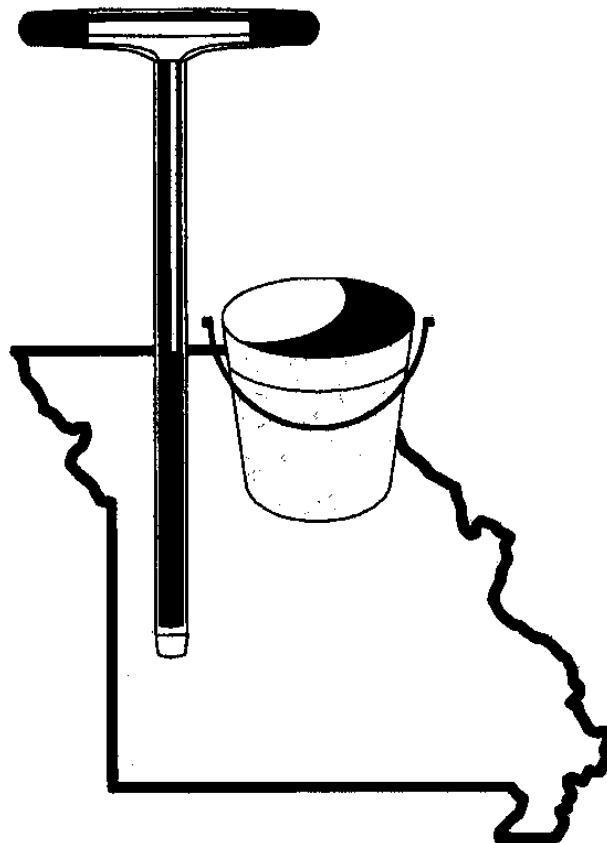


Soil Testing In Missouri

A Guide for Conducting
Soil Tests in Missouri



University Extension
Division of Plant Sciences, College of Agriculture, Food and Natural Resources
University of Missouri

Revised 1/2012

EC923

Soil Testing In Missouri

A Guide for Conducting
Soil Tests in Missouri

Manjula V. Nathan

John A. Stecker

Yichang Sun

Preface

Missouri Agricultural Experiment Station Bulletin 734, *An Explanation of Theory and Methods of Soil Testing* by E. R. Graham (1) was published in 1959. It served for years as a guide.

In 1977 Extension Circular 923, *Soil Testing in Missouri*, was published to replace Station Bulletin 734. Changes in soil testing methods that occurred since 1977 necessitated the first revision of EC923 in 1983. That revision replaced the procedures used in the county labs. This second revision adds several procedures for nutrient analyses not previously conducted by the laboratory. It also revises a couple of previously used analyses (soil organic matter and extractable zinc).

Acknowledgement is extended to John Garrett and T. R. Fisher, co-authors of the 1977 edition of EC923 and to J. R. Brown and R.R. Rodriguez, co-authors of the 1983 edition.

Contents

Introduction.....	5
Sampling.....	7
Sample Submission and Preparation.....	7
Extraction and Measurement.....	7
pH and Acidity Determination.....	8
Evaluation of Soil Tests.....	9
Procedures.....	10
Organic Matter <i>Loss on Ignition</i>	11
Potassium Calcium, Magnesium and Sodium <i>Ammonium Acetate</i> <i>Extraction</i>	13
Phosphorus <i>Bray I and Bray II Methods</i>	16
Soil pH <i>in Water (pH_w)</i>	20
Soil pH <i>in a Dilute Salt Solution (pH_s)</i>	22
Neutralizable Acidity (NA) <i>New Woodruff Buffer Method</i>	24
Zinc, Iron, Manganese and Copper <i>DPTA Extraction</i>	26
Electrical Conductivity.....	29
Sulfate-Sulfur <i>Monocalcium Phosphate Extraction</i>	32
Nitrate-Nitrogen <i>Cadmium Reduction Method</i>	34
Ammonium-Nitrogen <i>Phenolate Method</i>	37
Boron <i>Hot Water Extraction</i>	40
Chloride <i>Mercury (II) Thiocyanate Method</i>	42
Particle Size Analysis <i>Hydrometer Method</i>	44
Greenhouse Root Media	46
Calculated Cation Exchange Capacity.....	48
Literature Cited.....	48

Introduction

Soil testing is a process or a group of processes used to estimate the ability of a soil to supply plant nutrients or support plant growth. Soil test results enable evaluation of the fertility status of soil represented by a sample. Fertilizer and lime recommendations can then be made based on the soil's fertility status. This allows prudent and economical use of fertilizer and lime while providing crops with sufficient nutrients to reach production goals set for a field. In addition,

soil testing can be used to find excesses of certain nutrients.

The soil testing process consists of:

- sampling
- sample preparation
- nutrient extraction and chemical determination of these nutrients
- determination of pH and quantity of soil acidity, and
- evaluation of the tests resulting in fertilizer and lime recommendations.

The soil testing process in Missouri Soil Testing Labs begins when a soil sample arrives at the lab.

- (1) The soil sample is logged in and assigned a laboratory number on both the Soil Sample Information Form that should be submitted with the sample and on the soil bag or box containing the sample.
- (2) The sample is transferred to a drying rack and placed into a forced air, low temperature oven for drying.
- (3) The sample is dried, and then ground to pass a 2 mm screen.
- (4) The amount of soil required for individual soil test procedures is transferred to appropriate extraction containers using soil scoops.
- (5) An extracting solution is automatically dispensed into the flask or beaker.
- (6) The soil-extractant mixture is shaken for a specified time.
- (7) The soil-extractant suspension is filtered.
- (8) The soil extract is diluted with appropriate reagents using an automatic diluter.
- (9) An atomic absorption, flame emission is used to measure the calcium, magnesium, potassium and micronutrient concentrations in the diluted soil extract.
- (10) Soil acidity and lime requirement are determined with a pH meter.
- (11) Phosphorous is determined colorimetrically with a spectrophotometer.
- (12) Organic matter is determined by measuring a weight difference following burning of the soil in a high temperature oven.
- (13) Results are recorded directly onto a computer disk from the measuring instruments.
- (14) A computer program combines soil test data with samples' information which was provided by accompanying Soil Sample Information Forms.
- (15) Soil test reports are printed with soil test results, field information, and fertilizer and lime recommendations. Soil test reports are also transmitted via electronic mail. For county extension offices and firms or individuals who make appropriate arrangements, results can also be accessed via the web using a specifically assigned password.

Sampling

The two weakest links in a soil testing program are sampling and field calibration of soil test results with crop response to nutrients. The first of these weak links is discussed in this section and the second is covered starting on page 9, "Evaluation of Tests."

A soil sample should be representative of a volume of soil. For Missouri farmers that volume is usually the plow layer of a field. For homeowners that volume may be only the soil in a raised flowerbed. For Missouri farms a sample should represent no more than 20 acres. To obtain samples that represent this size or smaller, partition fields into areas based on past management, surface color, texture, and slope.

Once a field area is chosen, take 10 to 20 soil cores across the area. Place the soil cores into a clean plastic bucket, break apart the cores and mix. From this mixture, fill a clean soil sample box or bag. Identify the sample by a number or name on the sample container. If the sample is not taken to a University of Missouri Extension Center on the day it is collected, place it in a dust free location with the container open to allow drying of the sample. More details on sampling soils can be obtained from UMC Guide 9075 (3).

Sample Submission

Samples can be submitted to a county Extension Center or to one of the Soil Testing Laboratories, located in Columbia and Portageville. At the time of submission, clients are asked to complete Soil Information Sheets which provide the labs with information relevant to making recommendations. Fees for the soil test are also collected at submission.

Completion of the Soil Information Sheet is important to obtain the best possible recommendation based on the soil test, as this information is used to calculate recommendations. Information such as previous crop, soil region and yield goal (for horticulture samples, type of grass/plant and management level) is requested.

Upon arrival to the soil testing laboratory, samples are dried at low heat (less than 85° F) and ground to pass through a 2 mm screen. Any stones, sticks, plant material or foreign objects are removed at grinding. In addition to creating a fine and easily handled consistency, grinding provides a final mixing of the soil before extraction.

Extraction and Measurement

The specific details of each test are given in following sections. Phosphorus, potassium, calcium and magnesium are extracted from the soil with appropriate extractants. A small quantity of soil and the extractant are shaken for a specific time. The solution is filtered from the soil, and then the solution is analyzed for the extracted nutrients within the solution.

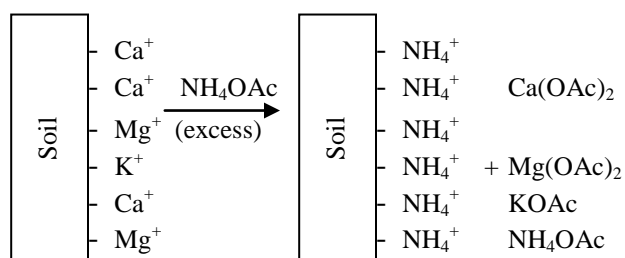
None of the extraction procedures are complete in their removal of nutrients from the soil to solution. However, they provide a good estimate of nutrients which would be available to growing plants. For instance, phosphorus exists

in the soil in the orthophosphate forms of H_2PO_4^- , HPO_4^{2-} or PO_4^{3-} . The first two phosphate anions dominate in most soils unless the soil is extremely acid. An acid ammonium fluoride extractant is used to extract acid soluble as well as water soluble phosphate. Calcium in the soil may cause reprecipitation of calcium phosphate in the extracting solution, but the fluoride ion in the extracting solution minimizes this by tying up the calcium.

The concentration of phosphorus in the soil extract is determined by colorimetry. The extract is treated with an acidic molybdate

solution to form a blue phosphomolybdate complex. The intensity of the blue color which develops is proportional to the amount of phosphorus extracted from the soil. A set of standards of known phosphorus concentration is analyzed for comparison. The intensity of the blue color is determined by a spectrophotometer by measuring the transmittance of a specific wavelength of light. The transmittance of each soil extract is then compared to that of the standards to determine the phosphorus concentration. Modern instrumentation automatically calculates the phosphorus concentration of an extract given its transmittance relative to that of a standard.

An ammonium acetate extracting solution removes exchangeable calcium (Ca), magnesium (Mg) and potassium (K) from the soil. As shown schematically below, ammonium ions exchange for calcium, magnesium and potassium ions on soil particles. The replaced ions go into solution.



The potassium concentration in the ammonium acetate soil extract is determined by flame emission. The extract sample is sucked

into a flame, and the energy of the flame excites the potassium atoms. When the potassium atoms leave the flame, they lose the excitation energy, and this energy is emitted as a light wavelength that is characteristic for potassium. The amount of light emitted is measured by an instrument. This emission is proportional to the amount of potassium in the sample. Standards of known potassium concentration are used to relate the light emitted to concentration.

Calcium and magnesium in the soil extract are determined by atomic absorption. Like flame emission, an extract sample is sucked into a flame. However, this technique uses a flame to place the calcium and magnesium atoms in chemical state to absorb light. A beam of light is passed through the flame. This beam of light is of a preselected wavelength (monochromatic). Calcium and magnesium atoms each absorb light of a specific wavelength. The amount of light absorbed and measured by the instrument is proportional to the quantity of calcium or magnesium atoms present in the extract. Standards of known concentration are used to relate the amount of absorption to the ion concentration.

Phosphorus, potassium, calcium and magnesium are all measured in parts per million but reported in pounds per acre. The conversion is calculated by multiplying parts per million by two. This is based on an estimated two million pounds of soil per furrow acre slice (six inch depth).

pH and Acidity Determination

Soils have varying degrees of acidity, which greatly impact the availability of nutrients, that of those already in the soil and those applied in fertilizer. Consequently, determining soil acidity is important toward assessing soil nutrients and is included in most soil testing systems.

In the University of Missouri soil testing program, soil pH is determined in a 0.01 M

CaCl₂ solution. This is based on the assumption that fertilizer will be applied, and most fertilizers are salts that when applied dissolve into the water in the soil. Plants growing in the soil contact this dilute salt solution. Hence it is logical to estimate the acidity in a chemical environment similar to that which plants contact, rather than an estimate of pH derived from distilled water and soil. An additional

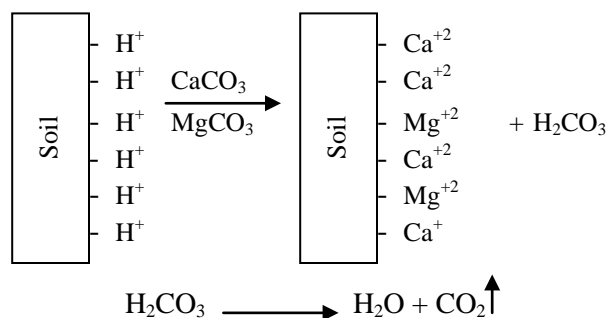
argument for using salt pH is that natural biological activity causes seasonal shifts in soil pH when measured in water. The 0.01 M CaCl₂ solution masks these shifts. A salt pH is reported as pH_s as opposed to a water pH (pH_w).

The pH determination is a measure of hydrogen ion (H⁺) activity in the soil solution. Formally defined, it is:

$$pH = \log \frac{1}{a_H}$$

where a_H is the activity of H⁺ in soil solution. In strongly acid soils (pH_s < 4.5), aluminum ions in the soil become more active, which thus are detrimental to crop root development. For a detailed discussion of soil pH, see the book edited by Pearson and Adams (4).

A pH measurement refers only to active acidity (hydrogen ions in the soil solution). All soils also have a reserve acidity (hydrogen ions attached to the soil particles). Usually the reserve acidity is many times larger than the active acidity. To completely neutralize a soil's acidity, both the active and reserve acidity must be neutralized. Hydrogen ions associated with reserve acidity are detached from soil particles by calcium and magnesium applied in limestone. This leads to removal of acidity from the soil. The classical "liming reactions" are diagrammed below.



C. M. Woodruff devised a buffer system to determine the total acidity in the soil (5). A buffer is chemically defined as a substance that resists change; in this case, the change is of that of active hydrogen. The combination of buffers devised by Woodruff changes pH in proportion to the amount of total acidity. Woodruff modified the original solution in the mid 1960s. These modifications were not formally published but are incorporated into this bulletin.

