LABORATORY METHODS RECOMMENDED

FOR CHEMICAL ANALYSIS OF MINED-LAND SPOILS AND OVERBURDEN IN WESTERN UNITED STATES

ABSTRACT

Sandoval, F. M. and Power, J. F. 1977. Laboratory methods recommended for chemical analysis of mined-land spoils and overburden in western United States. U.S. Department of Agriculture, Agriculture Handbook No. 525.

Guidelines are suggested for sampling and for chemical analysis of mine spoils and overburden samples. The handbook was compiled to meet an urgent need for uniform laboratory methods to evaluate plant growth capabilities and limitations associated with coal lands in western United States. Salinity associated with sodium and nutritional deficiencies commonly characterize these materials, therefore the procedures were selected accordingly. The authors drew heavily from methods recommended by the U.S. Salinity Laboratory, Riverside, Calif., and terminology common to saline-sodic soil technology was used. The procedures selected are those with which the authors have experience and which they believe are most widely accepted as reference or standard procedure for western mined lands and associated spoils. Other methods may be equally applicable, but those presented have been related to plant growth responses and may be used as a reference against which other methods may be compared.

Key words and phrases:
Laboratory analyses; chemistry of mine spoils; reclamation of mined-land; reclamation of saline-sodic spoils; diagnosis of mined land; salt-affected spoils; procedures of analyses.

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PREFACE

The material in this publication is intended to provide guidelines on acceptable methods for chemical analyses of mine spoils and overburden materials associated with the major coalfields in western United States. The methods selected are those which, in the judgment and experience of the authors, will provide data that can be interpreted in terms of plant growth potentials. Individuals with interest other than revegetation will undoubtedly be aware of other methods. Numerous methods of analyses were omitted from this publication either because they were not thought closely related to the subject or because we believed the methods selected were more appropriate.

In 1974, the authors prepared a preliminary listing of suggested laboratory procedures for the USDA Forest Service, Surface Environment and Mining (SEAM) Program, to serve as a guide for laboratories and agencies involved in the SEAM Program. To meet a later request from the U.S. Environmental Protection Agency (EPA), this publication was prepared by revising and further developing the 1974 draft. The authors acknowledge the interest and support from EPA for the development of this publication.

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Laboratory Methods Recommended For Chemical Analysis of Mined-Land Spoils And Overburden in Western United States

F. M. Sandoval and J. F. Power[1]

INTRODUCTION

Need for Uniform Procedures

The need is urgent for a uniform set of laboratory procedures to use in the evaluation of plant growth capabilities and limitations of mined-land spoils in the Western States. For analytical data on properties of spoils collected from one laboratory to be directly comparable with those from another laboratory, as many laboratories as possible should agree on a uniform set of analytical procedures. The adoption of uniform methods would increase the value of laboratory data acquired by the different laboratories—Federal, State, commercial, or industry owned. Although different procedures may result in similar conclusions regarding the relative revegetation potential of mine spoils, with uniform methods, reclamation specialists from Government and industry will be better able to define and directly compare land restoration problems and results.

Much laboratory work is needed to characterize and evaluate the wide array of land and management treatments associated with the restoration of plant growth potential to mined land in the Western United States. Information available shows that high salinity, sodic conditions, and plant nutrient deficiencies characterize many mine spoils. The laboratory methods suggested are selected with this fact in mind. Although we recommend specific procedures, we acknowledge that other procedures may also give acceptable data. Some individuals may prefer a different procedure, so long as the results are comparable. For this reason, we are also suggesting that a few standard soils be made available and their laboratory analyses be compiled and distributed to interested people.

Although the authors recognize the traditional distinction between soil and other materials from deeper depths, the procedures described

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apply equally to soil and mine spoils regardless of their original depth; therefore, "soil" in this publication includes all materials evaluated.

Most of the laboratory procedures suggested here are those recommended by the U.S. Salinity Laboratory (5)[2] and the American Society of Agronomy (1, 2). More detailed laboratory methodology is described in the references indicated at the beginning of each procedure.

Principles of Evaluation[3]

The term soluble salts, as applied to soils, refers to the inorganic constituents that are appreciably soluble in water. The determination of soluble salts consists essentially of two steps: the preparation of a soil-water extract and the measurement of the salt concentration of the extract.

The choice of a method for preparing a soil-water extract and for measuring its salt concentration depends upon the purpose of the determination and the accuracy required. In general, the higher the water content at which the extract is obtained, the easier to remove the extract but the less representative the extract is of the solution to which plant roots are exposed in the soil. Thus, if the purpose is to correlate soluble-salt concentration with plant growth, the extract should be obtained at a water content similar to that at which plants grow. The water content of soils in which plants grow fluctuates between a lower limit at which plants wilt permanently (the permanent wilting percentage) and an upper limit (the field capacity), which, for most soils, is approximately two times the water content at the permanent wilting percentage.

A satisfactory method for appraising the soluble salt content of soils in relation to plant growth must, therefore, take into account the variable water-retention characteristics of soils. Moreover, the method should use an extract having a composition as representative of the soil solution as possible. An ideal method would measure the salt concentration of an extract obtained at field capacity water content, but the difficulty of obtaining such extracts prohibits their routine use. The next higher feasible and readily identifiable water content is that at which the soil is mixed with water to a saturated paste.

On some soil materials, laboratory analyses may be feasibly conducted on soil:water ratio extracts wider than saturation and then arithmetically corrected to saturation (when the saturation percentage is known). This procedure assumes that the change in solubility of the salts present is linearly related to the soil:water ratio—an assumption

[2] Numbers in parentheses refer to references listed, p. 31.
[3] Abstracted in part from Bower and Wilcox *In* Black (1).

that may or may not be true. Consequently, in many cases, deviation from saturation may lead to considerable error in the estimate of concentration and composition of salts. Medium- to coarse-textured, chloride-dominant materials are in the first category; fine-textured, high-sulfate (especially if gypsiferous) materials are in the second category.

In 1954, the U.S. Salinity Laboratory developed, and has since recommended, the saturated paste extract as the best solution for soil salinity appraisal (5). Research to date suggests that this also applies for laboratory analyses of solutions extracted from spoils and overburden connected with strip mining.

The quantity of water required to mix a soil to a saturated paste that has certain definable characteristics is reasonably reproducible. It also quantitatively equals about four times the quantity of water held by the soil at permanent wilting and about twice that held at field capacity. The salt concentration of water in the paste, therefore, tends to be about one-fourth the concentration of that in the soil solution at the lower limit of field-water content and about one-half the concentration at the upper limit. Measurement of the salt concentration in water extracted from a saturated soil paste thus provides a quantitative value that automatically reflects the field water-holding characteristics of the soil and which can be related to plant response.

Sampling Method and Sample Preparation

Samples of overburden and spoils can be collected and prepared by many methods varying with available resources, time, and purposes. In selecting the method used, care must be exercised that the chemical properties of the samples are not altered during sampling and before analysis. No simple answers exist to the problem of collecting or to the question of frequency of sampling. Good judgment and experience are required.

Caution should be exercised in transporting and processing samples for laboratory analyses. Polyethylene plastic bags are recommended for transporting samples from the field. Canvas (unless lined) and ordinary paper bags are not recommended because these materials may absorb soluble salts from wet samples, and the glue in the paper bag may interfere with accurate analysis for boron. Galvanized equipment should be avoided if zinc is to be analyzed. Samples to be analyzed for nitrate-nitrogen cannot be stored moist under warm conditions. Moist or wet samples should be immediately frozen or spread to dry on waxed paper or similar water-proof material, ground to 2-mm size, and stored in closed water-resistant containers until analyzed. Knowledge of potential sources of contamination and chemical transformations that may occur in samples is required. Erroneous data are generally more

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harmful than no data. The principles of sampling are discussed by Peterson and Calvin in detail in ASA Monograph, Part 1, *In* Black (*1*).

Sampling by drilling methods that involves a circulating fluid may have a potential to affect the composition of soluble constituents in the sample, either by leaching out salts or by impregnating the sample with contaminants from the circulating fluid. This problem is particularly acute in sampling overburden and spoils in the Western United States. The authors of this publication have shown that the drilling method affects the chemical composition of overburden samples (*4*). Drilling fluids that used saline water (about 5 millimhos/cm electrical conductivity (EC)) or sodium bentonite as the drilling mud, or both, increased salinity and adsorbed sodium in samples, whereas drilling with air (pneumatic) or using water of relatively low salinity (about 1 millimhos/cm EC) did not appreciably change the sample composition. The use of an organic polymer developed for drilling fluid use did not appreciably change sample composition. In this work, laboratory data of samples collected directly from a freshly exposed highwall a few meters away were assumed to represent true values.

METHODS ON EARTH SAMPLES

1. Soil-Water Content

Procedure: Transfer a representative subsample of the soil to a tarred can with lid. For accuracy, use at least a 25-g sample. Weigh, oven dry to constant weight at 105° C, and weigh again.

