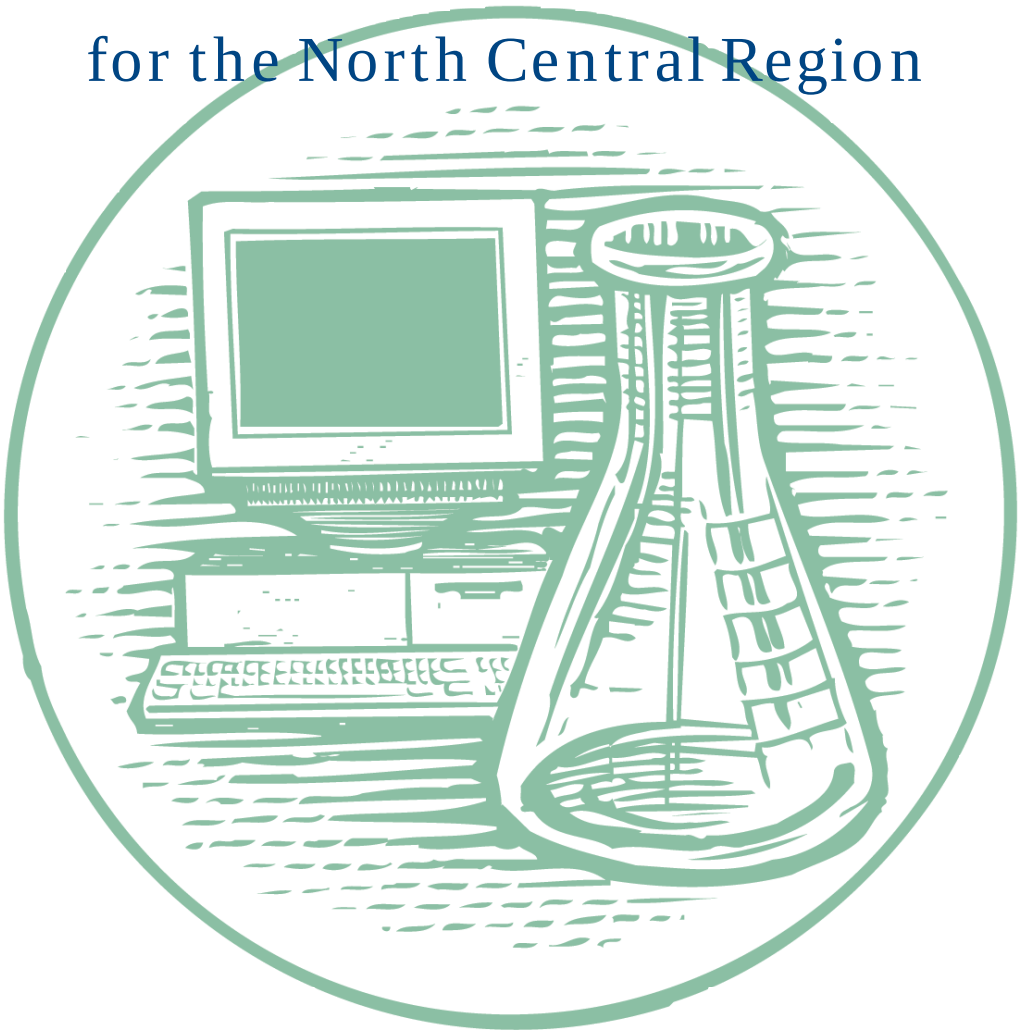
North Central Regional Research Publication No. 221 (Revised)

Recommended Chemical Soil Test Procedures

for the North Central Region



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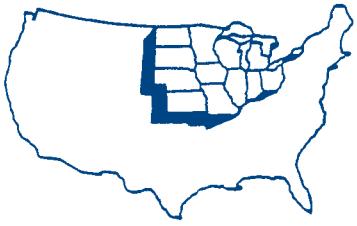

Missouri Agricultural Experiment Station SB 1001

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Foreword

Over the past 30 years, the NCR-13 Soil Testing and Plant Analysis Committee members have worked hard at standardizing the procedures of Soil Testing Laboratories with which they are associated. There have been numerous sample exchanges and experiments to determine the influence of testing method, sample size, soil extractant ratios, shaking time and speed, container size and shape, and other laboratory procedures on test results. As a result of these activities, the committee arrived at the recommended procedures for soil tests.

Experiments have shown that minor deviations in procedures may cause significant differences in test results. It is to the advantage of all laboratories that the credibility of soil testing be enhanced. The adoption of these recommended procedures by all laboratories would be a major step toward improving the image of soil testing and, hopefully, the integrity of fertilizer recommendations based on soil tests. Calibration studies conducted by the North Central Agricultural Experiment Stations over the past five decades have been used to calibrate these recommended procedures.

NCR-13 wants it clearly understood that the publication of these tests and procedures in no way implies that the ultimate has been reached. Research and innovation on methods of soil testing should continue. The committee strongly encourages increased research efforts to devise better, faster, less expensive and more accurate soil tests. With the high cost of fertilizer, and with the many soil related environmental concerns, it is more important than ever that fertilizer be applied only where needed and in the amount of each element needed for the response goal. The best hope of attaining this goal is better soil tests and better correlations with plant response. NCR-13 stands ready to evaluate promising new soil tests, and with clear justification will move quickly to revise their recommendations.

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R. R. Davis	1969-74
Clive Donoho, Jr.	1975-83
Leo Walsh	1984-90
Ben Jones	1991-92
H. R. Lund	1993
Jim Brown	1994
Robert Gast	1995
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Contents

Acknowledgments

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This publication is sponsored by the Agricultural Experiment Stations of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Pennsylvania, South Dakota and Wisconsin. The 1996-97 official representatives are listed below.

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Introduction

1997 Revision

J. R. Brown

This publication was revised in 1980 and 1988 under the leadership of Bill Dahnke who was the North Dakota representative to the NCR-13 committee until his retirement. His introduction to those two revisions is included below without change.

The NCR-13 committee on Soil Testing and Plant Analysis asked me to serve as editor for this revision, which I deemed an honor and a climax to my activities in soil testing and soil fertility since 1963. The committee made some changes in this edition, which includes the addition of the Mehlich 3 extractant to the recommended phosphorus procedures (Chapter 6), a chapter on Quality Assurance and Quality Control (Chapter 15), a glossary, and changes of a lesser nature in other chapters.

Users of this edition should read Dr. Dahnke's comments carefully and spend some time reflecting upon them. Time has passed and some tend to underestimate the importance of efforts put into soil testing during the past 100 years. The contributions of those such as Emil Truog (Wis.), Roger Bray (Ill.), R. A. "Prof." Olson (Neb.), E. O. McLean (Ohio), E. R. Graham (Mo.), John Grava (Minn.), Stan Barber (Ind.) Touby Kurtz (Ill.), and many others in the North Central Region made to our understanding of soil test measurements and plant growth relationships must not be discounted. Learning is a progressive activity; we must never forget that.

1980 and 1988 Edition

W. C. Dahnke

For more than a century, soil and plant scientists have been developing methods for determining the levels of plant-available nutrients in soils. One of the first quick soil tests for "active" (available) nutrients was that of Daubeny (1) in 1845. It involved extracting the soil with carbonated water. His suggested test, however, was never put to practical use because of analytical difficulties. The first known fertilizer recommendations based on a soil test were made by Dr. Bernard Dyer (2) in 1894. He recommended that phosphate fertilizer be applied to soils releasing less than 0.01percent P_2O_5 (.0044 percent P) when extracted with 1 percent citric acid.

Since 1845, many extracting solutions have been suggested and tried. Some of the tests have proved to be very successful in spite of the fact that many different chemical forms of each nutrient occur in the soil, each having a different level of availability to plants.

Research efforts in developing soil testing as a useful guide to soil management have been extensive in soils and agronomy departments in the region. In most departments one or more prominent soils scholars have been associated with soil testing research over considerable periods of time. This, plus the fact that many soils in this region are amenable to corrective management, has resulted in the extensive use of soil testing in the NCR-13 region.

The preliminary work for this bulletin was done several years ago when a soil sample exchange was conducted among the member states. The results of this exchange indicated that differences in procedure were possibly causing significant differences in soil test results. A cooperative study among several of the states was conducted to determine the importance of procedural differences. For example, temperature, time and speed of shaking, and shape of extraction vessel were found to have an influence on the amount of phosphorus and potassium extracted (see Chapter 4). Soil scoops of the same volume but different depth and diameter were found to influence the amount of soil they hold. To solve this variability problem, a standard soil scoop was suggested and is described in Chapter 2.

Another purpose of this bulletin is to describe the detailed procedures based partly on the above studies for soil pH, lime requirement, phosphorus, potassium nitrate-nitrogen, calcium, magnesium, CEC, zinc, iron, manganese, copper, boron, chloride, sulfate-sulfur, soil organic matter, soluble salts and greenhouse media. We believe that use of these procedures by all public, private and industrial soil testing laboratories in our region will do much to reduce any confusion connected with soil testing and thus lend greater credibility to its role in the fertility management of soils.

The intent of the NCR-13 committee is to encourage continued work on procedures for these as well as other plant nutrients. As a new soil test or innovation is developed, it will be studied; and, if it offers improvements over a procedure in this bulletin, it will be adopted in place of or as an alternative to the one described herein. In addition to our research on soil testing procedures we plan to spend a substantial amount of time on soil test interpretation and fertility recommendations.

A word of caution to readers of this bulletin: A soil test is only as successful and usable for a region as the degree to which it is correlated and calibrated for the soils and crops of the area. The procedures described in this bulletin are especially suited to our region. Do not assume that they will work in your area without doing the necessary research.

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Reference to Commercial Products or Manufacturers

Note: Reference to commercial products or manufacturers' names throughout this publication does not constitute an endorsement by the authors but, for the convenience of the reader, indicates the relative type of equipment needed.

Chapter 1

Soil Sample Preparation

R. H. Gelderman and A. P. Mallarino

Ideally, a soil should be tested without disturbing or altering it chemically or mechanically in the process of sample preparation. This would require testing in situ, which is not technically feasible today. For the convenience of handling and to provide a homogenous mix for subsampling, soil samples are usually dried and pulverized. Subsamples of the dry, pulverized soils are either weighed or measured by volume. Galvanized containers, cast iron mortars, rubber stoppers, brass screens and a variety of other tools can contribute to contamination with iron, zinc and other micronutrients, and should not be used.

Sample handling before analysis can affect soil test results. It has been shown (1, 11, 14) that drying can result in increased release of exchangeable potassium (K) in many soils and in fixation in others. The fixation tends to occur in recently fertilized soils at higher test levels. The extent of reversion on rewetting varies among soils and is seldom, if ever, complete. Increased temperature can also increase the exchangeable K levels (4). Dowdy and Hutcheson (5) found that illite was the source of K release on drying and that fixation could be attributed to vermiculite or montmorillonite. Early studies in Iowa (11) showed that the results from field-moist samples were better correlated with the potassium uptake by plants than the results from air-dried soils. Higher correlations with field-moist samples were also found in the regional K studies in the late 1950s and early 1960s (2, 8, 9). The K release on drying and the reversion on rewetting can be controlled with organic additives (12), but this procedure has not been evaluated in practical soil testing.

Drying and method of drying may also affect the results of the tests for mineralizable nitrogen (10), phosphorous (13), sulfur (3, 13, 16), zinc (7) and perhaps other micronutrients, but the correlations between the test results and the uptake of nutrients by plants have not been shown to be significantly affected by drying.

Primarily because of the effect of drying on potassium results, a method of testing undried soil samples was developed and put into use in the Iowa State University Soil Testing Laboratory until 1990. Because of the difficulties of analyzing moist samples and because most correlation and calibration studies have been done on air-dried soils, the undried soil analysis method has not been adopted widely. The traditional method of preparing dry samples is presented here.

Recommended Procedure for Handling Dry Soil Samples

Traditionally, most soil analysts have considered dry soil as the convenient state from which to start chemical tests. Because soil samples are received in a wide range of physical conditions, a common denominator in preparation is required to alleviate these problems and expedite processing.

Drying

Moist, well-mixed samples may be transferred to paper bags, cardboard boxes or aluminum trays of convenient size. The open sample container is then placed in a drying rack or cabinet equipped with exhaust fans to expedite air movement and moisture loss. If heat is necessary, the temperature of the cabinet should not exceed 40°C (104°F). This is especially critical for potassium analysis, which can be significantly influenced by drying temperatures. If nitrate analyses are involved, the soil should be dried or frozen within 12 hours of sampling. Such samples can be dried by spreading them out on a clean paper or cloth and blow drying them with a fan.

Where sample volume is not adequate to justify artificial drying, samples may be spread on clean surfaces, such as paper plates. Initial crushing of soil clods will decrease the time required for drying at room temperatures.

Microwave drying is a relatively rapid method to dry a few soil samples. For moisture determination, the method worked well (6). However, microwave-drying appears to change many nutrient analyses as compared to air-drying (15; Malo and Gelderman, unpublished data), and is not recommended.

Crushing and Sieving

The nature of analyses to be conducted, plus presence of rocks or limestone concretions, dictate initial steps to crushing. Crush samples designated

for mechanical analyses with a wooden rolling pin after removing all stony material from the soil.

Crush other samples with a flail-type grinder, a power-driven mortar and pestle, or some other crusher which is designed to minimize contamination through carryover from one sample to another.

If micronutrient analyses are to be performed, it is essential that all surfaces coming into contact with the soil be stainless steel, plastic or wooden, preferably in the order listed. Samples should be crushed until a major portion of the sample will pass a U.S. No. 10 (2 mm opening) sieve. Crushing to pass a finer mesh sieve may be desirable for analysis utilizing less than one gram of soil.

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Chapter 2

Standard Soil Scoop

T. R. Peck

For the purpose of this section, "soil testing" is restricted to the popular usage: rapid chemical analysis for assaying the fertility status of soil. Farmer use of soil testing is enhanced when laboratories provide rapid service. Therefore, testing techniques must be designed for expeditious handling of large numbers of samples without compromising requirements of a successful soil test (1, 2).

One step in soil testing is measuring an amount of soil from which the analysis will be performed. Controversy exists concerning the merits of using a measured volume of soil versus using a predetermined weight. Where a volume measurement of sample is taken, the results may be expressed either on a direct volume basis or on a corrected weight/volume basis. Because differences existed in the test values of soil samples exchanged among member laboratories using the "same" methods, an NCR-13 committee was established to evaluate the impact of sample measurement in 1965.

It became apparent early in the study that each of the different measurement techniques had its strong and weak points, and adoption of a standard technique would be a compromise between variations in soil bulk density and the fact that plants grow in a volume of soil, not a weight of soil.

Weight vs. Volume Measurement

Weight measurement offers the advantage of precision in determining sample size. It has the disadvantage of requiring more time, greater initial expense for weighing equipment and a larger work space area. In addition, an estimation of soil bulk density or measurement to correct for soil variation is required (unless appropriate compensation is made in the test calibration). Most research soil analyses are made on weighed samples.

Volume measurement is the technique most commonly used in soil testing. It has the advantage of being rapid, low cost, requires little space and integrates bulk density into the sample measurement. It has the disadvantage of reduced precision between replicate volume samples. Test results from volume sample measurements may be expressed in two ways: (a) some volume unit, or (b) a weight/volume basis. Reporting soil analysis on a strictly volume basis, e.g., mg/dm^3, is suggested by Mehlich (3). The weight-volume basis of reporting has been the conventional reporting method under the U.S. measurement system.

The concept of the weight-volume basis is that a scoop of an appropriate size will hold a unit amount of the typical soil weighing 2 million pounds per acre to a depth of 6⅔ inches. As one changes to the metric system these convenient, conventional reporting units may have conversion disadvantages.

The Historical Scoop

An initial study in 1965 showed that measurement scoops of two sizes were predominant in use among the 13 member states. These sizes were approximately 0.85 cc and 1.0 cc per gram of "typical soil." Scoop construction varied greatly, consisting of modified kitchen measuring spoons, calibrated copper tubing caps and machined brass scoops. The basis for calibrating scoops was undocumented and vague. Conditions of wear and shape varied greatly, contributing further to disarray in soil measurement.

A search into the heritage of the two scoop sizes showed that the 1.0 cc scoop was introduced in the late 1950s in Illinois during a modernization[1] of the soil testing program, and the 0.85 cc size scoop was used by developers of early soil testing methods. The magnitude of the variations in test results was not as serious as variations in scoop size due to the small degree of dissociation of nutrient forms measured by available tests.

NCR-13 Scoop Development

In 1967, the NCR-13 representatives using volume measurement elected to adopt a standard size, stainless-steel scoop to minimize the following problems: contamination[2] of soil samples, wear of the

[1] *The scoop was machined of more durable material and, hence, was an improvement.*

[2] *Brass and copper scoops may contribute contamination in zinc and copper soil tests.*

scoop and variation among laboratories. The committee members also decided to continue using the weight-volume basis of reporting soil test levels since soil testing with these terms has appreciable farm acceptance in the North Central Region. The usual layman term is "pounds per acre," and conversion to the metric system can be pp2m or ppm, designated with an asterisk to indicate scoop measurement.

Studies show that the 0.85 cc size scoop approximates a 1 gram measure of typical soil. This is an empirical conclusion arrived at from the observation of several hundred volume/weight measurements on a wide range of soils. The typical soil is defined as a medial silt-loam texture with 2.5 percent organic matter crushed to pass a 10-mesh screen. Bulk density of crushed, typical soil approximates 1.18, which compared with 1.32 for undisturbed soil. Experience with the 0.85 cc scoop shows that soil test results on a sample measured with such a scoop, when compared to a weighed sample analysis, differ by a factor equal to the difference in bulk density of the soil samples.

Table 1 shows the specifications for standard soil scoops as adopted by the NCR-13 Regional Soil Testing and Plant Analysis Committee. The scoops are illustrated in Figure 1. The relationship of pulverized soil scoop weight with unpulverized field bulk density is shown in Figure 2. There is close agreement between the scoop design and soil mass contained in the normal range of bulk density.

Procedure for Using Scoop

Suggested procedure for using a soil scoop to measure soil is as follows:

1. Stir the pulverized and screened soil sample with a spatula to loosen soil prior to measuring.
2. Dip into the center of the soil sample with the scoop, filling it heaping full.
3. Hold the scoop firmly. Tap the handle three times with a spatula from a distance of 2 to 3 inches.
4. Hold the spatula blade perpendicular to the top of the scoop and strike off excess soil.
5. Empty the scoop into an extraction vessel for the soil test.[3]
6. Calculate the analytical result using the scoop size (Table 1) as the assumed weight of soil and report soil test value in units of pounds per acre (acre will be understood to represent a volume of soil measuring 43,560 square feet to a depth of 6⅔ inches and weighing 2 million pounds).

[3]*Scooping technique can be evaluated by weighing scoop contents. Precision not to exceed plus or minus 10 percent should be expected.*

Table 1. NCR-13 standard soil scoop specifications (manufactured from stainless steel).

Scoop Size[1] g	Scoop Capacity cc	Outside Diameter in.	Inside Diameter[2] in.	Inside Depth[2] in.
1	0.85	5/8	1/2	17/64
2	1.70	3/4	5/8	22/64
5	4.25	1	7/8	28/64
10	8.51	1¼	1 1/8	34/64

[1]Grams of soil in terms of the typical soil weighing 2 million lb./acre to a depth of 6⅔ inch layer.
[2]Note the inside depth is approximately equal to one-half the inside diameter.