A sample of soil is placed into a container with the specified quantity of 0.01 M CaCl₂. A given quantity of the Woodruff buffer is added. After a period of equilibration, the pH is measured. The pH of the buffer is 7.0. As it reacts with an acid soil, the pH decreases to a stable value which is measured as pH_B. Each 0.1 unit decrease is equivalent to 1 meq H⁺ per 100 grams of soil if the soil solution ratio is not altered from that given in the detailed procedures (page 23). That is:

$$10(pH_{7.0} - pH_B = \text{Neutralizable acidity (meq / 100g)})$$

From the value of neutralizable acidity, a limestone recommendation is calculated.

Evaluation of Soil Tests

Tests for plant nutrients are estimates of the soil's ability to provide nutrients for a crop. For soil tests to be useful toward indicating a need for fertilizer, they must be calibrated to a crop's response to fertilizer in the field.

This calibration is done through field experiments and statistical evaluation of the resulting data. Plots are selected with different soil test levels. The plots are subdivided, and several rates of a plant nutrient are applied.

Study crops are grown and yields are determined. The data obtained indicate crop yield at a soil test level without fertilizer and the amount of yield increase (or decrease) associated with each rate of fertilizer. The degree to which the fertilizer changes the soil test is also measured. The more data of this type that are collected, the more reliable the soil test becomes as a basis for fertilizer recommendations.

Field calibration research should be a continuing process. As each new soil test procedure is developed, it should be either field calibrated or correlated to the old procedure that was calibrated for it to be a useful basis for making fertilizer recommendations.

In the evaluation of calibration data, fertilizer response equations are developed. The equations

form the basis of the computer program used to make the recommendations printed on the Soil Test Report Form. Data are analyzed to predict the frequency that a crop will respond to fertilizer for a measured soil test value. From this analysis, soil test ratings are developed, which are reported on the Soil Test Report Form.

Procedures

The following pages present the testing methods that the Missouri Regional Soil Testing laboratories use. The format is parallel to that used for procedures by the Council on Soil Testing and Plant Analysis in its reference handbook (6).

For each procedure, check samples of known values are analyzed along with the test samples. In each day's analysis of samples, every 20th sample is a check. This ensures quality control of the analyses.

Most of the procedures listed were evaluated by T. R. Fisher and J. Garrett prior to incorporation, in 1968, into the Delta Area Regional Soil Testing Laboratory. Modifications have been made in the analyses. Based on recent work and demand for the analyses, four new soil test procedures have been added: Hot Water Extraction for Boron, an Electrode method for measuring Chloride, the Cadmium Reduction method for Nitrate-Nitrogen, the Salicylate method for Ammonium-Nitrogen, Particle Size

Analysis by the Hydrometer method, and Greenhouse Root Media. For the determination of soil organic matter, the previously used Walkley-Black method has been replaced by the Loss on Ignition method. Some procedures differ slightly from reference or standard procedures (6, 7).

In this bulletin, there is a reference section at the end of the description of each procedure. These references will not be included in the general literature cited section (page 44).

The following procedures are those that consist of our regular soil analysis:

- Soil Organic Matter By Loss-On-Ignition
- Extractable Soil Phosphorus (Bray-1 method)
- Ammonium Acetate Extractable Calcium, Magnesium and Potassium
- Soil pH in Salt Solution (pH_s)
- Determination of Neutralizable Acidity (NA) – New Woodruff Buffer Method

SOIL ORGANIC MATTER

Loss-On-Ignition

Principle of Method

- 1.1 This method estimates organic matter by measuring weight loss that results from the ignition of organic matter (Loss On Ignition, LOI) in a high temperature oven. It requires that soil is adequately dried before ignition, and then organic matter is quantitatively destroyed without altering other soil constituents such that soil weight is changed.
- 1.2 Various methods using different heating times and temperatures have been investigated. These are noted in the references 8.1, 8.2 and 8.4. A minimum heating temperature of 105° C for 24 hours is necessary to eliminate hygroscopic water and water of hydration from minerals such as gypsum. Excessive heating may result in weight loss associated with carbonates, structural water of silicate clays, oxidation of Fe⁺² and dehydration of salts. The method noted here is adapted from Storer (8.7).

Range and Sensitivity

- 2.1 This method has been used with soils ranging in organic matter content from <1 to 45%. It has a sensitivity of 0.2 to 0.5% organic matter.

Sources of Error

- 3.1 Loss of water from incomplete preheating dehydration can result in over-estimation of organic matter. The problem is particularly likely in high clay soils with low organic matter, such as with subsoils. The method is not considered suitable for calcareous soils.

Precision and Accuracy

- 4.1 This method directly estimates organic matter, and it correlates well with organic carbon determinations. Yet it results in greater estimates of organic matter than with methods

previously used. So organic matter is estimated from this method by regression of data with other established methods.

- 4.2 Mineral composition and soil horizons may affect LOI results.
- 4.3 Consistent analytical results are possible with a range of sample sizes, ashing vessels, ashing temperatures and length of ashing times.
- 4.4 Repeated analyses should provide results with a maximum coefficient of variability of 1 to 4%.

Equipment

- 5.1 NCR-13 2-g scoop.
- 5.2 10 mL glass beakers
- 5.3 Oven capable of heating to approximately 360° C.
- 5.4 Stainless steel racks for holding beakers.
- 5.5 Balance sensitive to ± 1 mg in draft-free environment.

Procedure

- 6.1 Scoop or weigh 2 g of air-dried soil into tared 10-mL glass beakers.
- 6.2 Dry for at least 2 hours at 150° C.
- 6.3 Record pre-weight to ± 1 mg.
- 6.4 Heat at 360° C for 2 hours after oven temperature reaches 360° C.
- 6.5 Move the beakers from the oven to a lab bench; allow cooling approximately 15 minutes to cool. NOTE: if samples cannot be weighted immediately then they should be re-dried in an oven at 150° C for 2 hours prior to recording post-weight.
- 6.6 Record post-weight to ± 1 mg.

Calculations

7.1 Calculate loss of weight on ignition (LOI)

$$LOI \% = \left\{ \frac{\left[(Initial\ wt.\ at\ 150^{\circ}\ C -\ crucible\ wt.) - (Final\ wt.\ at\ 360^{\circ}\ C -\ crucible\ wt.) \right]}{Initial\ wt.\ at\ 150^{\circ}\ C -\ crucible\ wt.} \right\} * 100$$

7.2 Estimate soil organic matter

Estimation of organic matter from LOI is done by regression analysis. Sixty soils were selected at random from those submitted to the lab. LECO-C was determined on these samples as well as % LOI. Percent organic matter was determined from LECO-C by multiplying % C by 1.79. LOI was regressed on LECO-OM forcing the intercept through the origin. The resulting equation is used to convert % LOI values into % organic matter. The equation is:

$$\% \text{ Organic Matter} = \% \text{ LOI} * 0.956$$

References

- 8.1 Ball, D. F. 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *J. Soil Sci.* 15:84-92.
- 8.2 Combs, M. and M. V. Nathan. 1998. Soil Organic Matter. Ch. 12. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region, N.C. Reg. Res. Pub. 221 (Revised). (Mo. Agric. Exp. Stn. SB 1001).
- 8.3 Goldin, A. 1987. Reassessing the use of loss-on-ignition for estimating organic matter content in non-calcareous soils. *Commun. Soil Sci. Plant Anal.* 18:1111-1116.
- 8.4 Handbook on reference methods for soil analysis. 1999. Soil and Plant Analysis Council, Inc. CRC Press. Washington DC.
- 8.5 Michigan State University. Manual of Laboratory Procedures. Soil and Plant Nutrient Laboratory. Michigan State University. Dept. of Crop and Soil Sci. East Lansing, MI 48824.
- 8.6 Nelson, D. W. and L. E. Sommers, 1996. Total carbon, organic carbon, and organic matter. *In* D. L. Sparks (ed.). Methods of Soil Analysis, Chemical Methods, Part 3. Soil Science Soc. Am. Madison, WI.
- 8.7 Storer, D. A. 1984. A simple high sample volume ashing procedure for determining soil organic matter. *Commun. Soil Sci. Plant Anal.* 15:759-772.
- 8.8 Western States Laboratory Proficiency Testing Program, Soil and Plant Analytical Methods. 1998. Version 4.10.

Calcium, Magnesium, Potassium and Sodium Ammonium Acetate Extraction

Principle of the Method

- 1.1 This method uses 1N ammonium acetate (NH_4OAc) at pH 7.0 to extract basic cations (calcium, Ca; magnesium, Mg; potassium, K and sodium, Na) from the soil. The quantity of extracted basic cations is equivalent to the quantity considered exchangeable. The ammonium ion replaces the basic cations by cation exchange. Ammonium is selected as a replacing ion because of the relatively low levels of exchangeable ammonium in most arable soils, and because the quantity of cations extracted by ammonium acetate reaches a relatively stable quantity after a short period of time. The acetate buffers suspensions near a desirable level of acidity for most crops.
- 1.2 See references 12.1, 12.3, and 12.4 for detailed discussions of the method.

Range and Sensitivity

- 2.1 The procedure described here has a range of 0 to 8000 lb Ca/acre, 0 to 1200 lb Mg/acre, and 0 to 1000 lb K/acre. The range can be extended by dilution of the soil extract.
- 2.2 The sensitivity will depend on the instrument used and the extraction parameters.

Interferences

- 3.1 If free carbonates of Ca and Mg are present, the extracting reagent may dissolve some of the carbonates. If calcareous soils are extracted, the basic cations in the extract would be termed exchangeable plus soluble or extractable (12.2).
- 3.2 Lanthanum diluent for the atomic absorption spectrophotometer is used to suppress interfering substances in the soil extracts.

Precision and Accuracy

- 4.1 Extraction aliquots of the same soil sample should give coefficients of variation less than 10%. Samples testing near the upper end of the accuracy range will have more variability than those in the mid-to-low end of the range. Much of the variability is caused by soil heterogeneity rather than to the extraction or analysis method.
- 4.2 Sample drying tends to change the level of extractable K (usually an increase). However, the physical problems associated with routine testing of moist samples have caused most soil testing facilities to use dried samples.

Apparatus

- 5.1 Balance or 2 g scoop (NCR-13).
- 5.2 50 mL Erlenmeyer extraction flask.
- 5.3 Extracting solution dispenser (20 mL).
- 5.4 Mechanical shaker, 180 or more oscillations per minute.
- 5.5 Filter funnel (45 mm top ID).
- 5.6 Funnel rack.
- 5.7 Filter paper, Whatman No. 2 or equivalent, 9 cm.
- 5.8 Receiving beakers, 20 to 30 mL.
- 5.9 Diluter.
- 5.10 Atomic absorption spectrophotometer.
- 5.11 Flame photometer (if preferred for K analysis).

Reagents

6.1 Extracting Solution-Ammonium acetate-- NH₄OAc @ pH 7.0)

Pour 58 mL of acetic acid (HC₂H₃O₂), 95.5%, 1.05 sp. gr. into about 500 mL of deionized water. Add 70 mL of ammonium hydroxide (NH₄OH), 0.9 sp. gr. and mix. Dilute to about 950 mL and cool. Adjust the pH to 7.0 ± 0.05 with acetic acid or ammonium hydroxide. Dilute to one liter with deionized water.

6.2 Lanthanum Diluent (0.105% La).

Place 1.2314 g of lanthanum oxide (La₂O₃), low calcium grade, in a one liter volumetric flask. Add 4 mL of 6 N HCl to dissolve the La₂O₃, then dilute to one liter with deionized water.

Procedure

7.1 Extraction

Weigh or scoop 2 g of <10 mesh air dry soil into an extraction flask. Add 20 mL of extracting solution (6.1). Shake 5 minutes on a shaker, filter, and collect the filtrate in a 20 mL beaker.

7.2 Potassium Determination

7.21 Flame emission spectrometers may be used for determination of K directly in the extract. In such cases where no internal standard is used, use the potassium standards in 1 N NH₄OAc as in 8.3.

7.22 Potassium may be determined on some atomic absorption spectrophotometers. See the appropriate instrument instruction manual.

7.3 Alternate Potassium Determination

Use a 1:1 dilution of soil extract or standard and lithium solution. Transfer 5 mL of the extract into a beaker. Add 5 mL of Lithium Diluent (6.2) as an internal standard and determine on a flame photometer. A final Li internal standard concentration of 15 milliequivalents (meq) per liter is needed to meet internal standard requirements for flame photometers.

7.4 Sodium Determination

Sodium may be determined on the extracts used for K determination (7.2 or 7.3). Sodium standards must be used (8.4).

7.5 Calcium and Magnesium Determination

Dilute 0.5 mL of the soil extract (7.1) with 9.5 mL of the Lanthanum diluent (6.2). Determine the Ca and Mg concentration on an atomic absorption spectrophotometer.

Calibration and Standards

8.1 Calcium Standards

Calcium standards are made using a purchased 1000 ppm Ca standard solution (Ca Standard). The recipe given below is designed to make working standards that are to be used with diluted soil extracts. Different amounts of the Ca Standard solution are added to one liter volumetric flasks. The solutions are brought up to volume with 1 N NH₄OAc to result in the working standard solutions. Diluting 0.5 mL of the working standard solutions with 9.5 mL of the lanthanum diluent results in the final concentrations against which soil extracts are compared.

Concentrations			
1000 ppm Standard	Working Standards	Final	Equivalent Soil Ca
<i>mL/L</i>	<i>ppm</i>	<i>ppm</i>	<i>lb/A</i>
0	0	0	0
100	100	5	2000
200	200	10	4000
300	300	15	6000
400	400	20	8000
600	600	30*	12000

*Not normally used in routine runs

8.2 Magnesium Standards

Magnesium standards are made using a purchased 1000 ppm Mg standard solution (Mg Standard). The recipe given below is designed to make working standards that are to be used with diluted soil extracts. Magnesium working standards are made similar to those of calcium.

Concentrations			
1000 ppm Standard	Working Standards	Final	Equivalent Soil Mg
<i>mL/L</i>	<i>ppm</i>	<i>ppm</i>	<i>lb/A</i>
0	0	0	0
10	10	0.5	200
20	20	1.0	400
30	30	1.5	600
40	40	2.0	800
60	60	3.0*	1200

*Not normally used in routine runs.

8.3 Potassium Standards

Potassium standards are made using a purchased 1000 ppm K standard solution (K Standard). An alternative to using a standard K solution would be to dissolve 1.906 g KCl in deionized water and dilute to one liter. The recipe given below is designed to give standards to be used with soil extracts in 1 N NH₄OAc. Add appropriate amount of K Standard to one liter volumetric flasks and bring up to volume with 1 N NH₄OAc.