Calculations:

A. Water content percent (weight basis) = (loss in weight on drying) $\times$ 100/(weight of oven-dried soil).

B. Water content percent (volume basis) = water content percent, weight basis $\times$ bulk density, g/cc.

2. Saturation Extract and Saturation Percentage

References: (Complete citations, page 31.)
USDA Handbook 60, pp. 84, 107.
ASA Monograph No. 9, chap. 62-1.3.

Reagent: Sodium hexametaphosphate solution, 0.1 percent: Dissolve 0.1 g of sodium hexametaphosphate [$(NaPO_3)_6$] in water and dilute to 100 ml with distilled water.

Procedure: Weigh 200 to 1,000 g of air-dry soil of known water content and transfer it to a suitable container with a lid. Weigh the container and contents. Weighing is not necessary if the Saturation Percentage (SP) is omitted. Add distilled water to the soil and stir the mixture with a spatula until a condition of saturation is reached. Consolidate the mixture from time to time during the mixing process by

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tapping the container on the workbench. At saturation, the soil paste glistens as it reflects light, flows slightly when the container is tipped, and slides freely and cleanly off a spatula for all soils except those of high clay content.

After the mixing has been completed, cover the container and allow the sample to stand for 1 hr or more; then recheck the criteria for saturation. If the paste has stiffened markedly or lost its glisten, add more water and mix it again. Alternatively, if free water has collected on the surface of the paste, add an additional weighed quantity of dry soil and mix it again. Weigh the container and contents. Record the increase in weight as water added.

Calculate the SP from the weight of oven-dry soil and the sum of the weights of water added and that originally present in the air-dry sample. The SP may also be determined by oven-drying a subsample of the saturated soil paste, in which case recording the quantity of water and soil used is not necessary.

After allowing the saturated soil paste to stand 4 or more hours, pH may be determined (see **Method 4, p. 6**). Then transfer the paste to a Büchner or Richards filter funnel, fitted with low-ash, highly retentive filter paper. Apply vacuum and collect the filtrate in a test tube or small bottle. About one-fourth of the water in the paste can be extracted with ordinary laboratory suction filtration. If the initial filtrate is turbid, refilter or discard it. Terminate the filtration when air begins to pass through the filter. Add 1 drop of 0.1 percent sodium hexametaphosphate solution for each 25 ml of extract to prevent the precipitation of calcium carbonate ($CaCO_3$) on standing. This will increase the sodium content < 0.5 ppm, which is more acceptable than the loss of $CaCO_3$ by precipitation.

Comments on the saturation point: When sulfate content is minor, or when the extraction is made to make a broad general salinity evaluation, the extraction can take place a few minutes after preparation of the saturated paste. However, if the soil contains gypsum ($CaSO_4 \cdot 2 H_2O$), ionic content may increase by 10 or 20 meq/liter (1 or 2 millimhos/cm electrical conductivity) upon standing. Therefore, to allow for the presence of gypsum, allow the paste to stand several hours as suggested.

Special precautions must be taken with soils of extreme properties. Highly sodic-clay soils of low, organic-matter content puddle easily, frequently have a high affinity for water, and the saturation endpoint is difficult to obtain. To minimize puddling, and thus obtain a more definite endpoint with such soils, the water should be added initially with a minimum of stirring. Sands have a low saturation percentage; unless caution is taken, too much water will be added.

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The saturation extract may be used for the following determinations: electrical conductivity; calcium, magnesium, sodium, potassium, calculation of the sodium adsorption ratio (see exchangeable sodium percentage **Method 6**, p. 9), carbonates, bicarbonates, chlorides, and sulfates. See respective **Analysis** section for these determinations.

3. Alkaline-Earth Carbonates
from Acid Neutralization, Calcium Carbonate Equivalent

References: (Complete citations, page 31.)
USDA Handbook 60, pp. 84-88, 105-107.
ASA Monograph 9, Part 2, chap. 91-4.2.

Reagents:
1. Hydrochloric acid (HCl), 0.5 N, standardized.
2. Sodium hydroxide (NaOH), 0.25 N, standardized.
3. Phenolphthalein, 1 percent in 60 percent ethanol.

Procedure: Place 1 to 5 g of oven-dried soil in a 150-ml beaker, add 50 ml of reagent 1 by means of a pipet. Cover with a watchglass and boil gently for 5 min. Cool, filter, and wash all the acid from the soil with distilled water. Determine the amount of unused acid by adding 2 drops of reagent 3 and back-titrating with 2.

Calculation:

Calcium carbonate ($CaCO_3$) equivalent in percent
= (meq HCl added minus meq NaOH used) × 5/weight of sample in grams.

Note: The calculation gives the $CaCO_3$ equivalent. This is the amount of $CaCO_3$ required to react with the acid. The value is often somewhat high because soil constituents other than $CaCO_3$ may react with the acid.

4. pH Determination of Water Saturated Paste

References: (Complete citations, page 31.)
USDA Handbook 60, pp. 17-18 and 102.
ASA Monograph 9, Part 2, chap. 60.

Equipment: pH meter with glass electrode; standard pH buffers.

Procedure: Standardize the pH meter against known, standard buffer solutions having pH values approximately those of the samples. Prepare a saturated paste with distilled water as directed in **Method 2**, page 4, and allow the paste to stand at least 1 hr. Insert the electrodes into the paste and raise and lower repeatedly until a representative pH reading is obtained.

Note: Opinions vary as to the best way for making pH readings. The pH of soil suspensions frequently increase upon dilution by increasing the soil: water ratio. For this reason, we recommend the saturated paste method with water at the CO_2 pressure of the atmosphere after equilibrium with the soil.

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5. Extractable and Exchangeable Cations

References: (Complete citations, page 31.)
USDA Handbook 60, p. 101.
ASA Monograph 9, Part 2, chap. 57-2.1 and 57-3.2.

The procedure described below is by saturation with ammonium and is taken from the first reference listed. A slightly different ammonium saturation procedure is described in the second reference, as well as a method by sodium saturation.

A. Extractable cations (exchangeable plus soluble cations)

Apparatus: Centrifuge, 50-ml round-bottom, narrow-neck centrifuge tubes and reciprocating shaker.

Reagents:

1. Ammonium acetate solution, 1.0 N. To 700 or 800 ml of water add 57 ml of concentrated acetic acid (CH_3COOH) and then 68 ml of concentrated ammonium hydroxide (NH_4OH). Dilute to volume of 1 liter and adjust to pH 7 or to pH 8 by the addition of more ammonium hydroxide or acetic acid. pH 7 solution is used on noncalcareous soils; pH 8 solution is used on calcareous materials.

2. Nitric acid (HNO_3), concentrated.

3. Hydrochloric acid (HCl), concentrated.

4. Acetic acid, approximately 0.1 N.

Procedure: Ammonium acetate extractable cations: Samples for this determination should be approximately 4 g for medium- and fine-textured soils and 6 g for coarse-textured soils. Weigh samples to an accuracy of 1 percent and correct for the air-dry moisture content. Place the sample in a centrifuge tube. Add 33 ml of reagent 1 to the tube, stopper, and shake for 5 min. Remove the stopper and centrifuge at relative centrifugal force (RCF) = 1,000 until the supernatant liquid is clear. This usually requires 5 min. Decant the supernatant liquid as completely as possible into a 100-ml volumetric flask. Extract with reagent 1, a total of three times by this procedure, decanting into the same flask. Dilute to volume, mix, and determine the amounts of the various extracted cations by flame photometric or chemical methods. Flame photometric analyses (emission or atomic absorption) may be made directly upon aliquots of the extract.

If chemical methods are to be employed for the determination of cations, pretreat the extract in the following manner: Transfer to a 250-ml beaker and evaporate to dryness on a hot plate or steam bath. Wash down the walls of the beaker with a small quantity of distilled water and again evaporate to dryness. Add 1 ml of reagent 2 and 3 ml of 3, evaporate, and dissolve the residue in 20 ml of reagent 4. Filter

through low-ash content filter paper into a 50-ml volumetric flask, using water to wash the beaker and filter paper. Dilute to volume.

Soluble cations: Prepare a saturated soil paste as described in **Method 2**, page 4, using a 200- to 1,000-g sample of soil. The weight of soil will depend upon the number of cations to be determined, the analytical methods employed, and the salt content of the soil. Determine the saturation percentage and obtain the saturation extract as described in **Method 2**, page 4, and determine the soluble cation concentrations by flame photometric or chemical methods.

Calculations:

Ammonium acetate extractable cations in meq/100 g
  = (cation concentration of extract in meq/liter $\times$ 10)/(wt of sample in g).
Soluble cations in meq/100 g
  = (cation concentration of saturation extract in meq/liter) $\times$ (saturation percentage)/1,000.
Exchangeable cations in meq/100 g
  = (extractable cations in meq/100 g) minus (soluble cations in meq/100 g).

Note: To complete the calculations, determine the soluble cation content.

B. Cation exchange capacity

Apparatus: Centrifuge, 50-ml round-bottom, narrow-neck, centrifuge tubes, and reciprocating shaker.