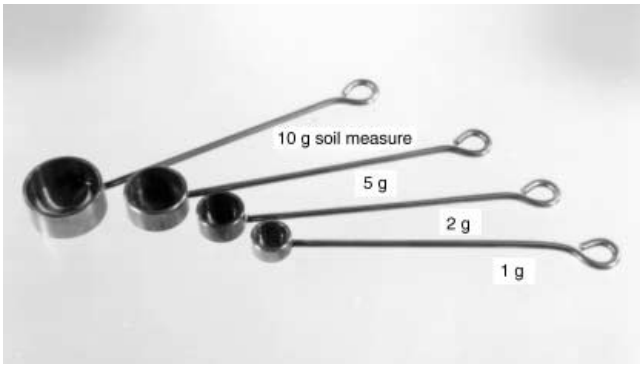

Figure 1. NCR-13 standard soil scoops.

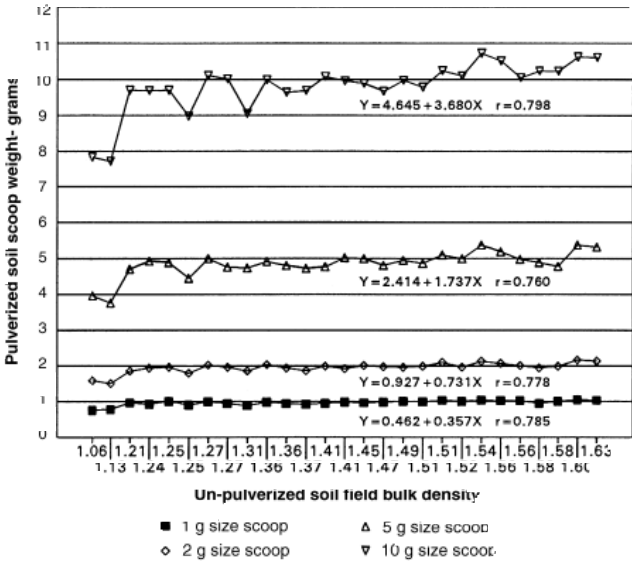

Figure 2. Relationship of pulverized soil scoop weight with unpulverized field bulk density.

Summary

Choice of a routine, rapid and accurate technique for measuring soil amounts for soil testing is an arbitrary one. In the experience of the NCR-13 com-

mittee, use of a scoop of the proposed size and shape will give soil test results comparable to weighed samples corrected for bulk density with a precision of plus or minus 10 percent.

Note: Information about the source of NCR-13 Standard Soil Scoops is available from the Illinois Soil Testing Association. Write to: Mowers Soil Testing Plus, Inc. P.O. Box 518, 117 E. Main, Toulon, IL 61483, or call: (309)286-2761.

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Reference to Soil Scoops

Note: Reference to a scoop or scooping in the procedures of this publication implies use of the appropriate NCR-13 scoop described in Chapter 2.

Chapter 3

Laboratory Factors of Importance to Soil Extraction

R. Eliason

One of the responsibilities of the NCR-13 committee is to standardize soil testing procedures for the North Central Region. These procedures include the chemical methods for extracting plant nutrients from the soil and their subsequent analysis by means that are accurate and free from interferences. However, sometimes overlooked are the details of exactly how those extractions are performed in a laboratory that is processing large numbers of samples under time pressure. This includes factors such as the means of shaking, rate of reciprocation, type of extraction vessel, extraction time and laboratory temperature. Although these factors are sometimes not given a lot of attention, they can have a significant impact on the test results. As laboratories work to improve the accuracy and reproducibility of their testing, it is important that they examine these factors and the impact they may have on test results. The more agreement that exists in this area, the better chance there will be for uniformity of test results across laboratories.

In the pursuit of consistency among laboratories, some of the following points should be considered when examining the techniques used in extracting plant nutrients by the recommended standard procedures:

Extraction Vessel Shape

Studies by Grava (1) have shown that Erlenmeyer flasks are preferred to ensure adequate mixing of the extracting solution and soil. The size of the flasks used in a particular test is determined by the volume of the extracting solution needed. The guideline to follow is that the flask should be about one-fourth full for best agitation. Wheaton bottles or similar straight sided bottles are discouraged due to the risk of variable and inadequate mixing.

Shaking vs. Stirring

Stirring has sometimes been used in place of shaking for mixing soil with an extracting solution. Grava (1) found this is acceptable if a stirring rate of 500 rpm is used. Agboola and Omueti (2) found that stirring extracted more P than shaking with the Bray P-1 test and felt shaking to be a better method for careful work.

Shaking Rates (Reciprocating Platform)

Studies by Munter (3) did not show large differences in extractability of nutrients with variable shaking rates over the range of 160 to 260 epm (excursions per minute). A study by Stone (4) reported lower sodium bicarbonate extractable phosphorus (P) with rates of 140 epm. Grava (1) recommended a shaking rate of 160 to 240 epm when using Erlenmeyer flasks. This recommendation was also endorsed by Munter.

Extraction Time

Each test has a recommended extraction (shaking/reflux) time that should be strictly followed. A number of studies have shown that for some tests, an extraction time other than the recommended time can have significant effects on the amount of nutrient extracted. For example, with the DTPA test, it has been found that shaking 15 minutes beyond the 2-hour recommended shaking time can result in a significant increase in the amount of micronutrients extracted for some soils (Unpublished data, Univ. of Minn., 1995). As demonstrated by Grava (1), it is inadvisable for laboratories to cut corners by reducing shaking times, especially for P and potassium (K). A study by Agboola and Omueti (2) paralleled the results of Bray and Kurtz (5) showing that Bray P-1 reached an equilibrium after 5 minutes, declined at 10 minutes of shaking and again increased at 20 minutes. These variations point out the importance of consistency in extraction time.

In addition, McGeehan et al. (6) have found that reflux and cooling times can strongly affect the results of the hot water extractable boron (B) soil test. They found that increased reflux time resulted in higher extractable B values, while increased cooling time decreased extractable B values. This points out the importance of following the recommended 5-minute reflux time and to carefully standardize the cooling time for this test. McGeehan et al. recommend a 10-minute cooling period.

Laboratory Temperature

The temperature of the laboratory is an often overlooked factor in laboratory analysis. There are several areas where this can have an impact. One area is in pH measurements. If pH reference buffers are not the same temperature as the samples or if the measurements are not temperature compensated, the error can be as much as 0.05 pH units for every 4°C change in temperature (7). It is recommended that all solutions be at ambient laboratory temperature. (This applies to all other soil tests as well.) Don't use reference buffers or calibration standards still cold from the refrigerator or distilled water directly from a cold tap. Make sure the pH meter is properly adjusted for temperature.

The extractability of nutrients has also been found to vary with changes in the ambient laboratory temperature. Stone (4) reported that the temperature of extraction was an important factor in sodium bicarbonate extractable P, the extractable P increasing with temperature over the range of 14 to 33°C. Olsen (8) found that sodium bicarbonate extractable P increased 0.43 ppm P with each 1°C increase in ambient temperature between 20 to 30°C. Munter (3) also reported strong temperature effects on Bray 1 extractable P, with P levels increasing as much as 126 percent with a temperature increase from 24 to 35°C. For this reason, Munter strongly recommended that laboratory temperatures be maintained between 24 to 27°C for routine extraction.

Summary

Although perfect agreement between laboratories on all aspects of processing soil samples may not be realistic, consideration of the above test parameters deserve attention when procedures are established for any laboratory. Consistency should be an overriding consideration for any technique, with considerable effort placed on mechanisms that allow for close control of even the small details in the procedure. Above all, closely follow the recommendations given in the procedure. This will provide the best opportunity for agreement of test results between laboratories.

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Chapter 4

pH and Lime Requirement

M. E. Watson and J. R. Brown

Soil pH is a measure of hydronium ion (H_3O^+ or, more commonly, H^+) activity in a soil suspension. This property influences many aspects of crop production and soil chemistry, including availability of nutrients and toxic substances, activity and diversity of microbial populations, and activity of certain pesticides. Soil pH is defined as the negative logarithm (base 10) of the H^+ activity (moles per liter) in the soil solution. As the activity of H^+ in the soil solution increases, the soil pH value decreases. Soils with pH values below 7 are referred to as "acid"; pH values above 7 are referred to as "alkaline"; soils at pH 7 are referred to as "neutral."

In most soils, the soil pH is buffered by several components of the solid phase, including hydroxy aluminum monomers and polymers, soil organic matter, and undissolved carbonates in soils. Lime requirement tests, which generate recommendations for effecting relatively long-term changes in soil pH, are designed to account for soil buffering capacity.

Soil pH Determination

Soil pH is usually measured potentiometrically in a slurry using an electronic pH meter (2). A H^+ sensitive electrode and a reference electrode are also used. Combination electrodes that contain the H^+ sensitive electrode and the reference electrode as one unit can be used if the combination electrode is robust enough to withstand continued wear from the soil slurry over time. Instructions for the correct pH meter operation are provided by the manufacturer.

Several precautions should be taken when measuring pH of a soil/liquid slurry. Electrodes should be checked and maintained frequently to prevent surface residue buildup, which may affect the measurement. Rinsing between each soil sample, however, is not usually necessary.

Electrodes should be protected to prevent insertion to the very bottom of the slurry-containing vessel. If this is not done, abrasion of the sensing surfaces will occur, decreasing the life of the electrode and leading to inaccurate pH readings. All meters should be calibrated routinely at two points with buffer solutions of known pH before measuring the pH of a soil sample. One point of calibration should be at pH 7.0, while the other point should be chosen based on the range of soil pH normally encountered by the laboratory. A laboratory testing mainly acid soils should calibrate across the acid range (second point at pH 4, for example), while a laboratory testing mainly alkaline soils should calibrate across the alkaline range (second point at pH 9 or 10).

Reference and/or combination electrodes for measuring soil pH should be chosen carefully because flow rates at the liquid junction can affect the accuracy of soil pH readings. Laboratories should use a set of reference soil samples of known pH to evaluate the performance of electrodes. Such samples should be stored and handled under carefully controlled conditions to prevent changes in soil properties over time. The reference soil pH of these samples should be determined using the average reading of several meters over several days. Electrodes that have been calibrated with clear buffer solutions, but fail to produce pH readings of the reference soils consistent with established values, should be discarded. However, the properties of the reference soils must not have changed.

Soil pH is normally measured in a soil/water slurry. The presence of soluble salts in a soil sample will affect pH. For that reason, some analysts prefer to measure pH in a mixture of soil and 0.01 M $CaCl_2$ (1, 6). The excess salt in this solution masks the effects of differential soluble salt concentrations in individual samples. Below are procedures for each method.

Equipment and Reagents

1. NCR-13, standard 5 g soil scoop
2. pH meter with appropriate electrode(s)
3. Pipettes
4. 1 oz. paper cups or equivalent
5. Distilled or deionized water
6. 0.01 or 1.0 M $CaCl_2$
7. Appropriate buffer solutions for calibrating the pH meter

Procedure

1. Calibrate the pH meter over the appropriate range using the manufacturer's instructions.
2. Use the scoop to measure a 5 g soil sample into a paper cup.

3. Add 5 mL distilled or deionized water to the sample.
4. Stir vigorously for 5 seconds and let stand for 10 minutes.
5. Place electrodes in the slurry, swirl carefully and read the pH immediately. Ensure that the electrode tips are in the swirled slurry and not in the overlying solution.
6. For the $CaCl_2$ measurement, add one drop of 1.0 M $CaCl_2$ solution to the previous sample, or prepare a sample as in Steps 2 and 3, using 0.01 M $CaCl_2$ instead of water. Stir vigorously and let stand 30 minutes, with occasional stirring. Read the pH as in Step 5.

Lime Requirement Determination

The SMP buffer method described below was designed for soils with large lime requirements and significant reserves of exchangeable aluminum (7). The procedure may be inaccurate on low lime requirement soils (<2 T/A), soils with organic matter contents greater than 10 percent, sandy soils or soils with a predominance of kaolinite and hydroxy oxides of aluminum and iron in their clay fractions (3). For most North Central Region soils, however, the SMP method appears to yield satisfactory results. For more precise determination of very low lime requirements, the double-buffer modification of the SMP procedure (4, 5) may prove useful.

Equipment and Reagents

1. Equipment needed for pH determination
2. Mechanical shaker
3. SMP buffer solution (below)

SMP Buffer Solution (Bulk Preparation)

1. Weigh into an 18 L bottle:
   a. 32.4 g paranitrophenol[1];
   b. 54.0 g potassium chromate;
   c. 955.8 g calcium chloride dihydrate.
2. Add 9 L distilled or deionized water, shaking vigorously during addition.
3. Weigh 36.0 g calcium acetate into a separate container and dissolve in 5 L of distilled or deionized water.
4. Combine solutions 2 and 3, shaking during mixing and every 15 to 20 minutes for 2 to 3 hours.
5. Add 45 mL triethanolamine, shaking during addition and periodically thereafter until completely dissolved (may take up to 8 hours). A magnetic stirrer can be use as an alternative to periodic shaking.
6. Dilute to 18 L with distilled or deionized water, adjust to pH 7.50 using 15 percent NaOH, and filter. To minimize air bubbles, avoid excessive agitation of the solution after pH adjustment.
7. Store in a container with the air inlet protected by drierite and ascarite to prevent contamination by water vapor and carbon dioxide.

Measuring Soil-Buffer pH

1. Add 10 mL of SMP buffer solution to the soil/water slurry saved from the pH determination.
2. Place in a mechanical shaker, close tightly, shake at 250 excursions per minute for 10 minutes, and let stand for 30 minutes. (Fifteen minutes shaking and 15 minutes standing is also acceptable. See Table 1.)
3. Swirl and read the pH. Read to the nearest 0.01 pH unit, particularly if using the double-buffer option described below.
4. Use the resulting soil-buffer pH to determine the lime requirement. The relationship of lime requirement for mineral soils and SMP soil-buffer pH is given in Table 2. An example of the relationship between lime requirement and soil pH for organic soils is shown in Table 3 (8).

Double-Buffer Option of the SMP Test

A double-buffer option for the SMP test has been developed which may improve the accuracy of predicting lime needs of soils with low lime requirements (4, 5). This procedure essentially develops the lime requirement/buffer pH relationship for each individual soil sample rather than using a generalized relationship. It can be run as a simple add-on procedure to the standard SMP method. In contrast to the standard single-buffer method, certain properties of each batch of buffer should be determined precisely before using the double-buffer procedure. These properties (See Preliminary Steps.) may vary from one batch to the next, and their determination should be included in every preparation.

Preliminary Steps

1. Prepare an HCl solution of sufficient concentration that 1 mL will lower the pH of 10 mL of SMP buffer from pH 7.50 to pH 6.00. This solution should be approximately 0.21 M.
2. Titrate 10 mL of the pH 7.50 SMP buffer with HCl (from Step 1, above) to determine the meq acidity neutralized per unit change in pH. Record this value as a_1. It should be approximately 0.137 meq.

[1]*Safety considerations for paranitrophenol: May cause eye irritation and irreversible eye injury; may be absorbed through skin in harmful amounts; harmful if ingested.*

3. Add 1 mL HCl (prepared in Step 1) to 10 mL of the pH 7.50 buffer, mix, let stand 30 minutes, and titrate with HCl to determine meq acidity neutralized per unit change in pH. Record the value as a_2. This should be about 0.129 meq.

Procedure for Double-Buffer Option

1. Record the buffer pH from the standard SMP test as pH_1.
2. Add 1 mL of the HCl solution (prepared in Preliminary Step 1.) to the soil-buffer mix and repeat the 10-minute shaking and 30-minute standing (or 15-minute shaking and 15-minute standing).
3. Read the pH of this mixture and record as pH_2.
4. Calculating the lime requirement
   a. Calculate the acidity to be neutralized to achieve desired pH in meq/5 g sample:

$$a_f = [(7.5 - pH_1)a_1 - (6 - pH_2)a_2]\ [(pH_f - pH_2)/(pH_1 - pH_2)] + (6 - pH_2)\, a_2$$

a_f = acidity to be neutralized
pH_f = desired pH

(All other values defined in previous procedures.)

   b. Calculate the lime requirement as follows:

$$LR\ (meq/100g) = 33.8a_f - 0.86$$

For 6 $^2/_3$ inch furrow slice (2 million lb soil/acre):

$$LR\ (tons\ CaCO_3/acre) = 16.9\ a_f - 0.43$$

For 8 inch furrow slice (2.4 miilion lb soil/acre):

$$LR\ (tons\ CaCO_3/acre) = 20.3a_f - 0.52$$

Note: All values for constants are based on averages across a wide range of soils. As with the standard SMP Method, constants derived from calibrations on local soils may be more accurate than those presented here.

Table 1. Effects of shaking and standing time following shaking on average soil-buffer pH of 15 U.S. soils.

Shaking Time (min.)	Standing Time (min.)			
	0	15	30	45
	pH			
5	6.32	6.24	6.20	6.21
10	6.30	6.27	6.19	6.22
15	6.25	6.19	6.21	6.19
20	6.21	6.20	6.14	6.20

Table 2. Amounts of lime required to bring mineral soils to indicated pH according to soil-buffer pH.

Soil-buffer pH	Desired soil pH			
	7.0	Mineral soils 7.0	6.5	6.0
	Pure $CaCO_3$	Ag-ground limestone[1]		
	tons/acre 8" of soil			
6.8	1.1	1.4	1.2	1.0
6.7	1.8	2.4	2.1	1.7
6.6	2.4	3.4	2.9	2.4
6.5	3.1	4.5	3.8	3.1
6.4	4.0	5.5	4.7	3.8
6.3	4.7	6.5	5.5	4.5
6.2	5.4	7.5	6.4	5.2
6.1	6.0	8.6	7.2	5.9
6.0	6.8	9.6	8.1	6.6
5.9	7.7	10.6	9.0	7.3
5.8	8.3	11.7	9.8	8.0
5.7	9.0	12.7	10.7	8.7
5.6	9.7	13.7	11.6	9.4
5.5	10.4	14.8	12.5	10.2
5.4	11.3	15.8	13.4	10.9
5.3	11.9	16.9	14.2	11.6
5.2	12.7	17.9	15.1	12.3
5.1	13.5	19.0	16.0	13.0
5.0	14.2	20.0	16.9	13.7
4.9	15.0	21.1	17.8	14.4
4.8	15.6	22.1	18.6	15.1

[1]Ag-ground lime of 90% plus total neutralizing power (TNP) or $CaCO_3$ equivalent, and fineness of 40% < 100 mesh, 50% < 60 mesh, 70% < 20 mesh, and 95% < 8 mesh. Adjustments in the application rate should be made for liming materials with different particle sizes, neutralizing values and depth of incorporation.

Table 3. Example of lime required to bring organic soils to desired pH as used by Indiana, Ohio and Michigan (8).

Organic Soils	
Soil pH	5.3 Desired pH Tons/Acre[1]
5.2	0.0
5.1	0.7
5.0	1.3
4.9	2.0
4.8	2.6
4.7	3.2
4.6	3.9
4.5	4.5
4.4	5.1

[1]These values are based on liming to 8 in. of depth with agricultural limestone and a neutralizing value of 90 %. Adjustments in the application rate should be made for liming materials with different particle sizes, neutralizing values and depths of incorporation.