Concentrations		
1000 ppm Standard	Working Standards	Equivalent Soil K
<i>mL/L</i>	<i>ppm</i>	<i>lb/A</i>
0	0	0
5	5	100
10	10	200
15	15	300
20	20	400
30	30	600
50	50	1000

8.4 Sodium Standards

Sodium standards are made using a purchased 1000 ppm sodium standard solution (Na Standard). An alternative to using a standard Na solution would be to dissolve 3.6971 g NaNO₃ in deionized water and dilute to one liter. To make working standards, follow the recipe for K standards (8.3), but substitute the Na standard.

Calculations

9.1 In Missouri, cation results are reported in pounds/acre, assuming 2 million pounds. in a 6 2/3 inch furrow slice.

9.2 The instrument readings are converted to pounds per acre using the appropriate standard curves or instrument readout.

Storage

10.1 Soil samples that are stored air-dry in closed containers should not change cation concentrations appreciably in one year, but there may be long-term changes depending on the mineralogy and potassium content of the soil.

10.2 Soil extracts should not be stored for more than 4 hours unless placed in closed containers with appropriate provisions made for the suppression of microbial growth.

Interpretation

11.1 The test must be calibrated to field response in order for soil test results to be useful. Once calibrated the test can be used to predict yields and to predict the probability of response to fertilizers. See the appropriate extension publications for proper interpretation.

Reference

- 12.1** Chapman, H. D. 1965. Total Exchangeable Bases. Ch. 58. *In* C. A. Black (ed.). *Methods of Soil Analysis, Part 2*. Soil Sci. Soc. of Amer., Madison, WI.
- 12.2** Handbook on Reference Methods for Soil Analysis. 1999. Soil and Plant Analysis Council Inc. CRC Press. Washington D.C. .
- 12.3** Jackson, M. L. 1958. *Soil Chemical Analysis*. Prentice-Hall, Inc., Englewood Cliffs, N.J.
- 12.4** Warnke, D. and J. R. Brown. 1998. Potassium and Other Basic Cations. Ch. 7. *In* J. R. Brown (ed.). *Recommended Chemical Soil Test Procedures for the North Central Region*, N.C. Reg. Res. Pub. 221 (Revised). (Mo. Agric. Exp. Stn. SB 1001).

Extractable Soil Phosphorus

Bray I and Bray II Methods

Principle of the Method

- 1.1 This soil test procedure for P is a modification of the procedure originally developed in Illinois by Roger Bray and co-workers S. R. Dickman and Touby Kurtz (12.1). During subsequent years the procedure has been evaluated and modified (12.2, 12.8, 12.9). The ascorbic acid method of developing color has been adapted for use with soil extracts (12.10, 12.11). The tests used in the Missouri county soil testing laboratories and at the Delta Center laboratory have been outlined by Graham and Fisher (12.6, 12.5). In recent years attempts have been made to eliminate procedural variability between states (12.3). The procedure given here is the one proposed as standard for the North Central States with a modification to include the Bray II test (12.4).
- 1.2 The HCl in the Bray extractants extracts a portion of the acid soluble P in soils. The Bray-I (weak, 0.025 N HCl) is less reactive than the Bray-II (strong, 0.1 N HCl). The Bray-I extractant is used routinely. In Missouri, the Bray-II method has previously been used, because it tends to identify soils that had received rock phosphate from those that had not. In states such as Iowa, very little rock phosphate has been used, hence the Bray-I test has been preferred.

The F⁻ ion in the extractant tends to suppress the activity of Al and Ca. These two cations combine with ortho-phosphate anions (H₂PO₄⁻, H₂PO₄²⁻, PO₄³⁻). Thus the F⁻ ion helps maintain phosphates in solution during extraction. The Bray extractants should not be used on alkaline soils because (1) the acid tends to be neutralized and/or (2) excessive calcium phosphates may be extracted, giving a false high test for available P.

Range and Sensitivity

- 2.1 The Fiske-Subbarow standard curve is essentially linear to about 10 ppm P in the extract. The Ascorbic Acid variation is linear to about 7 ppm P in the extract.
- 2.2 The test is sensitive to about 0.1 ppm P in the extract or 2 pounds P/acre if the ascorbic acid variation is used.

Interferences

3.1 Arsenic

Normal field soils do not generally have sufficient arsenic to be a problem. However because arsenic has been used as a pesticide in orchards, arsenic in orchard soils may be sufficiently high to be additive to the P test (12.11). Jackson outlines steps to remove arsenic interference (12.6).

3.2 Fluoride

Fluoride may interfere with color development. Boric acid may be added to some reagents to prevent such interference.

Precision and Accuracy

- 4.1 If fresh reagents are used and times and action correspond to the procedure as outlined, coefficients of variation of 5% should be expected on repeat runs. This does not, however, consider field sampling variability.

Equipment

- 5.1 Balance or 2 g scoop (NCR-13).
- 5.2 Erlenmeyer extraction flask, 50 mL.
- 5.3 Rack for extraction flasks.
- 5.4 Automatic dispensers and diluters (kind and quantity dependent on laboratory arrangement and volume).
- 5.5 Shaker (> 180 oscillations per minute).

- 5.6 Funnel (45 mm diameter with a 50 mm stem).
- 5.7 Funnel rack.
- 5.8 Filter paper (Whatman No. 2 or equivalent, 9 cm).
- 5.9 Receiving beaker.
- 5.10 Spectrophotometer tubes (or automatic flow through cell).
- 5.11 Spectrophotometer.

Reagents

6.1 Bray I Extracting Reagent

Dissolve 11.11 g of reagent grade ammonium fluoride (NH_4F) in about 9000 mL of deionized water. Add 21.6 mL of concentrated hydrochloric acid (sp. gr. 1.19, 37.5%). Dilute to 10 liters and mix. Store in a polyethylene container. This solution should be 0.03 N NH_4F in 0.025 N HCl.

6.2 Bray II Extracting Reagent

Dissolve 11.11 grams of reagent grade ammonium fluoride in about 8000 mL of deionized water and add 83 mL of concentrated hydrochloric acid (sp. gr. 1.19, 37.5%). Dilute to 10 liters with deionized water and mix. Store in a polyethylene container. This solution should be 0.03 N NH_4F in 0.1 N HCl.

6.3 Color Development Reagents-Ascorbic Acid

6.31 Acid Molybdate Stock

Dissolve 120 g of ammonium molybdate molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$] in 200 mL of warm (60° C) deionized water. Cool. Dissolve 2.910 g antimony potassium tartrate in the aqueous molybdate solution. Slowly add 1400 mL of concentrated sulfuric acid (H_2SO_4). Cool and dilute to 2 liters. Store in a dark refrigerated compartment. This solution may be blue but will clear when diluted for use.

6.32 Ascorbic Acid Stock

Dissolve 132 g ascorbic acid in deionized water and dilute to a final volume of one liter. Store in a dark refrigerated compartment.

6.33 Working Solution

Add 25 mL of acid molybdate stock to 800 mL deionized water. Add 10 mL of ascorbic acid stock. Dilute to 1 liter with deionized water. MAKE FRESH DAILY.

6.4 Color development reagents--Fiske-Subbarow Variation.

6.41 Acid Molybdate Solution

Dissolve 75.25 g ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) in 490 mL warm (60° C) deionized water. Cool. Add 1500 mL of concentrated HCl (sp. gr. 1.19, 37.5%) and mix. Cool and dilute to 2 liters with distilled water. Store in a glass stoppered brown bottle to which 100 g of boric acid has been added.

6.42 Dry Reducing Powder

Mix 5 g 1-amino-4-sulfonic acid and 10 g sodium sulfite (Na_2SO_3) with 292.5 g of sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$). Grind the mixture to a fine powder. Store in a brown bottle in a dark, cool place. Shelf life approximately 1 year if properly stored.

6.43 Dilute Reducing Solution

Dissolve 16 g of the dry reducing solution in 100 mL of warm (60° C) deionized water. Cool and store in a brown bottle. Maximum shelf life is 3 weeks.

Procedure

7.1 Extraction

Weigh or scoop 2 g of < 10 mesh soil and place in a 50 mL Erlenmeyer extraction beaker. Add 20 mL of extracting reagent and shake 5 minutes at 180 or more oscillations per minute.

7.2 Filtration

Filter into the receiving beaker. Refilter if filtrate is not clear.

7.3 Color Development.

7.31 Ascorbic Acid.

In a 1:4 ratio combine aliquots of extract and working solution in a test tube.

- 7.311 Transfer a 1.5 mL aliquot to a test tube.
- 7.312 Add 6 mL of working solution in a manner to insure mixing in the test tube.
- 7.313 Allow 20 minutes for color development. Read percent transmittance (or optical density) on a spectrophotometer set at 660 nm with a blank (0 ppm P standard) that has been diluted with the working solution giving 100% transmittance. The color is relatively stable for at least 2 hours.

7.32 *Fiske-Subbarrow Method. Variation*

- 7.321 Transfer a 5 mL aliquot to a test tube.
- 7.322 Add 0.25 mL acid molybdate solution.
- 7.323 Add 0.25 mL dilute reducing solution. Shake.
- 7.324 Read percent transmittance (or optical density) on a spectrophotometer set at 660 nm between 15 and 45 minutes after addition of dilute reducing solution. Use a blank (0 ppm P standard) that has been diluted with acid molybdate and dilute reducing solutions to set 100% transmittance

Dilute 10 mL of the standard stock solution to 1000 mL with the appropriate extracting reagent in a volumetric flask.

8.3 Operating Standards

Use the following table to make the appropriate standards. Use transfer pipettes and one liter volumetric flasks. Fill to volume with the appropriate extracting solution.

Equivalent Concentration in the Soil					
1000ppm Working Standard	Working Conc.	Ascorbic Acid		Fiske-Subbarrow	
mL	ppm	ppm P	lb/A P	ppm P	lb/A P
50	0.5	5	10	5	10
100	1	10	20	10	20
250	2.5	25	50	25	50
500	5	50	100	50	100

8.4 Standard Curve

Prepare a standard curve by starting the procedure at paragraph 7.3 using the operating standards instead of soil extracts. Read the percent transmittance in the same way as for the soil extracts and enter values into the spectrophotometer. Also enter the appropriate conversion factor for the standards read. If a standard curve is to be developed independently from the spectrophotometer, plot percent transmittance on the logarithmic axis of a semi-log graph and concentration on the linear axis. If optical density is used, an ordinary linear graph is appropriate. If all reagents are operating properly, a straight line should result (except perhaps with the most concentrated standard).

Calibration and Standards

8.1 Standard Stock Solution - 1000 ppm P.

In a minimum quantity of deionized water, dissolve 4.3936 g of reagent grade potassium dihydrogen phosphate (KH₂PO₄), which has been oven dried. Dilute to one liter with the appropriate extracting reagent (Bray I or Bray II). Storage life is indefinite in a stoppered polyethylene container.

8.2 Working Standard Solution - 10 ppm P.

Calculations

- 9.1 The results may be reported as ppm P, lb P/acre or lb P₂O₅/acre as desired (see paragraph 8.3). This procedure assumes a weight relationship of 2 million pounds of soil per acre furrow slice of 6 2/3 inches.

Effects of Storage

- 10.1 Soil samples may be stored for several months with no change in extractable P.
- 10.2 Soil extracts should be stored no longer than 24 hours if in an air tight container. Once the

color has been developed follow the time directions in paragraph 7.31 or 7.32.

10.3 The extracting reagent is quite stable when stored in polyethylene. Shelf life of the color development reagents is given in paragraph 6.3 and 6.4.

10.4 The working stock solution (8.2) and operating standards (8.3) should be stable.

Interpretation

11.1 Accurate fertilizer recommendations for P are based upon calibration of the test with response to fertilizer P. As data are collected, recommendations are modified thus the appropriate current extension publication should be consulted.

Literature Cited

12.1 Much of the early work on the test was done at the University of Illinois under the direction of Dr. Roger Bray. Listed in this paragraph are some of the early citations:

- (a) Bray, R. H. 1929. A Test for Available Phosphorus in Soils. Univ. of IL, Bul. 337.
- (b) Dickman, S. R. and R. H. Bray. 1941. Replacement of Absorbed Phosphate from Kaolinite by Fluoride. *Soil Sci.* 52:263-273.
- (c) Bray, R. H. and S. R. Dickman. 1942. Tentative Fluoride Extraction Methods for Soil Phosphorus. Univ. of IL., Agric. Exp. Stn. Mimeo AG 1006.
- (d) Bray, R. H. 1942. Rapid Tests for Measuring and Differentiating Between the Absorbed and Acid-Soluble Forms of Phosphate in Soils. Univ. of IL., Agron. Mimeo.
- (e) Bray, R. H. and L. T. Kurtz. 1945. Determination of Total, Organic, and Available Forms of Phosphorus in Soil. *Soil. Sci.* 59:39-45.
- (f) Bray, R. H. 1948. Correlation of Soil Tests With Crop Response to Added Fertilizers

and With Fertilizer Requirement. Ch. 11 *In* Diagnostic Techniques for Soils and Crops. H. B. Kitchen, ed., Amer. Potash Institute, Washington, D.C.

- 12.2** Arnold, C. Y. and Touby Kurtz. 1946. Photometer Method for Determining Available Phosphorus in Soils. Univ. of IL, Agron. Dept. Mimeo AG1306.
- 12.3** Handbook on Reference Methods for Soil Analysis. 1999. Soil and Plant Analysis Council, Inc. CRC Press, Washington DC...
- 12.4** Frank, K., D. Beegle and J. Denning. 1998. Phosphorus. Ch. 7. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).
- 12.5** Fisher, T. R. 1969. Soil Testing Laboratory Improvements in Missouri. Univ. of MO. Agron. Dept. Unpublished Mimeo.
- 12.6** Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. Univ. of MO. Agric. Exp. Stn. Bul. 734.
- 12.7** Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall, Inc. Englewood Cliffs, N. J.
- 12.8** Laverty, J. C. 1963. The Illinois Method for Determining Available Phosphorus in Soils. Univ. of IL., Agron. Dept. Mimeo AG1861.
- 12.9** Laverty, I. C. 1963. A Modified Procedure for the Determination of Phosphorus in Soil Extracts. *Soil Sci. Soc. Amer. Proc.* 27:360-361.
- 12.10** Murphy, J. and J. R. Riley. 1962. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters *Anal. Chem. Acta* 27:31-36.
- 12.11** Watanabe, F. S. and S. R. Olsen. 1965. Ascorbic Acid Method for Determining Phosphorus in Water and NaHCO₃ Extracts from Soil. *Soil Sci. Soc. Amer. Proc.* 29:677-678.