Reagents:

  1. Sodium acetate solution, 1.0 N. Dissolve 136 g of sodium acetate trihydrate in water and dilute to a volume of 1 liter. The pH value of the solution should be approximately 8.2.

  2. Ethanol, 95 percent.

  3. Ammonium acetate solution, 1.0 N. To 700 or 800 ml of water add 57 ml of concentrated acetic acid and then 68 ml of concentrated ammonium hydroxide. Dilute to volume of 1 liter and adjust to pH 7 or 8 as under (A-1) for extractable cations.

Procedure: Samples for this determination should be approximately 4 g for medium- and fine-textured soils and 6 g for coarse-textured soils. Weigh samples to an accuracy of 1 percent and correct for the air-dry moisture content. Place the sample in a centrifuge tube. Add 33 ml of reagent 1, stopper the tube, and shake for 5 min. Unstopper and centrifuge at RCF = 1,000 until the supernatant liquid is clear. This usually requires 5 min. Decant the supernatant liquid as completely as possible and discard. Treat the sample in this manner with 33-ml portions of reagent 1, a total of four times, discarding the supernatant liquid each time. Add 33 ml of reagent 2 to the tube, stopper, shake for 5 min, unstopper, and centrifuge until the supernatant liquid

is clear. Decant and discard the supernatant liquid. Wash the sample with 33-ml portions of reagent 2 a total of three times. The electrical conductivity of the supernatant liquid from the third washing should be less than 40 micromhos/cm. Replace the adsorbed sodium from the sample by extraction with three 33-ml portions of reagent 3 and determine the sodium concentration of the combined extracts after dilution to 100 ml as described under **Method 5-A.**

Calculation:

Cation-exchange capacity in meq/100 g
= (Na concentration of extract in meq/liter × 10)/(wt of sample in g).

6. Exchangeable Cations
and Exchangeable Sodium Percentage

References: (Complete citations, page 31.)

USDA Handbook 60, pp. 101-103.
Wilcox, L. V., 1963. Factors for calculating the sodium absorption ratio. U.S. Salinity Laboratory, Riverside, Calif., Publ. No. 376.

A. Direct determination

Procedure: Determine the exchangeable-cation content and the cation-exchange capacity (CEC), using A and B from **Method 5, page 6.**

Calculation:

Exchangeable-cation percentage
= (exchangeable cation content in meq/100 g × 100)/(cation exchange capacity in meq/100 g).

B. Soluble cations or empirical method

Procedure: Prepare a saturation extract of the soil as described in **Method 2, page 4.** Determine the calcium, magnesium (or Ca plus Mg), and sodium concentrations of the saturation extract, using methods described in **Analyses of Soil Extracts and Water Solutions, page 22.**

Calculations:

Exchangeable sodium percentage, ESP

$$ESP = \frac{100(-0.0126 + 0.01475X)}{1 + (0.0126 + 0.01475X)}$$

where X is equal to the sodium adsorption ratio.

Sodium adsorption ratio, SAR

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

where ionic concentrations are expressed in milliequivalents per liter.

A nomogram which relates soluble sodium and calcium plus magnesium concentrations to the SAR is given in USDA Handbook 60, page 103. Included on the nomogram is a scale for estimating the corresponding ESP. A helpful set of factors to facilitate accurate calculation of the SAR has been prepared by Wilcox of the U.S. Salinity Laboratory (5).

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7. Gypsum

Reference: (Complete citation, page 31.)
USDA Handbook 60, pp. 102-104.

A. Precipitation with acetone (qualitative)

Reagent: Acetone.

Procedure: Weigh 10 to 20 g of air-dried soil into an 8-oz bottle and add a measured volume of water sufficient to dissolve the gypsum present. Stopper the bottle and shake by hand six times at 15-min intervals or agitate for 15 min in a mechanical shaker. Filter the extract through paper of medium porosity. Place about 5 ml of the extract in a test tube, add an approximately equal volume of acetone, and mix. The formation of a precipitate indicates the presence of gypsum in the soil.

Remarks: The soil should not be oven-dried because heating promotes the conversion of gypsum ($CaSO_4 \cdot 2\ H_2O$) to the half-hydrate form ($CaSO_4 \cdot 0.5\ H_2O$). The latter hydrate has a higher solubility in water for an indefinite period following its solution.

B. Precipitation with acetone (quantitative)

Apparatus: Centrifuge, 50-ml conical centrifuge tubes, conductivity cell, and electrical conductivity bridge.

Reagent: Acetone.

Procedure: Transfer a 20-ml aliquot of the filtered extract obtained as described under A into a 50-ml conical centrifuge tube. Add 20 ml of acetone and mix. Let stand until the precipitate flocculates. This usually requires 5 to 10 min. Centrifuge at relative centrifugal force (RCF) = 1,000 for 3 min, decant the supernatant liquid, invert the tube, and drain on filter paper for 5 min. Disperse the precipitate and rinse the wall of the tube with a stream of 10 ml of acetone blown from a pipet. Again, centrifuge for 3 min, decant supernatant liquid, invert tube and drain on filter paper for about 5 min. Add exactly 40 ml of distilled water to the tube, stopper, and shake until the precipitate is completely dissolved. Measure the electrical conductivity of the solution, using **Analysis 1,** page 22, and correct the conductivity reading to 25° C. Determine the concentration of gypsum in the solution by reference to a graph showing the relationship between the concentration and the electrical conductivity of gypsum solutions. This graph may be constructed by means of the following data from the International Critical Tables, Vol. VI.

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CaSO₄ concentration Meq/liter	Electrical conductivity at 25° C. Millimhos/cm
1	0.121
2	.226
5	.500
10	.900
20	1.584
30.5	2.205

Calculations:

Milliequivalents of $CaSO_4$ in aliquot
= (meq/liter of $CaSO_4$ from conductivity reading) × (ml of water used to dissolve precipitate)/1,000.

Milliequivalents of gypsum per 100 g of soil
= 100 × (meq of $CaSO_4$ in aliquot)/(soil:water ratio × ml of soil-water extract used).

Remarks: Sodium and potassium sulfates when present in sufficiently high concentrations are also precipitated by acetone. The maximum concentrations of sodium sulfate and of potassium sulfate that may be tolerated are 50 and 10 meq/liter.

At a 1:5 soil-water ratio, water will dissolve approximately 15 meq of gypsum per 100 g of soil. If the gypsum content of the soil is found to approach 15 meq/100 g by use of a 1:5 soil-water extract, the determination should be repeated, using a more dilute extract.

C. Increase in soluble calcium plus magnesium content upon dilution

Procedure: Determine the saturation percentage and obtain a saturation extract of the soil using method described in **Method 2, page 4.** Prepare another water extract of the soil, using a moisture content sufficient to dissolve the gypsum present as described under method A. Determine the calcium plus magnesium concentrations of the two extracts by methods described in **Analyses of Soil Extracts and Water Solutions.**

Calculations:

Soluble Ca + Mg at the saturation percentage in meq/100 g
= (Ca+ Mg concentration of saturation extract in meq/liter) × (saturation percentage)/1,000.

Soluble Ca + Mg at the high moisture percentage in meq/100 g
= (Ca + Mg concentration of dilute extract in meq/liter) × (moisture percentage)/1,000.

Gypsum in meq/100 g of soil
= (soluble Ca + Mg at the high moisture percentage in meq/100 g) — (soluble Ca + Mg at the saturation percentage in meq/100 g).

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8. Organic Carbon (Walkley-Black Method)

References: (Complete citations, page 31.)

ASA Monograph No. 9, Part 2, pp. 1373-1376.

Jackson, M. L., Soil Chemical Analysis, pp. 219-222.

Apparatus: Magnetic stirrer, burette, and appropriate glassware.

Reagents:

1. Potassium dichromate ($K_2Cr_2O_7$), 1 N: Dissolve 49.04 g of reagent-grade $K_2Cr_2O_7$ (dried at 105° C) in water, and dilute to 1 liter.

2. Sulfuric acid (H_2SO_4), concentrated (not less than 96 percent): if chloride is present, add silver sulfate (Ag_2SO_4) at the rate of 15 g per liter of acid.

3. Orthophosphoric acid (H_3PO_4), concentrated.

4. o-phenanthroline-ferrous complex, 0.025 N: Dissolve 14.85 g of o-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) and 6.95 g of ferrous sulfate ($FeSO_4 \cdot 7 H_2O$) in distilled water, and dilute to 1 liter.

5. Barium diphenylamine sulfonate [$(C_6H_5NHC_6H_4\text{-}4\text{-}SO_3)_2$ Ba] solution: Prepare a 0.16 percent aqueous solution. This reagent is an optional substitute for No. 4.

6. Ferrous sulfate solution, 0.5 N: Dissolve 140 g of reagent-grade $FeSO_4 \cdot 7 H_2O$ in distilled water, add 15 ml of concentrated H_2SO_4, cool the solution, and dilute to 1 liter. Standardize this reagent daily by titrating it against 10 ml of 1 N $K_2CR_2O_7$, as directed below.