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Chapter 5

Nitrate-Nitrogen

R. H. Gelderman and D. Beegle

Pre-plant Soil Nitrate Test

Pre-plant Soil Nitrate Tests (PPNT) have been used for decades to predict crop nitrogen (N) needs in the Great Plains region. In these low-rainfall areas, nitrate carryover from the previous growing season is frequent due to low potential for nitrate loss through leaching and denitrification (12, 17). Recent work in humid areas of the Midwest shows that the PPNT is a useful method of adjusting crop N recommendations for the amounts of residual nitrate in soil profiles (6, 7, 10, 14, 29). In humid regions, the PPNT is likely to be most useful on medium and fine-textured soils where previous-year precipitation was normal or below normal, and where previous-year N applications exceeded crop N needs (9).

In general, the PPNT consists of measuring nitrate-N in some portion of the crop root zone and crediting this N against the N needs of the crop to be grown. The PPNT differs in principle from the Pre-sidedress Nitrate Test (PSNT) discussed later in this chapter in that the PPNT provides a direct crediting of soil nitrate against crop N needs, while the PSNT provides an index of N availability that is related to crop N response through test calibration data. Therefore, the PPNT does not provide a direct assessment of the amounts of N likely to be released from organic N sources during the growing season.

Procedures for using the PPNT have recently been summarized by Bundy and Meisinger (8). Soil sampling for the PPNT can be done in the fall (subhumid areas only) or before crops are planted in the spring. This provides more time for sampling and analysis than is usually available for the PSNT. Samples are usually taken to a minimum depth of 2 feet. Some states recommend deeper samples. Standard analytical procedures are appropriate for extraction and analysis of nitrate in the soil samples. Samples should be dried or frozen soon after collection, and moist samples should be protected from warm temperatures.

Interpretation and use of PPNT results to develop fertilizer recommendations for crops varies among states and regions, but direct crediting of nitrate-N against crop N needs is usually involved. Examples of interpretation procedures for PPNT results in humid regions are provided in Bundy and Sturgul (9) and Schmitt and Randall (29).

Pre-sidedress Soil Nitrate Test for Corn

In humid regions, the nitrate-N level in the top foot of soil, measured just prior to sidedressing corn, has been shown to be related to the N-supplying capability of the soil and thus, the probability of a corn yield response to sidedress application of N fertilizer (4, 23, 24). This test, which is called the Pre-sidedress Soil Nitrate Test (PSNT), is essentially an in situ incubation method which provides an index of the N-supplying capability of a soil. It is not used to reduce recommendations by the amount of extracted nitrate-N such as is done with deep nitrate tests in the Great Plains. The PSNT has been especially useful in helping to estimate the probability of corn response to N where manure has been applied. While this test is designed primarily to determine the probability of response to sidedress N, it can also provide some guidance for improving N rate recommendations when a response is predicted.

Standard recommended procedures for extraction and analysis of the soil nitrate-N can be used. However, the timing and method of sampling for the PSNT is unique. Samples must be taken when the corn is approximately 12 inches tall. Samples are taken to a 12 inch depth and must be dried within 24 hours. If they cannot be dried immediately, they must be frozen until they can be dried for analysis. In addition to the standard recommended procedures for extraction and analysis for soil nitrate-N, quick-test methods have been developed in Pennsylvania and Iowa in response to the need for rapid turnaround with this analysis. These kits have been shown to agree well with standard laboratory procedures and have been used successfully (27, 28).

Interpretation of the soil nitrate-N levels and the method of making recommendations for sideidressing N vary from state to state. Research from the Northeast to the Midwest has indicated that the critical level for the PSNT generally ranges from 21 to 25 ppm nitrate-N. Above this level, a response to sidedress N is not expected. Below this level, recommendations can be adjusted based on the nitrate-N level from the PSNT (2, 5, 19).

Extraction

The high solubility of NO_3^- in water makes extraction with water possible for most soils of the North Central Region. Soils with significant anion-exchange properties should be extracted with 1 or 2 molar KCl, unless Cl^- or K^+ ions interfere with the determination method.

Time of extraction varies from 5 to 30 minutes for various states(15). Kelly and Brown (20) found that shaking the sample for 5 minutes gave similar results to shaking for 8 hours. Oien and Selmer-Olsen (26) found a 2-minute shaking time sufficient to extract nitrates.

The extraction of NO_3^- is relatively simple; however, many methods of determination exist. Errors can arise in each of these methods due to interferences, biological transformations, poor lab technique and many other sources. Variations due to method of determination are of relatively minor importance, though, compared to those due to field sampling techniques and those due to interpretation of the test from field response to added N.

The most commonly used procedures of NO_3^- determination among states using the test are the Nitrate Electrode and the Cadmium Reduction methods (3). These two methods are presented here. Any method used to determine NO_3^- should be scrutinized by using standard lab "check" soils, known additions and comparisons to reference procedures, such as steam distillation (21).

Nitrate Electrode Method

The function of the nitrate-specific ion electrode as explained by Dahnke (11) is similar to a conventional pH electrode, but instead of developing a potential across a glass membrane, a potential develops across a thin layer of water-immiscible liquid or gel ion exchanger that is selective for NO_3^- ions. This layer of ion exchanger is held in place by a porous membrane.

The aqueous internal filling solution contains fixed levels of NO_3^- ion and provides a stable potential between the inside surface of the membrane and the internal Ag/AgCl reference element. The NO_3^- electrode responds only to the activity of the free, unassociated ions, not to NO_3^- ions which are bound to complexing agents. If the activity of the NO_3^- ion is greater in the sample solution than in the internal filling solution, there is a net diffusion of NO_3^- ions into the electrode; or if the activity is less than in the sample solution, there is a net diffusion out of the electrode. The diffusion of NO_3^- ions into or out of the electrode will continue until a state of equilibrium is reached, at which time the electrical potential developed across the membrane prevents any further net diffusion of NO_3^- ions.

The lower limit of accurate detection of the NO_3^- electrode is about 1 to 2 ppm NO_3^-–N in solution. This fact largely determines the smallest soil to solution ratios that can be used. Oien and Selmer-Olsen (26) studied ratios (g to mL) of 5-to-50, 10-to-50, 20-to-50, 30-to-50, and 50-to-50. They found that the 5-50 ratio was too large to determine NO_3^- accurately in most soils because the NO_3^- contents are too low. They report that the 20-50 ratio can be used to determine accurately as little as 2 ppm of NO_3^-–N. When they used the 50-50 ratio, the NO_3^- values decreased slightly when expressed as mg NO_3^-–N per 100 g dry soil.

As ionic strength increases, the activity of the NO_3^- ion decreases. For this reason, numerous extractants have been developed to dampen this effect. The modified extracting solution of Millham et al. (25) is listed below. If chloride and nitrite (NO_2^-) are not serious interferences, the silver sulfate and sulfamic acid can be eliminated from this extractant. Using present day module-type electrodes, many workers have found that this extractant is an improvement over water. The electrode can be placed in a filtrate of the extract or directly in the soil/water slurry.

Equipment

1. Nitrate ion-sensitive electrode
2. A pH/ion meter or pH-millivolt meter
3. NCR-13, 10 g scoop

Reagents

1. Extracting Solution
   a. Distilled water or
   b. Ionic strength adjusting solution: 0.01 M $Al_2(SO_4)_3$, 0.02 M H_3BO_3, 0.01 M Ag_2SO_4 and 0.02 M NH_2HSO_3 (sulfamic acid): Dissolve 67 g of $Al_2(SO_4)_3 \cdot 18H_2O$, 12 g of H_3BO_3, 20 g of Ag_2SO_4 and 19 g of NH_2HSO_3 in water and dilute to10 L.
2. Standard nitrate solutions: To a 1,000 mL volumetric flask, add 0.7221 g of oven-dry KNO_3; make up to volume with extracting solution. This gives a solution containing 100 ppm of NO_3^-–N.

Procedure

1. Measure 20 g of soil into a 100 mL cylindrical container.
2. Add 50 mL of extracting solution.
3. Shake for 5 minutes on a reciprocal shaker.
4. Read the potential while suspension is being stirred with magnetic stirrer.
5. Record the millivolt reading (if using a calibration curve technique) or read the NO_3–N concentration directly from a pH/ion meter.

Table 1. Working standard solutions for NO_3^-–N test

Volume of 100 ppm Stock Solution	Final Volume	Concentration of NO_3^-–N in Working Standards
mL	mL	ppm
1	100	1
5	100	5
10	100	10
15	100	15
20	100	20

Cadmium Reduction Method

This method of determining nitrate reduces NO_3^- to NO_2^- using copperized cadmium. Once reduced, the NO_2^- is usually determined using a modified Griess- Ilosvay method. This method is based on the principle that NO_2^- reacts with aromatic amines (diazotizing agents) in acidic solutions to give diazo salts. These salts couple with aromatic agents to form colored azo compounds or dyes. The color intensity is then determined with a spectrophotometer.

The range of detection for soil extracts using this method has been reported from 0.2 to 15 ppm NO_3^-–N (16). This should be a sufficient range for most soils without additional dilutions. Precision values of 2.1 to 3.4 percent (coefficients of determination) have been reported using a manual method (13).

Other advantages of this method include the sensitivity of the Griess-Ilosvay procedure. This allows sufficient dilution to effectively eliminate any colored extract interference. The procedure is relatively rapid using automated instrumentation. From 40 to 100 samples per hour can be analyzed using automated procedures after samples are extracted. Instrumentation, however, is relatively expensive. Manual methods for cadmium reduction have been described (13, 18, 22). An estimate of 36 samples (previously extracted) analyzed per hour, using four columns, was made by Dorich and Nelson (13). The color of the azo compounds are very stable (1). Nitrite-N is determined simultaneously with NO_3^-–N. However, NO_2^- can be determined separately by not passing one aliquot of the extract through the reducer column. The NO_3^-–N is then determined by subtraction. Alternatively, NO_2^- can be removed from the extract by addition of sulfamic acid.

Extraction can be accomplished with 2 M KCl (13) or with water (18). A procedure will not be specifically described here because of the lengthy methods involved. Each instrument will have its specific literature and method following the above principles. The reader is referred to Keeney and Nelson (22) or Huffman and Barbarick (18) for Manual Cadmium Reduction methods.

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Chapter 6

Phosphorus

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All of the state soil testing laboratories in the North Central Region, except two, use the Bray and Kurtz P-1 (3) procedure for phosphorus (P). The exceptions are North Dakota and South Dakota where soils are predominantly calcareous. Consequently, the Sodium Bicarbonate (Olsen) Method (5) is used. Most of the states and provinces that border the North Central Region also use one of these two methods. Each state experiment station has developed correlations and calibrations for the soil conditions within its own state.

The Bray and Kurtz P-1 Test results are well-correlated with yield response on most acid and neutral soils in the region. This test is used for soils that contain small amounts (less than 2 percent) of dolomite or calcium carbonate (1, 9, 12). It should not be used for soils containing large amounts of lime. Since the phosphorus may be precipitated during extraction, the result is very low test values (1,12).

The Sodium Bicarbonate (Olsen) test for P (10,13) is preferred for highly calcareous soils. The test results are well-correlated with crop response to P fertilization on both calcareous and noncalcareous soils. The Sodium Bicarbonate (Olsen) Test values are more highly correlated with yield response on calcareous soils than the Bray and Kurtz P-1 (1:10 ratio). In some cases, the correlation-to-yield was equal to or superior to the Bray and Kurtz P-1 on noncalcareous soils (1, 9, 12).

If the Bray and Kurtz P-1 is the primary method used in the laboratory for extracting ortho-phosphate, the Sodium Bicarbonate (Olsen) Method should be used for highly calcareous soils that test very low in the Bray and Kurtz P-1 method. In general, the Bray and Kurtz P-1 method will extract about the same amount of P as the Sodium Bicarbonate (Olsen) Method in the low range. The Bray and Kurtz P-1 method will extract more P in the medium range than the Olsen method. In the high range, except on highly calcareous soils, the Bray and Kurtz P-1 extracts more P than the Sodium Bicarbonate (Olsen) method. Each of these tests have a separate calibrations to yield response (6).

Another extractant for determining P is the Mehlich 3 procedure (7). This procedure exhibits a good correlation with the Sodium Bicarbonate (Olsen) method on calcareous and non-calcareous soils.. However, Bray and Kurtz P-1 only correlates with Mehlich 3 on non-calcareous soils. Calibrations-to-yield response are more recent where they exist. Research is continuing to supply the calibration data. The response patterns of the Mehlich 3 extractant are similar to the Bray and Kurtz P-1 and the Sodium Bicarbonate (Olsen) tests. Mehlich 3 extracts more P from the soil than does the Bray and Kurtz P-1 or Sodium Bicarbonate (Olsen) tests on acid and neutral soils (6).

The Mehlich 3, Bray and Kurtz P-1 and Sodium Bicarbonate (Olsen) procedures can be used with various reducing agents. The procedures presented here use ascorbic acid with potassium antimony tartrate or an alternative using the Fiske-Subbarrow reducing agent (aminonaphtho-sulfonic acid) (4). The Fiske-Subbarrow procedure is somewhat less sensitive and provides a wider range of soil test values without dilution. The ascorbic acid reducing method (13) is well-adapted to the Olsen method. A 1:10 soil-to-extractant ratio for Bray and Kurtz P-1 and Mehlich 3 (1:20 soil-to-extractant ratio for Sodium Bicarbonate (Olsen)) should be maintained for either volume-to-volume or volume-to-weight ratios.

Bray and Kurtz P-1 Test for Phosphorus

Background

The Bray and Kurtz P-1 method of testing for “adsorbed” P was first published in 1945 by Roger H. Bray and Touby Kurtz (3) of the Illinois Agricultural Experiment Station. Research showed the Bray and Kurtz P-1 to be best correlated with crop response to phosphate fertilizer. Most states implemented it into the routine soil test operation with various minor modifications. Surveys and sample exchanges conducted by the NCR-13 committee revealed diversity of phosphate concentrations extracted by the Bray and Kurtz P-1 procedure. Primarily, the differences were caused by extraction techniques that were not adequate. Results of these studies are presented by Munter in his discussion on extraction techniques (8).

A detailed study of the soil-to-solution ratio, type of extraction vessel, shaking speed and time, and the chemistry involved produced the following procedures. Using these procedures should provide the

conditions necessary to obtain satisfactory replication of results among laboratories. The method detection limit is approximately 1.0 mg kg^{-1} (dry soil basis) and can be reproduced plus or minus 10 percent. The color development procedure can be accomplished manually or by automated techniques as described in the appendix to this chapter (4).

Equipment

1. No. 10 (2 mm opening) sieve
2. Standard NCR-13, 1 g and 2 g soil scoop
3. Automatic extractant dispenser, 25 mL capacity.(If preferred, pipettes are acceptable.)
4. 50 mL Erlenmeyer extraction flasks
5. Rotating or reciprocating shaker with a capability of 200 excursions per minute (epm)
6. Filter funnels, 9 to 11 cm
7. Whatman No. 42 or No. 2 (or equivalent) filter paper, 9 to 11 cm. (Acid resistant filter paper may be needed if using automated method of determining concentration by intensity of color. Bits of filter paper may cause an obstruction in the injection valves.)
8. Funnel rack
9. Appropriate vials for color development
10. Volumetric flasks and pipettes required for preparation of reagents and standard solutions; pipettes or a dilutor used for color development
11. Photometric colorimeter (manual or automated) suitable for measurement in the 882 nm range (610 to 660 for Fiske-Subbarrow)
12. A computer or calculator, used for calculation of the concentrations of phosphorus in the soil

Extractant: 0.025 M HCl in 0.03 M NH_4F

1. Dissolve 11.11 g of reagent-grade ammonium fluoride (NH_4F) in about 9 L of distilled water.
2. Add 250 mL of 1.00 M HCl (previously standardized) and make to 10 L volume with distilled water.
3. Mix thoroughly.
4. The pH of the resulting solution should be 2.6 plus or minus .05. The adjustments to pH are made using HCl or ammonium hydroxide (NH_4OH).
5. Store in polyethylene.

Phosphorus Standards

1. Stock Standard Phosphorus Solution (50 ppm P)
   a. Dissolve 0.2197 g of oven-dried, reagent-grade potassium dihydrogen phosphate (KH_2PO_4) in about 25 mL of distilled water.
   b. Dilute to a final volume of 1,000 mL with extracting solution. (If this solution is stored at 40°F, its shelf life should be approximately 6 months.)
2. Working Standard Solutions
   a. Using the information in Table 1 for Bray and Kurtz P-1, pipette appropriate volumes of 50 ppm stock standard P solution into proper volumetric flasks.
   b. Use the extracting solution to bring each standard to the proper volume.

Table 1. Working standard solutions for Bray and Kurtz P-1 and Mehlich 3 tests.

50 ppm Stock Solution	Final Volume	Concentration of Working Standard	Equivalent Soil Concentration	
			Ascorbic Acid	Fiske-Subbarow[1]
mL	mL	ppm P	ppm P	ppm P
1	250	0.2	2.0	2.0
1	100	0.5	5.0	5.0
2	100	1.0	10.0	10.0
4	100	2.0	20.0	20.0
6	100	3.0	30.0	30.0
8	100	4.0	40.0	40.0
10	100	5.0	50.0	50.0
12	100	6.0	–	60.0

[1]Standards appropriate for the range of each method of color development are listed under the respective columns.

Ascorbic Acid Method Reagents

1 Acid Molybdate Stock Solution
   a. Dissolve 60 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 200 mL of distilled water. If necessary, heat to about 60°C until solution is clear and allow to cool.
   b. Dissolve 1.455 g of antimony potassium tartrate in the molybdate solution.
   c. Add slowly 700 mL of concentrated sulfuric acid.
   d. Cool and dilute to a final volume of 1,000 mL. This solution may be blue, but will clear when diluted for use.
   e. Refrigerate this reagent in the dark.
2. Ascorbic Acid Stock Solution
   a. Dissolve 13.2 g of ascorbic acid in distilled water and dilute to a final volume of 100 mL.
   b. Refrigerate this reagent in the dark.
3. Working Solution
   a. Prepare fresh each day by adding 25 mL of acid molybdate stock solution to a volumetric flask containing about 800 mL of distilled water.
2. Mix thoroughly.
3. Add 10 mL of ascorbic acid stock solution.
4. Add distilled water to final volume of 1,000 mL.

Fiske-Subbarow Method Reagents

1. Acid Molybdate Stock Solution(P-B Solution)
   a. Dissolve 75.25 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 500 mL of distilled water heated to 60°C.
   b. Cool the solution and mix with 1,500 mL HCl (sp. gr. 1.19, 37.5 percent).
   c. Dilute the solution to 2,000 mL with distilled H_2O in a volumetric flask.
   d. Store in a glass-stoppered, brown bottle to which 100 g of boric acid (H_3BO_3) has been added.
2. Dry Reducing Agent: Aminonaphthol-sulfonic Acid (P-C Powder)
   a. Mix 5 g of 1-amino-2-napthol-4 sulfonic acid with 10 g of sodium sulfite (Na_2SO_3) and 292.5 g of sodium pyrosulfite ($Na_2S_2O_5$).
   b. Grind the mixture to a fine powder.
   c. If stored in a cool place in a sealed brown bottle, this reagent will keep for a year. Otherwise, discard after 6 months.
1. Dilute Reducing Agent (P-C Solution)
   a. Dissolve 16 g of dry reducing agent in 100 mL of distilled water heated to 60°C.
   b. Cool and store in brown bottle.
   c. Make fresh every 3 weeks.

Extraction

1. Scoop 2 g of soil (ratio of soil-to-solution is 1:10, see Chapter 2).
2. Add measured volume of soil to a 50 mL Erlenmeyer flask, tapping the scoop on the funnel or flask to remove all of the soil from the scoop.
3. Add 20 mL of extracting solution to each flask and shake at 200 or more epm for 5 minutes with the room temperature at 24 to 27°C (8).
4. Filter extracts through Whatman No. 42 filter paper or through a similar grade of paper. Refilter if extracts are not clear.