Soil pH in Water (pH_w)

Principle

- 1.1 This procedure estimates the pH of soil solutions in a 1:1 soil to water suspension. Reference 12.1 presents the basic chemistry of soil acidity. In theory as the pH value decreases 1 unit, the concentration of H^+ ions increases 10 fold. Commercially available pH meters with a glass electrode and a calomel reference electrode are used to determine soil pH_w . The measurement is an estimate of the activity of H^+ ions in solution.
- 1.2 This procedure is a modification of the procedure given in Reference 12.2

Range and Sensitivity

- 2.1 A pH range of 3.2 to 8.5 can be obtained with most commercial pH meters and will be adequate for the majority of soils.
- 2.2 In routine soil testing, it is necessary to read pH_w only to 0.1 unit. Most commercial pH meters easily meet this requirement if the glass and calomel electrodes are in good condition.

Interferences

- 3.1 Most interferences are discussed in reference 12.1. This reference should be consulted to obtain a working knowledge of problems inherent in determining pH_w . Scratched glass electrodes and plugged reference electrodes cause most of the problems in the determination of pH_w .
- 3.2 In alkaline soils atmospheric CO_2 may have an appreciable effect on soil pH.

Precision and Accuracy

- 4.1 Random variation of 0.1 to 0.2 pH unit can be expected in replicates of the same sample or in

exchanges of the same sample between laboratories.

Apparatus

- 5.1 Balance or 5 g scoop (NCR-13).
- 5.2 Cup, 30 mL capacity (glass, plastic or paper).
- 5.3 Dispenser, 5 mL.
- 5.4 Stirrer, shaker or glass rod.
- 5.5 pH meter, line or battery operated, with a glass electrode and a calomel reference electrode (or a combination electrode).

Reagents

- 6.1 **pH 7.0 Buffer**
Solution is commercially available.
- 6.2 **pH 4.0 Buffer**
Solution is commercially available.

Procedure

- 7.1 Weigh or scoop 5 g of air-dry, <10 mesh soil into a cup (see 5.2). Add 5 mL of distilled deionized. Shake for 30 minutes or stir intermittently several times over a 30 minute period. With a stirring motion lower the electrodes into the soil-water suspension. When a stable number is achieved on the pH meter, record the meter reading as pH_w to the nearest 0.1 unit.
- 7.2 Save the sample if a buffer pH determination is desired.

Calibration and Standards

- 8.1 The pH meter is calibrated using pH 7 and pH 4 buffers (see 6.1, 6.2) according to instrument instructions.

- 8.2** A set of check soil samples of known pH levels should be used daily to assure proper operation of the meter and electrodes.

Calculation

- 9.1** The result is the direct reading from the pH meter and is reported as pH_w .

Storage Effects

- 10.1** Storage of air-dry samples for several months in closed containers will not affect the pH_w .
- 10.2** Follow the manufacturer's instructions for storage of the pH meter and electrodes to maintain accuracy and reliability of results.

Interpretation

- 11.1** See appropriate extension and agronomic research publications for state or region.

References

- 12.1** Coleman, N. T. and G. W. Thomas. 1967. The Basic Chemistry of Soil Acidity. Ch 1. *In* Soil Acidity and Liming, R. W. Pearson and F. Adams, ed. Agronomy No. 12. Amer. Soc. of Agron., Madison, WI.
- 12.2** Handbook on Reference Methods for Soil Analysis. 1999. Soil and Plant Analysis Council, INC. CRC Press, Washinton DC. Athen, GA.

Soil pH

in a Dilute Salt Solution (pH_s)

Principle of the Method

- 1.1 This method estimates the activity of H^+ ions in a soil suspension in the presence of 0.01 M CaCl_2 which approximates a constant ionic strength for soils regardless of past management, mineralogical composition, and fertility level.
- 1.2 The use of 0.01 M CaCl_2 in soil pH measurement was proposed by Schofield and Taylor (12.4). Peech (12.3) summarized the advantages of using 0.01 M CaCl_2 for measuring soil pH values. McLean (12.2) and Woodruff (12.6) give additional discussions of the merits of determining soil pH in a constant salt level.

Range and Sensitivity

- 2.1 Commercially available standard pH meters have an adequate range to measure the pH in 0.01 M CaCl_2 of acid soils (pH_s 2.5 to 7.0).
- 2.2 The sensitivity will depend on the instrument. In routine soil testing it is necessary to read pH only to the 0.1 unit.
- 2.3 The pH in 0.01 M CaCl_2 may be estimated with a brom cresol purple solution (12.5).

Interferences

- 3.1 The main advantage of soil pH measurement in 0.01 M CaCl_2 is the elimination of interferences and suspension effects that result from variable salt contents.

Precision and Accuracy

- 4.1 Soil pH measurements in 0.01 M CaCl_2 are more precise than those made in water due to elimination of interferences (3.1).

Apparatus

- 5.1 Balance or 5 g scoop (NCR-13)

- 5.2 Cup, 30 mL capacity (glass, plastic or paper).
- 5.3 Dispenser, 5 mL.
- 5.4 Stirrer, shaker, or glass rod.
- 5.5 pH meter, line or battery operated, with a glass electrode and a calomel reference electrode (or a combination electrode).

Reagents

- 6.1 **0.01 M Calcium chloride (CaCl_2)**
Dissolve 1.47 g of calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water and dilute to one liter.
- 6.2 **pH 7.0 Buffer**
Solution is commercially available.
- 6.3 **pH 4.0 Buffer**
Solution is commercially available.
- 6.4 **(alternative) 1 M Calcium chloride (CaCl_2)**
Dissolve 147 g of calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water and dilute to one liter.

Procedure

- 7.1 Weigh or scoop 5 g of < 10 mesh soil into a 30 mL beaker (or comparable container—5.2). Add 5 mL of 0.01 M CaCl_2 solution and stir for 30 minutes on a mechanical stirrer or shaker (or periodically with a glass rod for a period of 30 minutes). Calibrate the pH meter according to instructions supplied with the specific meter. With a stirring motion lower the electrodes into the 0.01 M CaCl_2 -soil suspension. When a stable number is achieved on the pH meter, record the meter reading as pH_s (or pH in 0.01 M CaCl_2) to the nearest 0.1 unit.

- 7.2** In laboratories desiring both a soil pH in water and a soil pH in 0.01 M CaCl₂, 5 mL of distilled water can be substituted for the 5 mL of 0.01 M CaCl₂ in 7.1. After the pH_w is determined, one drop of 1 M CaCl₂ can be placed in the soil-water suspension; the suspension is stirred for 30 minutes, and the pH read. Report the pH as pH_s or pH in 0.01 M CaCl₂.
- 7.3** In laboratories using the Woodruff Buffer method of determining neutralizable acidity, the Woodruff Buffer may be added to the samples after pH is determined.
- 7.4** Alterations in quantities of soil and solution will not affect the results if the ratio given in paragraph 7.1 is maintained.

Calibration and Standards

8.1 Buffer Solutions

The pH meter is calibrated using commercially available buffer solutions of pH 7.0 and pH 4.0 according to the instrument instruction manual.

Calculations

- 9.1** The results are reported as pH_s or pH in 0.01 M CaCl₂.

Effects of Storage

- 10.1** Air dry soils may be stored several months in closed containers without affecting the pH measurement.

- 10.2** Follow the manufacturer's instructions for storage of the pH meter and electrodes to maintain accuracy and reliability of results.

Interpretation

See 12.1 or 12.6

References

- 12.1** Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. MO. Agric. Exp. Stn. Bul. 734.
- 12.2** McLean, E. O. 1973. Testing Soils for pH and Lime Requirement. Ch. 7. *In* Walsh, L. M. and J. D. Beaton, (ed.). Soil Testing and Plant Analysis Rev. Ed. Soil Sci. Soc. of Amer. Madison, WI.
- 12.3** Peech, M. 1965. Hydrogen-Ion Activity. Ch. 60. *In* Black, C. A. (ed.). Methods of Soil Analysis Part 2. Chemical and Microbiological Properties. Amer. Soc. Agron. Madison, WI.
- 12.4** Schofield, R. K. and A. W. Taylor. 1955. The Measurement of Soil pH. Soil Sci. Soc. Amer. Proc. 19:164-167.
- 12.5** Woodruff, C. M. 1961. Brom Cresol Purple as an Indicator of Soil pH. Soil Sci. 91:272.
- 12.6** Woodruff, C. M. 1967. Crop Response to Lime in the Midwestern United States. Ch. 5. *In* Pearson, R. W. and F. Adams (ed.). Soil Acidity and Liming. Amer. Soc. of Agron. Madison, WI.

Neutralizable Acidity (NA)

New Woodruff Buffer Method

Principle of the Method

- 1.1 This procedure estimates a soil's lime requirement by the new Woodruff buffer method. This is a modification of the original Woodruff buffer method (12.2, 12.4, 12.5). The lime requirement in practical terms is the quantity of agricultural limestone required to raise the pH level of a soil to a desired level. The desired level depends upon the soil and the crops to be grown. This procedure was evaluated by Cisco (12.1) by comparison with the older Woodruff method (12.5) and the "SMP" method (12.3). In addition the data were related to soil pH changes due to application of CaCO_3 . In all cases the New Woodruff method gave the best correlation with the true lime requirement.
- 1.2 After the Woodruff buffer solution is added to and mixed with an acid soil sample, the pH of the suspension will be lower than the original buffer pH. This depression in buffer pH is due to the acidity that agricultural limestone will neutralize, and it is called neutralizable acidity. The new Woodruff buffer is designed so that 0.1 pH depression equals 1 milliequivalent (meq) of neutralizable acidity per 100 g of soil when the soil to buffer ratio given in paragraph 7.1 is used.

Range and Sensitivity

- 2.1 This procedure is useful for soils with neutralizable acidity ≤ 10 meq per 100 g. If the pH depression exceeds 1 pH unit, rerun the procedure with one-half the designated quantity of soil and double the results.
- 2.2 Neutralizable acidity (NA) should be determined to the nearest 1 meq per 100 g.

Interferences

- 3.1 Alteration of the buffer's exposure time to the soil to the may alter the measurement of neutralizable acidity.

Precision and Accuracy

- 4.1 A sensitivity of 0.1 pH unit is required of the pH meter used in this determination.

Apparatus

- 5.1 Balance or 5 g scoop (NCR-13).
- 5.2 Cup or beaker, 30 mL capacity (glass, plastic or paper).
- 5.3 Dispensers, 5 mL (2).
- 5.4 Shaker, stirrer or glass rod.
- 5.5 pH meter, line or battery operated, with a glass electrode and a calomel reference electrode (or a combination electrode).

Reagents

- 6.1 **0.01 M Calcium chloride (CaCl_2)**

- 6.2 **Woodruff Buffer Solution (New).**

Dissolve 10 g calcium acetate [$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$] and 4.0 g calcium hydroxide [$\text{Ca}(\text{OH})_2$] in 500 mL of cool deionized water. Heat 200 mL of distilled water to 70°C and dissolve 12.0 g of para-nitrophenol in the hot water. Add 10.0 g salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) to the acetate-hydroxide solution and mix vigorously for one to two minutes. Pour in the para-nitrophenol solution and mix. A delay in adding the para-nitrophenol solution will cause undesirable side reactions. Bring the resulting solution to one liter while adjusting the pH to 7.0 ± 0.05 with 6 N NaOH or 6 N HCl.

- 6.3 **pH 7.0 Buffer solution**

Solution is commercially available.

- 6.4 **pH 4.0 Buffer solution**

Solution is commercially available.

Procedure

- 7.1 Weigh or scoop 5 g of < 10 mesh soil into a 30 mL container. Add 5 mL of 0.01 M CaCl_2 solution. (If pH_s is desired, determine it first on the stirred sample after 30 minutes). Add 5 mL of the Woodruff Buffer Solution (6.2), stir

intermittently over a 30-minute period. With the pH meter set at pH 7.00 with the Woodruff Buffer Solution, lower the electrodes into the buffer–soil suspension using a stirring motion. When a stable number is achieved on the pH meter, record the meter reading as pH_b to the nearest 0.1 unit.

- 7.2** When the pH depression measured with the Woodruff Buffer suspension is greater than 1.0 pH unit (10 meq NA per 100 g), the solution should be diluted and another measurement taken. Add a second 5 mL of distilled water and 5 mL of Woodruff Buffer plus 2 more drops of $CaCl_2$. Measure again as in 7.1.

Calibration

- 8.1** The pH meter is set at pH 7.00 with the Woodruff Buffer Solution (7.1).

Calculation

- 9.1** The buffer solution is at pH 7.0 when added to the soil. $pH\ 7.0 - pH_B = pH\ depression$.
- 9.2** $10 \times pH\ depression = neutralizable\ acidity\ (NA)\ in\ meq\ per\ 100\ g\ soil$.
- 9.3** When a dilution is made as in 7.2, double the measured NA.

Effects of Storage

- 10.1** Air dry soil may be stored in closed containers for several months with no effect on pH_s .
- 10.2** The electrodes should be stored according to the manufacturer's instructions.

- 10.3** The buffer solution should be stored in a container protected from air.

Interpretation

- 11.1** The lime requirement of the soil depends upon the neutralizable acidity of the soil and the neutralizing value of the limestone used. Consult extension publication G9107 for the correct interpretation.

References

- 12.1** Cisco, J. R. 1981. Estimating the Lime Requirements of Missouri Soils. Unpublished M.S. Thesis. Library, University of Missouri Columbia.
- 12.2** Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. Mo. Agric. Exp. Stn. Bul. 734.
- 12.3** Watson, M. E. and J. R. Brown. 1998. pH and Lime Requirement. Ch. 4. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).
- 12.4** Woodruff, C. M. 1948. Determination of the Exchangeable Hydrogen and Lime Requirement of the Soil by Means of the Glass Electrode and a Buffered Solution. Soil Sci. Soc. Amer. Proc. 12:141-142.
- 12.5** Woodruff, C. M. 1948. Testing Soils for Lime Requirement by Means of a Buffered Solution and the Glass Electrode. Soil Sci. 66:53-63.

