add 25 ml of buffer solution.
   2. Swirl the flask occasionally during a 30-minute period to mix the sample suspension.
   3. Prepare a 250-ml suction flask fitted with a Gooch crucible which contains a moistened Whatman No. 42 paper.
   4. Transfer quantitatively the sample suspension to the Gooch crucible, and use an additional 25 ml of buffer solution to remove sample from the original 125-ml Erlenmeyer flask. Adjust the filtration rate so that this filtration requires at least 30 minutes.
   5. Leach the soil sample with an additional 100 ml of the replacement solution (Reagent 2) by adding repeatedly small increments of the solution to the sample contained in the crucible.
   6. Add 10 drops of mixed indicator to the filtrate and titrate with standardized HCl.
   7. Prepare a blank solution which contains 50 ml of buffer solution, using standardized HCl titrate 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:

\[
\text{Exchangeable hydrogen in meq per 100 g of soil sample} = \frac{(\text{Blank-sample titration in ml}) \times N \times 100}{10 \text{ g of sample}}
\]

D. Comments

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.

Peech and others (15) indicate that subtraction of the metal cations (Ca, Mg, K, Na and Mn) from the exchange capacity as determined by the ammonium adsorption method provides an alternate approach for determining exchangeable hydrogen. The exchangeable Na content of acid soils of the humid regions is usually small, and may be neglected in the calculation. With certain soils, the quantity of exchangeable hydrogen determined by the ammonium acetate method may vary widely from that obtained by the triethanolamine method.
A. Reagents

1. Reducing agent

   Mix 300 ml of hydriodic acid (Sp. G. 1.7, 55-58%), 75 ml hypophosphorus acid (50 percent), and 150 ml formic acid (90 percent). Boil gently with a stream of nitrogen flowing through this solution for about 10 minutes after the temperature has reached 115°C. Do not let the temperature of the solution exceed 117°C. Do not attempt to recover spent reagent by distillation.

   Caution. Extremely poisonous fumes of phosphine (PH₃) 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

   Dissolve 100 g of sodium dihydrogen phosphate (NaH₂PO₄·H₂O) in a liter of glass-distilled water. Crush 150 grams of crystalline pyrogallol (pyrogallic acid, C₆H₃(OH)₃ using a mortar and pestle and store in a tightly stoppered glass container. To prepare the wash solution, proceed in the following manner:
   a. Weigh 1+ gram of crushed pyrogallol into a 150-ml beaker for each distillation unit to be used (i.e., 7 grams for a six-unit system).
   b. Saturate the atmosphere in the beaker with N₂ gas. This can be accomplished by holding the end of a Tygon tube from which an audible stream of N₂ gas is flowing near the bottom of the beaker for about 1 minute.
   c. Add 72 mls of the sodium dihydrogen phosphate solution and stir with a magnetic stirrer until the pyrogallol crystals are dissolved. An atmosphere of N₂ should 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 grams of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and 12.5 grams of sodium acetate trihydrate (CH₃COONa·3H₂O) in sulfide-free, copper-free distilled water. Make to 1 liter volume and filter if turbid. Solution is facilitated by bubbling a stream of nitrogen gas through the system. A bulk supply of a dilute zinc acetate-sodium acetate can be made by diluting the above solution to a seven liter volume with glass-distilled water.

4. Amino dimethylaniline solution - Dissolve 2 grams of p-amino dimethylaniline sulfate in 1500 ml of glass-distilled water. Add to this solution 400 ml of concentrated reagent grade sulfuric acid. Dilute the cooled solution to 2 liters.
5. **Ferric ammonium sulfate solution** - To 25 grams of ferric ammonium sulfate (Fe₃(SO₄)₂(NH₄)₂.24H₂O) add 5 ml of concentrated sulfuric acid and 195 ml distilled water (in this order). The salt dissolves slowly, often requiring two to three days with frequent shaking.

6. **Standard sulfate solutions**
   a. **Stock solution** - Dissolve 5.434 grams of reagent grade potassium sulfate (K₂SO₄) in glass-distilled water and make to one liter. This makes a 1000 ppm SO₄²⁻ solution.
   b. **Working solution** - A 100 ppm stock solution is made by diluting an aliquot of the 1000 ppm stock solution ten times with 1N KCl extracting solution. Working standards of 1, 3, 5, 7, and 10 ppm are then made by diluting a suitable sized aliquot of the 100 ppm stock solution to 100 mls with 1 N KCl extracting solution.

7. **1N KCl extracting solution** - Dissolve 74.56 g reagent grade potassium chloride (KCl) in one liter of glass-distilled water. A large supply of extracting solution can be made by multiplying 74.56 g KCl times the number of liters of solution desired.

8. **Nitrogen gas, (water pumped or prepure).**

9. **Sulfur-free ground joint lubricant** - Most ground joint lubricants contain appreciable sulfur which must be removed before use. Many lubricants deteriorate quickly when exposed to the hot reducing reagent. Dow-Corning silicone stopcock lubricant has been found suitable if freed from sulfur contaminant. Place about 5 grams of the silicone lubricant in a 100-ml beaker, add 10 ml of an equal volume mixture of the hydriodic and hypophosphorus acids (the formic acid is unnecessary in this procedure and produces obnoxious fumes, so is omitted). Fill one of the 50-ml boiling flasks with cold water and set on top of beaker to act as a condenser. Boil the mixture gently with frequent stirrings for about 45 minutes. Pour off the acid mixture and wash the lubricant thoroughly with sulfur-free distilled water.