For steps 5 through 9, select either the Ascorbic Acid or Fiske Subbarrow color development procedure.

Ascorbic Acid Method Procedure

5. Transfer a 2 mL aliquot of the extract to a test tube (or remove quantitatively all but 2 mL from the filter tube if color is to be developed in the filter tube).
6. Add 8 mL of working solution so that thorough agitation and mixing occurs.
7. Allow 10 minutes for color development. Read percentage of transmittance or optical density on a colorimeter or spectrophotometer set at 882 nm. Color is stable for about 2 hours.
8. Prepare a standard curve by pipetting a 5 mL aliquot of each working standard, developing color and reading intensity in the same manner as with the soil extracts. Plot intensity against concentration of working standards. Determine concentration in soil extracts from intensity and the standard curve.
9. Convert ppm concentration in filtrate to concentration in the soil:

$$\text{ppm P in soil} = \text{ppm P in filtrate} \times 10$$
$$\text{lb/acre P insoil} = \text{ppm P in filtrate} \times 20$$

For an automated flow injection procedure, see Appendix 1.

Fiske-Subbarrow Method Procedure

5. Transfer a 5 mL aliquot of the extract to a test tube (or remove quantitatively all but 5 mL from the filter tube if color is to be developed in the filter tube).
6. Add 0.25 mL acid molybdate solution (P-B solution). Shake to mix with filtrate.
7. Add 0.25 mL dilute-reducing agent (P-C solution). Allow color to develop 15 minutes before reading samples. Read percentage of transmittance or optical density on a colorimeter or spectrophotometer set at 660 nm within 45 minutes after adding reducing agent.
8. Prepare a standard curve by pipetting a 5 mL aliquot of each working standard, developing color and reading intensity in the same manner as with the soil extracts. Plot intensity against concentration of working standards. Determine concentration in soil extracts from intensity and the standard curve.
9. Convert ppm concentration in filtrate to concentration in the soil:

$$\text{ppm P in soil} = \text{ppm P in filtrate} \times 10$$
$$\text{lb/acre P insoil} = \text{ppm P in filtrate} \times 20$$

For an automated flow injection procedure, see Appendix 1.

Mehlich 3 Test for Phosphorus

Background

The Mehlich 3 extraction of P is applicable for a wide range of soil properties ranging in reaction from acid to basic. This extractant was developed by Adolf Mehlich (7). The present Mehlich 3 procedure was developed to improve upon the Mehlich 1 and Mehlich 2 methods. Mehlich 1 did not correlate well with crop growth or yield when used on neutral to alkaline soils where apatite was the predominant source of available P. Mehlich 2 did not extract copper

adequately and caused corrosive damage to the laboratory and equipment. The Mehlich 3 extraction was developed on a 1:10 soil-to-solution ratio and a 5-minute shaking period at 200 epm. The detection limit of Mehlich 3 procedure is approximately 1.0 mg kg^{-1} (dry soil basis) and can be reproduced plus or minus 10 percent. The color development procedure can be accomplished manually or by automated techniques.

Equipment

1. No. 10 (2 mm opening) sieve
2 Standard NCR-13, 1 g and 2 g soil scoop
3. Automatic extractant dispenser, 25 mL capacity (If preferred, pipettes are acceptable.)
4. 50 mL Erlenmeyer extraction flasks
5. Rotating or reciprocating shaker with a capability of 200 excursions per minute (epm)
6. Filter funnels, 9 to 11 cm
7. Whatman No. 42 or No. 2 (or equivalent) filter paper, 9 to 11 cm (Acid resistant filter paper may be needed if using automated method of determining concentration by intensity of color. Bits of filter paper may cause an obstruction in the injection valves.)
8. Funnel tube rack
9. Appropriate vials for color development
10. Volumetric flasks and pipettes required for preparation of reagents and standard solutions; pipettes or a dilutor used for color development
11. Photometric colorimeter (manual or automated), suitable for measurement in the 880 nm range (610 to 660 is acceptable)
12. A computer or calculator, used for calculation of the concentrations of phosphorus in the soil

Mehlich 3 Extracting Solution

0.2 N CH_3COOH (acetic acid, glacial: 99.5 percent, fw 60.04, 17.4 N), 0.25 N NH_4NO_3 (ammonium nitrate: fw 80.05), 0.015 N NH_4F (ammonium fluoride: fw 37.4), 0.013 N HNO_3 (nitric acid: 68 to 70 percent, fw 63.02, 15.5 N), 0.001 M EDTA $[(HOOCH_2)_2NCH_2NCCH_2COOH)_2$, ethylenediaminetetraacetic acid: fw 292.24].

1. Use ACS grade chemicals and distilled water, unless noted, to prepare solutions.
2. Ammonium fluoride, EDTA stock solution (3.75 M NH_4F: 0.25 M EDTA)
   a. Add 1,200 mL of distilled water to a 2 L volumetric flask.
   b. Add 277.8 g of ammonium fluoride and mix.
   c. Add 146.1 g EDTA to the solution.
   d. Bring solution to 2 L, mix thoroughly and store in plastic (stock solution for 10,000 samples).
3. Mehlich 3 extractant preparation
   a. Add 8 L of distilled water to a 10 L carboy.
   b. Dissolve 200 g of ammonium nitrate in the distilled water.
   c. Add 40 mL NH_4F-EDTA stock solution. Mix.
   d. Add 11.5 mL acetic acid.
   e. Add 8.2 mL of nitric acid.
   f. Add distilled water to bring volume to 10 L. Mix thoroughly (provides enough extractant for 400 samples).

Phosphorus Standards

1. Stock Standard Phosphorus Solution (50 ppm P):
   a. Dissolve 0.2197 g of dry, reagent-grade potassium dihydrogen phosphate (KH_2PO_4) in about 25 mL of distilled water.
   b. Dilute to a final volume of 1,000 mL with extracting solution. (If this solution is stored at 40°F, its shelf life should be approximately 6 months.)
2. Working Standard Solutions
   a. Using the information in Table 1 for Mehlich 3, pipette appropriate volumes of 50 ppm stock standard phosphorus solution into proper volumetric flasks.
   b. Bring each flask to volume with extracting solution.

Acid Molybdate Stock Solution

1. Dissolve 60 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 200 mL of distilled water. If necessary, heat to about 60°C until solution is clear and allow to cool.
2. Dissolve 1.455 g of antimony potassium tartrate in the molybdate solution.
3. Add slowly 700 mL of concentrated sulfuric acid.
4. Cool and dilute to a final volume of 1,000 mL. This solution may be blue, but will clear when diluted for use.
5. Store in the dark under refrigeration.

Ascorbic Acid Stock Solution

1. Dissolve 13.2 g of ascorbic acid in distilled water and dilute to a final volume of 100 mL.
2. Store in the dark under refrigeration.

Working Solution

1. Prepare fresh daily by adding 25 mL of acid molybdate stock solution to a volumetric flask containing about 800 mL of distilled water.
2. Mix thoroughly.
3. Add 10 mL of ascorbic acid stock solution.
4. Add distilled water to a final volume of 1,000 mL.

Procedure

1. Scoop 2 g of soil (see Chapter 2).
2. Add measured volume of soil to a 50 mL Erlenmeyer flask, tapping the scoop on the funnel or

flask to remove all of the soil from the scoop.
3. Add 20 mL of extracting solution to each flask and shake at 200 or more epm for 5 minutes with the room temperature at 24 to 27°C (8).
4. Filter extracts through Whatman No. 42 filter paper or through a similar grade of paper. Refilter if extracts are not clear.
5. Transfer a 2 mL aliquot to a test tube (or remove quantitatively all but 2 mL from the filter tube if color is to be developed in the filter tube).
6. Add 8 mL of working solution so that thorough agitation and mixing occurs.
7. Allow 10 minutes for color development. Read percentage transmittance or optical density on a colorimeter or spectrophotometer set at 882 nm. Color is stable for about 2 hours.
8. Prepare a standard curve by aliquoting 2 mL of each of working standards, developing color and reading intensity in the same manner as the soil extracts. Plot color intensity against P concentration of the standards.
9. Determine ppm P in the extracts (Step 7) using the standard curve and convert ppm concentration in filtrate to concentration in the soil as follows:

$$\text{ppm P in soil} = \text{ppm P in filtrate} \times 10$$
$$\text{lb/acre P in soil} = \text{ppm P in filtrate} \times 20$$

Olsen ($NaHCO_3$) Phosphorus Test

Background

The Sodium Bicarbonate Method of extracting soil P was first published as USDA Circular 939 in 1954 by Dr. Sterling R. Olsen et al. (10). It was the result of a search for an extractant that would correlate crop response to fertilizer on calcareous soils. This procedure is recommended for calcareous soils, particularly those containing more than 2 percent calcium carbonate. The amount of P extracted will vary with temperature and shaking speed (8). The detection limits of the Sodium Carbonate (Olson) Method is approximately 2.0 mg kg^{-1} (air dried soil basis) and varies plus or minus 12 percent.

Equipment

1. No. 10 (2 mm opening) sieve
2. Standard NCR-13, 1 g and 2 g soil scoop (1:20 soil-to-solution)
3. Automatic extractant dispenser, 25 mL capacity (If preferred, pipettes are acceptable.)
4. 50 mL Erlenmeyer extraction flasks (125 mL flask if 2:40 soil-to-solution)
5. Rotating or reciprocating shaker with a capability of 200 excursions per minute (epm)
6. Filter funnels, 9 to 11 cm
7. Whatman No. 42 or No. 2 (or equivalent) filter paper, 9-11 cm (Acid-resistant filter paper may be needed if using automated method of determining concentration by intensity of color. Bits of filter paper may cause an obstruction in the injection valves.)
8. Funnel rack
9. Appropriate vials for color development
10. Volumetric flasks and pipettes required for preparation of reagents and standard solutions; pipettes or a dilutor used for color development
11. Photometric colorimeter (manual or automated), suitable for measurement in the 880 nm range (610 to 660 is acceptable)
12. A computer or calculator, used for calculation of the concentrations of phosphorus in the soil

Extracting Solution: (0.5 M $NaHCO_3$, pH 8.5)

1. Dissolve 420 g commercial-grade sodium bicarbonate in distilled water.
2. Make to a volume of 10 L.
3. A magnetic stirrer or electric mixer is needed to dissolve the $NaHCO_3$.
4. Adjust to pH 8.5 with 50 percent sodium hydroxide.

Acid Molybdate Stock Solution

Reagent A

1. Dissolve 60 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, in 1,250 mL of distilled water.
2. Dissolve 1.455 g of antimony potassium tartrate in 500 mL of distilled water.
3. Add both of these solutions to 5,000 mL of 2.5 M H_2S0_4 (ADD THE ACID TO THE WATER–148 mL of concentrated H_2S0_4 per liter of water).
4. Mix and dilute to 10,000 mL with distilled water.
5. Store in a glass, pyrex bottle in a dark, cool place.

Reagent B

1. Dissolve 2.639 g of ascorbic acid in 500 mL of reagent A. This reagent must be prepared each day as needed since it will not keep for more than 24 hours.

Stock Standard Solution: 50 ppm

1. Dissolve 0.2197 g of reagent-grade, dry potassium dihydrogen phosphate (KH_2PO_4) in about 25 mL of distilled water.
2. Dilute to a final volume of 1,000 mL with extracting solution.
3. Store in the dark under refrigeration.
4. This standard should be stable for 6 months.

Working Standards

1. Referring to Table 2, pipette appropriate amounts of 50 ppm stock standard phosphorus solution into volumetric flasks.
2. Bring flasks to volume with extracting solution.

Procedure

1. Scoop 2 g of soil (see Chapter 2).
2. Add measured volume of soil to a 50 mL Erlenmeyer flask, tapping the scoop on the funnel or flask to remove all of the soil from the scoop.
3 Add 20 mL of extracting solution to each flask and shake at 200 or more epm for 30 minutes with the room temperature at 24 to 27°C (8).
4. Filter extracts through Whatman No. 2 filter paper or a similar grade of paper. Refilter if extracts are not clear.
5. Transfer a 5 mL aliquot to a beaker or Erlenmeyer flask (50 mL or larger).
6. Add 15 mL of distilled water.
7. Add 5 mL of Reagent B and agitate flask so that thorough mixing occurs.
8. Allow 10 minutes for color development. Read percentage transmittance or optical density on a colorimeter set at 882 nm. Color is stable for at least 2 hours.
9. Prepare a standard curve by pipetting a 5 mL aliquot of each of the working standards, developing color and reading intensity in the same manner as with the soil extracts. Plot intensity against concentration of the working standards. Determine concentration in soil extract from intensity and standard curve.

Calculations

1. Convert ppm concentration in filtrate to concentration in the soil:

$$\text{ppm P in soil} = \text{ppm P in filtrate} \times 20$$
$$\text{lb\acre in soil} = \text{ppm P in filtrate} \times 40$$

Table 2. Working standard solutions for the Olsen Test.

Volume of 50 ppm Stock Solution	Final Volume[1]	Concentration of Working Standard	Equivalent Concentration in Soil
mL	mL	ppm P	ppmP
1	250	0.2	4.0
1	100	0.5	10.0
2	100	1.0	20.0
4	100	2.0	40.0
6	100	3.0	60.0
8	100	4.0	80.0
10	100	5.0	100.0

[1]Standards appropriate for the range of each method of color development are listed under the respective columns.

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Appendix

QuikChem Method No. 12-115-01-1-A

Parameter: Phosphorus as orthophosphate
Matrix: Bray or Mehlich No. 1 extracts of soils
Range: 0.4 to 20 mg P/L in the extract
Sample Throughput: 90 samples/hour; 40 s/sample

Principle

Soil samples are extracted with either a Bray No. 1 or Bray No. 2 solution. Approximately 0.02 mL of this extract sample is injected on the method's manifold where it is diluted. The orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 660 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

Interferences

1. Silica forms a pale blue complex which also absorbs at 660 nm. This interference is generally insignificant as a silica concentration of approximately 4,000 ppm would be required to produce a 1 ppm positive error in orthophosphate.
2. Concentrations of ferric iron greater than 50 mg/L will cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates.
3. The determination of phosphorus is sensitive to variations in acid concentrations in the sample since there is no buffer. The higher the acidity, the smaller the sensitivity of the method is. Samples, standards and blanks should be prepared in a similar matrix.

Sample Preparation: Example Extraction Procedure

1. Scoop 2 mL of soil into an extraction flask. Add 20 mL of the Bray No. 1, Bray No. 2 or Mehlich No. 1 solution (Reagents 2, 3 and 4, below).
2. Shake rapidly for 5 minutes.
3. Filter sample through a Lachat QuikFilter (Part No. 1000-000) or Whatman #2 filter paper.

Note: Any changes from this example may cause changes in the method. The standards described below are made up to match the extract matrix.

Reagent Preparation

Use deionized water (10 megohm) for all solutions.

1. Degassing with helium(He): To prevent bubble formation, degas all solutions except the standards with helium. Use He at 20 lb/inch^2 through a fritted gas dispersion tube. Bubble He vigorously through the solution for 1 minute.
2. Bray No. 1 "Weak Bray" Extracting Solution for Midwest soils (0.025 M HCl, 0.03 M NH_4F)
   a. To a 1 L container, add 1.0 L or 1.0 Kg of water. Then add 2.1 mL or 2.5 g of concentrated hydrochloric acid and 1.1 g of ammonium fluoride (NH_4F) and shake until dissolved.
3. Bray No. 2 Extracting Solution (0.1 M HCl, 0.03 M NH_4F)
   a. To a 1 L container, add 1.0 L or 1.0 Kg of water. Then add 8.4 mL or 10.0 g of concentrated hydrochloric acid and 1.1 g of ammonium fluoride (NH_4F) and shake until dissolved.
4. Mehlich No. 1 Extraction Solution for Southeast soils (0.05 M HCl, 0.012 M H_2SO_4)
   a. To a 1 L container, add 1.0 L or 1.0 Kg of water. Then add 4.2 mL or 5.0 g of concentrated hydrochloric acid and 0.7 mL or 1.2 g of concentrated sulfuric acid. Shake to mix.
5. Stock Ammonium Molybdate Solution
   a. By volume: In a 1 L volumetric flask dissolve 40.0 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in approximately 800 mL of water. Dilute to the mark and invert three times. Store in plastic and refrigerate.
   b. By weight: To a tared 1 L container, add 40.0 g ammoniumn molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot_4H_2O$] and 983 g water. Stir or shake until dissolved. Store in plastic and refrigerate.
6. Stock Antimony Potassium Tartrate Solution
   a. By volume: In a 1 L volumetric flask, dissolve 3.0 g of antimony potassium tartrate (potassium antimony) tartrate hemihydrate $K(SbO)C_2H_40_6\cdot\frac{1}{2}\ H_2O$) in approximately 800 mL of water. Dilute to the mark and invert three times. Store in a dark bottle and refrigerate.
   b. By weight: To a 1 L dark, tared container, add 3.0 g antimony potassium tartrate (potassi-

um antimonyl tartrate hemihydrate $K(SbO)C_2H_40_6 \cdot {}^1/_2\ H_2O$) and 995 g water. Stir or shake until dissolved. Refrigerate.

7. Molybdate Color Reagent
   a. By volume: To a 1 L volumetric flask, add 72.0 mL of the Stock Antimony Potassium Tartrate Solution (Reagent 6, above) and 213 mL of the Stock Ammonium Molybdate Solution (5, above). Dilute to the mark and invert three times. Degas with helium
   b. By weight: To a tared 1 L container, add 772 g water, 72.0 g of the Stock Antimony Potassium Tartrate Solution (Reagent 6) and 213 g of the Stock Ammonium Molybdate Solution (Reagent 5). Shake and degas with helium.
8. Ascorbic Acid Reducing Solution
   a. By volume: In a 1 L volumetric flask, dissolve 60 g ascorbic acid in about 700 mL of water. Dilute to the mark and invert three times. Prepare fresh weekly.
   b. By weight: To a tared 1 L container, add 60 g ascorbic acid and 975 g water. Stir or shake until dissolved. Prepare fresh weekly.
9. 0.8 M Acid Carrier Solution
   a. To a 1.1 L container, add 1.0 kg or 1.0 L of water, and 43.5 mL or 80.0 g concentrated sulfuric acid. CAUTION: Solution will get hot. Invert to mix.
10. Sodium Hydroxide - EDTA Rinse
    a. Dissolve 65 g of sodium hydroxide (NaOH) and 6 g of tetrasodium ethylendiamine tetraacetic acid (Na_4EDTA) in 1.0 L or 1.0 kg of water.