Zinc, Iron, Manganese and Copper DTPA Extraction

Principle of the Method

1.1 This method was developed as a nonequilibrium extraction by Lindsay and Norvell (13.5). DTPA (diethylenetriamine-penta-acetic acid) will chelate iron (Fe), manganese (Mn), zinc (Zn) and copper (Cu), hence it serves as an effective extracting agent. In the two-hour shaking time provided in the procedure, equilibrium is not attained and, as pointed out by Whitney (13.9), conditions such as pH, shaking time, and laboratory temperature will affect the results. As a result, any modifications of the procedure "must be carefully monitored to adjust the interpretation levels" (13.9). Kennedy (13.4) evaluated this procedure and found the results for zinc in Missouri soils could be interpreted for DTPA extracts as described by Soltanpour et al. (13.6).

Range and Sensitivity

2.1 This procedure can extract and determine soil nutrient concentrations without dilution in the following ranges: Zn, 0.1 to 10 ppm; Fe, 0.1 to 10 ppm; Mn, 0.1 to 10 ppm; and Cu, 0.1 to 10 ppm. Concentrations above these ranges may be extracted by diluting the extracted filtrate prior to analysis.

2.2 The sensitivity will vary with the type of instrument used and the wavelength selected.

Interferences

3.1 Triethanolamine (TEA) is used to keep the pH close to 7.3.

3.2 Before use all apparatus that will come in direct contact with the extractant and extraction filtrate must be thoroughly washed and rinsed in redistilled dilute HCl and pure water. Avoid contact with rubber and metals.

3.3 Contamination of soil samples, especially for Zn and Fe, may occur from either the sampling equipment or the soil grinding equipment.

Precision and Accuracy

4.1 Repeated analysis of the same soil with medium concentration ranges of Zn, Fe, Mn, and Cu will give coefficients of variability of 10 to 15%. A major portion of the variability is related to heterogeneity of the soil rather than the extraction procedure or the method of analysis.

Apparatus

5.1 Balance or 10 g scoop (NCR-13).

5.2 50 mL Erlenmeyer extraction flask.

5.3 Mechanical reciprocating shaker, 180 oscillations per minute.

5.4 Filter funnel.

5.5 Whatman No. 42 ash less filter paper (or equivalent).

5.6 Atomic Absorption Spectrophotometer.

Reagents

6.1 Extracting Reagent (DTPA-diethylenetriaminepenta-acetic acid)

Weigh 1.96 g DTPA* into a one liter volumetric flask. Add 14.92 g TEA (Triethanolamine). Bring volume to approximately 950 mL with deionized water. Add 1.47 g calcium chloride (CaCl₂·2H₂O). Bring volume to 1 liter with deionized water while adjusting the pH to exactly 7.3 with redistilled 6 N HCl. The final concentration will be 0.005 M DTPA, 0.1 M TEA, and 0.1 M CaCl₂.

* Note: The DTPA reagent should be the acid form.

6.2 Zinc Standard (1000 ppm)

Zinc standards are made using a purchased 1000 ppm Zn standard solution. An alternative to using a standard Zn solution would be to dissolve 1.00 g pure Zn metal in 5 to 10 mL concentrated HCl. Evaporate almost to dryness and dilute to one liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the standard solution with extracting reagent (see 6.1) to cover the anticipated range in concentration found in the soil extraction filtrate. Working standards from 0.1 to 1.0 ppm Zn should be sufficient for most soils.

6.3 Iron Standard (1000 ppm)

Iron standards are made using a purchased 1000 ppm Fe standard solution. An alternative to using a standard Fe solution would be to dissolve 1.000 g pure Fe wire in 5-10 mL concentrated HCl. Evaporate almost to dryness and dilute to one liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the standard solution with extracting reagent to cover the anticipated range in concentration in the soil filtrate. Working standards from 0.1 to 10 ppm Fe should be sufficient for most soils.

6.4 Manganese Standard (1000 ppm)

Manganese standards are made using a purchased 1000 ppm Mn standard solution. An alternative to using a standard Mn solution would be to dissolve 1.582 g manganese oxide (MnO_2) in 5 mL concentrated HCl. Evaporate almost to dryness and dilute to 1 liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the standard solution with extracting reagent to cover the anticipated range in concentration in the soil filtrate. Working standards from 0.1 to 10 ppm Mn should be sufficient for most soils.

6.5 Copper Standard (1000 ppm)

Copper standards are made using a purchased 1000 ppm Cu standard solution. An alternative to using a standard Cu solution would be to dissolve 1.000 g pure Cu metal in a minimum amount concentrated HNO_3 and add 5 mL concentrated HCl. Evaporate almost

to dryness and dilute to 1 liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the stock solution with extracting reagent to cover the anticipated range in concentration in the soil filtrate. Working standards from 0.1 to 10 ppm Cu should be sufficient for most soils.

Procedure

7.1 Extraction

Weigh or scoop 10 g of air-dry <10 mesh (2 mm) soil into a 50 mL extraction flask (see 5.2). Add 20 mL of extracting reagent (see 6.1) and shake on a reciprocating shaker for 2 hours. Samples shaken longer than 2 hours will give high results because a final equilibrium of the metal and soil is not reached in 2 hours. Filter and collect the filtrate.

7.2 Analysis

The elements Zn, Mn, Fe, and Cu in the filtrate can be determined by atomic absorption spectroscopy. Because instruments vary in their operating conditions, no specific details are given. It is recommended that the procedure described by Isaac and Kerber (see 13.3) is followed.

Calibration and Standards

8.1 Working Standards

Working standards should be prepared as described in section 6.2 through 6.5. If element concentrations are found outside the range of the instrument or standards, suitable dilutions should be prepared starting with a 1:2 extract to extracting reagent dilution.

8.2 Calibration

Calibration procedures vary with instrument techniques and the type of instrument. Carefully follow the proper procedures and manufacturer recommendations for the operation and calibration of the instrument used.

Calculations

9.1 To express results in ppm of soil, use the following formula:

ppm in soil = ppm in solution x 2

Effects of Storage

- 10.1** Soils may be stored in an air-dry condition for several months with no effect on the extractability of Zn, Fe, Mn, and Cu.

Interpretation

- 11.1** Accurate micronutrient fertilizer recommendations are based on soil test results, field response for individual crops and local field conditions. Interpretative data for critical levels established by Viets and Lindsay for Colorado soils are available (see 13.5). Boawn did work with DTPA for Zn on Washington soils (see 13.1) and Kennedy evaluated DTPA for Missouri soils (see 13.4).

Comments

- 12.1** Grinding can change the amount of DTPA extractable micronutrients, especially iron (Fe). Therefore, it is imperative that grinding procedures be standardized along with extraction procedures. Grinding should be equivalent to using a wooden roller to crush the soil aggregates (see 13.6).

References

- 13.1** Boawn, L. C. 1971. Evaluation of DTPA extractable zinc as a zinc soil test for Washington soils. Proc. 22nd Annual Pac. N. W. Fert. Conf. Bozeman, Mont., Pacific NW Plant Food Assoc., p. 143-147.
- 13.2** Handbook on Reference Methods for Soil Analysis. 1999. Soil and Plant Analysis Council, Inc. CRC Press, Washington D.C.
- 13.3** Isaac, R. A. and J. D. Kerber. 1972. Atomic Adsorption and flame photometry: techniques

and uses in soil, plant, and water analysis. p. 17-24. *In* L. M. Walsh, (ed.). Instrumental Methods for Analysis in Soils and Plant Tissue, revised edition. Soil Sci. Soc. Amer., Madison, WI.

- 13.4** Kennedy, Ann C. 1979. Evaluation of Three Zinc Soil Tests for Missouri Soils. Unpublished M.S. Thesis, Library, University of Missouri-Columbia.
- 13.5** Lindsay, W. L. and W. A. Norvell. 1969. Development of a DTPA micronutrient soil test. Agron. Abstracts, p. 84. Equilibrium relationships of Zn^{+2} , Fe^{+2} , Ca^{+2} , and H^+ with EDTA and DTPA. *In* Soil. Soil Sci. Soc. Amer. Proc. 33:62-68.
- 13.6** Soltanpour, P. N., A. Khan, and W. L. Lindsay. 1976. Factors affecting DTPA-extractable Zn, Fe, Mn and Cu. *Comm. Soil Sci. Plant Anal.* 7:797-821.
- 13.7** Soltanpour, P. N. and A. P. Schwab. 1977. A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils. *Comm. in Soil Sci. and Plant Analysis* 8:195-207.
- 13.8** Viets, Jr., F. G. and W. L. Lindsay. 1973. Testing soils for zinc, copper, manganese, and iron. p.153-172. *In* L. M. Walsh and J. D. Beaton (ed.). Soil Testing and Plant Analysis, revised edition. Soil Sci. Soc. Amer., Madison, WI.
- 13.9** Whitney, D. A. 1998. Micronutrient Soil Tests - Zinc, Iron, Manganese and Copper. Ch. 9. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).

Electrical Conductivity

Principle of the Method

- 1.1 This method estimates salt concentration in a soil-water extract. Ideally, the salinity of the soil solution should be monitored in the field moisture range. This is best accomplished in the laboratory by using a water saturated soil paste (saturation extract) as recommended by the U.S. Salinity Lab (11.4). However for ease of measurement and reproducibility of results, many labs use a 1:1 (weight: volume) ratio of soil to water.
- 1.2 Electrical conductivity (EC) is measured using a modified Wheatstone bridge with alternating currents. A pipette or dip-type conductivity cell with platinized electrodes should be used. The cell should be approximately 1.0 reciprocal centimeter. For instructions on replatinizing electrodes, see reference 11.4.
- 1.3 This method is a rapid and reasonably precise determination that does not alter or consume the sample.

Range and Sensitivity

- 2.1 This procedure is useful for a wide range of soil-water extract conductivities. The range can be extended by dilution of the extract.

Interferences

- 3.1 Only deionized water from which salts have been removed should be used to make extracts.
- 3.2 Clean and well-platinized electrodes are essential for reproducible results.
- 3.3 As temperature of the extract rises, the conductivity measurement will also rise. If the temperature of the sample extract and the standard are different, correct all readings to 25°C (see table 8.3).

Precision and Accuracy

- 4.1 Report electrical conductivity in mmho/cm to the closest 0.01 for values less than 1.0, or to the closest 0.1 for values of 1.0 and greater.

Apparatus

- 5.1 Balance or 10 g scoop (NCR-13)
- 5.2 125 mL Erlenmeyer flask with stopper
- 5.3 Mechanical shaker
- 5.4 Buchner funnel
- 5.5 Filter paper, Whatman #2 or equivalent
- 5.6 500 mL filtering flask
- 5.7 Test tube, 25 mm x 150 mm
- 5.8 Vacuum pump or aspirator
- 5.9 Appropriate size tubing
- 5.10 Thermometer

Reagent

6.1 Potassium Chloride (KCl) Standard

Dissolve 0.7456 g anhydrous KCl in freshly boiled and cooled deionized water. Dilute to one liter. At 25°C this solution has an electrical conductivity of 1.413 mmho/cm. Store in a glass stoppered Pyrex bottle.

Procedure

- 7.1 Scoop or weigh 40 g of < 10 mesh soil into an extraction flask. Add 40 mL of deionized water. Stopper and shake on a mechanical shaker for 15 minutes. Allow contents to stand one hour, then agitate again for 5 minutes. Filter the extract using vacuum suction into a test tube.
- 7.2 Measure the temperature of the sample extract and the standard.

7.3 Measure the conductivity of the sample extract and standard according to the operating instructions of the particular conductivity bridge used. Rinse electrode with

deionized water between each sample. Then rinse electrode with part of the sample extract before each reading.

Table 1. Temperature factors (f_t) for correcting resistance and conductivity data on soil extracts to the standard temperature of 25°C*

$$EC_{25} = EC_t \times f_t ; EC_{25} = (k/R_t) \times f_t ; R_{25} = R_t/f_t$$

°C	°F	f_t	°C	°F	f_t	°C	°F	f_t
3.0	37.4	1.709	22.0	71.6	1.064	29.0	84.2	0.925
4.0	39.2	1.660	22.2	72.0	1.060	29.2	84.6	.921
5.0	41.0	1.613	22.4	72.3	1.055	29.4	84.9	.918
6.0	42.8	1.569	22.6	72.7	1.051	29.6	85.3	.914
7.0	44.6	1.528	22.8	73.0	1.047	29.8	85.6	.911
8.0	46.4	1.488	23.0	73.4	1.043	30.0	86.0	.907
9.0	48.2	1.448	23.2	73.8	1.038	30.2	86.4	.904
10.0	50.0	1.411	23.4	74.1	1.034	30.4	86.7	.901
11.0	51.8	1.375	23.6	74.5	1.029	30.6	87.1	.897
12.0	53.6	1.341	23.8	74.8	1.025	30.8	87.4	.894
13.0	55.4	1.309	24.0	75.2	1.020	31.0	87.8	.890
14.0	57.2	1.277	24.2	75.6	1.016	31.2	88.2	.887
15.0	59.0	1.247	24.4	75.9	1.012	31.4	88.5	.884
16.0	60.8	1.218	24.6	76.3	1.008	31.6	88.9	.880
17.0	62.6	1.189	24.8	76.6	1.004	31.8	89.2	.877
18.0	64.4	1.163	25.0	77.0	1.000	32.0	89.6	.873
18.2	64.8	1.157	25.2	77.4	.996	32.2	90.0	.870
18.4	65.1	1.152	25.4	77.7	.992	32.4	90.3	.867
18.6	65.5	1.147	25.6	78.1	.988	32.6	90.7	.864
18.8	65.8	1.142	25.8	78.5	.983	32.8	91.0	.861
19.0	66.2	1.136	26.0	78.8	.979	33.0	91.4	.858
19.2	66.6	1.131	26.2	79.2	.975	34.0	93.2	.843
19.4	66.9	1.127	26.4	79.5	.971	35.0	95.0	.829
19.6	67.3	1.122	26.6	79.9	.967	36.0	96.8	.815
19.8	67.6	1.117	26.8	80.2	.964	37.0	98.6	.801
20.0	68.0	1.112	27.0	80.6	.960	38.0	100.2	.788
20.2	68.4	1.107	27.2	81.0	.956	39.0	102.2	.775
20.4	68.7	1.102	27.4	81.3	.953	40.0	104.0	.763
20.6	69.1	1.097	27.6	81.7	.950	41.0	105.8	.750
20.8	69.4	1.092	27.8	82.0	.947	42.0	107.6	.739
21.0	69.8	1.087	28.0	82.4	.943	43.0	109.4	.727
21.2	70.2	1.082	28.2	82.8	.940	44.0	111.2	.716
21.4	70.5	1.078	28.4	83.1	.936	45.0	113.0	.705
21.6	70.9	1.073	28.6	83.5	.932	46.0	114.8	.694
21.8	71.2	1.068	28.8	83.8	.929	47.0	116.6	.683

*Adapted from Agricultural Handbook 60, USDA, p. 90

Calculations

- 8.1** If temperatures of the samples and standards are the same,

$$EC_{mmho/cm} = \frac{1.413 \text{ mmho/cm} \times EC_{sam} \text{ mmho/cm}}{EC_{std} \text{ mmho/cm}}$$

- 8.2** If temperatures are different, correct all readings, including standard, to 25°C using Table 1, and then calculate EC by the above formula.