**B. Procedure**

1. **Extraction of SO₄²⁻**
   a. Weigh 10 g of soil into a plastic bottle which can be stoppered with glass or plastic.
   b. Add 20 ml of the 1N 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 #42 Whatman filter paper (or equivalent) into sulfur-free filter tubes.

2. **Determination of SO₄²⁻**
   a. Lubricate all spherical joints with a minimal amount of the treated lubricant. Place 10 ml of the pyrogallol-sodium phosphate solution in the gas washing column of the digestion-distillation apparatus. The washing column should be filled
with N₂ gas before the washing solution is added to reduce the possibility of the oxidation of the pyrogallol. Saturate the system (digestion-distillation apparatus and washing solution) with H₂S by using one of the standard solutions and following the procedure described below, with the following exception: H₂S-N₂ is vented into the atmosphere when the system is being saturated. Note: This step is necessary only after the system has been washed and/or when new washing solution has been introduced.

b. Place 35 ml of the dilute zinc acetate-sodium acetate solution in a 50-ml volumetric flask. Connect the glass delivery tube to the side arm of the gas washing column and clamp the receiving flask in place. The delivery tube should be near the bottom of the receiving flask.

c. Place 4 ml of the reducing reagent (hydriodic, hypophosphorus, formic acid mixture) into a boiling flask. Transfer 2 ml of a standard solution or a soil extract to the boiling flask containing the reducing reagent.

d. Attach the boiling flask to the condenser and connect the tube from the nitrogen supply. Adjust the nitrogen flow rate so that about two bubbles per second issue from the receiving flask. The rate is not extremely critical. Make certain cool water is flowing through the condenser. After about five minutes of nitrogen flow, light the microburner; with nitrogen continuing to flow, maintain the contents of the boiling flask at a low boil for 45 minutes.

e. Remove the receiving flask, leaving the glass delivery tube in the zinc acetate solution. Using a rapid delivery pipette, add 5 mls of the p-amino dimethylaniline solution. Quickly stopper the volumetric flask and mix thoroughly, then add one ml of the ferric ammonium sulfate solution; mix again, remove the glass delivery tubes, then make to volume with glass-distilled water and mix thoroughly. The methylene blue color is stable and may be read after 10 minutes but within 24 hours after development at wavelength of 670 mp. If the color is too intense to read, make the appropriate dilution with a solution containing 10 ml of the p-amendimethyl-aniline solution and 2 mls of the ferric ammonium solution in 100 ml of glass-distilled water. Dilution with water alone causes changes in color intensity which render the readings useless.

D. Comments
The methylene blue method for the determination of sulfur as described by Johnson and Nishita (9) is followed except for the following modifications.

a. 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 15 samples can be run before the solution becomes discolored.

b. The zinc acetate-sodium acetate is made up in the dilute form.

c. A 50-ml volumetric flask is used instead of a 100-ml one. This is done to concentrate the sulfur, since most soils are generally very low in sulfur. The KCl solution is used because of problems encountered with dispersion of clays. Water could be used for eastern Oregon soils if the soil colloids do not disperse.
LITERATURE CITED


Appendix I

Water Ca, Mg, and Na

A. Reagents
1. Distilled water
2. 500 ppm standard solutions for Ca, Mg, Na
3. Dilute standard solutions

<table>
<thead>
<tr>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>175 ppm</td>
<td>40 ppm</td>
<td>25 ppm</td>
</tr>
<tr>
<td>125 ppm</td>
<td>25 ppm</td>
<td>20 ppm</td>
</tr>
<tr>
<td>75 ppm</td>
<td>75 ppm</td>
<td>10 ppm</td>
</tr>
<tr>
<td>25 ppm</td>
<td>5 ppm</td>
<td>5 ppm</td>
</tr>
</tbody>
</table>

B. Procedure
1. Dilute samples and sets of standards 25 times with H₂O, using
   Custom Lab Equip. hand diluter.
2. Read diluted standards and sample on Atomic Absorption Spectrophotometer

C. Calculations

\[
\text{meg of cation/liter} = \frac{\text{ppm (mg/l) of cation in sample}}{\text{meq Wt of cation.}}
\]
Water Boron

A. Reagents
1. Curcumin - oxalic acid solution - Dissolve 0.4 g finely ground curcumin in about 500 ml 95% alcohol by warming slightly in a warm water bath and crushing crystals with string rod. Dissolve 50g oxalic acid in the curcumin solution and cool. Bring to volume of 1 liter with 95% ethyl alcohol and store in a refrigerator for at least two days before using. When stored in a refrigerator, the reagent should keep up to two weeks.
2. Ethyl alcohol - 95%.
3. Standard boron stock solution, 100 ppm - Dissolve 0.5716 g of C.P. boric acid in distilled water contained in a liter volumetric flask and dilute to volume. Prepare a standard solution which contains 5 ppm boron by diluting a 5 ml aliquot of the 100 ppm stock solution to 100 ml. Starting with the diluted stock solution, prepare a series of standard solutions (0.2, 0.4, 0.6, 1.0, 1.4 and 2.0 ppm used at OSU) ranging in concentration from 0.2 to 2 ppm B.