Standards Preparation Recipes

1. Stock Standard 1,000 mg P/L as PO_4^{3-}
   a. In a 1 L volumetric flask, dissolve 4.394 g of primary standard grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried for 2 hours at 110°C in about 800 mL of the extracting solution (Reagents 2-4). Dilute to the mark with the extracting solution and invert three times.
2. Working Standard Solution 80.0 mg P/L
   a. By volume: In a 1 L volumetric flask, dilute 80.0 mL of the Stock Standard (Standard 1, above) to the mark with the extracting solution (Reagents 2-4). Invert three times.
   b. By weight: To a tared 1 L container, add about 80 g of the Stock Standard (Standard 1). Divide the actual weight of the added solution by 0.08, and make up to this resulting total weight with the extracting solution (Reagents 2-4) using a wash bottle for the last 10 g or so. Shake.
3. Working Standards Set of Six Standards: 0.4-20 mg P/L in the extract A subset of these standards can be used depending on the application.
   a. By volume: To six 200 mL volumetric flasks, add respectively, 50.0, 30.0, 10.0, 5.00, 2.00, and 1.00 mL of the Working Stock Standard (Standard 2) This makes 20.0, 12.00, 4.00, 2.00, 0.800, and 0.400 mg P/L standards, respectively. Dilute each to the mark with the extracting solution described in 2-4 of Reagent Preparation, and invert three times.
   b. By weight: To six tared 200 mL containers, add respectively, about 50, 30, 10, 5, 2, and 1 g of the Working Stock Standard (Standard 2). For each in turn, measure the exact weight of solution added and divide this weight by 0.25, 0.15, 0.05, 0.025, 0.010, and 0.005, respectively. This will, in turn, give you the total weight of the diluted solution to be made. Make up each solution to this total weight using a wash bottle filled with the extracting solution described in Reagent Preparation 2-4. Shake before using. This makes 20.0, 12.00, 4.00, 2.00, 0.800, and 0.400 mg P/L standards, respectively.

   If samples often fall within a narrower range, more standards within this narrower range can be added and standards outside this narower range can be dropped.

Apparatus: Lachat QuikChem Automatic Flow Injection Ion Analyzer, which includes:

1. Automatic sampler
2. Proportioning pump
3. Injection module with a microloop
4. Colorimeter
   a. Flow cell: 10 mm, 80 uL
   b. Interference filter, 660 nm
5. Heating bath with temperature controller and a circulating cell: 4 in. coil, 0.81 mm i.d., double wrapped
6. Reaction module 12-115-01-1-A
7. QuikCalc II software or chart recorder

Injection Timing

- Pump speed: 35
- Cycle period: 40 s
- Load period: 10 s
- Inject period: 30 s
- Inject to start of peak period: 18 s
- Inject to end of peak period: 46 s

Gain

$$\text{Gain} = 900 \times 1$$

System Operation

1. Inspect all modules for proper connections.
2. Turn on power and all modules, except sampler. Allow heating bath to warm up to 60°C.
3. Place reagent feedlines into proper containers.
4. Pump system until a stable baseline is attained.
5. Set zero on colorimeter. If necessary, manually inject a high standard to set gain on colorimeter.
6. Program data system to initial parameters or those empirically determined.
7. Place calibration standards and blank in sample tray in descending order of concentration followed by unknowns and check standards.
8. At end of run, place the color reagent and ascorbic acid feedlines into the NaOH-EDTA solution (Reagent 8.). Pump this solution for approximately 5 minutes to remove precipitated reaction products. Then place these lines in water and pump for an additional 5 minutes. Then pump dry all lines.
9. Turn off pump, all modules, and release levers on pump tube cassettes.

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Chapter 7

Potassium and Other Basic Cations

D. Warncke and J. R. Brown

Potassium (K), calcium (Ca), and magnesium (Mg) availabilities in soil are generally estimated by measurement of the water soluble and exchangeable forms. The amounts of K, Ca, and Mg in the soil solution are quite small relative to the amounts in the exchangeable form. Hence, the quantities of these three cations extracted in most soil test procedures are simply referred to as exchangeable K, Ca, and Mg. Available K levels in soils of the region are important for determining the appropriate rates of supplemental K to apply. Calcium in most North Central Region soils is rarely limiting as a plant nutrient. The measurement of exchangeable Ca may be used with the measurements of the other exchangeable cations to calculate an estimate of the cation exchange capacity of soils and/or to calculate the percentage of base saturation as an index for the need to neutralize excess soil acidity. Magnesium deficiencies have occurred with sufficient frequency in the region to justify testing for Mg. A determination of available Mg will be helpful in deciding when to use dolomitic limestone.

The literature abounds with methodology used to measure exchangeable cations and cation exchange capacity. These methods were recently condensed (4, 6). The reader is referred to these references for details of the most accurate and precise procedures for determining plant available and exchangeable cations.

Soil testing or quick testing compromises some degree of accuracy for speed of determination. Therefore, standard or reference methods of soil testing have been developed to estimate nutrient availability. These estimates are then calibrated for recommendations based upon field trials with crop species of interest. A reference method, such as the one described herein for potassium, must be calibrated for the soil/crop/environment continuum for which it is to be used. These calibrations carried out in the various states and/or soil association areas provide the data for interpretation of the soil tests in terms of fertilizer needs. Thus, if different crop/environment combinations give different yield responses in different soil association areas, different recommendations may result for the same soil test level. K extractable with neutral 1 M NH_4OAc has been calibrated with crop responses and supplemental K needs for the varied soils of the North Central Region.

The cation exchange capacity (CEC) of soils is important in determining the supplemental K needs and the appropriate quantities of soil-applied herbicides to use. The precise determination of CEC is time consuming. Soil testing labs in the region have determined that estimation of CEC by summation of exchangeable K, Ca and Mg and neutralizable acidity is acceptable for most soils. In Michigan, Warncke et al. (7) found that CEC by summation is a good estimate of the actual CEC in acid, neutral and calcareous soils. Gelderman (2) reports that CEC measures by summation may be inflated in calcareous soils by dissolution of $CaCO_3$ in the neutral 1 M NH_4OAc. Sodium acetate is a better replacing solution to use in the determination of CEC in calcareous soils.

The Mehlich 3 extractant has been adapted by many laboratories as a near-universal extractant (Mehlich 1984). Workers in the North Central Region have been evaluating the Mehlich 3 as indicated in Chapter 6 for P. The results suggest that Mehlich 3 is a satisfactory extractant for K and for Ca and Mg on non-calcareous soils. These results show that either 1 M ammonium acetate or Mehlich 3 may be used to extract K. However, Mehlich 3 is not recommended as a substitute for 1 M ammonium acetate as an extractant for Ca and Mg from calcareous soils.

Estimate of Available Potassium

The following procedure is slightly modified from the "NCR-13 Exchangeable Potassium Procedure" as written by Carson in earlier editions of this publication (1).

Equipment

1. Standard NCR-13, 1 or 2 g scoop
2. Automatic or semi-automatic extracting solution dispenser (10 or 20 mL)
3. Extracting flasks (50 mL Erlenmeyer or conical flasks)
4. Funnels (or filter holding devices) and filter paper.

5. Receiving receptacle (20 to 30 mL beakers or test tubes)
6. Rotating or reciprocating shaker capable of 200 excursions per minute (epm)
7. Atomic absorption/emission spectrometer (set in the emission mode for K)

Note: Most high volume soil testing labs have racks of extracting flasks, funnels and receiving receptacles designed to handle multiple soil samples at one time.

Reagents

1. Extracting Solution (1 M NH_4OAc at pH 7.0)
   a. Place approximately 500 mL of distilled water into the mixing vessel. Add 57 mL of glacial acetic acid (99.5 percent) then add 69 mL of concentrated ammonium hydroxide (MIX IN THE FUME HOOD). Bring the volume to about 900 mL with distilled water. Adjust to pH 7.0 with 3 M NH_4OH or 3M acetic acid. After cooling to room temperature, bring the solution to a volume of 1 L and recheck the pH.
   b. Alternative: Reagent grade ammonium acetate may be used. Add 77.1 g of NH_4OAc to 900 mL of distilled water. After dissolution of the salt, adjust the pH to 7.0 as above. Dilute to a final volume of 1 L. (Check this solution for potassium contamination from the salt.)
2. Extracting Solution (Mehlich-3)
   0.2 N Ch_3COOH (acetic acid, glacial: 99.5 percent, fw 60.04, 17.4 N), 0.25 N NH_4NO_3 (ammonium nitrate: fw 80.05), 0.015 N NH_4F (ammonium fluoride: fw 37.4), 0.013 N HNO_3 (nitric acid:68 to 70 percent, fw 63.02, 15.5 N), 0.001 M EDTA [$(HOOCH_2)_2NCH_2NCCH_2COOH)_2$, ethylenediaminetetraacetic acid: fw 292.24].
   a. Add 8 L of distilled water to a 10 L carboy.
   b. Dissolve 200 g of ammonium nitrate in the distilled water.
   c. Add 40 mL NH_4F-EDTA stock solution and mix.
   d. Add 11.5 mL acetic acid.
   e. Add 8.2 mL of nitric acid.
   f. Add distilled water to bring volume to 10 L. Mix throroughly (provides enough extractant for 400 samples).
3. Standards
   a. Stock solution (1,000 ppm K)
      Dissolve 1.9073 g oven dry, reagent grade KCl in 1 M NH_4OAc at pH 7.0. Bring to a volume of 1,000 mL with the extracting solution and mix well.
   b. Prepare a 100 ppm standard by diluting 100 mL of the 1,000 ppm K stock solution to 1 L with extracting solution. Pipette 10, 20, 30, 40 and 50 mL of the 100 ppm K solution into 100 mL volumetric flasks and bring each to volume with extracting solution. These solutions will contain 10, 20, 30, 40 and 50 ppm K, respectively. The extracting solution serves as the 0 ppm standard.
4. Reference Soil
   One or more reference soil samples of medium to low levels of exchangeable K should be available to carry through each run of unknowns. These reference samples should be prepared in bulk by regular sample preparation methods and stored in sealed containers at cool temperatures (4 to 20°C).

Procedure

1. Scoop 2 g of prepared soil into an extraction flask. (See Chapter 2 for scooping techniques. Use the appropriate number of blanks and reference samples per laboratory quality assurance/quality control procedures.)
2. Add 20 mL of extracting solution to the extraction flask. (*Note:* The quantity of soil and extracting solution may be varied as long as the 1:10 ratio is maintained.)
3. Shake for 5 minutes on the shaker at 200 epm. Recheck speed weekly.
4. Filter the suspensions through Whatman No. 2 or equivalent filter paper. Refilter or repeat if the extract is cloudy.
5. Set up the atomic adsorption/emission spectrometer for K by emission. After warmup, determine the standard curve using the standards and obtain the concentrations of K in the soil extracts.
6. To convert K concentration (ppm) in the soil extract solution to ppm in a soil (mg K/kg), multiply by 10. To convert to pounds of K per acre, multiply by 20.

Estimates of Exchangeable Ca, Mg and Na

Some soil testing laboratories test soils for other exchangeable bases or use such determinations for estimation of the cation exchange capacity.

Equipment

The same as for potassium.

Reagents

1. Extracting Solution: 1 M NH_4OAc at pH 7.0. Mehlich 3 may be substituted for non-calcareous soils.

2. Standards

   Using a protocol similar to that for K, make up a 1,000 ppm stock solution of Ca ($CaCO_3$ dissolved in a minimum of HCl), Mg (Mg metal dissolved in HCl), and Na (NaCl). Commercially available stock solutions may be used.

   Make working standards for Ca of 0, 10, 20, 30, 40 and 50 ppm and Mg of 0, 1, 2, 3, 4 and 5 ppm using the extracting solution and sufficient lanthanum to give a final concentration of 1percent (wt./vol.). Concentrations of the Na working standards should be the same as for K; 0, 10, 20, 30, 40 and 50 ppm.

Procedure

Follow the procedure as outlined for K. The same extracts used for K may be used for Ca, Mg and Na. Dilution will be necessary. Make dilutions for Ca and Mg analysis with the extracting solution contaiing 1 percent lanthanum (wt./vol.). The final dilution for Ca and Mg analysis should contain the same lanthanum concentration as the working standards. Ca and Mg are determined by atomic adsorption and Na by emission. The results will be expressed in the same units as for K.

Cation Exchange Capacity

An estimate of the Cation Exchange Capacity (CEC) may be obtained by summing the meq exchangeable bases per 100 g (cmol kg^{-1}) and the meq exchangeable acidity per 100 g (cmol kg^{-1}).

Estimates of meq per 100 g (or cmol kg^{-1}) may be obtained as follows:

$$(\text{extract ppm K} \times 10) \div 390 = \text{K meq per 100 g (cmol kg}^{-1}\text{)}$$

$$(\text{extract ppm Ca} \times 10) \div 200 = \text{Ca meq per 100 g (cmol kg}^{-1}\text{)}$$

$$(\text{extract ppm Mg} \times 10) \div 120 = \text{Mg meq per 100 g (cmol kg}^{-1}\text{)}$$

$$(\text{extract ppm Na} \times 10) \div 230 = \text{Na meq per 100 g (cmol kg}^{-1}\text{)}$$

Exchangeable acidity may be estimated from the SMP buffer pH measurement:

$$\text{meq acidity per 100 g} = 12\,(7.0 - \text{SMP buffer pH})$$

This calculation is based upon the Ph.D. thesis by Shoemaker (5) which led to development of the SMP buffer (see Chapter 4).

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Chapter 8

Sulfate-Sulfur

S. M. Combs, J. L. Denning and K. D. Frank

Testing the soil for plant available sulfur (S) and response to fertilization occurs mainly in the northwestern and western areas of the North Central Region. These areas have few industrial centers that produce gaseous or solid waste byproducts of S. Minnesota, Nebraska and Wisconsin report areas that show consistent plant response to S mainly on sandy soils low in organic matter (5, 11, 21). Soil test summaries often identify numerous soil tests of surface samples in the "low" category (Eik, K. 1980. Unpublished summary of soil test results from Iowa State University Soil Testing Lab, 1974-1979; and Schulte, E. 1986. Unpublished soil test summaries, Wisconsin, 1982-1985). However, field experiments show small or no crop response from S fertilization on the fields many of these samples represent (34).

Several states in the North Central Region and two Canadian provinces offer the plant available S soil test to the public. This interest in S tests reflects an increase in client demand. However, there is a need to compile information, develop techniques for analysis, and correlate the test results with response data. Three additional states are using the test only for research. Recommending applications of S on the basis that the amount applied is equivalent to crop removal or as "insurance" neglects contributions of S from the atmosphere, applied manure, the subsoil, and, for irrigated fields, any S in irrigation water.

The Nature of Available Sulfur (S)

Most of the S in the surface soils (95 to 99 percent in Iowa soils) occurs in organic combinations (29, 35). Mineralization of organic S is an important source of plant available S. Plants can also absorb SO_2 directly from the atmosphere (10, 19, 24, 32). The sulfate ion is the usual S form utilized by plants.

Inorganic S occurs as the sulfate ion (SO_4^{-2}) in combination with cations in soil solution (well drained, arable soil) or precipitated as a salt in conjunction with the existing cations (arid soil) and adsorbed by 1:1 clays and oxides of iron and aluminum. The adsorption increases as soil pH decreases below a value of 6.5 (15). The concentration of inorganic S determines the nutritional status of the crop (22) since both the soluble and the adsorbed fractions are available. Soil test analysis usually measures the inorganic S or the inorganic and some organic S. The quantity of inorganic S present at any given time is small. It is continually undergoing changes due to: (1) mineralization and immobilization by microorganisms (2) leaching (3) additions from the atmosphere in gaseous form or with precipitation (1, 12, 14, 20, 30) and (4) additions from the application of manure. Lower horizons of the soil profile and irrigation water may contain available S. Measurements of inorganic S in surface soil at a given time do not always reflect all of the sources of readily or potentially available S. Other methods of predicting readily or potentially available S have serious shortcomings. Mineralization is slow and difficult to measure for prediction purposes. The atmospheric contribution fluctuates with the the season and may be impractical to monitor except on a regional basis. Since the movement, retention and absorption of available S by plants occur predominately in the sulfate form, it is the fraction usually measured.

North Central Region S Tests

Sporadic responses to S, mainly by alfalfa, are recorded in parts of North and South Dakota, Nebraska, Minnesota and Wisconsin. Elsewhere in the North Central Region, S response has been minimal. Atmospheric precipitation, manure and subsoil are contributing S sources which may not be measured in the soil test. A 2-year average of 20 pounds S per acre per year was measured in precipitation in nonresponsive areas of Wisconsin and only half that amount in responsive areas (1). A study of profile subsoil sulfate-S in six Wisconsin soils at eight sites gave amounts ranging from 11 kg/ha to 90 cm in a loamy sand to 179 kg/ha to 150 cm in a silt loam soil (33). The average profile S to 90 cm was 72 kg/ha. Sulfate-S through the profile correlated with organic matter in the 0 to 30 cm depth and was negatively correlated with pH. The sulfate-S concentration in medium and fine textured soils averaged from 3.3 to 7.4 kg/ha in the first foot, 5.9 to 13.1 kg/ha in the second foot and 8.9 to 18.5 kg/ha in the third foot increment based on data from 2,226 profiles submitted to the University of Wisconsin Soil and Plant Analysis

Lab-Madison for residual NO_3-N analysis in 1989-1991 (4). A previous manure application tended to slightly increase the average SO_4-S concentration in each foot increment whereas having grown a legume crop tended to result in less average SO_4-S in each foot increment. These results help explain why response to S fertilizer is sometimes not obtained when analysis of surface samples would predict a response.

Considering S sources, a sample testing program similar to that for Nitrate-N (testing subsoil samples) and/or plant analysis may be the best predictors of the status of plant available S. Wisconsin is currently using a model to determine the need for additional S that includes S in precipitation, S released from soil organic matter, S from applied manure and S in subsoil, in addition to the sulfate-S soil test (16). The plant available S is the sum of these inputs and is expressed as the S availability index (SAI).

Monocalcium Phosphate Extraction Procedure

Extensive reviews of S reactions in soils as they relate to availability and measurement are available (3, 7, 8, 11, 13, 22, 23, 34). Water soluble inorganic S is usually extracted with salt solutions such as calcium chloride ($CaCl_2$), lithium chloride (LiCl) or sodium chloride (NaCl) (34). Pure water tends to deflocculate soil and may dissolve some nonavailable organic S (27). Calcium phosphate [$Ca(H_2PO_4)_2$] or potassium phosphate (KH_2PO_4) are the extractants of choice when an appreciable amount of sorbed sulfate is present. The phosphate ion has a greater strength of adsorption than does sulfate, nitrate or chloride ions (23). The extraction process causes the sulfate, nitrate and chloride ions to go into solution. The Ca in calcium phosphate depresses the solubility of organic matter and produces a clearer filtrate than results from a potassium phosphate extraction (9). If the soil contains gypsum, test results may be low (27).

Equipment for Extraction

1. Balance with sensitivity of plus or minus 0.0l g or NCR-13, 10 g scoop
2. Erlenmeyer flasks, 50 mL or larger
3. Automatic pipette or dispenser capable of dispensing 25 mL
4. Funnels
5. Reciprocating shaker capable of approximately 200 excursions per minute (epm)
6. Whatman no. 42 filter paper or its equivalent

Reagents

1. Extracting solution to contain 500 ppm phosphorus: Dissolve 36.6 g of analytical grade $Ca(H_2PO_4)\cdot 2H_2O$ in deionized water and bring to 18 L.
2. Standard sulfate stock solution, 500 ppm S: Weigh out 2.717 g of analytical grade K_2SO_4 (oven dry at 100°C) and transfer to 1 L volumetric flask. Fill to volume with extracting solution.