Procedure: Grind material to pass a 0.5-mm sieve, avoiding iron or steel mortars. Transfer a weighed sample, containing 10 to 25 mg of organic-C, but not in excess of 10 g total weight, into a 500-ml widemouth Erlenmeyer flask.[4] Add 10 ml of 1 N $K_2Cr_2O_7$, and swirl the flask gently to disperse the material in the solution. Then rapidly add 20 ml of concentrated H_2SO_4, directing the stream into the suspension. Immediately swirl the flask gently until soil and reagents are mixed, then more vigorously for a total of 1 min. Allow the flask to stand on a sheet of asbestos for about 30 min. Then add 200 ml of water to the flask and filter the suspension if experience shows that the endpoint of the titration cannot otherwise be clearly discerned. Add three to four drops of o-phenanthroline indicator and titrate the solution with 0.5 N $FeSO_4$. As the endpoint is approached, the solution takes on a greenish cast and then changes to dark green. At this point, add the ferrous sulfate drop by drop until the color changes sharply from blue to red (maroon in reflected light against a white background). Make a blank determination in the same manner, but without soil, to standardize the

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[4] Trade names are used in this publication solely for the purpose of providing specific information and do not constitute a warranty of the product by the U.S. Department of Agriculture or an endorsement over products not mentioned.

dichrotate ion ($Cr_2O_7^{2-}$). Repeat the determination with less soil if more than 75 percent of the dichromate is reduced.

Calculation:

Calculate the results according to the following formula, using a correction factor $f = 1.33$ or a more suitable value found experimentally:

$$\text{Organic-C, percent} = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4) \times 0.003 \times 100}{\text{soil wt, g}} \times (f).$$

Note: This method is not well suited for determining organic carbon contents of spoils in which coal fragments are intermixed because carbon in coal, lignite, charcoal, or other resistant forms is only partially oxidized.

9. Sodium Bicarbonate Soluble Phosphorus (Olsen Method)

References: (Complete citations, page 31.)

ASA Monograph No. 9, Part 2, pp. 1044-1047.

Jackson, M. L., Soil Chemical Analysis, pp. 162-165.

Murphy, J. and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural water. Analytica Chimica Acta. 27:31-36.

Apparatus: Shaker, colorimeter.

Reagents:

1. Sodium bicarbonate ($NaHCO_3$) solution, 0.5 N: Adjust pH to 8.5 with 1 N sodium hydroxide (NaOH). Add mineral oil (about 1 cm layer) to avoid exposure of the solution to the air. Prepare a fresh solution if it has been standing over 1 month in a glass container. The solution may be stored in a polyethylene container for longer periods, but check pH monthly.

2. Carbon black: Use carbon black G as received.

3. Ammonium molybdate solution: Dissolve 15 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$] in 300 ml of warm distilled water. Filter the mixture, if necessary, and allow to cool; add 342 ml of concentrated HCl gradually with mixing and dilute to 1 liter with distilled water. This solution contains an extra 50 ml of concentrated HCl to neutralize the $NaHCO_3$ in a 5-ml aliquot.

4. Stannous chloride ($SnCl_2 \cdot 2\ H_2O$), concentrated solution: Dissolve 10 g of stannous chloride in 25 ml of concentrated HCl. Prepare a fresh solution every 2 months or less. Use large crystals of $SnCl_2 \cdot 2\ H_2O$ rather than fine powder. Store solution in a refrigerator.

5. Stannous chloride, dilute solution: Add 0.5 ml of the concentrated $SnCl_2$ solution to 66 ml of distilled water. Prepare the dilute solution for each set of determinations.

6. Standard phosphorus (P) solution: Weigh 0.4393 g of monobasic potassium phosphate (KH_2PO_4) into a 1-liter, volumetric flask.

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Add 500 ml of distilled water and shake until the salt dissolves. Dilute to 1 liter with distilled water. Add 5 drops of toluene to diminish microbial activity. This solution contains 0.1 mg of P per ml.

7. Dilute P solution: Dilute 20 ml of the standard P solution to 1 liter with distilled water. This solution contains 2 µg of P per ml.

Procedure: Add 5 g of soil, 1 tsp of carbon black, and 100 ml of the extracting solution (reagent 1) to a 250-ml Erlenmeyer flask. Shake the flask for 30 min with a suitable shaker. Filter the suspension through Whatman No. 40 paper. Add more carbon black if necessary to obtain a clear filtrate. Shake the flask immediately before pouring the suspension into the funnel.

Place a 5-ml aliquot of the extract in a 25-ml volumetric flask. Slowly add 5 ml of the ammonium molybdate solution directly into the flask. After rapid evolution of CO_2 has ceased, shake the flask gently to mix contents. Wash down the neck of the flask with distilled water to avoid direct contact of the $SnCl_2$ solution with the concentrated ammonium molybdate solution. Dilute the contents to about 22 ml with distilled water. Add 1.0 ml of the dilute $SnCl_2$ solution to one or two flasks, dilute the solution to volume and mix the contents immediately. Measure the transmittance of the solution in the colorimeter 10 min after addition of the stannous chloride solution. Use 660 nm incident light in the colorimeter.

Calculation: Prepare a standard curve as follows: Pipet aliquots of the dilute P solution containing from 2 to 25 µg of P into 25-ml volumetric flasks and add 5 ml of the $NaHCO_3$ extracting solution to each flask. Develop the color as stated above. Plot percentage transmittance against P concentration on single-cycle, semilog, graph paper. Express the results of P in ppm of soil, that is, µg of P per 5 ml of the unknown $\times$ 4 equals ppm of P for the procedure described here.

Note: Ascorbic acid may be substituted for the $SnCl_2 \cdot 2\ H_2O$ reagent. However, with spoil materials, continue to use carbon-black even with ascorbic acid to prevent discolored extract giving erroneous colorimeter readings.

10. Total Nitrogen (Macro-Kjeldahl Method)

References: (Complete citations, page 31.)
ASA Monograph No. 9, Part 2, pp. 1162-1164.
Jackson, M. L., Soil Chemical Analysis, pp. 183-190.

Apparatus: Macro-Kjeldahl digestion and distillation apparatus with fume exhaust, associated glassware.

Reagents:

1. Sulfuric acid (H_2SO_4), concentrated.
2. Potassium sulfate (K_2SO_4).

3. Copper sulfate ($CuSO_4 \cdot 5H_2O$).

4. Selenium (Se).

5. Sodium hydroxide (NaOH), approximately 10 N: Place 4.2 kg of NaOH in a heavy-walled 10-liter Pyrex flask, add 4 liters of water, and swirl the flask until the alkali is dissolved. Place a rubber stopper on the flask while cooling to prevent absorption of atmospheric carbon dioxide (CO_2) and allow to stand for several days to permit any sodium carbonate (Na_2CO_3) present to settle. Siphon the clear supernatant liquid into a large Pyrex bottle which contains about 1.5 liters of CO_2-free water and is marked to indicate a volume of 10 liters, and make the solution to 10 liters by addition of CO_2-free water. Then swirl the bottle vigorously to mix the contents, and fit the neck with some arrangement which permits the alkali to be stored and dispensed with protection from atmospheric CO_2.

6. Boric acid-indicator solution: Place 80 g of pure boric acid (H_3BO_3) in a 5-liter flask marked to indicate a volume of 4 liters, add about 3,800 ml of water, and heat and swirl the flask until the H_3BO_3 is dissolved. Cool the solution and add 80 ml of mixed indicator solution prepared by dissolving 0.099 g of bromocresol green and 0.066 g of methyl red in 100 ml of ethanol. Then cautiously add 0.1 N NaOH until the solution assumes a reddish-purple tint (about pH 5.0), and make the solution to 4 liters by addition of water. Mix thoroughly before use.

7. Sulfuric (or hydrochloric) acid (H_2SO_4 or HCl), 0.05 N standard.

Procedure: Place a sample containing about 10 mg of N in a dry Macro-Kjeldahl flask, add 20 ml of water; and, after swirling the flask for 5 to 10 min, allow it to stand for an additional 30 min. Then add 10 g of K_2SO_4, 1 g of $CuSO_4 \cdot 5H_2O$, 0.1 g of Se, and 30 ml of concentrated H_2SO_4, and heat the flask cautiously on the digestion stand. When water has been removed (frothing has ceased), increase heat until the digest clears, and thereafter boil the mixture gently up to 5 hr. Regulate the heating during this boiling so that the H_2SO_4 condenses about one-third of the way up the neck of the flask. Time of boiling varies somewhat with materials and may need to be determined independently for different materials. Temperature of the solution while boiling should be maintained in the 350° to 410° C range.

After completion of digestion, allow the flask to cool, and add about 100 ml of water (slowly, and with shaking). Then cool the flask under a cold-water tap and transfer the contents to a 1-liter conical (or 800-ml Kjeldahl) flask for distillation. As far as practicable, retain sandy residue in the digestion flask during this transfer because sand can cause severe bumping during Kjeldahl distillation. Four washings of

the sandy residue with 50 ml of water are usually adequate for quantitative transfer of the ammonium in the digest.