B. Procedure
1. Place 1 ml of the water sample in a Coors No. 000 evaporating dish.
2. Add 4 ml curcumin oxalic acid solution and mix thoroughly by rotating the evaporating dish.
3. Evaporate to dryness on a water bath at 55° ± 3° C, and then continue to bake the residue at this temperature for a minimum of 15 minutes to insure complete dryness.
4. After the residue has cooled, dissolve it with 25 ml of 95% ethyl alcohol.
5. Filter through a Whatman No. 1 (or equivalent) filter paper.
6. Read the absorbance of the filtrate with a colorimeter or spectrophotometer at 540 μm within two hours after dissolving the residue in alcohol.
7. Determine the amount of B from a standard curve prepared by running a series of standard solution which contains 0.2 to 2.0 ppm of B. Place 1 ml of each sample in an evaporating dish and treat as you do samples.
Water Carbonates and Bicarbonates

A. Reagent
   1. 0.1 N standardized HCl
   2. Mixed indicator: Dissolve 0.1 g brom cresol green and 0.02 g methyl red indicators in 100 ml of 95% ethyl alcohol.

B. Procedure
   1. Pipette 50 ml of water sample into 125 ml Erlenmeyer flask.
   2. Add 6 drops mixed indicator
   3. Titrate with 0.1N HCl

C. Calculations
   \[ \text{meq CO}_3^- + \text{HCO}_3^- / \text{liter} = \text{mls acid} \times N \times 20 \]
Water Organic-N + NH₄-N  Micro Kjeldahl

A. Reagents
1. Sulfuric acid concentrated tech. grade.
2. Sodium hydroxide, 40% solution - Add 10 kg sodium hydroxide flakes (tech. grade) to 15 liters of distilled water. Add flakes slowly with constant stirring.
3. Hydrochloric acid, 0.1N - standardized.
4. Digestion accelerator - Prepare a mixture which contains 1000 g Na₉SO₄, 25 g CuSO₄ and 10 g selenium powder. Do not breathe CuS₄ and Se dust.
5. Boric acid-indicator solution - Dissolve 0.5 gm bromocresol green and 0.1 gm methyl red in 100 ml of 95% ethanol. Add 60 ml of this and 1.2 gm p-nitrophenol to 12 liters of 4% boric acid indicator solution and adjust to pH 4.6. 4% boric acid is 480 gm boric acid in 12 liters.

B. Procedure
1. Place 25 mls water sample in 75 ml digestion flask.
2. Add one scoop 1/4 tsp of digestion accelerator.
3. Add 10 ml concentrated sulfuric acid.
4. Swirl flask and place in digestion unit. Increase temperature gradually (over 3 to 4 hours) until the temperature is 350°C.
5. Digest at 350°C for an hour.
6. Transfer digest to 300 ml Kjeldahl flask, rinsing out digestion tube with distilled water and adding this to 300 ml flask.
7. Place on distilling unit and distill about 75 mls of solution over into 125 ml Erlenmeyer flask containing 10 mls indicator.
8. Remove Erlenmeyer flask and titrate with the 0.1 N HCl.
(Note: use the acid with the normality which gives the best precision.) The color change will be from green to blue and then to an orange end point. If overtitrated, it will go to bright peach.
9. Run a blank at least once a day.
Water \(\ NO_3^-\text{-N and NH}_4^-\text{-N} \) Micro Kjeldahl

A. Reagents
1. Magnesium oxide Heat heavy magnesium oxide (U.S.P.) in an electric muffle furnace at 600° C to 700° C for 2-4 hrs. Cool and store in a desiccator containing KOH pellets.
3. Devarda alloy - Grind reagent - grade alloy in a ball mill until the product will pass a 100-mesh sieve or at least 75% of it will pass a 200-mesh sieve.
4. Hydrochloric acid 0.02N standardized.

B. Procedures
1. Place 100 mls (25 mls manure) water sample in 300 mls Kjeldahl flask.
2. Add 2 large scoops (0.8 g) MgO.
3. Place on distillation unit and distill over 75 mls into 125 ml Erlenmeyer flask with 10 mls indicator in it if \(\text{NH}_4^-\text{N}\) test is required. If \(\text{NH}_4^-\text{N}\) test is not needed, put into empty flask and this distillate may be discarded.
4. Place another Erlenmeyer flask on the unit and add three scoops (0.8) Devarda alloy through funnel on top of unit.
5. Distill over about 75 mls.
6. Titrate with 0.02 HCl.
Water Total Salts

A. Reagent
   1. Potassium chloride solution 0.01 N.

B. Procedure
   1. Calibrate the solu-bridge by placing instrument indicator on 1.41 by turning the temperature indicator.
   2. Record the electrical conductivity reading for each sample.