Storage

- 9.1** If properly stored, soil samples may be kept several months. Dry soils should be stored in containers which are impervious to water vapor. Otherwise, soils that contain deliquescent salts may accumulate enough moisture when stored to decompose a paper bag.

Interpretations

- 10.1** Crops vary in their sensitivity to salt content. For interpretation of results see Agricultural Handbook No. 60, USDA., or current pertinent literature.

References

- 11.1** Bower, C. A. and L. V. Wilcox. Soluble Salts. Ch. 62. *In* C. A. Black (ed.). Methods of Soil Analysis, Part 2. Soil Science Society of America, Madison, WI.
- 11.2** Handbook on Reference Methods for Soil Analysis. 1999. Soil and Plant analysis Inc. CRC Press, Washington DC.
- 11.3** Jurinak, J. I. 1978. Salt-Affected Soils (unpublished class text). Department of Soil Science and Biometerology, Utah State University, Logan, UT.
- 11.4** United States Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkaline soils. U.S.D.A. Handbook No. 60.

Extractable Sulfate-Sulfur Monophosphate Calcium Extraction

Principle of the Method

- 1.1 Hoeft et al. reviewed the work on soil sulfur (S) (12.4). Their study concluded that the best available sulfate-sulfur ($\text{SO}_4\text{-S}$) extractant for soils was 2 N acetic acid containing 500 ppm P as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The phosphate is present as an anion, which can replace adsorbed sulfate sulfur. Because phosphate is adsorbed more strongly than sulfate, the replaced sulfate tends to remain in solution. The acid system tends to prevent reprecipitation of the sulfate from the extract. Thom (12.5) evaluated ammonium acetate based extractants and concluded that the phosphate was essential for sulfate extraction. Hanson (12.3) and Barton (12.1) used a procedure modified from that published by Hoeft et al.
- 1.2 The procedure reported in this manual varies from the standard reference procedure proposed for the North Central Region (12.2). The procedure is based upon the Hoeft et al. method as modified by Hanson (12.3).

Range and Sensitivity

- 2.1 Hoeft et al. (12.1) reported ranges in soil sulfate sulfur up to 18 ppm.

Interferences

- 3.1 Most soil testing laboratories use a turbidimetric method of analyzing the soil extract for sulfate sulfur. In these methods, a suspension of BaSO_4 is developed by adding an excess of barium chloride to the acid soil extract. Gum arabic is used as a stabilizing agent. The speed of BaSO_4 formation, suspension stability and optical properties of the suspension are affected by many factors including temperature, acidity of the solution, size and quantity of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals and the presence of foreign materials (12.2). Time is always a factor with which to contend.

Precision and Accuracy

- 4.1 The technician who runs the sulfate-sulfur soil test must practice with known samples to develop the skill necessary to obtain accurate and precise results. A skilled technician who carries out the procedure consistently the same way on each run can develop reasonable precision ($\text{CV} = 10\text{-}15\%$).

Apparatus

- 5.1 Balance or 10 g scoop (NCR-13)
- 5.2 Extraction flask (50 or 125 mL)
- 5.3 Mechanical shaker (180 or more oscillations per minute)
- 5.4 Dispenser for extracting solution
- 5.5 Filter funnel
- 5.6 Filter paper (Whatman No. 2 or equivalent)
- 5.7 Aliquoter or pipette - 10 mL
- 5.8 Folin-Wu or similar tubes (50 mL capacity)
- 5.9 Spectrophotometer or nephelometer with 420 nm wavelength setting with cuvetts or sampling cell.

Reagents

- 6.1 **Extracting solution-500 ppm P in 2 N Acetic Acid**
Dissolve 2.03 g of calcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] in about 800 mL of deionized water. To this, add 115 mL of glacial acetic acid and dilute to one liter.
- 6.2 **Gum arabic- BaCl_2 -Acetic Acid Buffer**
Dissolve 5 g of gum arabic in about 500 mL of hot, deionized water and filter if cloudy. Add 50 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and 450 mL of glacial acetic acid and dilute to 1 liter.

6.3 Purified Free Activated Charcoal

Shake approximately 20 g of activated charcoal into about 200 mL of extracting solution for 30 minutes, filter under suction, wash with deionized water and dry in oven at 100°C.

Procedure

- 7.1 Weigh or scoop 10 g of < 10 mesh soil into an extraction flask.
- 7.2 Add 0.1 g of activated charcoal (6.3). Then add 25 mL of the extracting solution (6.1).
- 7.3 Shake the suspension for 15 minutes and filter through Whatman No. 2 (or equivalent) filter paper that has been previously washed with diluted acetic acid and dried to remove sulfate-sulfur impurities.
- 7.4 A 10 mL aliquot of filtrate is transferred to a 50 mL Folin Wu tube or other suitable container. Add 10 mL of the gum arabic-BaCl₂-acetic acid solution (6.2) and shake for 10 minutes.
- 7.5 Allow 20 minutes for color development.
- 7.5 Transfer the solution to a cuvet, a spectrophotometer cell or a nephelometer and read % transmittance at a wavelength of 420 nanometers.
- 7.6 If dilutions are needed, dilute the original filtrate with the extracting solution and proceed with the addition of gum arabic-BaCl₂-acetic acid solution.

Calibration and Standards

8.1 Standard Sulfur solution (100 ppm S)

Dissolve 0.544 g of oven dried (105°C) K₂SO₄ in about 500 mL of deionized water. Add 10 mL of acetic acid as a preservative and dilute to one liter with deionized water. A standard curve is determined with each run of samples.

8.2 Working Sulfur Standards

Transfer 0, 2, 4, 6, 8, and 10 mL of the 100 ppm sulfur standard to 100 mL volumetric flasks. Add 25 mL of a 2000 ppm P and 8N acetic acid solution, (8.12 g of Ca(H₂PO₄)₂·H₂O plus 460 mL of glacial acetic acid diluted to one liter) and dilute to 100 mL.

This will result in 0, 2, 4, 6, 8, and 10 ppm S working standards.

- 8.3 Treat a 10 mL aliquot of each working standard the same as the soil extracts. The instrument is adjusted to read 0% transmittance with the zero sulfur standard.

Calculations

$$9.1 \quad ppm \text{ SO}_4 - S \text{ in soil} = ppm \text{ S in extract} \times \frac{25}{10}$$

$$9.2 \quad lbs \text{ SO}_4 - S \text{ in soil} = ppm \text{ S in extract} \times \frac{25}{10} \times 2$$

- 9.3 If the samples are diluted (7.6), appropriate dilution factors must be calculated.

Storage

- 10.1 Air-dry soil samples may be stored for several months without significant changes in SO₄-S.
- 10.2 Once extraction is complete, determine SO₄-S in the extract with a minimum delay.

Interpretations

- 11.1 The test must be calibrated to field response. Consult current extension service guides.

References

- 12.1 Barton, M. J. 1982. A study of sulfur effect on cotton growth and nutrient status on two southeast Missouri soils. M.S. Thesis, Library, University of Missouri-Columbia.
- 12.2 Combs, S. M., J. L. Denning and K. D. Frank. 1998. Sulfate-Sulfur. Ch. 8. In J. R. Brown (ed.), Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).
- 12.3 Hanson, R. G. 1979. Extractable soil sulfate-sulfur test. Unpublished mimeo, Agron. Dept. University of Missouri-Columbia.
- 12.4 Hoefl, R. G., L. M. Walsh and D. R. Keeney. 1973. Evaluation of various extractants for available soil sulfur. Soil Sci. Soc. Amer. Proc. 37:401-404.
- 12.5 Thom, W. O. 1972. Estimating plant available sulfur in selected soils of the Southeastern Missouri Delta region. M.S. Thesis, Library, University of Missouri-Columbia.

SOIL NITRATE-N CADMIUM REDUCTION METHOD

Principle of the Method

- 1.1 The nitrate ion (NO_3^-) is soluble in any water-based solution. However, because nitrate extraction is done in tandem with ammonium, the extracting solution is 2 M potassium chloride (KCl). Ammonium ions (NH_4^+) on colloidal exchange sites are brought into solution by exchange with potassium (K^+) ions.
- 1.2 Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. Once reduced the nitrite is then determined by using a modified Griess-Ilosvay method in which nitrite is diazotized with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm.
- 1.3 The procedure outlined here is for use with a Lachat Flow Injection Autoanalyzer.

Range and Sensitivity

- 2.1 The procedure has a soil extract detection range of 0.02 to 20.0 ppm $\text{NO}_3\text{-N}$.

Interferences

- 3.1 If unfiltered suspended matter in the reduction column may restrict sample flow.
- 3.2 High concentrations of iron, copper and other heavy metals can result in low values.

Precision and Accuracy

- 4.1 Coefficients of variation of 2.1 to 3.4% have been reported.

Equipment

- 5.1 Balance or 10 g scoop (NCR-13).
- 5.2 50 mL Erlenmeyer flasks.

- 5.3 Extracting solution dispenser (25 mL).
- 5.4 Reciprocating shaker, capable of 180 or more opm (oscillation per minute).
- 5.5 Nitrate-free filter paper (Schleicher and Schuel # SA720).
- 5.6 Filter funnels.
- 5.7 30 mL receiving beakers.
- 5.8 10 mL test tubes.
- 5.9 A refrigerator.
- 5.10 Flow Injection Autoanalyzer.

Reagents

6.1 2 M Potassium Chloride (KCl) Extracting Solution

Dissolve 150 g of KCl in one liter volumetric flask and bring to volume with deionized water. Thoroughly mix then transfer to a clean, labeled plastic bottle.

6.2 15 M Sodium Hydroxide(NaOH) Solution

Dissolve 150 g of NaOH very slowly in 250 mL of distilled water in a 500 mL beaker. CAUTION: solution becomes very hot! Swirl until completely dissolved. Cool and store in a glass flask.

6.3 Ammonium Chloride Buffer (pH 8.5).

In a hood, add 500 mL of deionized water, 105 mL of concentrated HCl, 95 mL NH_4OH , and 1.0 g of disodium EDTA to a one liter volumetric flask. Adjust the pH to 8.5 with 15 M NaOH solution. Dilute to the mark, invert to mix, then store in a glass flask.

6.4 Sulfanilamide Color Reagent

Dissolve 40.0 g of sulfanilamide and 1.0 g of N-1-naphthylethylenediamine dihydrochloride (NED) into 600 mL of deionized water in a

one liter volumetric flask. Add 100 mL of 85% phosphoric acid (H₃PO₄). Stir for 20 minutes. Dilute to the mark and invert to mix. Store in a dark brown bottle. Discard when solution turns pink.

Procedure

- 7.1 Scoop or weigh 10 g of air-dried soil into a 50 mL Erlenmeyer flask.
- 7.2 Include at least one blank and one reference sample per run.
- 7.3 Add 25 mL of 2 M KCl solution using an extracting solution dispenser.
- 7.4 Shake for 5 minutes at 180-200 oscillations per minute.
- 7.5 Filter the soil suspension into 30 mL receiving beakers using nitrate-free filter paper that will provide a clean filtrate without contributing measurable amounts of nitrate-N to the filtrate.
- 7.6 Transfer a portion of the filtrate to 10 mL test tubes for analysis.
- 7.7 Nitrate-N content of the filtrated soil extracts is determined by using the nitrate reduction method (Quikchem No. 12-107-04-1-B) through the Lachat Flow Injection Analyzer.

Calibration and Standards

8.1 Standard Stock Solution - 1000 ppm as NO₃⁻-N in 2 M KCl

Weigh 1.444 g of potassium nitrate (KNO₃) into a 200 mL of volumetric flask with 2M KCl extracting solution. Dilute to the mark and invert three times to mix. Store in a refrigerator.

8.2 Working Stock Solution - 100 ppm as NO₃⁻-N in 2M KCl

Pipette 20 mL of the 1000 ppm standard stock solution into a 200 mL volumetric flask. Dilute to the mark with 2M KCl extracting solution and invert three times to mix.

8.3 Working Standards

Pipette the following volumes of 100 ppm working stock solution into the corresponding volumetric flasks and dilute to volume with extracting solution:

100 ppm Working Solution	Volumetric Flask	Working Standard Conc. NO ₃ ⁻ -N
mL	mL	ppm
5	500	1
25	500	5
25	250	10
50	250	20

Store in glass bottles and keep in the refrigerator until ready to use.

Calculations

$$\text{ppm as NO}_3^- - \text{N in soil} = \text{ppm as NO}_3^- - \text{N in reading} \times \frac{\text{Extracting solution volume}}{\text{soil weight}}$$

$$\text{ppm as NO}_3^- - \text{N in soil} = \text{ppm as NO}_3^- - \text{N in reading} \times \frac{25}{10}$$

$$\text{ppm as NO}_3^- - \text{N in soil} = \text{ppm as NO}_3^- - \text{N in reading} \times 2.5$$

References

- 9.1** Gelderman, R. H. and D. Beegle. 1998. Nitrate-Nitrogen. Ch. 5. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).
- 9.2** Griffin, G., W. Jokela, and R. Donald. 1995. Recommended Soil Nitrate-N Tests. *In* Recommended Soil Testing Procedures for the Northeastern United States, 2nd Edition. pp. 22-29. Northeastern Regional Publication #493, December 1995. Agricultural Experiment Station, University of Delaware, Newark DE 19717-1303.
- 9.3** Keeney, D. R. and D. W. Nelson. 1982. Nitrogen-inorganic forms. *In* A. L. Page, R. H. Miller and D. R. Keeney (ed.). Methods of soil analysis. Part 2—Chemical and microbiological properties. (2nd Ed.). Agronomy 9:643-698.
- 9.4** Lachat Instruments. 1993. Nitrate in 2 M KCl Soil Extracts (QuikChem Method 12-107-04-1-B). *In* QuikChem automatic ion analyzer methods manual. Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218.
- 9.5** McElreath, D. L. and G.V. Johnson. 1990. Soil nitrate-nitrogen in Laboratory Procedures Manual. Oklahoma State University Soil, Water, and Forage analytical Laboratory. AGRON 90-1.