To determine the ammonium-N liberated by digestion, place a 500-ml Erlenmeyer flask containing 50 ml of boric acid-indicator solution under the condenser of the distillation apparatus so the end of the condenser is below the surface of the H_3BO_3. Then hold the distillation flask at a 45° angle, add a teaspoonful of pumice, and pour about 150 ml of 10 N NaOH down the neck so the alkali reaches the bottom of the flask without mixing appreciably with the digest. Attach the flask as quickly as possible to the distillation apparatus, mix the contents thoroughly by swirling, and immediately commence distillation. Regulate the heating to prevent suck-back of H_3BO_3 and to minimize frothing or bumping during distillation and check that the flow of cold water through the condenser is sufficient to keep the temperature of the distillate < 35° C.

When about 150 ml of distillate have been collected, lower the receiver flask so the end of the condenser is above the surface of the distillate, and after rinsing the end of the condenser with water, remove the flask and stop distillation. Determine ammonium-N in the distillate by titration with 0.05 N H_2SO_4 using a 25-ml burette graduated at 0.1-ml intervals (1 ml 0.05 N H_2SO_4 $\simeq$ 0.7 mg ammonium-N). The color change at the end point is from green to pink.

Calculation:

$$\text{Percent N in sample} = (T - B) \times N \times 1.4/s$$

where T = ml standard acid used in sample titration,
B = ml standard acid used in blank titration,
N = normality of standard acid, and
s = oven dry weight of sample in grams.

Note: Many alterations of the basic method are commonly employed, particularly in respect to apparatus, sample size, and catalysts. Material should be ground to pass at least a 40-mesh sieve to insure thorough digestion, especially when semi-micro methods are used. Also procedure may be modified to include nitrates and nitrites if desired.

11. Inorganic Nitrogen

A. Nitrate-nitrogen by phenoldisulfonic acid method

References: (Complete citations, page 31.)
ASA Monograph No. 9, Part 2, pp. 1216-1218.
Soil Chemical Analysis, pp. 197-201.
Apparatus: Colorimeter, appropriate glassware.
Reagents:
1. Calcium sulfate ($CaSO_4 \cdot 2H_2O$), reagent-grade, powdered.
2. Phenoldisulfonic acid: Dissolve 25 g of pure, white phenol in

150 ml of concentrated sulfuric acid (H_2SO_4) (sp gr 1.84) in a 500-ml Erlenmeyer flask. Then add 75 ml of fuming H_2SO_4 (13 percent SO_3), mix, and place the flask (loosely stoppered) in boiling water for 2 hr. Store the resulting solution of phenoldisulfonic acid in a glass-stoppered, amber bottle. Alternatively, dissolve 25 g of pure, white phenol in 225 ml of concentrated H_2SO_4, and heat the solution in a loosely stoppered bottle or flask in boiling water for 6 hr. Store the product in a glass-stoppered, amber bottle.

    3. Ammonium hydroxide solution (NH_4OH): Prepare by mixing 1 liter of reagent-grade NH_4OH (sp gr 0.89 to 0.90) with 1 liter of water.

    4. Calcium carbonate ($CaCO_3$), reagent-grade, finely powered.

    5. Standard nitrate solution: Dissolve 0.722 g of potassium nitrate (KNO_3) in water, and dilute to a volume of 1,000 ml in a volumetric flask. If pure, dry KNO_3 is used, this solution contains 100 μg of nitrate-N per ml. Store the solution in a refrigerator.

    6. Silver sulfate (Ag_2SO_4), reagent-grade, powdered.

    7. Calcium hydroxide [$Ca(OH)_2$], reagent-grade, powdered.

    8. Magnesium carbonate ($MgCO_3$), reagent-grade powdered.

Procedure: Preparation of soil extract. Place 50 g of soil in a 500-ml, wide-mouth bottle and add 0.5 g of $CaSO_4$ and 250 ml of water. Stopper the bottle and shake it for 10 min on a mechanical shaker. Allow the suspension to settle for a few minutes and decant and filter the supernatant liquid through a large, dry, fluted filter paper (Whatman No. 42 or Schleicher and Schull No. 597 paper).[4] If the first portion of the filtrate is not clear, return it to the filter and collect the filtrate in a clean receiver flask.

Pipet an aliquot (usually 25 ml) of the extract into a 150-ml beaker (or an 8-cm evaporating dish), add about 0.05 g of $CaCO_3$, and evaporate the sample to dryness on a steam plate. Perform the evaporation in an atmosphere free of nitric acid (HNO_3) fumes and do not continue heating beyond the point of dryness. Allow the beaker to cool and add 2 ml of phenoldisulfonic acid from a rapid-delivery pipet. Rotate the beaker so that the phenoldisulfonic acid comes into contact with the entire residue in the beaker. After allowing the beaker to stand for 10 min, add 20 ml of water and stir with a glass rod until the residue is in solution. Then add NH_4OH solution (slowly and with stirring) from a dispensing burette until the solution is slightly alkaline (as indicated by the development of a yellow color) and add an additional 2 ml to ensure an excess of this reagent. Transfer the solution to a 100-ml volumetric flask and dilute to volume with water. Then mix thoroughly and measure color intensity at 420 nm against a reagent blank solution.

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Determine the nitrate content of the sample by reference to a calibration graph plotted from the results obtained with samples containing 0, 10, 20, 40, 70, and 100 µg of nitrate-N. To prepare this graph, dilute 10 ml of the standard nitrate solution (reagent 5) to 100 ml with water in a volumetric flask and mix thoroughly. Then add 0-, 1-, 2-, 4-, 7-, and 10-ml volumes of this diluted standard solution (from a 10-ml burette graduated at 0.02-ml intervals) to 150-ml Pyrex beakers and measure the intensities of the colors obtained with these samples by the procedure described for analysis of the extract.

Calculation:

ppm NO_3-N in soil

= ppm from standard curve × aliquot dilution × soil dilution

= ppm from standard curve × ml final volume/ml aliquot × ml extracting solution/gm oven dry soil

$$= \text{ppm from standard curve} \times \frac{100}{25} \times \frac{250 + \text{ml soil water}}{50 - \text{ml soil water}}$$

Note: If high chlorides are suspected, remove with $AgSO_4$ first. Procedure is capable of high precision and is frequently used as a standard method to which results from other methods are commonly referred.

B. Nitrogen by steam distillation method (ammonium, nitrate, and nitrite)

References: (Complete citations, page 31.)
ASA Monograph No. 9, Part 2, pp. 1195-1201.

Apparatus: Steam-distillation apparatus, 100-ml Pyrex distillation with side-arm, microburette, and other appropriate glassware.

Reagents:

1. Magnesium oxide (MgO): Heat heavy powder MgO in an electric muffle furnace at 600° to 700° C for 2 hr. Cool the product in a desiccator containing potassium hydroxide (KOH) pellets and store it in a tightly stoppered bottle.

2. Boric acid-indicator solution: Dissolve 20 g of pure H_3BO_3 in about 700 ml of hot water and transfer the cooled solution to a 1-liter volumetric flask containing 200 ml of ethanol and 20 ml of mixed indicator solution prepared by dissolving 0.330 g of bromocresol green and 0.165 g of methyl red in 500 ml of ethanol. After mixing the contents of the flask, cautiously add approximately 0.05 N sodium hydroxide (NaOH) until a color change from pink to pale green is just detectable when 1 ml of the solution is treated with 1 ml of water. Then dilute the solution to volume with water and mix thoroughly.

3. Devarda alloy: Prepare this reagent by ball-milling, reagent grade, Devarda alloy until the product will pass a 100-mesh screen and

at least 75 percent of it will pass a 300-mesh screen. Store the finely ground alloy in a tightly stoppered bottle.

4. Sulfamic acid (NH_2SO_3H) : Purify sulfamic acid by crystallization from hot water and dissolve 2 g of the purified reagent in 100 ml of water. Store the solution in a refrigerator.

5. Sulfuric acid (H_2SO_4), 0.005 N standard.

6. Standard (ammonium + nitrate)–N solution: Dissolve 0.236 g of $(NH_4)_2SO_4$ and 0.361 g of potassium nitrate (KNO_3) in water, dilute to a volume of 1,000 ml in a volumetric flask, and mix thoroughly. If pure, dry reagents are used, this solution contains 50 μg of ammonium-N and 50 μg of nitrate-N per ml. Store the solution in a refrigerator.

7. Standard (ammonium + nitrate + nitrite)-N solution: Dissolve 0.236 g of $(NH_4)_2SO_4$, 0.123 g of $NaNO_2$, and 0.361 g of KNO_3 in water, dilute the solution to a volume of 1,000 ml in a volumetric flask and mix thoroughly. If pure, dry reagents are used, this solution contains 50 μg of ammonium-N, 25 μg of nitrite-N and 50 μg of nitrate-N per ml. Store the solution in a refrigerator.