Procedure

1. Pass air-dried soil through a 10-mesh sieve.
2. a. Mineral soils: Scoop 10 g of dried, crushed (10-mesh) soil into 50 mL Erlenmeyer flasks.
   b. Peats and mucks: Due to the high water holding capacity of organic soils, 50 mL of extracting solution must be used. (see Procedure, paragraph 3, below). Therefore, record the weight of organic soil delivered by the 10 g scoop. The extra dilution from the 50 mL of extracting solution will require doubling the S reading obtained from the standard curve. To allow for the low bulk density of organic soils, record the weight of soil delivered in the 10 g scoop. Then multiply the calculated "ppm in soil" (see Step 6 in the determination procedure) by 10 g per actual weight.
3. Add 25 mL of calcium phosphate solution (maintain 2.5:1 extractant to mineral soil ratio) to each flask and shake at 200 or more epm for 30 minutes.
4. Filter the extracts into sample tubes suitable for analysis. If necessary for the analysis, use charcoal to obtain a clear filtrate.

Instrumentation Methods Used to Determine Extracted S

Sulfate-S in a monocalcium phosphate extract is measured either with a nephelometer or by ion chromotography. The nephelometer anaysis is a measure of turbidity developed by adding $BaCl_2$ to the soil extract (24). The sulfate-S extracted from the soil is measured using an ion exchange resin in the ion chromotography (IC) procedure (31, 36). Extracted sulfur may be measured using inductively coupled plasma (ICP). The ICP method measures all S in the extract (both organic and inorganic forms) (31). The chief advantage of ICP is the low standard error of the method (25).

Turbidimetric Procedure

Most soil testing laboratories use turbidimetric methods for the determination of sulfate-S in the extract. This method involves development of a suspension of $BaSO_4$ precipitate in a slightly acid medium when excess $BaCl_2\cdot 2H_2O$ is added to a solution containing sulfate-S. Gum acacia, gelatin or glycerol is usually included to stabilize the suspension. The density of the suspension is read in a colorimeter or neph-

elometer. The turbidimetric methods require exact duplication of the conditions under which the suspension is formed. The speed and extent of formation, stability and optical qualities of the suspension are affected by the temperature of the solution, acidity, size of $BaCl_2 \cdot 2H_2O$ granules, quantity of $BaCl_2 \cdot 2H_2O$ added, time and rate of stirring, time standing of the suspension before measurement, and the presence of foreign salts or organic matter (12, 17, 23).

The presence of acid is required to prevent precipitation of the barium salts of such anions as carbonate and phosphate. Co-precipitation of barium hydroxide is also prevented in slightly acid medium. In the presence of mineral acids the solubility of barium sulfate increases with increased acidity. It has been found that the most suitable hydrochloric acid concentration for precipitation is 0.05 M (17). Most procedures used in soil testing laboratories prescribe approximately 0.5 M HCl in final solution, presumably because it will give coarser precipitates. However, one laboratory is using the method of Tabatabai (28), which involves the addition of barium chloride-gelatin reagent to a sample approximately 0.045 M in HCl. In most turbidimetric procedures a known quantity of sulfate-S is added to serve as the nucleus ("seed solution") for formation of barium sulfate crystals (18).

In solutions containing small amounts of sulfate, dissolved organic matter acts as a protective colloid and causes low results, whereas at high concentrations of sulfate, organic matter co-precipitates with barium sulfate and causes high results (12). The interference of organic matter can be eliminated by adding activated charcoal to the soil extract (2) or by digestion with hydrogen peroxide or with nitric and perchloric acids. The digestion methods may lead to slightly higher results (23).

Equipment

1. Scoops
   a. One to hold 0.15 g charcoal
   b. One to hold 0.3 g $BaCl_2 \cdot 2H_2O$ crystals
2. Magnetic stirrer and ½ inch stirring bars
3. Timer with a second hand
4. A nephelometer with a 420 nm filter

Reagents

1. "Seed solution": 20 ppm S in 5.8 M HCl. Dissolve 0.1087 g analytical grade K_2SO_4 in 500 mL of deionized H_2O and add 500 mL of concentrated hydrochloric acid. Drop in a teflon-coated magnet and place on a magnetic stirrer. Add 2 g of powdered gum acacia slowly while stirring to avoid formation of lumps. Keep refrigerated.
2. Barium chloride crystals for turbidimetry ($BaCl_2 \cdot 2H_2O$, 20 to 30 mesh).
3. Darco G-6-activated carbon. Add $Ca(H_2PO_4)_2$ extracting solution to thoroughly wet the carbon. Cap the container, shake and filter slowly with suction using a Buchner funnel. Wash three times with deionized water. Sample the last increment and test for sulfate-S by adding $BaCl_2$ and HCl. If leachate contains S, pour carbon into beaker and add deionized water. Repeat above procedure. When no S is detected, dry in oven and keep dry charcoal in a closed bottle.
4. Working standards:

Fig. 1. Working standards.

Volume of 500 ppm S Solution	Final Volume[1]	$SO_4^{-2}S$ in Solution	$SO_4^{-2}S$ in Soil
mL	mL	ppm	ppm
1.0	500	1.0	2.5
2.0	500	2.0	5.0
4.0	500	4.0	10.0
6.0	500	6.0	15.0
8.0	500	8.0	20.0
12.0	500	12.0	30.0

[1]Bring working standards to volume with the extracting solution.

Procedure (Filtrate Obtained by the Extraction Procedure)

1. Add 0.15 g charcoal to each sample and shake for an additional 3 minutes.
2. Filter through Whatman no. 42 filter paper or a similar grade of paper.
3. Shake 25 mL portions of a series of working standards with 0.15 g of carbon for 3 minutes and filter.
4. To 10 mL aliquot of soil extracts (Step 1) and standards (Step 3), add 1 mL of "seed solution." Swirl.
5. Place flask on a magnetic stirrer. Add 0.3 g $BaCl_2 \cdot 2H_2O$ crystals. Stir for 1 minute. At the end of 1 minute, read percentage transmittance or optical density on a spectrophotometer or colorimeter at 420 nm. Set 100 percent transmittance or zero optical density with distilled water or extracting solution to which no reagents have been added.
6. Plot the percentage transmittance reading against concentrations on semi-log graph paper; or if an instrument is used which provides readings directly proportional to concentrations (optical density), such as Klett-Summerson, plot readings against concentrations on linear graph paper. Read the ppm sulfate-S in the soil extracts from the standard curve and multiply by 2.5 to get ppm in the dry soil sample.

Liquid Ion Chromatography Procedure[1]

The Ion Chromatographic (IC) technique was first reported by Small, Stevens and Baumann in 1975 (26). The process was patented by Dow Chemicals and the technology was licensed to Dionex Corp. Dick and Tabatabai (6) found the analysis of soil extracts for sulfate-S were reproducible and results agreed with the Methylene Blue Method. They also concluded the detection limit for the sulfate-S method was approximately 0.2 ppm in the soil extract or 0.5 ppm sulfate-S in the soil.

Soil Sulfate-S Standards, Extraction Procedure and Analysis

Equipment

1. Dionex DX-100 Ion Chromatograph
2. Dionex Anion Micro Membrane Suppressor, model AMMS-1
3. AS3 Separator Column and AG3 Guard Column. An equivalent column may be used. The conditions and concentration of eluent and regenerant will differ with use of equivalent columns.

Reagents

1. Stock Standard: 500 mL of 250 ppm SO_4^{-2}-S Weigh 0.5539 g of sodium sulfate into a 500 mL volumetric flask. Add deionized, distilled (d/d) water until the volume of 500 mL is attained.

   500 mL of 250 ppm SO_4-S = 0.5539 g Na_2SO_4/500 mL

2. Weigh 2.02 g of calcium phosphate monobasic into a 1 L volumetric flask. Bring the solution to 1 L volume with d/d water. Stir until calcium phosphate dissolves.

   8.0 mM $Ca(H_2PO_4)_2H_2O$ = 2.02 g $Ca(H_2PO_4)_2 \cdot H_2O$/L, which yields 1 L of 500 ppm P

3. Regenerant: 25 mM H_2SO_4 = 28 mL concentrated H_2SO_4/20 L double d/d water
4. Eluent:
   a. 2.3 mM Na_2CO_3 = 24.38 g Na_2CO_3/L (for 100 x concentration)
   b. 2.9 mM $NaHCO_3$ = 24.36 g $NaHCO_3$/L (for 100 x concentration)
   c. Weigh the Na_2CO_3 and the $NaHCO_3$ into a 1 L volumetric flask. Add d/d water to bring to volume. This is the concentrate stored for future use.
   d. Dilution of 10 mL of concentrate (4 c.) to 1 L yields the working eluent.

Figure 2. Working standards.

Microliters of 250 ppm SO_4^{-2}-S	Microliters of 500 ppm PO_4^{-2}-P	SO_4^{-2}-S ppm in Solution	SO_4^{-2}-S pm in Soil
10	4,990	0.50	1.25
20	4,980	1.00	2.50
50	4,950	2.50	6.25
100	4,900	5.00	12.50
150	4,850	7.50	18.75
200	4,800	10.00	25.00
Quality Control Standards.			
50	4,950	2.50	-

Procedure

The following procedural steps are currently in used in the University of Nebraska Agronomy Lab for determining S by IC.

1. Weigh 10.0 g crushed soil into plastic 50 mL Erlenmeyer flask.
2. Add 25 mL $Ca(H_2PO_4)_2 \cdot H_2O$ solution using an automatic dispenser. (Note: dilution factor = 2.5)
3. Shake for 30 minutes on the reciprocating shaker at 200 epm
4. Wash 11 cm no. 2 Whatman filter papers. Fold the filters first, set in plastic funnels and rinse with 0.1 M HCl. Allow to run through. Rinse with d/d water. Allow to run through. (Note: acid washing the filter paper prevents contamination of the sample with S that may be in the filter paper.)
5. Filter samples through prewashed no. 2 filter papers into 30 mL tubes. Place tubes in test tube racks. Allow adequate space between tubes or risk cross contamination of samples when filter funnels touch. Allow approximately 45 minutes.
6. Wash the Erlenmeyer flask out with hot water and a brush. Rinse three times with d/d water.
7. Remove the funnels. Discard the filters and soil.
8. Wash the funnels and tubes with hot water and a brush. Soak in 0.1 M HCl acid bath for a minimum of 15 minutes. Rinse three times with d/d water.
9. Analyze samples using the Dionex DX-100 Ion Chromatograph or equivalent with an AS3 or equivalent column with adequate separation of phosphorus (PO_4^{-3}-P)and S(SO_4^{-2}-S).
10. Calculate results using computer software to integrate the area under the SO_4^{-2} peaks of the working standards. Calculate the relationship of the areas at given concentrations and solve for

[1] *Authors wish to acknowledge Diane McCallister's support in organizing the Ion Chromatographic Sulfur Procedure.*

the areas of the unknowns.

a. The average area of the blanks, if detectable, should be subtracted from the areas of the standard peaks before calculation.
b. Quality control results should be evaluated and a judgement of the precision and accuracy of the results determined. The results are either accepted or rejected based on statistics gathered from previous runs.
c. The concentration is multiplied by 2.5 dilution factor to obtain the result for the soil sample.

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Chapter 9

Micronutrients: Zinc, Iron, Manganese and Copper

D. A. Whitney

Deficiencies of zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) are known to occur in the North Central Region. Of the total crop acreage in the region, however, only a small percentage is affected by micronutrient deficiencies. Zn deficiency has been recognized throughout the region; Fe, Mn, and Cu deficiencies are limited primarily to specific areas.

Over the past three decades, micronutrient soil tests have improved markedly, in part because of improved instrumentation. However, many tests have been developed within a particular problem area and have not been extensively tested for their usefulness across wide areas. More work is needed on relating micronutrient soil tests across geographic and climatic conditions. Most of the state soil testing laboratories in the North Central Region offer tests for one or more of the micronutrients.

Cox and Kamprath (2) found in their extensive review of many extraction procedures, which have been tried for the various micronutrients, that test results need to be supplemented with other information, such as pH, texture and presence of free lime for reliable interpretation.

Micronutrient contamination of samples can occur quite easily if care is not taken in collection and preparation of samples. Soil probes, sample containers and soil grinding equipment should all be checked for potential contamination before being used (see Chapter 1). The effects of sampling and sample storage time on test results have not been fully researched, so before incorporating the tests described in this section into a soil test program, one should study such effects for the specific soil/climatic conditions of a given region.

Sample preparation should follow the guidelines in Chapter 1 of this publication. Additional care in laboratory techniques over those used for the macronutrient tests must be taken within the laboratory in preparing all reagents, cleaning glassware and selecting reagents to avoid contamination.

DTPA Extraction

The DTPA (diethylenetriaminepentaacetic acid) test, a nonequilibrium extraction developed by Lindsay and Norvell (6), has gained wide acceptance because of good correlation for Zn on calcareous soils and the potential for using the same extract for Fe, Mn and Cu. The DTPA test also shows considerable promise for use in monitoring cadmium, nickel and lead in soils that have received sludge applications. The DTPA test is presently being used as the soil test for Zn in Iowa, Kansas, Minnesota, Missouri, Nebraska, North Dakota and South Dakota. In addition, Kansas uses the DTPA test for Fe and Missouri uses the test for Cu, Fe, and Mn when requested.

Lindsay and Norvell (6) showed that the amount of nutrient extracted by the DTPA method is affected by extractant pH, soil-to-solution ratio, chelating agent concentration, shaking time and extraction temperature. Subsequent work by others has shown that extraction intensity and sample preparation also affect the results (4, 5, 10).

Control of extraction conditions is very important for comparable results among laboratories. Most laboratories are following the procedure as developed by Lindsay and Norvell (6), and deviations from this procedure must be carefully monitored to adjust the interpretation levels.

Equipment

1. Atomic absorption, inductively coupled atomic emission (ICP) or direct current plasma atomic emission spectrometers
2. Reciprocating or rotating shaker, capable of at least 180 excursions per minute (epm)
3. Burets or automatic pipettes, 50 mL Erlenmeyer flasks and filter funnels for extraction
4. Standard NCR-13, 10 g soil scoop, (0.85 cc/g)
5. Soil pulverizer with 10-mesh, stainless steel sieve checked for micronutrient contamination

Reagents

1. Extracting Solution: 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA) adjusted to pH 7.3. For 18 L of solution, dissolve 35.4 g of DTPA in 268.6 g of TEA and about 200 mL of demineralized water and stir until dissolved. DTPA is slowly soluble in water but dissolves rapidly in the TEA–H_2O. Add 26.5 g of $CaCl_2 \cdot 2H_2O$ to about 10 L of micronutrient-free, demineralized water; then add the DTPA/TEA

mixture and bring to about 17 L with demineralized water. Adjust the pH to 7.3 using concentrated HCl and bring to the 18 L mark. Approximately 70 to 75 mL of HCl will be necessary.
2. Stock Standards: 1,000 ppm Zn, 1,000 ppm Fe, 1,000 ppm Mn, 1,000 ppm Cu.
3. Working Standards: Standards should be made up in the DTPA extracting solution. Concentration range for standards should cover Zn, 0 to 5 ppm; Fe, 0 to 10 ppm; Mn, 0 to 10 ppm; and Cu, 0 to 2 ppm.

Procedure

1. Air dry soil samples and crush to pass a 10-mesh stainless steel sieve. (See Chapter 1 on sample preparation.)
2. Scoop 10 g of soil without pressing the soil against the side of the container. Firmly tap the handle of the scoop three times with an 8 inch spatula and level off the soil by passing the spatula over the scoop, holding the spatula at a 90° angle. (See Chapter 2 on the standard soil scoop.)
3. Add the measured volume of soil to a 50 mL Erlenmeyer flask, tapping the scoop on the funnel or flask to remove all of the soil from the scoop.
4. Add 20 mL of extracting solution (1:2 soil-to-solution ratio) to each flask and shake at 180 or more epm for 2 hours.
5. Filter through Whatman No. 42 filter paper or similar grade paper. Refilter if extract is cloudy. Those samples high in extractable Fe will have a yellow color.
6. Carry a blank through the entire procedure with each run.
7. Read samples on the AA, ICP or DCP spectrometer unit using appropriate standards and instrument settings.
8. Report as ppm Zn, Fe, Mn or Cu in the soil:

$$\text{ppm in soil} = \text{ppm in extract} \times 2.$$

0.1 M HCl Extraction for Zinc

This procedure is based on the assumption that all or a portion of the soil Zn that will become available for plant uptake during a growing season is acid soluble. The quantity of acid-soluble Zn extracted serves as an index of Zn availability (12). The method is primarily for determining acid-extractable Zn in neutral and acid soils. It is not suitable for alkaline soils with excess calcium carbonate because of the neutralization of the acid in the extracting solution, unless some adjustment in the interpretation of results is made for the excess lime. Nelson, Boawn, and Viets (8) used "titratable alkalinity" as a correction. They also recommended repeated extractions on highly calcareous soils until the pH of the suspension is below 2.0. On calcareous soils, the DTPA test is recommended over the 0.1 M HCl procedure.

The 0.1 M HCl test has been used quite successfully throughout the North Central Region and is presently used in Michigan, Ohio and Wisconsin. The 0.1 M HCl test was developed with little coordination of procedures among states. Thus, procedural differences exist among laboratories. Sorensen et al. (11) showed that soil properties, soil-to-solution ratio and length of extraction all affected the amount of Zn extracted. Variations in the method used must be taken into account when comparing Zn extracted and the interpretation of the results. The method presented here is the procedure developed at the University of Missouri (1).

Equipment

1. Atomic absorption spectrophotometer
2. Reciprocating or rotary shaker capable of at least 180 epm
3. Standard NCR-13, 5 g scoop (85 cc/g)
4. Burets or automatic pipettes, 50 mL Erlenmeyer flasks and filter funnels for extraction
5. Soil pulverizer and 10-mesh stainless steel sieve checked for Zn contamination

Reagents

1. Zn-free, demineralized water
2. Redistilled 6 M HCl (reagent-grade concentrated HCl could be used if Zn-free)
3. Zn stock standard 1,000 ppm Zn
4. Working Zn Standards: Prepare working standards by diluting aliquot of the stock (1,000 ppm Zn) with the extracting solution to cover the normal range in the soil. Standards of 0, 0.1, 0.5, 1.0 and 2.0 ppm will cover the critical range.
5. Extracting Solution: Add 300 mL of the redistilled 6 M HCl to about 10 L of the Zn-free, demineralized water and mix. Bring to a final volume of 18 L with demineralized water and mix well.

Procedure

1. Air dry soil samples and crush to pass a 10-mesh sieve (see Chapter 1 on sample preparation).
2. Scoop 5 g of soil without pressing the soil against the side of the container. Firmly tap the handle of the scoop three times with an 8 inch spatula and level off the soil by passing the spatula over the scoop, holding the spatula at a 90° angle (see Chapter 2 on the standard soil scoop).

3. Add the measured volume of soil to a 50 mL Erlenmeyer flask, tapping the scoop on the transfer funnel or flask to remove all of the soil from the scoop.
4. Add 20 mL of the extracting solution to each flask, place on the shaker and shake at 180 epm or more for 30 minutes.
5. Filter through washed Whatman No. 2 filter paper (or equivalent) into 30 mL polypropylene beakers.
6. Carry a blank through the entire procedure with each run.
7. Determine Zn in the extracts with the AA unit using appropriate instrument settings and Zn standards.
8. Report results as ppm Zn in the soil:

$$\text{ppm in soil} = \text{ppm in extract} \times 4.$$

0.033 M H_3PO_4 Extraction for Manganese

Three states in the North Central Region: Michigan, Ohio, and Wisconsin, are testing for Mn. Wisconsin is using 0.033 M H_3PO_4 (3) as their extracting solution. Ohio and Michigan are using 0.1 M HCl. The method presented here is the procedure developed in the Ohio Agricultural Research and Development Center Research-Extension Analytical Laboratory, Ohio State University, Wooster.