SOIL AMMONIUM-N PHENOLATE METHOD

Principle of the Method

- 1.4 The extracting solution is 2 M potassium chloride (KCl). Ammonium ions (NH_4^+) on colloidal exchange sites are brought into solution by exchange with potassium (K^+) ions.
- 1.5 Ammonium is reacted with alkaline phenol. Subsequent reaction with sodium hypochlorite forms indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. With a spectrophotometer absorbance is read at 630 nm.
- 1.6 The procedure outlined here is for use with a Lachat Flow Injection Autoanalyzer.

Range and Sensitivity

- 2.1 The procedure has a soil extract detection range of 1.0 to 20.0 ppm $\text{NH}_4\text{-N}$.

Interferences

- 3.3 If unfiltered, suspended matter may interfere with reading absorbance.
- 3.4 High concentrations of calcium and magnesium ions may precipitate.

Precision and Accuracy

- 4.1 Coefficients of variation of 2.1 to 3.4 % have been reported.

Equipment

- 5.1 Balance or 10 g scoop (NCR-13).
- 5.2 50 mL Erlenmeyer flasks.
- 5.3 Extracting solution dispenser (25 mL).
- 5.4 Reciprocating shaker, capable of 180 or more opm (oscillation per minute).
- 5.5 Filter funnels.

- 5.6 30 mL receiving beakers.
- 5.7 10 mL test tubes.
- 5.8 A refrigerator.
- 5.9 Flow Injection Autoanalyzer.

Reagents

6.1 2 M Potassium Chloride (KCl) Extracting Solution

Dissolve 150 g of KCl in a one liter volumetric flask and bring to volume with deionized water. Thoroughly mix then transfer to a clean, labeled plastic bottle.

6.2 Sodium Phenolate Solution

In a one liter volumetric flask, dissolve 88 ml of 88% liquefied phenol in about 600 ml of water. While stirring, slowly add 32 g of sodium hydroxide (NaOH). Cool, dilute to volume and invert three times to mix. CAUTION: Wear gloves. Phenol causes severe skin burns and is rapidly absorbed into the skin.

6.3 Sodium hypochlorite

Dilute 250 mL of regular Clorox bleach to 500 mL with water. Degas with helium.

6.4 Buffer

In a one liter volumetric flask, dissolve 50.0 g of disodium ethylenediamine tetracetate (Na_2EDTA) and 5.5 g of sodium hydroxide (NaOH) in about 900 mL of water. Dilute to volume and invert three times to mix. Degas with helium.

6.5 Sodium Nitroprusside

Dissolve 3.50 g of sodium nitroprusside in one liter of water. Degas with helium.

Procedure

- 7.1 Scoop or weigh 10 g of air-dried soil into a 50 mL Erlenmeyer flask.
- 7.2 Include at least one blank and one reference sample per run.
- 7.3 Add 25 mL of 2 M KCl solution using an extracting solution dispenser.
- 7.4 Shake for 5 minutes at 180-200 oscillations per minute.
- 7.5 Filter the soil suspension into 30 mL receiving beakers using nitrate-free filter paper that will provide a clean filtrate without contributing measurable amounts of nitrate-N to the filtrate. This filter paper is available from Schleicher and Schuell Inc., Keene NH.
- 7.6 Transfer a portion of the filtrate to 10 mL test tubes for analysis.
- 7.7 Ammonium-N content of the filtrated soil extracts is determined by using the ammonia phenolate method (Quikchem No. 12-107-06-1-B) through the Lachat Flow Injection Analyzer.

Calibration and Standards

8.1 Standard Stock Solution - 1000 ppm as $\text{NH}_4^+\text{-N}$ in 2 M KCl

Weigh 3.819 g of ammonium chloride (NH_4Cl) into a 200 mL of volumetric flask

Calculations

$$\text{ppm as } \text{NH}_4^+ - \text{N in soil} = \text{ppm as } \text{NH}_4^+ - \text{N in reading} \times \frac{\text{Extracting solution volume}}{\text{soil weight}}$$

$$\text{ppm as } \text{NH}_4^+ - \text{N in soil} = \text{ppm as } \text{NH}_4^+ - \text{N in reading} \times \frac{25}{10}$$

$$\text{ppm as } \text{NH}_4^+ - \text{N in soil} = \text{ppm as } \text{NH}_4^+ - \text{N in reading} \times 2.5$$

References

- 9.1 Gelderman, R. H. and D. Beegle. 1998. Nitrate-Nitrogen. Ch. 5. In J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).
- 9.2 Griffin, G., W. Jokela, and R. Donald. 1995. Recommended Soil Nitrate-N Tests. In Recommended Soil Testing Procedures for the Northeastern United States, 2nd Edition. pp.

with 2 M KCl extracting solution. Dilute to the mark and invert three times to mix. Store in a refrigerator.

8.2 Working Stock Solution - 100 ppm as $\text{NH}_4^+\text{-N}$ in 2 M KCl

Pipette 20 mL of the 1000 ppm standard stock solution into a 200 mL volumetric flask. Dilute to the mark with 2 M KCl extracting solution and invert three times to mix.

8.3 Working Standards

Pipette the following volumes of 100 ppm working stock solution into the corresponding volumetric flasks and dilute to volume with extracting solution:

100 ppm Working Solution	Volumetric Flask	Working Standard Conc. $\text{NH}_4^+\text{-N}$
mL	mL	ppm
5	500	1
25	500	5
25	250	10
50	250	20

Store in glass bottles and keep in the refrigerator until ready to use.

22-29. Northeastern Regional Publication #493, December 1995. Agricultural Experiment Station, University of Delaware, Newark DE 19717-1303.

9.3 Keeney, D. R. and D. W. Nelson. 1982. Nitrogen-inorganic forms. *In* A. L. Page, R. H. Miller and D. R. Keeney (ed.). Methods of soil analysis. Part 2—Chemical and microbiological properties. (2nd Ed.). *Agronomy* 9:643-698.

9.4 Lachat Instruments. 1997. Ammonia (phenolate) in 2 M KCl Soil Extracts (QuikChem Method 12-107-06-1-B). *In*

QuikChem automatic ion analyzer methods manual. Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218.

9.5 McElreath, D. L. and G.V. Johnson. 1990. Soil nitrate-nitrogen in Laboratory Procedures Manual. Oklahoma State University Soil, Water, and Forage analytical Laboratory. AGRON 90-1.

SOIL BORON

HOT WATER EXTRACTION

Principle of Method

- 1.1 This method is based on work that has shown water-soluble boron (B) to be correlated to crop response, and that boron added to a mineral soil can be recovered by a boiling water extraction. This procedure is also calibrated to a number of important crops and vegetables. So realistic interpretations of soil boron are available.
- 1.2 This is a colorimetric method in which azomethine-H is used to form a colored complex with H_3BO_3 in aqueous media. The predominant form of boron in the soil is H_3BO_3 . In this procedure a standard spectrophotometer is used.

Range and Sensitivity

- 2.1 The azomethine-H forms a stable complex with H_3BO_3 across a range of 0.5 to 10 ppm.

Interferences

- 3.1 Iron, molybdenum, titanium and zirconium interfere only in unusually high amounts (10.5).

Precision and Accuracy

- 4.1 The soil boron working range for this method is 0 to 3.2 ppm.

Apparatus

- 5.1 Balance or NCR-13-10-g scoop.
- 5.2 125 mL Erlenmeyer flasks.
- 5.3 HCl washed charcoal.
- 5.4 Boiling glass beads.
- 5.5 Reflux funnels.
- 5.6 Hot plate.
- 5.7 Timer.

- 5.8 Whatman No. 42 filter paper.
- 5.9 10 mL plastic beakers.
- 5.10 Adjustable pipette.
- 5.11 10 mL test tubes.
- 5.12 Spectrophotometer.

Preparation of Glassware

- 6.1 Boil all Pyrex glassware with a 3:1 mixture of concentrated HNO_3 and concentrated $HClO_4$ at $225^\circ C$ for two hours.
- 6.2 Soak glassware overnight in a 2 M HCl acid bath. Rinse thoroughly with deionized water.

Reagents

7.1 Extracting Solution

Dissolve 1.00 g of $CaCl_2$ in a one liter volumetric flask and bring to volume with distilled water. Transfer to a clean, labeled plastic bottle.

7.2 Buffer-Masking Solution

Dissolve 250 g of ammonium acetate and 15 g of ethylenediamine-tetraacetic acid disodium salt in 400 mL high quality deionized water and slowly add 125 mL of glacial acetic acid.

7.3 Azomethine-H Solution

Dissolve 0.45 g of azomethine-H in 100 mL of 1% (1 g/100 mL water) L-ascorbic acid solution. Let stand for 24 hours prior to using. This reagent will keep in a refrigerator for two weeks at $40^\circ F$. This reagent is light sensitive and should be kept in a brown plastic bottle or a plastic bottle wrapped in aluminum foil.

Procedure

- 8.1 Scoop 10 g of air-dried soil into a 125 mL Erlenmeyer flask. Run duplicate samples.
- 8.2 Include at least one blank and one check sample per run.
- 8.3 Add 0.06 g of washed charcoal and 2 boiling glass beads to each flask.
- 8.4 Add 20 mL of extracting solution into each flask.
- 8.5 Cover with reflux funnel and place on pre-warmed hot plate.
- 8.6 When samples come to a rolling boil, set a timer for 5 minutes and continue boiling.
- 8.7 When the timer goes off, remove samples from hot plate and cool in a pan of cold tap water.
- 8.8 Using Whatman No. 42 filter paper, filter into a plastic beaker.
- 8.9 Pipette 1.0 mL of filtrate into a test tube and add 2 mL buffer-masking solution and 2 mL of azomethine-H solution. Thoroughly mix by swirling.
- 8.10 Allow the mixture to stand for 30 minutes and read transmittance on a spectrophotometer at a wavelength of 420 nm. Set 100% transmittance with a reagent blank--1.0 mL extracting solution, 2 mL buffer-masking solution and 2 mL of azomethine-H solution (8.9).
- 8.11 All of working standards should follow steps 9 and 10.

Calibration and Standards

9.1 1000 ppm Boron Stock Solution

Weigh 0.5716 g of boric acid and dilute to 100 mL with deionized water in a volumetric flask.

9.6 10 ppm Boron Working Stock Solution

Dilute one mL of 1000 ppm B stock solution to 100 mL with deionized water in a volumetric flask.

9.2 Working Standards

Pipette the following volumes of 10 ppm B working stock solution into 50 mL volumetric

flasks and dilute to volume with extracting solution:

10 ppm B Working Stock Solution	Working Standard B Conc.	Boron Conc. In Soil
mL	ppm	ppm
2	0.4	0.8
6	1.2	2.4
10	2.0	4.0

Store in plastic bottles and keep in the refrigerator until ready to use.

Calculations

$$B \text{ ppm in soil} = B \text{ ppm in reading} \times 2$$

References

- 10.1 Lohse G. 1982. Micro-analytical azomethine-H method for boron determination in plant tissue. *Commun. Soil Sci. Plant Anal.*, 13(2), 127-134.
- 10.2 McElreath, D. L. and Johnson, G. V. 1990. Soil Boron In laboratory procedures manual. Oklahoma state university soil, water, and forage analytical laboratory. AGRON 90-1.
- 10.3 Parker, D. R. and E. H. Gardner. 1981. The determination of hot-water-soluble boron in some acid Oregon soils using a modified azomethine-H procedure. *Comm. Soil Sci. Plant Anal.* 12(12): 1311-1322.
- 10.4 Spouncer, L. R., R. O. Nable, and B. Cartwright. 1992. A procedure for the determination of soluble boron in soils ranging widely in boron concentrations, sodicity, and pH. *Commun. Soil Sci. Plant Anal.*, 23(5&6), 441-453.
- 10.4 Watson, M. E. 1998. Boron. Ch 10. *In* J. R. Brown (ed.). Recommended chemical soil test procedures for the North Central Region. NCR Publication No. 221 (Revised). Missouri Agri. Exp. Stn. SB 1001.

SOIL CHLORIDE

Mercury (II) Thiocyanate Method

Principle of the Method

- 1.1 Chloride (Cl^-) is extracted from soils using 0.01 M calcium nitrate-- $\text{Ca}(\text{NO}_3)_2$.
- 1.2 For spectrophotometric determination, Cl^- displaces thiocyanate from mercury thiocyanate. In the presence of ferric iron, a highly colored and stable ferric thiocyanate complex is formed, which is proportional to the Cl^- concentration.

Range and Sensitivity

- 2.1 The procedure has a detection limit of 1 ppm Cl^- in soil.

Interferences

- 3.1 Nitrate, sulfide, cyanide, thiocyanate, bromide and iodide can interfere with the formation of the thiocyanate complex, but they are usually are not present in amounts sufficient to be a problem.

Precision and Accuracy

- 4.1 Precision varies with the soil Cl^- level. Coefficients of variation range from 9 to 24% with Cl^- levels greater than 12 ppm and from 15 to 25% with Cl^- levels less than 10 ppm.

Equipment

- 5.1 Balance with a resolution of ± 0.1 g.
- 5.2 Repipette dispenser calibrated to 25.0 ± 0.2 mL.
- 5.3 Reciprocating horizontal mechanical shaker, capable of 180 oscillations per minute (opm).
- 5.4 Extraction vessels and associated filtration vessel.
- 5.5 Whatman No. 42 or equivalent highly retentive filter paper.

- 5.6 Flow injection analyzer instrument.

Reagents

6.1 Stock mercuric thiocyanate-- $[\text{Hg}(\text{SCN})_2]$ solution.

In a one liter volumetric flask, dissolve 4.17 g $\text{Hg}(\text{SCN})_2$ in about 500 mL of methanol. Dilute to volume with methanol and invert to mix.