Procedure (using 2 N KCl soil extracts): The steam required for distillation is generated by heating distilled water in a 5-liter flask, which contains pumice or glass beads (to promote smooth boiling) and a small amount of H_2SO_4 (to trap any ammonium in the distilled water). Before use, the distillation apparatus should be steamed out for about 10 min to remove traces of NH_3, and the rate of steam generation should be adjusted so that 7 to 8 ml of distillate are collected per min. The flow of cold water through the condenser of the apparatus should be such that the temperature of the distillate obtained using this rate of distillation does not exceed 22° C. The desired rate of distillation is obtained if the steam generator flask is heated by an electric heating mantle and if the power supply to the mantle is controlled by a variable transformer. A trap at the base of the water jacket on the condenser is used to prevent water condensing on the external surface of the condenser from entering the flask used to collect the distillate.

Ammonium-N. Add 5 ml of H_3BO_3–indicator solution to a 50-ml Erlenmeyer flask, which is marked to indicate a volume of 30 ml, and place the flask under the condenser of the steam-distillation apparatus so that the end of the condenser is about 4 cm above the surface of the H_3BO_3. Pipet an aliquot (usually 10 to 20 ml) of a 2 N KCl soil extract (10 ml per 100 g soil) into a distillation flask and add 0.2 g of MgO through a dry powder funnel having a long stem that reaches down into the bulb of the flask. Attach the flask to the steam-distillation apparatus and immediately commence steam distillation. When the distillate reaches the 30-ml mark on the receiver flask, stop the distillation, rinse the end of the condenser, and determine ammonium-N in the

distillate by titration with 0.005 N H_2SO_4 from a microburette (1 ml of 0.005 N $H_2SO_4 \simeq 70$ μg of ammonium-N). The color change at the endpoint is from green to a permanent, faint pink.

(Nitrate + Nitrite)–N. After removal of ammonium-N from the sample as described in the previous section, remove the stopper from the side-arm of the flask, add 0.2 g of Devarda alloy rapidly through a dry powder funnel that reaches down into the flask to about the base of the side-arm and immediately replace the stopper in the neck of the side-arm. Then determine the amount of ammonium-N liberated by steam distillation as described above.

(Ammonium + Nitrate + Nitrite)-N. Proceed as described for ammonium-N but add 0.2 g of Devarda alloy to the distillation flask immediately after the addition of MgO and before connection of the flask to the distillation apparatus.

(Ammonium + Nitrate)-N. Proceed as described in the previous paragraph, but treat the sample in the distillation flask with 1 ml of sulfamic acid solution and swirl the flask for a few seconds to destroy nitrite before addition of MgO and Devarda alloy.

Nitrate-N. Follow the procedure described for determination of (nitrate + nitrite)-N, but perform the analysis on a sample which has been treated with sulfamic acid to destroy nitrite as described in the previous paragraph.

Note: Steam distillation procedures are especially suited to operations in the small- and medium-sized laboratories where up to a few thousand analyses are anticipated annually. Cost of equipment is nominal, and precision of the method is generally adequate for most purposes. The procedure for nitrates described gives results that agree closely with those obtained by the phenoldisulfonic acid method **(Method 11-A,** page 16). This procedure has the advantage that the three forms of inorganic N (ammonium, nitrate, and nitrite) can be determined on the same soil extract.

12. Hot-Water Soluble Boron

References: (Complete citations, page 31.)
   ASA Monograph 9, Part 2, pp. 1062-1063.
Apparatus:
   Low-boron glassware.
Reagents:
   1. Ethyl alcohol, 95 percent.
   2. Curcumin-oxalic acid reagent: Dissolve 0.04 g finely ground curcumin and 5 g oxalic acid in 100 ml of 95 percent ethyl alcohol and store in refrigerator in stoppered low-boron bottle.

3. Calcium hydroxide [$Ca(OH)_2$]: Add 0.4 g reagent-grade $Ca(OH)_2$ to 100 ml of distilled water.

4. Hydrochloric acid (HCl), 2.5 N.

5. Phenolphthalein indicator.

6. Standard solution A: Dissolve 0.5716 g of boric acid (H_3BO_3) in distilled water and dilute to 1 liter in a volumetric flask. 1 ml contains 0.1 mg Boron.

7. Standard solution B: Transfer 10 ml of solution A to a 1-liter volumetric flask and dilute to volume with water. One ml contains 0.001 mg Boron.

8. Barium chloride ($BaCl_2$), 10 percent solution.

Procedure: Place 20 g of air-dry, 20-mesh soil in a 250-ml, Corning, low-boron, Erlenmeyer flask and add 40 ml of distilled water and 0.5 ml of 10 percent $BaCl_2$ solution. Attach a water-cooled reflux condenser. Heat the flask until the first sign of boiling and then reflux the contents for exactly 5 min. Allow the flask to cool without removing the condenser. Decant the suspension into a 50-ml, round-bottom, centrifuge tube and centrifuge the suspension for 15 min at 1,500 to 2,000 rpm. Transfer an aliquot containing 1 to 5 µg of boron to a Coors evaporating dish. The usual aliquot sizes range from 1 to 20 ml. If the aliquot size exceeds 1 ml, evaporate the aliquot with 5 ml of $Ca(OH)_2$ suspension as directed below in the discussion of standards. Add 4 ml of the curcumin-oxalic acid solution and rotate the dish to bring the solution in contact with all the sample.

Place the dish on a mesh support located about 1.5 cm below the water surface in a water bath at $55° \pm 3°$ C. If a controlled water bath is not available, regulate the temperature by a gas burner. Allow the dish to bake for 15 min after drying before removing it from the bath. Moisten the residue with alcohol, using a wash bottle with a fine nozzle. After a few minutes, transfer the contents to a 15-ml centrifuge tube with additional alcohol, using a policeman to aid in the transfer. (At this stage of the procedure, low-boron glassware is not required because no additional color will develop if the solution is contaminated with boron.) Centrifuge the tube for 10 min at 1,500 rpm. Decant the solution into a 25-ml volumetric flask and add alcohol to bring the total volume to 25 ml. (The trace of solution remaining in the centrifuge tube is not added to either unknowns or standards.)

Place the blank solution in a colorimeter equipped with a green filter (approximately 540 nm) and adjust the galvanometer to indicate zero absorbence or 100 percent transmittance. Then measure the absorbence of the test solution without readjusting the galvanometer. Find the concentration of boron in the test solution by reference to a calibration

curve and calculate the content of boron in the original soil sample. The color is stable for a period of 1 to 2 hr.

Prepare a calibration curve by pipetting 0-, 1-, 2-, 3-, 4-, and 5-ml quantities of standard solution B into separate 75-mm evaporating dishes. Then treat each member of the series as follows: Add 5 ml of $Ca(OH)_2$ suspension and evaporate the contents to dryness. Allow the dish to cool and then add one drop of phenolphthalein indicator. Add 2.5 N HCl dropwise until the color of the indicator disappears and then add 0.5 ml of acid in excess. Add 4 ml of curcumin-oxalic acid solution and rotate the dish to bring the solution into contact with all the sample. Continue the procedure in the manner described above for soil samples, setting the galvanometer to indicate zero absorbence or 100 percent transmittance with the solution to which no boron has been added. Plot the absorbence or percentage transmittance against the quantities of boron added to obtain a calibration curve.

Note: In laboratories with atomic absorption (AA) equipment, use of AA spectroscopy for boron analysis is probably more convenient than the method described.

ANALYSES OF SOIL EXTRACTS
AND WATER SOLUTIONS[5]

1. Electrical Conductivity
To Estimate Soluble Salt Concentration

References: (Complete citations, page 31.)
USDA Handbook 60, pp. 7-13, 89-90.
ASA Monograph No. 9, Part 2, chap. 62-2.

Apparatus:

1. Electrical conductivity (EC) bridge, alternating-current (a.c.) type, suitable for EC measurements: This may be an older 1,000-cycle, a.c. bridge with telephone receivers, a 60-cycle, a.c. bridge with an a.c. galvanometer, or one of the newer bridges employing a cathode ray tube as the null indicator. Battery-operated bridges are also available that give satisfactory readings.

2. EC cell, pipet-type, with platinized platinum electrodes: The cell constant should be approximately 1.0 reciprocal cm. A higher cell constant of 10 reciprocal cm will increase the working EC range, which may be helpful when highly saline soils are analyzed. Keep cells clean and rinse them thoroughly after use. When not in use, keep cells filled with distilled water. Refer to references and manufacturers' instructions for replatinizing cells and how to clean dirty cells.

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[5] Also see **Method 2,** page 4.

Reagents: An array of standard solutions of known salt concentration and EC should be prepared. Salts of reagent grade that may be used are sodium chloride (NaCl) and potassium chloride (KCl). Solutions of KCl of 10 and 100 meq/liter (0.01 and 0.10 N) will have EC's of 1.41 and 12.86 millimhos/cm, respectively, at 25° C. To prepare a 0.01 N KCl solution, dissolve 0.7456 g/liter of distilled water; for a 0.10 N KCl solution, dissolve 6.456 g/liter.