Equipment

1. Atomic absorption spectrophotometer
2. Reciprocating or rotary shaker, capable of at least 180 epm
3. Standard NCR-13, 1 g stainless steel scoop (.85 cc/g)
4. Burets or automatic pipettes, 50 mL Erlenmeyer flasks and filter funnels for extraction
5. Soil pulverizer and 10-mesh stainless steel sieve checked for Mn contamination

Reagents

1. Manganese-free, demineralized water
2. Concentrated H_3PO_4 (85.5 percent)
3. Mn stock standard of 1,000 ppm Mn
4. Extraction Solution: Dilute 2.25 mL of concentrated H_3PO_4 to a volume of 1.0 L with the manganese-free, demineralized water.
5. Mn Working Standards: From the 1,000 ppm Mn standard, prepare working standards of 0, 0.5, 1.0, 2.0 and 4.0 ppm Mn in the extracting solution. Additional standards may be necessary for samples low in extractable Mn.

Procedure

1. Air dry soil samples and crush to pass a 10-mesh sieve. (See Chapter 1 on sample preparation.)
2. Scoop 1 g of soil without pressing the soil against the side of the container. Firmly tap the scoop handle three times with an 8 inch spatula and level off the soil by passing the spatula over the scoop, holding the spatula at a 90° angle. (See Chapter 2.)
3. Add the measured volume of soil to a 50 mL Erlenmeyer flask, tapping the scoop on the transfer funnel or flask to remove all of the soil from the scoop.
4. Add 10 mL of the extracting solution to each flask, place on the shaker and shake for 10 minutes at 180 epm.
5. Filter through Whatman No. 1 filter paper or similar grade filter paper.
6. Carry a blank through the entire procedure with each run.
7. Determine Mn in the extracts with the AA unit using appropriate instrument settings and Mn standards. For precise Mn readings on samples testing less than 1 ppm Mn, the AA should be recalibrated on lower standards than shown for the working standards. Randall (9) has reported calcium (Ca) interference in determination of Mn by atomic absorption using an H_2 and air flame. The addition of a final concentration of 150 ppm Ca and 0.24 M HCl to the soil extracts and standards effectively masked the interference. Watson (Ohio State, personal communication) has reported no Ca interference from up to 300 ppm Ca in determination of Mn by atomic absorption using an acetylene and air flame or by inductive coupled plasma (ICP) emission spectroscopy. Each laboratory should check for interferences within their laboratory technique before using the procedure.
8. Report results as ppm Mn in the soil:

$$\text{ppm Mn in soil} = \text{ppm in extract} \times 10.$$

1 M HCl Extraction for Copper in Organic Soils

The 1 M HCI extraction for Cu currently being used in Michigan is for organic soils (7) and is not recommended for use on mineral soils. The procedure presented here is the procedure used at the Michigan State University, Soil and Plant Nutrient Laboratory.

Equipment

1. Atomic absorption spectrophotometer
2. Balance with 0.01 g readability
3. 50 mL Erlenmeyer flasks
4. Reciprocating or rotating shaker capable of at least 180 excursions per minute (epm)
5. Burets and beakers

Reagents

1. Extracting Solution: For 1 M HCl, dilute 86.2 mL of concentrated HCl to a volume of 1.0 L with distilled, deionized water.
2. Working Copper Standards: From a 1,000 ppm standard solution, prepare working standards of 0, 1.0, 2.0, 3.0, 4.0, and 5.0 ppm. Make to volume with the extracting solution.

Procedure

1. Air dry soil samples and crush to pass a 10-mesh sieve. (See Chapter 1 on sample preparation.)
2. Weigh out 2.0 g of soil and transfer soil to a 50 mL Erlenmeyer flask.
3. Add 20 mL of extracting solution and shake for 1 hour on a rotating or reciprocating shaker at 180 epm.
4. Filter extracts through Whatman No.2 or similar grade filter paper.
5. Carry a blank through the entire procedure with each run.
6. Determine Cu in the extracts with the AA unit using appropriate instrument settings and Cu standards.
7. Report results as ppm Cu in the soil:

$$\text{ppm in soil} = \text{ppm in extract} \times 10.$$

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Chapter 10

Boron

M. E. Watson

Boron (B) is an essential nutrient to living plants (16). It has been characterized as a micronutrient because of the small quantity required to support optimum plant growth. B concentrations usually range from 5 to 80 µg per gram of dry plant tissue across plant species. The interval between deficiency and toxicity is narrow for most plant species. Some of the plants most sensitive to B deficiency are celery, cauliflower, cabbage, brussels sprouts, alfalfa, red clover, white clover, apple trees and pear trees.

Plants obtain B from soluble B forms present in the soil. According to Lindsay (8), H_3BO_3 is the predominant B species in soil solution. Only at pH above 9.2 is the H_2BO_3 species expected to become predominant in soils.

Ideally, the test for soil B should measure the form of B that is most important to plants. A successful soil B test must, however, be able to measure the amount of B that is immediately available, as well as that potentially available to plant roots. The better the correlation between plant absorption of B and the measure of B in the soil, the more useful the test. The B test must be sensitive enough to allow accurate measurements of concentrations (either high or low) which are important to the plant. In addition, the test must be free from major interferences caused by other chemical constituents in the soil extract.

Berger and Truog (2) divided soil B into three categories: total B, acid-soluble B (H_2SO_4), and water-soluble B. They concluded that water-soluble B correlated best with the incidence of black spot in garden beets. Work by Berger and Truog (3), as well as Starck, Truog and Attoe (17), showed that all the B added to a mineral soil could be recovered with a boiling hot water extraction. In 1966, Miljkovic, Matthews and Miller (10) related the uptake of B by sunflowers from eight different soils to the concentration of soil B as determined by a hot water extraction. Next to water-soluble B, clay content had the most influence on B uptake. These two variables in a curvilinear regression accounted for 79 percent of the variability in uptake from cultivated surface soil samples.

Hot-water soluble B can be affected by many soil factors. Clays and oxides of iron and aluminum can fix B (5, 15). Also, the soil organic matter content has been shown to be important, particularly for soils that are not highly cultivated (13, 9). The absorption of hot-water soluble B by lucerne (alfalfa) was shown to be greater from coarse texture soils than from fine texture soils (20). A survey by Ouellette and Lachance (12) revealed that when lucerne was the dominant plant species, B deficiency occurred more frequently on coarse texture soils than on fine texture soils. They concluded that about 0.8 lb of B per acre was necessary for normal growth of lucerne on fine texture soils compared to 0.5 lb of B per acre on coarse texture soils. Variations in soil moisture and cultivation may also affect the amount of hot-water soluble B present. Work by Winsor (21) showed that the concentration of hot-water soluble B increased as the soil moisture level increased. The increase occurred both in virgin and cultivated soils, but was much more in virgin soils. The soil texture in this research was fine sand.

Methods that have commonly been used in the past to measure B have been those using quinalizarin and curcumin dyes (2,11). Azomethine-H has been used to complex the B in plant tissue and soil extracts (1, 6, 14, 22, 23). Kowalenko and Luvkulich (7) used a modified curcumin procedure and an acetate buffer extraction (pH 4.8) to measure available soil B.

It must be emphasized that it is extremely important to use the instrument of detection that is recommended by the method. For example, if the method indicates that an inductively coupled plasma spectrograph (ICP) be used, then a colorimeter should not be substituted. Arbitrarily using another type of instrument can lead to serious errors in the analysis.

The Curcumin Method has generally replaced the Quinalizarin Method because concentrated sulfuric acid is not required for curcumin. Disadvantages of the Curcumin Method are that water must be evaporated from the sample, and a great deal of handling is thus required. An advantage of the Curcumin Method over the Azomethine-H Method is that of greater sensitivity. Methods that use ICP have greatly simplified the measurement of B.

Hot-Water Extractable Boron

Equipment

1. Standard NCR-13, 10 g soil scoop
2. Fiber digestion beakers (600 mL)
3. Fiber digestion apparatus
4. Centrifuge
5. Plastic centrifuge tubes
6. Plasticware and/or low boron glassware

Reagents

1. Extracting Solution: Dissolve 1 g of $CaCl_2 \cdot 2H_2O$ in deionized water. Make to 1 L volume with high quality, deionized water. Calcium chloride is added to promote soil flocculation.

Procedure

1. Scoop 10 g of soil into a 600 mL fiber digestion beaker. Add 20 mL of extracting solution, attach beaker to the condenser of a fiber digestion apparatus, and boil for 5 minutes. Allow solution to cool slightly before removal, but keep warm.
2. Remove from apparatus and immediately transfer the suspension to a plastic centrifuge tube. Centrifuge for 15 minutes at 2,700 g. Decant an aliquot from the supernatant extract for analysis.

Measurement of Boron Concentration in Extract

Curcumin Method

Equipment

1. Spectrophotometer or colorimeter capable of measuring absorbance at 545 nm wavelength
2. Plastic beakers
3. Waterbath

Reagents

1. Stock Standard (1,000 ppm B): Dissolve 5.716 g of H_3BO_3 in about 900 mL of deionized water and dilute to 1 L. Store in polyethylene bottle.
2. Working Standard (5 ppm B): Dilute 5.0 mL of 1,000 ppm B solution to 1,000 mL of deionized water.
3. Ethyl Alcohol: Use absolute ethyl alcohol to avoid moisture problems, which hinder proper color development.
4. Curcumin-oxalic Acid Solution: Dissolve 0.04 g of curcumin and 5.0 g of oxalic acid in 100 mL of absolute alcohol. Keep in a cool, dark place. Use reagent within 2 days; 250 mL of reagent will color 55 samples plus 5 standards.

Procedure

1. Pipet a 2 mL aliquot of extract into a plastic beaker. Add 4 mL of curcumin-oxalic acid solution and mix thoroughly by rotating the beaker.
2. Evaporate on a waterbath at 55 plus or minus 3°C until the last sample is dry and then continue to heat the residue for at least 15 minutes to ensure dryness.
3. Cool and add 25 mL of absolute alcohol. Filter into a clean vial or centrifuge. Read samples in colorimeter at 545 nm.
4. Prepare a standard curve by measuring exactly 20 mL of the deionized water into each of five plastic beakers. Add to each beaker exactly the volume of 5.0 ppm B standard as indicated in Table 1. Take a 2 mL aliquot of each solution and follow steps 1, 2 and 3 in the same manner as for the samples.

Table 1. Boron working standards for Curcumin Method·

Beaker	Deionized Water	Volume of 5 ppm B Standard	Boron in Solution	Boron in Soil
	mL	mL	ppm	mg/kg
1	20	0	0	0
2	20	0.5	0.12	0.24
3	20	1.0	0.24	0.475
4	20	2.0	0.455	0.91
5	20	3.0	0.65	1.30

Comments

To avoid B contamination, it is best to use plasticware where possible. Nitrate at quantities in excess of 20 µg per aliquot can interfere. Evaporation and gentle ignition in the presence of $Ca(OH)_2$ will eliminate nitrate. Heating acid solutions containing B to temperatures above 55°C may result in loss of B if $Ca(OH)_2$ has not been added. To prevent loss of B from acid solutions, add sufficient $Ca(OH)_2$ to make the solution alkaline.

Iron, molybdenum, titanium and zirconium interfere only in unusually high amounts (more than 300 ppm in B solution to be analyzed) (19).

Azomethine-H Method

Equipment

1. Spectrophotometer or colorimeter capable of measuring absorbance at 420 nm wavelength
2. Plasticware
3. Whatman No. 42 filter paper or a similar grade of paper

Reagents

1. Buffer-masking Solution: Dissolve 250 g of ammonium acetate and 15 g of ethylenedinitrilo-tetraacetic acid disodium salt (i.e., disodium ethylenediamine tetraacetate, EDTA disodium salt) in 400 mL of high-quality, deionized water and slowly add 125 mL of glacial acetic acid.
2. Azomethine-H Solution: Dissolve 0.45 g of Azomethine-H in 100 mL of 1 percent L-ascorbic acid solution. Prepare fresh reagent each week and store in the refrigerator.
3. Boron Stock Solution (1,000 ppm B): Weigh 5.716 g boric acid (H_3BO_3) into a 1 L volumetric flask and dilute to volume with deionized water.
4. Boron Stock Solution (20 ppm B): Pipet 20 mL of 1,000 ppm B solution into 1,000 mL volumetric flask and dilute to volume with deionized water.
5. Working Standards: Pipet the appropriate volumes of 20 ppm B into 100 mL volumetric flasks and dilute to volume with deionized water. (See Table 2.)

Table 2. Boron working standards for Azomethine-H Method.

Beaker	Volume of 20 ppm Boron Standard	Boron Final Volume	Boron in Solution	Boron in Soil
	mL	mL	ppm	mg/kg
1	0	100	0	0
2	1	100	0.2	0.4
3	2	100	0.4	0.8
4	4	100	0.8	1.6
5	5	100	1.6	3.2

Procedure

1. If necessary, filter supernatant solution through Whatman No. 42 filter paper (or similar grade paper) fitted in plastic funnels. Inspect filtrate for clarity and refilter if necessary. If filtrate is strongly yellow, refilter with one-half teaspoon of activated charcoal in the filter paper cone.
2. Pipet a 1 mL aliquot of soil extract into a plastic tube or small beaker, followed by 2 mL of the buffer-masking solution. Thoroughly mix by swirling.
3. Add 2 mL of Azomethine-H reagent and mix the contents thoroughly.
4. Allow mixture to stand 30 minutes, then measure light transmission at 420 nm wavelength.
5. Prepare a standard curve by adding 1 mL of each of the B working standards (Table 2) to a plastic tube or beaker and follow steps 2 through 4 as applied to soil extracts. Plot percentage transmittancy versus B concentration in lb/acre.

Comments

If it is necessary to use charcoal, it should be washed several times with dilute HCl to remove possible B contamination. It is important that the solutions be mixed thoroughly.

Inductively Coupled Plasma Optical Emission Spectrophotometric Method

The Spectrophotometric Method (ICP) is highly correlated with the Curcumin Method (r = 0.985) and the Azomethine-H Method (r = 0.990) for the measurement of B extracted from many soils (4, 18). However, if the hot-water extracting solution were to remove organic compounds that contain bound B, then it is likely that the ICP method would result in a higher B concentration value than would other methods which measure only the free B in solution. The high temperature plasma of the ICP would cause the release of the B from the organic compound. Based on the correlation with other methods, this does not appear to be a problem.

Equipment

1. Inductively Coupled Plasma Optical Emission Spectrograph
2. Whatman No. 2 filter paper or similar grade paper
3. 10 mL plastic tubes

Reagents

1. Stock Standard (1,000 ppm B): Dissolve 5.716 g of H_3BO_3 in about 900 mL of deionized water and dilute to 1 L. Store in a polyethylene bottle.
2. Working Standard (5 ppm B): Dilute 5 mL of 1,000 ppm B stock solution to 1,000 mL with deionized water.

Procedure

1. If necessary, filter the centrifuged extracts through Whatman No. 2 filter paper or similar grade paper into small plastic tubes. Aspirate the supernatant into the standardized ICP.
2. Prepare B standards by accurately measuring exactly 20 mL of deionized water into each of five plastic beakers. Add to each beaker exactly the volume of 5 ppm B standard as indicated in Table 3.
3. Use the prepared standards to standardize the ICP across the full range of B standards.
4. Carry a blank (a beaker containing only deionized water) through the entire procedure to esti-

mate any B contamination that may be present.
5. Use a 40 second preburn setting and a 10 second integration time. Three, 10 second integrations should be done.

Table 3. Boron working standards for ICP Method.

Beaker	Deionized Water	Volume of 5 ppm Boron Standard	Boron in Solution	Boron in Soil
	mL	mL	ppm	mg/kg
1	20	0	0	0
2	20	0.5	0.12	0.24
3	20	1.0	0.24	0.475
4	20	2.0	0.455	0.91
5	20	3.0	0.65	1.30

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Chapter 11

Chlorides

R. H. Gelderman, J. L. Denning and R. J. Goos

Historically, soil chloride (Cl^-) analysis has been conducted primarily for the purpose of salinity characterization and irrigation management. However, recent research in the northwestern United States and in the northern Great Plains has indicated positive cereal responses to Cl^- additions (1, 2, 3, 4). Studies in South Dakota have indicated that soil Cl^- level is a factor influencing the probability of obtaining a yield response to Cl^- (5). The procedures that will be discussed here are intended for determining Cl^- fertilizer needs rather than for salinity evaluation. Therefore, detection of relatively low Cl^- concentrations is emphasized.

Chloride is similar to nitrate in solubility and mobility in the soil. A 2 foot sampling depth was found to be superior to shallower or deeper depths for predicting wheat plant Cl^- concentrations in eastern South Dakota (5).

Chloride is a ubiquitous ion, and precautions must be taken to avoid contamination during sampling and in the laboratory. Many common laboratory reagents and cleansers contain Cl^-. Other possible sources of contamination include dust, perspiration, filter paper, glassware, water and paper bags (6). Plastic gloves should be worn when handling filter paper for Cl^- determination.

Standard soil sample preparation procedures, as discussed in Chapter 1, appear to be adequate for Cl^- determination. Considerable flexibility exists in extraction techniques. Extractants that have been used include H_2O (5), 0.1 M $NaNO_3$ (7), 0.5 M K_2SO_4 (8) and 0.01 M $Ca(NO_3)_2$ (9). Theoretically, these should give similar results; however, the method of determination used may make some extractants more convenient than others. Time required for extraction appears to be similar to nitrate extraction. Gaines et al. (7) showed that a 5 minute extraction on Georgia soils was adequate. Other investigators have adopted longer extraction periods of 15 (5), 30 (8), or 60 (9) minutes. Minimum extraction times should be determined through recovery studies on the soils to be analyzed. Comparison of soil-to-solution g to mL ratios of 1:2 or 1:2.5 showed much better precision levels than ratios of 1:4 or 1:5 using the Mercury Thiocyanate Method of Cl^- determination (15).

Several methods have been developed to determine Cl^- in soil extracts. Many of these are not suited for routine soil testing and will not be discussed here. The procedures presented are those that have been successfully used in soil testing laboratories in the North Central Region.

A comparison of the Mercury Thiocyanate and Potentiometric Known Addition Methods on a silt loam soil with a mean Cl^- concentration of 12 ppm found coeffecients of variance (CV's) of 9 and 24 percent, respectively (15). Precision values for most soil chloride methods are generally poor for samples with Cl^- levels of less than 10 ppm. Typical CV's are 15 to 25 percent for such samples (16). Duplicate or triplicate analysis should be performed for these samples.

Mercury (II) Thiocyanate Method

The Mercury (II) Thiocyanate Method is a modification of the procedure of Adriano and Doner (10) for Cl^- determination and uses an extraction procedure similar to that suggested by Bolton (9). In this colorimetric method, Cl^- displaces thiocyanate which, in the presence of ferric iron, forms a highly colored ferric thiocyanate complex:

$$2Cl^- + Hg(SCN)_2 + 2\ Fe^{3+} \longrightarrow HgCl_2 + 2\ Fe(SCN)^{2+}$$

The resulting solution's color is stable and proportional to the original chloride ion concentration.

The procedure is very sensitive and has a detection limit of approximately 1 $\mu g Cl^- g^{-1}$ soil. Nitrate, sulfide, cyanide, thiocyanate, bromide and iodide can cause interferences, but are usually not present in sufficient amounts to be a problem. Similar procedures have been modified for use with auto-analyzers.