6.2 Stock Ferric (III) nitrate-- $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ solution.

In a one liter volumetric flask, dissolve 202 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in approximately 800 mL of deionized. Add 25 mL concentrated nitric acid (HNO_3). Dilute to final volume and invert to mix.

6.3 Combined Color Reagent

In a 500 mL volumetric flask, mix 75 mL stock mercuric thiocyanate solution with 75 mL stock ferric nitrate reagent. Dilute to volume and invert to mix. Vacuum filter through a 0.45 micromembrane filter.

Procedure

- 7.1 Weigh 10.0 ± 0.1 g of air-dried soil, pulverized to pass a 10 mesh sieve (< 2 mm), into an extraction vessel. Add 25.0 mL of calcium nitrate extracting solution, 0.01 M $\text{Ca}(\text{NO}_3)_2$ using a repipette dispenser. Include a method blank.
- 7.2 Place extraction vessel(s) on a reciprocating horizontal mechanical shaker for fifteen (15) minutes.
- 7.3 Filter extract. Refilter if filtrate is cloudy.
- 7.4 Chloride content of the extract is determined using a flow injection autoanalyzer (Lachat Quickchem 8000) using the Quickchem

method no. 10-117-07-1-A. Determine Cl⁻ concentration of filtered extracts, and a method blank. Record results as ppm of Cl⁻.

Calibration and Standards

8.1 1000 ppm Cl⁻ Standard Stock Solution

Dissolve 0.2103 g of reagent grade potassium chloride (KCl) in approximately 50 mL of extracting solution. Dilute to volume with extracting solution.

8.2 Working standards

Pipette the following volumes of the 1000 ppm Standard Stock Solution into 100 mL volumetric flasks. Dilute to volume with extracting solution:

1000 ppm Chloride Stock Solution	Working Standard Cl ⁻ Conc.	Chloride Conc. In Soil
mL	ppm	ppm
1.2	12	30
2.4	24	60
3.6	36	90
4.8	48	120

Store in plastic bottles and keep in the refrigerator until ready to use

Calculations

$$Cl \text{ ppm in soil} = (Cl \text{ ppm in filtrate} - \text{method blank}) \times 2.5$$

Report soil chloride concentration to the nearest 0.1 ppm.

References

- 9.1 Gelderman, R. H., J. L. Denning and R. J. Goos. 1998. Chlorides. Ch. 11. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. NCR Publication No. 221 (Revised). Missouri Agri. Exp. Stn. SB 1001.
- 9.2 Keeney, D. R. and D. W. Nelson. 1982. Nitrogen-inorganic forms. p. 643-698. *In* A. L. Page (ed.). Methods of soil analysis, part 2. Agron. Monogr. 9, 2nd ed. ASA and SSSA, Madison, WI.

PARTICLE SIZE ANALYSIS

HYDROMETER METHOD

Principle of the Method

- 1.1 This method quantitatively determines the proportions of sand, silt and clay soil particles based on their settling rates in aqueous solution using a hydrometer. Settling rates are based on the principle of sedimentation as described by Stokes' Law.
- 1.2 The use of an ASTM 152H-type hydrometer is based on a temperature of 20°C and a particle size density of 2.65 g cm⁻³.
- 1.3 Dispersion is achieved with a 5% solution of sodium hexametaphosphate.

Range and Sensitivity

- 2.1 The method has a detection limit of 2% sand, silt and clay on a dry basis.

Interferences

- 3.1 Soluble salts, organic matter, carbonates and iron oxides may need to be removed by pretreatment.

Precision and Accuracy

- 4.1 The method is reproducible to ± 8%.

Equipment

- 5.1 Balance.
- 5.2 Mixer.
- 5.3 Sodium hexametaphosphate (Calgon™).
- 5.4 Settling cylinder with a one liter mark that is 36 ± 2 cm from the bottom.
- 5.5 Hydrometer (Bouyoucus).
- 5.6 Plunger.
- 5.7 Timer.
- 5.8 Thermometer.

- 5.9 Watch glass.

Preparation

- 6.1 Prepare the sodium hexametaphosphate solution by dissolving 50 g in 1000 mL of deionized water.

Procedure

- 7.1 Weigh 40.0 g of air-dried soil.
- 7.2 Transfer soil into mixer. Add 100 mL of sodium hexametaphosphate solution and 300 mL of deionized water.
- 7.3 Mix 1 minute in the mixer on the low speed setting.
- 7.4 Transfer the suspension quantitatively into settling cylinder.
- 7.5 Add deionized water to bring volume to 1000 mL
- 7.6 Fill a cylinder with 100 mL of 5% hexametaphosphate and 900 mL of deionized water. This will be the blank sample.
- 7.7 Allow suspensions to come to room temperature (22 to 27°C)—approximately two hours.
- 7.8 Insert plunger into the cylinder and carefully move up and down to thoroughly mix the contents of the cylinder. Be sure to displace sediment on the bottom of the cylinder. Finish mixing with two to three smooth strokes.
- 7.9 Remove the plunger and lower the hydrometer into the suspension.
- 7.10 After 30 seconds from the plunger removal, record the hydrometer reading as hydrometer #1 reading. Record a reading on the blank.
- 7.11 Remove the hydrometer carefully, rinse the surface and wipe it dry.

- 7.12** Cover cylinders with watch glasses to prevent foreign material from entering solutions during the settling period.
- 7.13** After 6 hours record temperature and refer to the temperature correction table (taken from the Western States Laboratory Proficiency Testing Program (9.3). Do not move the cylinder or reshape the suspension during the standing period.
- 7.14** Reread hydrometer at the prescribed time. Record as hydrometer #2 reading. Repeat a reading on the blank.

Calculations

$$8.1 \quad \% \text{ sand} = \frac{40 - (\text{Hydrometer \#1 reading} - \text{blank \#1})}{40} * 100$$

$$8.2 \quad \% \text{ clay} = \frac{(\text{Hydrometer \#2 reading} - \text{blank \#2})}{40} * 100$$

$$8.3 \quad \% \text{ silt} = 100 - (\% \text{ sand} + \% \text{ clay})$$

Table 1. Suspension temperature effect on time of hydrometer reading for clay determination

Temperature	Settling time for clay
°C	hours and minutes
18	8:09
19	7:57
20	7:45
21	7:35
22	7:24
23	7:13
24	7:03
25	6:53
26	6:44
27	6:35
28	6:27

Classification of soil texture

Soil texture can be classified by the guide for textural classification from the USDA Natural Resource Conservation Service. In the USDA textural triangle below, the corners represent 100 percent sand, silt, or clay (gravel and organic soils are not included). The triangle is divided into 10 percent portions of clay, silt, and sand. Heavy lines show the divisions between the 12 basic soil textural classes. If the percentage for any two of the soil separates is known, the correct textural class can be determined. However, the summation of the three percentages must total 100 percent. Sometimes the point representing the texture of a soil sample falls exactly on the line between two texture names. It is customary to use the finer texture class when this happens. For example, a sample containing 40 percent clay, 30 percent silt, and 30 percent sand is called clay rather than clay loam.

References

- 9.1** McElreath, D. L. and Johnson, G.V. 1990. Soil texture-hydrometer method. *In* Laboratory Procedures Manual. Oklahoma State University Soil, Water, and Forage Analytical Laboratory.
- 9.2** Michigan State University. Manual of Laboratory Procedures. Soil and Plant Nutrient Laboratory. Michigan State University. Dept. of Crop and Soil Sci. East Lansing, MI 48824.
- 9.3** Miller, R. O., J. Kotuby-Amacher, and J. B. Rodriguez. 1998. Western States Laboratory Proficiency Testing Program-Soil Plant and Analytical Methods. Ver. 4.10.

Greenhouse Root Media

Principle of the Method

- 1.1 Saturation extracts of greenhouse media provide a dependable measure of available nutrients for peat based mixes. The method was developed by Michigan State University. Extraction is performed on moist samples.
- 1.2 Using relatively large sample sizes (400 cm³), handling and sampling errors of heterogeneous materials can be avoided.
- 1.3 Root media that contain slow release fertilizer can be extracted with very little inflation of the test results.

Interferences

- 2.1 This method is designed for greenhouse root media in the state that they arrive from a greenhouse. Storage in either the dry or moist state can affect nitrate-N and soluble salt levels. Refrigerate samples if they are not to be extracted within two hours of arrival.

Equipment

- 3.1 600 mL plastic beaker
- 3.2 Spatula
- 3.3 Buchner funnel, 11 cm
- 3.4 Filter paper (Whatman No. 2), 11 cm
- 3.5 Vacuum flask, 500 mL
- 3.6 Vacuum pump
- 3.7 Vial, snap-cap 100 mL
- 3.8 Conductivity meter
- 3.9 Dipping type conductivity cell
- 3.10 Thermometer
- 3.11 pH meter with expanded scale
- 3.12 pH glass electrode with a paired calomel reference electrode

- 3.13 Lachat Quikchem 8000 for measuring nitrate
- 3.14 Colorimeter
- 3.15 Atomic absorption spectrophotometer
- 3.16 Volumetric flasks and pipettes as required for preparation of reagents and standard solutions

Reagents

- 4.1 Deionized water
- 4.2 0.01 M potassium chloride--KCl (for standardizing solubridge)
- 4.3 Reagents for determining pH, nitrate-N, phosphorus, potassium, calcium, magnesium and micronutrients of interest.

Procedure

- 5.1 Fill a 600 mL beaker to about two-thirds full with the root medium. Gradually add deionized water while mixing until the sample is saturated. At saturation the sample will flow slightly when the container is tipped and is easy to work with a spatula. After mixing allow the sample to equilibrate for 1 hour and then recheck the criteria for saturation. The saturated sample should have no appreciable free water on the surface, nor should it have stiffened. Adjust as necessary by addition of root medium or deionized water. Then allow an additional 30 minutes for a final equilibration.
- 5.2 Determine the pH of the saturated sample by carefully inserting the electrodes into the saturated sample. Wiggle the electrodes gently to attain good solution contact.
- 5.3 Attach a Buchner funnel lined with filter paper to a vacuum flask. Apply a vacuum and transfer the saturated sample into the Buchner funnel. Level the sample with a spatula and tap the funnel to eliminate entrapped air and to

insure good contact between the saturated sample and the filter. Continue the vacuum, collecting the extract in the flask. No more than 15 minutes of vacuum should be required. Transfer the extract to a snap-cap vial. All subsequent analyses are done on the extracted solution.

- 5.4 Soluble salts (see procedure for Electrical Conductivity).
- 5.5 Nitrate-N and ammonium-N (see procedure for Nitrate-N).
- 5.6 Determine phosphorus on an aliquot of the extract using the colormetric procedure described in the procedure for phosphorus.
- 5.7 Determine potassium, calcium and magnesium on an aliquot of the extract using flame emission or atomic absorption spectroscopy.

Calculations

Soluble salts are reported as dS m^{-1} . To convert total soluble salt concentration to ppm multiply

electrical conductivity by 700. Once total soluble salt concentration is calculated, nutrient balance can be calculated for individual nutrients as follows:

$$\% \text{ nutrient} = \frac{(\text{nutrient conc.})(100)}{\text{Total soluble salt conc.}}$$

Interpretations

Desirable soluble salt and nutrient levels vary with the greenhouse or nursery crop being grown or the management practices. General guidelines are given in the table below.

References

- 6.1 Gelderman, R. H. and D. Beegle. 1998. Nitrate-Nitrogen. Ch. 5. *In* J. R. Brown (ed.). Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (Mo. Agric. Exp. Stn. SB 1001).

Analysis	Rating				
	Low	Acceptable	Optimum	High	Very High
Soluble salt (mmho/cm)	0 - 0.75	0.75 - 2.0	2.0 - 3.5	3.5 - 5	> 5.0
Nitrate-N (ppm)	0 - 39	40 - 99	100 - 199	200 - 299	> 300
Phosphorus (ppm)	0 - 2	3 - 5	6 - 10	11 - 18	> 19
Potassium (ppm)	0 - 59	60 - 149	150 - 249	250 - 349	> 350
Calcium (ppm)	0 - 79	80 - 199	> 200	-	-
Magnesium(ppm)	0 - 29	30 - 69	> 70	-	-

Calculated Cation Exchange Capacity

The **cation exchange capacity** (CEC) is estimated from the extractable K, Ca, and Mg results and the measure of neutralizable acidity. The resulting CEC is used to calculate percentages of saturation with Ca, Mg, and K.

The calculations are based on the assumption that the sample represents an acre furrow slice which weighs 2 million pounds (air dry). Based on this assumption and the chemical equivalent weights of Ca, Mg, and K the following equations hold:

$$\text{meq Ca} / 100 \text{ g} = \text{lbs Ca} / A \div 400 \text{ lbs} / \text{meq}$$

$$\text{meq Mg} / 100 \text{ g} = \text{lbs Mg} / A \div 240 \text{ lbs} / \text{meq}$$

$$\text{meq K} / 100 \text{ g} = \text{lbs K} / A \div 780 \text{ lbs} / \text{meq}$$

$$\text{meq Na} / 100 \text{ g} = \text{lbs Na} / A \div 460 \text{ lbs} / \text{meq}$$

The calculated CEC is the sum of the three basic cations, Ca, Mg, and K, expressed in milliequivalents (meq) per 100 grams of soil plus the quantity of neutralizable acidity (NA)

Literature Cited

- (1) Graham, E. R. 1959. An explanation of theory and methods of soil testing. Mo. Agric. Exp. Stn. Bull. 734.
- (2) Fisher, T. R. 1974. Some Considerations Regarding Soil Test Interpretations for Phosphorus and Potassium. Mo. Agric. Exp. Stn. Bull. 1007.
- (3) Christy, C. M. 1970. How to take a good soil sample, Univ. of Mo. Ext. Div. Science and Technology Guide 9075.
- (4) Pearson, R. W. and F. Adams. 1967. ed. Soil Acidity and Liming. Agronomy Monograph 12. American Society of Agronomy, Madison, WI.
- (5) Woodruff, C. M. 1948. Testing soils for lime requirements by means of a buffered solution and the glass electrode. Soil Sci. 66:53-63.
- (6) Handbook on Reference Methods for Soil Analysis. 1999. Soil and Plant Analysis Council, Inc. CRC Press, Washington DC.
- (7) Recommended Chemical Soil Test Procedures for the North Central Region. 1998. North Central Regional Publication 221(revised). Missouri Agric. Exp. Stn. Bull. SB 1001.