Procedure: Allow the standard salt solutions and samples of soil: water extracts to adjust uniformly to room temperature. The specific temperature within the range 20° to 30° C is not important, but the standard solution and samples must be at the same temperature. When greater precision is required, bring the standard solution and samples to a temperature of 25° in a thermostat or constant temperature room.

Depending on the EC meter used, the EC determination is obtained by either manually correcting for temperature on the meter or by multiplying the meter reading by the appropriate temperature factor to correct to the standard 25° C.

Comments: EC (also called specific conductance) readings on solutions are highly correlated with total ionic concentration and thus the osmotic potential of water extracts. The units of conductivity recom-

TABLE 1.—*Temperature correcting factors for electrical conductivity data to standard 25° C*

C°	Factor	C°	Factor	C°	Factor
18.0	1.163	23.2	1.038	27.0	0.960
19.0	1.136	23.4	1.034	27.2	0.956
19.5	1.124	23.6	1.029	27.4	0.953
20.0	1.112	23.8	1.025	27.6	0.950
20.2	1.107	24.0	1.020	27.8	0.947
20.4	1.102	24.2	1.016	28.0	0.943
20.6	1.097	24.4	1.012	28.2	0.940
20.8	1.092	24.6	1.008	28.4	0.936
21.0	1.087	24.8	1.004	28.6	0.932
21.2	1.082	25.0	1.000	28.8	0.929
21.4	1.078	25.2	0.996	29.0	0.925
21.6	1.073	25.4	0.992	29.2	0.921
21.8	1.068	25.6	0.988	29.4	0.918
22.0	1.064	25.8	0.983	29.6	0.914
22.2	1.060	26.0	0.979	29.8	0.911
22.4	1.055	26.2	0.975	30.0	0.907
22.6	1.051	26.4	0.971	30.5	0.899
22.8	1.047	26.6	0.967	31.0	0.890
23.0	1.043	26.8	0.964	32.0	0.873

mended are millimhos per cm (EC $\times$ 10³) for extracts from soil materials and micromhos per cm (EC $\times$ 10⁶) for waters. For water solutions associated with mined lands in the West, we found the following empirical conversion factors useful:

EC, millimhos/cm $\times$	Factor	$=$	mg/liter (ppm)
0 to 3	650		(ppm expressed on solution basis, not on soil basis.)
3 to 7	700		
7 to 15	750		
15 to 25	800		

2. Cations Calcium, Magnesium, Sodium, and Potassium by Atomic Absorption Spectroscopy

References: (Complete citations, page 31.)

Analytical Methods Handbook available from manufacturer for specific instrument used.

ASA Monograph No. 9, Part 2, chap. 54, 55, 62.

Robinson, J. W. 1966. Atomic Absorption Spectroscopy. Marcel Dekker, Inc., New York, N.Y. 204 pp.

Slavin, W. 1968. Atomic Absorption Spectroscopy. Interscience Publishers, New York, N.Y. 305 pp.

Atomic absorption (AA) spectroscopy techniques and instrumentation are invaluable for identifying and measuring metals in soil and water solutions and are recommended to analyze for calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K). The principle of AA is simple in theory but not in actual practice. Use of AA instrumentation requires a competent analyst to recognize and compensate for light-scattering errors that are introduced. Samples in solution are sprayed into a flame to dissociate the sample into atoms. Then a light source is beamed in, and depending on the wave length used, the individual atoms of a particular metal selectively absorb the light. The wave length absorbed by a particular metal is specific for the metal and therefore identifies it. The amount of light absorbed is proportional to the metal concentration and therefore determines quantity.

Detailed procedures of AA analysis vary depending on the type of instrument and burners employed and on other factors. A review of the instrument methods handbook plus other references is necessary.

Apparatus, principal:

1. AA instrument with appropriate lamps and hooked up with air-acetylene for the flame, adequately vented in a room free of noxious fumes and dusts.

2. Equipment for preparing accurate dilutions.

3. Miscellaneous laboratory glass and hardware.

Procedure (generalized): Prepare a single-standard solution containing the standard elements of determination. This minimizes standard

preparation time and storage requirements. Like all analytical procedures, a minimum and a maximum concentration range of application exists. Generally, low range analyses present minor problems, and detection is a function of concentration limits under optimum conditions. High concentration limits frequently present problems but often can be manipulated. The upper limit can be extended by three methods: (1) The sample solution is diluted until the concentration is in a good analytical range; (2) use of long path burners and changing the position of the burner. By placing the burner perpendicular, or at an angle, to the light path rather than parallel to it, much of the flame is taken out of the light path, and the number of absorbing atoms is reduced, however, there is a loss of sensitivity; and (3) use of secondary absorption wave length lines with low oscillator strengths. For example: with Na, 3320 Angstrom (A) instead of the more sensitive 5890 A; with Ca, 2399 A instead of the primary line at 4227 A.

During analysis, a good technique is to run one or more standard samples with each group of unknowns because results are varied by such things as sample feed rate caused by salt incrustations on the burner or change in liquid viscosity caused by temperature. Unsuspected errors may also be detected and compensated for if frequent calibration checks are performed.

3. Cations Sodium and Potassium by Flame Emission Photometry

Apparatus: Flame spectrophotometer and associated equipment. The monovalents, sodium (Na) and potassium (K) can be accurately determined by using emission flame photometry techniques. Interferences are much less of a problem with Na and K than with the divalents, Ca and Mg. For this reason, analysis for the divalents is not popular with emission flame spectrophotometers. Detailed procedures for the analyses vary depending on the type of instrument used and on other factors. A review of the instrument methods handbook is necessary plus references like those suggested. The most prominent emission lines of Na and K and the radiations most usable for analysis of soil and water solution work are the doublets at 5890 A and 5896 A for Na and at 7665 A and 7699 A for K. A series of standards of known Na and K content containing similar reagents as the unknowns are prepared.

4. Cations Calcium and Magnesium by Titration With EDTA

References: (Complete citations, page 31.)
USDA Handbook 60, pp. 94-95.
ASA Monograph No. 9, Part 2, chap. 62, 68-3.2.

Apparatus: Magnetic stirrer, 10-ml titration assembly, and other miscellaneous lab ware.

Reagents:

1. Ammonium chloride (NH_4Cl)-ammonium hydroxide (NH_4OH) buffer solution: Dissolve 33.76 g of NH_4Cl in 285 ml of concentrated (15 N) NH_4OH, add 5 g of disodium magnesium ethylenediamine tetraacetate (Na_2Mg EDTA) and dilute the solution to a volume of 500 ml.

2. Sodium hydroxide (NaOH), approximately 4 N: Dissolve 40 g of NaOH in water, and dilute the solution to a volume of 250 ml.

3. Standard calcium chloride ($CaCl_2$) solution, 0.02 N: Dissolve 1.000 g of pure calcite crystals ($CaCO_3$) in 20 ml of approximately 3 N hydrochloric acid (HCl) and dilute the solution to a volume of 1 liter.

4. Eriochrome Black T indicator solution: Dissolve 0.5 g of reagent grade Eriochrome Black T powder and 4.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 ml of 95 percent ethyl alcohol. Alternatively, prepare a somewhat more stable solution by dissolving 0.5 g of Eriochrome Black T in 100 ml of diethanolamine [($HOCH_2$ $CH_2)_2NH$].

5. Murexide (acid ammonium purpurate) indicator: Thoroughly mix 0.5 g of murexide ($C_8H_8N_6O_6 \cdot H_2O$) with 100 g of powdered potassium sulfate (K_2SO_4).

6. Standard disodium dihydrogen ethylenediamine tetraacetate (EDTA) solution, 0.02 N: Dissolve 3.723 g of reagent grade disodium ethylenediamine tetraacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) in water and dilute the solution to a volume of 1 liter. Standardize this EDTA solution against the standard $CaCl_2$ solution (reagent 3), following the titration procedure for Ca + Mg given below.

7. Sodium diethyldithiocarbamate solution: Dissolve 1 g of reagent grade sodium diethyldithiocarbamate [$(C_2H_5)_2$ NCSS Na $\cdot 3H_2O$] in 100 ml of water. Because this solution decomposes rapidly, some workers prefer to add the crystals directly to the sample. The quantity is not critical, but 5 mg are adequate. This reagent complexes the heavy-metal ions and thus reduces or eliminates interference from these ions.

8. Hydrochloric acid (HCl), concentrated (12 N).

Procedure: To measure calcium (Ca) concentration, pipet an aliquot of the soil-water extract containing 0.02 to 0.20 meq of Ca into a beaker. Place the beaker in the titration assembly and start the stirrer. Add 5 drops of the sodium diethyldithiocarbamate solution (reagent 7), 1 drop of NaOH (reagent 2) for each 5 ml of aliquot, and a suitable amount (about 5 to 10 mg per 5 ml aliquot) of murexide indicator (reagent 5), mixing the solution after the addition of each reagent. Titrate the solution with the standard EDTA (reagent 6). The color

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change at the end point is from pink to purple. As the end point is approached, add the titrant slowly—a drop every 5 to 10 seconds. At the end point, the addition of a small increment of titrant will not cause a deepening of the purple color. Reserve the solution for the determination of magnesium (Mg).

Calculation:

$$\text{Meq of Ca per liter} = \frac{1,000}{\text{ml of sample}} \times (\text{ml of standard EDTA} \times \text{normality of EDTA}).$$

To measure the Mg concentration, add 3 or 4 drops of concentrated HCl (reagent 8) to the sample just titrated for Ca and stir the solution until the murexide is destroyed. Add 1 ml of the NH_4Cl-NH_4OH buffer solution (reagent 1) and 1 or 2 drops of Eriochrome Black T indicator (reagent 4) and titrate the solution with the standard EDTA (reagent 6). The color at the end point should be clear blue with no tinge of red.

Calculation:

$$\text{Meq of Mg per liter} = \frac{1,000}{\text{ml of sample}} \times (\text{ml of standard EDTA} \times \text{normality of EDTA}).$$

To measure the Ca + Mg concentration, pipet an aliquot containing 0.02 to 0.20 meq of Ca + Mg into a beaker. Place the beaker in the titration assembly and start the stirrer. Add 5 drops of the sodium diethyl-dithiocarbamate solution (reagent 7), 1 ml of the NH_4Cl-NH_4OH solution (reagent 1), and 1 or 2 drops of the Eriochrome Black T indicator solution (reagent 4). Titrate the solution with the standard EDTA (reagent 6). The color change at the end point is from wine red to clear blue.

Calculation:

$$\text{Meq of Ca + Mg per liter} = \frac{1,000}{\text{ml of sample}} \times (\text{ml of standard EDTA} \times \text{normality of EDTA}).$$

5. Carbonate and Bicarbonate

References: (Complete citations, page 31.)
USDA Handbook 60, pp. 98-99.
ASA Monograph No. 9, chap. 62-3.4.

Apparatus: Magnetic stirrer, 10-ml titration burette assembly, and other miscellaneous lab ware.

Reagents:

1. Phenolphthalein indicator: Dissolve 0.25 g of phenolphthalein powder in 100 ml of 50 percent alcohol.

2. Methyl orange indicator: Dissolve 0.1 g of methyl orange powder in 100 ml of water.

3. Sulfuric acid (H_2SO_4), standard, 0.01 N.

Procedure: Pipet an aliquot (usually 5 ml) of the soil-water extract, containing not more than 0.05 meq of bicarbonate (HCO_3) into a beaker. Place the beaker in the titration assembly and start the stirrer. Add 2 drops of phenolphthalein (reagent 1), and, when a pink color is produced, titrate the solution with standard H_2SO_4 (reagent 3), adding a drop every 2 or 3 sec, until the pink color disappears. Note the burette reading. To the colorless solution from this titration, or to the original solution if no color is produced with phenolphthalein, add 1 or 2 drops of methyl orange (reagent 2), and continue the titration to the methyl orange end point. Note the total volume of standard H_2SO_4 used from the burette. Reserve the solution for the determination of chloride (Cl). Make blank determinations after adding the appropriate reagents to CO_2-free water, and make corrections if necessary.

Calculation:

Meq of carbonate (CO_3^{2-}) per liter

$$= \frac{1,000}{\text{ml of sample}} \times (2P \times \text{normality of standard } H_2SO_4)$$

where P = ml of standard H_2SO_4 required to reach the phenolphthalein end point.

Calculation:

Meq of bicarbonate (HCO_3^-) per liter

$$= \frac{1,000}{\text{ml of sample}} (T - \text{blank} - 2P) \times (\text{normality of standard } H_2SO_4)$$

where T = total ml of standard H_2SO_4 required to reach the methyl orange end point, and P = ml of standard H_2SO_4 required to reach the phenolphthalein end point.

Note: Water extracts from sodic mine spoils are often so dark in color that titration with color indicators are difficult. Under such conditions the titration can be made by using a pH meter and glass electrode—carbonate to pH 8.2 and bicarbonate to pH 4.5.

6. Chloride

A. Titration with silver nitrate

References:
USDA Handbook 60, pp. 98-99.
ASA Monograph No. 9, chap. 62-3.5.

Apparatus: Magnetic stirrer, 10-ml titration assembly, and other miscellaneous lab ware.

Reagents:

1. Potassium chromate (K_2CrO_4) indicator: Dissolve 5 g of K_2CrO_4 in approximately 75 ml of water. Add a saturated solution of silver nitrate ($AgNO_3$) until a small quantity of red silver chromate

(Ag_2CrO_4) precipitates. Set the solution in the dark for 24 hr. Then filter it to remove the Ag_2CrO_4 and make the volume to 100 ml.

2. Standard $AgNO_3$ solution, 0.025 N: Dissolve 4.2472 g of reagent grade $AgNO_3$ in water and dilute the solution to a volume of 1 liter. Check the normality by titrating an aliquot of the 0.01 N potassium chloride (KCl) conductivity reference solution reagent (**Analysis 1, page 22**).

3. Sodium bicarbonate ($NaHCO_3$) saturated solution: Renew the solution every few weeks because it has a tendency to lose CO_2 and become too alkaline. Dispense the solution from a dropping bottle.

Procedure: Place the solution from the carbonate-bicarbonate titration (**Analysis 5, p. 27**) in the titration assembly and start the stirrer. If this solution is not available, take a new aliquot of the sample. Adjust the pH with $NaHCO_3$ solution (reagent 3) so the solution is alkaline to methyl orange but acid to phenolphthalein. Usually a single drop of the $NaHCO_3$ solution is sufficient. Add K_2CrO_4 indicator (reagent 1), 1 drop per 5-ml aliquot, and titrate the solution with the standard $AgNO_3$ solution (reagent 2) until the appearance of a red or reddish-brown precipitate.

Determine a blank correction by titrating a like volume of chloride-free distilled water. The normal blank correction is 0.02 to 0.05 ml, depending on the final volume.

Calculation:

Meq of chloride (Cl^-) per liter

$$= \frac{1,000}{\text{ml of sample}} \times (\text{ml of } AgNO_3 - \text{blank}) \times \text{normality of } AgNO_3.$$

B. Potentiometric or coulometric methods

Reference:

ASA Monograph No. 9, chap. 81-3.

Frequently, some extracts from sodic mine spoils are highly colored and are difficult to analyze colorimetrically; such samples can best be analyzed by potentiometric titration using equipment and the procedure such as described in the above reference.

Chloride determinations are also made by using specialized automatic titrator equipment which employs the principle of coulometric generation of reagent (a silver wire) and amperometric indication of the endpoint.

7. Sulfate

A. Precipitation as barium sulfate

References:

USDA Handbook 60, p. 99.
ASA Monograph No. 9, chap. 62-3.1.

Apparatus: Centrifuge and 12-ml conical tubes.

Reagents:

1. Methyl orange, 0.01 percent in water.

2. Hydrochloric acid (HCl), approximately 1 N.

3. Barium chloride, approximately 1 N. Dissolve 122 g of barium chloride dihydrate ($BaCl_2 \cdot 2 H_2O$) in water and dilute to 1 liter.

4. Ethanol, 50 percent by volume.

Procedure: Pipet an aliquot containing 0.05 to 0.5 meq of sulfate (SO_4^{-2}) into a clean 12-ml conical centrifuge tube of known weight. Dilute or evaporate to about 5 ml. Add 2 drops of reagent 1, then 2 dropwise until pink, and then 1 ml of 2 in excess. Heat to boiling in water bath. While twirling the tube, add 1 ml of 3 dropwise. Return to the hot-water bath for 30 min and then cool at least 1 hr in air.

Centrifuge at RCF = 1,000 for 5 min. Carefully decant and let drain by inversion on filter paper for 10 min. Wipe the mouth of the tube with a clean towel or lintless filter paper.

Stir the precipitate and rinse the sides of the tube with a stream of 5 ml of reagent 4 blown from a pipet. If necessary, loosen precipitate from bottom of tube with a bent wire. Centrifuge for 5 min and decant but do not drain. Repeat this washing and decanting operation once. Wipe the outside of tube carefully with chamois and do not subsequently touch with fingers. Dry overnight in an oven at 105° C. Cool in a desiccator and weigh.

Calculation:

Meq per liter of sulfate (SO_4) = (mg of $BaSO_4$ precipitate $\times$ 8.568)/(ml in aliquot).

Note: Care must be taken in the preparation or concentration of the unknowns so as not to precipitate foreign material that might be weighed as $BaSO_4$.

B. Content calculation by difference

Estimating sulfate concentration is often adequate as the difference between the sum of the determined cations and the sum of the determined anions expressed in meq per liter. When nitrate content is significant, it should also be subtracted.

$$SO_4 = (Ca + Mg + Na + K) - (CO_3 + HCO_3 + Cl)$$

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