Equipment

1. Standard NCR-13, 10 g scoop
2. Spectrophotometer
3. Shaker
4. 50 mL Erlenmeyer flasks, filter funnels or tubes

Reagents

1. Extracting Solution (0.01M $Ca(NO_3)_2 \cdot 4H_2O$): Weigh 4.72 g into a 2 L volumetric flask. Bring to volume with distilled water.

2. Saturated Mercury (II) Thiocyanate [$Hg(SCN)_2$] Solution, 0.075 percent: Add approximately 0.75 g $Hg(SCN)_2$ to 1 L of distilled water and stir overnight. Filter through Whatman No. 42 paper. It is important that this solution be saturated because it may then be stored for long periods of time.
3. Ferric Nitrate Solution: Dissolve 20.2 g $Fe(NO_3)_3 \cdot 9H_2O$ (Ferric (III) nitrate nonahydrate) in approximately 500 mL of distilled water and add concentrated nitric acid (HNO_3) until the solution is almost colorless (20 to 30 mL). Make up to 1 L with distilled water. Excess HNO_3 is unimportant as long as there is enough to prevent darkening of stored solution.
4. Charcoal washed in 0.01M $Ca(NO_3)_2$ and dried.
5. Chloride Standard Stock Solution (1,000 ppm Cl^-): Dissolve 0.2103 g reagent-grade KCl in approximately 50 mL of extracting solution. Bring up to 100 mL.
6. Chloride Standard Intermediate Solution (100 ppm): Dilute 10 mL of stock solution to 100 mL with extracting solution.
7. Chloride Standard Working Solutions: Dilute 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 mL of 100 ppm standard solution to 100 mL with extracting solution. This is equivalent to 0.5, 1.0, 2.0, 4.0, 5.0, and 10.0 ppm Cl^-.

Procedure

1. Scoop 10 g of crushed soil into a 50 mL Erlenmeyer flask. Do duplicate or triplicate analyses. Include a blank.
2. Add approximately 25 mg washed charcoal (dried).
3. Add 25 mL extracting solution.
4. Shake for 15 minutes at 180 or more excursions per minute (epm) and filter immediately following shaking using Whatman No. 42 filter paper or equivalent.
5. Transfer a 10 mL aliquot to a 50 mL beaker.
6. Add 4 mL each of the thiocyanate and the ferric nitrate solutions. Swirl to mix.
7. Allow 10 minutes for color development and read at 460 nm. Set 100 percent transmittancy with extracting solution.
8. Prepare a standard curve by pipetting a 10 mL aliquot of each of the working standards and proceeding as with the soil extracts. Plot transmittance or absorbance against concentration of the working standards.
9. Determine chloride concentration in the extract from the meter reading and standard curve. Subtract the chloride in the blank and convert to ppm in soil by multiplying by a dilution factor of 2.5.

Potentiometric Known Addition Method

Direct reading of soil extracts with the solid state Cl^- electrode has not been reliable across diverse soils and may give high readings (11). The electrode has worked well when used as an endpoint indicator in titrations. A more convenient alternative to potentiometric titrations is the Potentiometric Known Addition Method outlined here. It is particularly well-suited for situations where occasional analysis for Cl^- concentration is needed since no calibration is necessary.

The basic approach of the method was reported by Bruton (12) for Cl^- and fluoride determination in phosphates, and involves measuring the electrode potential before and after addition of a known quantity of Cl^- to a sample. The change in potential is then related to sample concentration by assuming a Nernst-type relationship and a theoretical electrode response of 59.1 mV per 10-fold change in concentration. This electrode response should be verified by measuring the potential after successive additions of the standard.

Equipment

1. Standard NCR-13, 10 g scoop
2. Shaker
3. Solid state Cl^- electrode and double junction reference electrode
4. pH/ion meter or pH millivolt meter
5. Magnetic stirrer

Reagents

1. Extracting Solution (0.5 M K_2SO_4): Weigh 87.0 g of K_2SO_4 into a 1 L volumetric flask. Bring to volume with distilled water.
2. Chloride Standard Stock Solution (1,000 ppm Cl^-): Dissolve 0.2103 g reagent-grade KCl in approximately 50 mL of extracting solution. Bring up to 100 mL volume with extracting solution.
3. Chloride Standard Working Solution, 50 ppm Cl^-: Dilute 5 mL of stock solution to 100 mL with extracting solution.

Procedure

1. Scoop 10 g of crushed soil into a 50 mL Erlenmeyer flask. Do duplicate or triplicate analyses. Include a blank sample.
2. Add 30 mL of extracting solution.
3. Shake for 15 minutes at 180 or more epm. Samples can be either filtered (No. 42 Whatman or equivalent), centrifuged, or left to settle to produce clear solutions.
4. Pipette 20 mL of the solution into a 50 mL beaker.

5. Place beaker on a stirrer, add magnet and mix.
6. Immerse Cl^- electrode into the beaker and record mv reading once the meter has stabilized.
7. Add 2 mL of 50 ppm Cl^- solution and record mv reading when meter has stabilized.
8. The difference between the first and second readings is ΔE.
9. Sample concentration can be determined by either of the following approaches:
   a. Obtain a Q value which corresponds to the ΔE value from a known addition table that is usually supplied with the electrode. Multiply the Q value by the concentration of the standard (50 ppm) and subtract the blank concentration to determine the sample concentration.
   b. Calculate the concentration directly as follows:

$$C = \frac{(C_S)(V_S)}{V+V_S} \times [10^{-\Delta E/59.1} - V/(V+V_S)]^{-1}$$

C = concentration of sample
C_S = concentration of standard
V = mL of sample
V_S = mL of standard

In this procedure the equation simplifies to:

$$C = \frac{4.545}{10^{-\Delta E/59.1} - 0.909}$$

10. Subtract the blank concentration from C.
11. Convert extract concentration to ppm in soil by multiplying by a dilution factor of 3.0.

Ion Exchange Chromatographic Method

Chemically suppressed ion chromatography was introduced by Small, Stevens, and Bauman (14) in 1975. The main advantages of this method are high sensitivity, the ability to separate and quantify similar types of ions (i.e. F^-, Cl^- and Br^-), multiple element analyses and increased freedom from sample matric effect. Mosko (13) demonstrated some problems encountered in the analyses of a range of aqueous samples.

Equipment

1. Balance (0.01 g)
2. Reciprocating shaker, capable of approximately 200 epm
3. Dispenser or buret, capable of dispensing 25 mL
4. 50 mL Erlenmeyer flasks and filter-funnel tubes
5. Mechanical vacuum extractor (Centurion) and syringes
6. Ion chromatography system, including appropriate inline filters, column(s) and detector
7. Strip chart recorder and/or micro computer aided data acquisition

Reagents

1. Extracting Solution: Calcium hydroxide (saturated solution). Add calcium oxide to water (3 g/L of distilled water); shake thoroughly. Filtration of the solution is desirable, but not necessary.
2. Eluant for Ion Chromatograph: Weigh 0.2544 g of sodium carbonate and 0.2520 g sodium bicarbonate into a liter volumetric flask and make to volume with double-distilled or distilled, deionized (DDI) water.
3. Regenerant for Chemically Suppressed Ion Chromatography System Utilizing a Micromembrane Suppressor: Add 1.5 mL concentrated sulfuric acid to a 1 L volumetric flask and make to volume with DDI water.
4. Chloride Stock Standard Solution (1,000 ppm Cl^-): Dissolve 0.1648 g reagent-grade sodium chloride in approximately 50 mL extracting solution. Make to 100 mL volume with extracting solution.
5. Chloride Standard Intermediate Solution (100 ppm Cl^-): Pipette 10 mL of stock solution into a 100 mL volumetric flask and bring to volume with extracting solution.
6. Ion Exchange Resin: Dowex 50W-X8 or equivalent (Bjorad 50W-X8) 50 to 100-mesh (prevents divalent and trivalent cations from poisoning separator and suppressor columns).

Table 1. Chloride working standards: Ion Chromatographic Method.

Beaker	Volume of 100 ppm Cl-	Final Volume	Chloride Concentrate Solution	Equivalent Concentrate in Soil
	mL	mL	ppm	ppm
1	0	100	0	0
2	0.5	100	0.5	1.25
3	1	100	1	2.5
4	5	100	5	12.5
5	10	100	10	25.0
6	20	100	20	50.0

Procedure

1. Weigh 10.0 g of crushed soil into a 50 mL Erlenmeyer flask.
2. Dispense 25 mL of extracting solution into each flask. (Alternatively add approximately 0.1 to 0.2 g of calcium oxide to each flask, then despense 25 mL DDI water into each flask.)
3. Shake for 5 minutes at 180 or more epm.
4. Filter sample into filter tubes through Whatman No. 2 filter papers that have been washed with DDI water.
5. Set up mechanized vacuum extractor utilizing 0.2 micron filters. (As an alternative to this procedure (# 5-7), samples can be clarified by centrifuging for 30 minutes at 35,000 to 40,000 rpm. Decant samples into test tubes for analysis.)
6. Pour the filtered sample extract or standard into each syringe and allow it to equilibrate with the exchange resin about 5 minutes.
7. Extract samples and/or standards through 0.2 micron filters.
8. Set ion chromatographic analysis parameters.
   a. Eluent flow rate
   b. Regenerant flow rate
   c. Retention time for Cl^- (determined experimentally)
9. Inject samples using strip-chart recorder and/or micro computer to acquire the chromatographic data.
11. Results are calculated by measuring peak height or peak area from strip-chart recording or by computer software when sample run is complete.
    a. Fit of standards to the standard calibration curve must be checked.
    b. Dilution factors are checked and data is checked for error.
    c. Quality control standards (soil extracts and solution standards) are checked.
12. Cleanup of labware.
    a. Rinse with distilled water.
    b. Soak in a dilute acid bath at least 30 minutes.
    c. Rinse three times with DDI water.

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Chapter 12

Soil Organic Matter

S. M. Combs and M. V. Nathan

The importance of soil organic matter (OM) in supplying nutrients, contributing to cation exchange capacity, improving soil structure, etc., is well recognized. In many states, OM content of the soil is used to adjust nitrogen (N), sulfur, herbicide, and/or lime recommendations. OM is also important in adjusting herbicide application rates and in calculating loading rates for sewage sludge and other wastes.

OM determinations are usually based on either 1) determination of some constituent which comprises a relatively constant percentage of the OM, such as N or carbon (C) or 2) weight loss on removal of the OM from the mineral fraction by oxidation with H_2O_2, ignition or ignition after decomposition of silicates with HF.

Mehlich (13) extracted "humic matter" with 0.2 M NaOH – 0.0032 M DTPA – 2 percent ethanol from North Carolina soils. Use of this procedure on Wisconsin soils resulted in poor reproducibility in replicate samples. It is believed that mobilization of clay may be partly responsible.

Carbon Determination

Estimation of OM by determination of C is used extensively. Determining total N is not widely used because of the relatively wide variation of N content in organic materials from different sources. C can be determined by:

1. Dry combustion after removal of carbonates and measurement of CO_2 evolved .
2. Chromic acid oxidation after removal of carbonates and measurement of CO_2 evolved .
3. Chromic acid oxidation for determination of easily oxidized material (external heat applied).
4. Chromic acid oxidation for determination of easily oxidized material (spontaneous heating).

The dry combustion method measures total C whereas the chromic acid methods determine only that C which is easily oxidizable, i.e. C in graphite and coal is not oxidized by chromic acid. The methods involving measurement of evolved CO_2 requires special apparatus and are not well adapted to rapid analysis of a large number of samples common to routine testing. Consequently, the methods which involve chromic acid oxidation for the determination of easily oxidizable C are most widely used. These methods (3 and 4) differ primarily in the source and amount of heat used to drive the reaction. Method 3 utilizes an external source of heat which permits heating to a higher temperature that can be achieved with Method 4, which derives its heat from the heat of dilution of concentrated H_2SO_4. Consequently, the reaction in Method 3 is much faster and oxidation of the OM more complete. However, conditions must be carefully controlled to achieve reproducible results.

A temperature of approximately 120°C is obtained in the heat-of-dilution reaction of concentrated H_2SO_4 (2). This is sufficient to oxidize the active forms of organic C but not the more inert forms. Walkley and Black (20) recovered 60 to 86 percent of the organic C in the soils they studied. As a result of this and other work, a recovery factor of 77 percent is commonly used to convert "easily oxidizable" organic C to total organic C. Later work (1), however, showed that the recovery factor varied from 59 to 94 percent. The use of external heat, such as employed in the Schollenberger Method (14, 15), gives a higher recovery of organic C and less variation in percentage recovery among different groups of samples.

When external heat is applied, temperature control is extremely important. The actual temperature selected is not too critical so long as the procedure is standardized for that temperature. As temperature increases, reaction time required should decrease and precision increase.

Three main sources of error arise with chromic acid digestion (19): 1) interfering inorganic constituents, 2) differences in digestion conditions and reagent composition, and 3) variable composition of the OM itself.

Chlorides, if present, reduce $Cr_2O_7^{2-}$ and lead to high results. They can be rendered ineffective by precipitation with Ag_2SO_4 added to the digestion acid or by water leaching prior to digestion. The presence of Fe^{2+} also leads to high results, but drying soils containing Fe^{2+} during sample preparation oxidizes Fe^{2+} to Fe^{3+} and minimizes the amount of Fe^{2+} present. Higher oxides of manganese compete with $Cr_2O_7^{2-}$ for oxidation of OM, leading to low results. Usually this is not a serious error. Carbonates and elemental C do not introduce any significant error.

Equations

1. Reaction of $Cr_2O_7^{2-}$ with organic matter.
   a. The $Cr^2O_7^{2-}$ will react with C as follows:

$$2Cr_2O_7^{2-} + 3C^0 + 16\ H^+ \xrightarrow{\Delta}$$

$$4Cr^{3+} + 3CO_2 + 8H_2O$$

   b. Similarly, $Cr_2O_7^{2-}$ will react with organic hydrogen as follows:

$$Cr_2O_7^{2-} + 6H^0 + 8\ H^+ \xrightarrow{\Delta} 2Cr^{3+} + 7H_2O$$

   c. The presence of organic oxygen will decrease the amount of total C oxidized by the $Cr_2O_7^{2-}$ because of the following reaction:

$$RCOOH \xrightarrow{\Delta} RH + CO_2$$

Reaction b tends to compensate for the loss of C due to Reaction c so that the assumption that each C atom is oxidized from C^0 to C^{4+} reflects the overall electron change in the reaction. Excess $Cr_2O_7^{2-}$ is back titrated with standard Fe^{2+} solution to determine the amount that has reacted.

2. Reaction of ferrous iron (Fe^{2+}) with $Cr_2O_7^{2-}$:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H + \xrightarrow{\Delta}$$

$$2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Weight Loss Determination

Recent interest in weight loss methods has arisen out of a desire to eliminate the use of chromic acid because of concern for disposal of the chromium and hazards associated with its use. Even though weight loss determinations can be subject to errors caused by volatilization of substances other than organic materials and incomplete oxidation of carbonaceous materials, they are a promising alternative. Ball (3) compared the weight loss of 117 upland, 22 lowland, and 11 organic soils of North Wales at 850 and 375°C with OM determined by a modification of the Walkley and Black (20) procedure. Results at both temperatures were highly correlated with OM by the Walkley and Black procedure, but the lower temperature was deemed preferable. Goldin (9) compared loss of weight on ignition of 60 noncalcareous soils of northwestern Washington and British Columbia with organic carbon determined with a Leco carbon analyzer and found the two methods to be highly correlated ($R^2 = 0.98$). Storer (18) automated the procedure with a computerized weighing system.

High temperature heating (more than 500°C) can result in loss of CO_2 from carbonates, structural water from clay minerals, oxidation of Fe^{2+} and decomposition of hydrated salts (3, 5, 12). However, heating below 500°C should eliminate these potential errors. Davies (7) for example compared the weight loss-on-ignition (LOI) at 430°C for 17 British soils containing 9 to 36.5 percent $CaCO_3$ with OM determined by the Walkley-Black Method. The relationship indicated no interference from the carbonates ($r = 0.974$). Addition of $CaCO_3$ to a pH 6.8 soil to give soil to $CaCO_3$ ratios of 10:0 to 10:5 had no effect on LOI.

Water loss by minerals between 105 and 360°C may occur. Results of thermo-gravimetric analysis of several Israeli arid zone soils and two synthetic mixes showed that heating samples for 24 hours at 105°C was necessary to remove hygroscopic water which would otherwise be interpreted as OM (5). Selecting a temperature above 105°C as the base temperature but below which the OM decomposes should help minimize water loss from minerals.

OM may be overestimated when preheated at 105° C in low OM soils (Nathan, M. V., unpublished data). Preheating at 150° C gave LOI results better correlated to Walkley-Black results. Gypsum ($CaSO_4 \cdot 2HO$) in soils of subhumid and arid regions could present a problem with LOI (16, Jensen, T., personal communication). Gypsum contains 20.9 percent water and loses $1^1/_2$ H_2O at 128°C and the remaining H_2O at 163°C (10). Therefore, preheating at 150°C or higher should eliminate much of the problem with gypsum. Schulte and Hopkins (16) found that drying soils for 24 hours at 105°C removed all the water from gypsum and that 50 percent was lost in 2 hours. Gypsum was found completely dehydrated in 2 hours at 150°C. To ensure complete dehydration of gypsiferous soils, a minimum of 2 hours at 150°C or overnight at 105°C is necessary (16). Other hydrated salts such as Epsom salts ($MgSO_4 \cdot 7H_2O$) and calcium chloride ($CaCl_2 \cdot 6H_2O$), lose some water at temperatures greater than 150°C (10). Sodium salts ($Na_2CO_3 \cdot 10H_2O$ and $Na_2SO_4 \cdot 10H_2O$) have the potential to decompose to NaOH and CO_2 at 270°C, but the effect of heating at 105 or 150°C on water loss from these salts is not known (10).

The use of LOI to estimate OM has given higher values than other methods (Table 1). Hence, a regression equation is needed to estimate OM from LOI. The differences in slopes shown in Table 1 result from differences in heating times and temperature and, possibly, from differences in the nature of the clay and OM fractions. Goldin (9) and David (6), for example, obtained different regression equations for mineral soils than for forest floor litter. Peters (personal communication) and Storer (18) obtained different slopes and intercepts when high OM samples were excluded from the regression analysis.

Table 1. Heating times and temperature reported in the literature for loss-on-ignition (LOI).

Reference	°C	Hours	--------- y = bx + a --------- [1] b	a	R^2	n
Peters (1991) Personal Comm.	360	2	0.73	0.08	0.93	63
Peters (1991) Personal Comm.[2]	360	2	0.66	0.04	0.84	60
Schulte et al. (1991)	360	2	1.04	-0.36	0.97	356
Schulte et al. (1991)[3]	360	2	0.97	-0.33	0.90	316
Ball (1964)	375	16	0.79	-0.7	-	65
Ben-Dor & Banin (1989)	400	8	0.84	-0.32	0.97	91
Donkin (1991)	400	0.57	-	-	0.98	55
Davies (1974)	430	24	0.85	0.56	0.99	174
David (1988)	450	12	0.90	-0.02	0.92	174
David (1988)[4]	450	12	[5]	[5]	0.89	164
Lowther et al. (1990)	450	16	0.78	-0.20	0.99	38
Storer (1984)	500	4	0.81	-1.47	0.98	215
Storer (1984)[3]	500	4	0.60	-0.33	0.87	210
Goldin (1987)[6]	600	6	0.70	-1.24	0.86	60
Goldin (1987)[4]	600	6	0.72	-4.29	0.89	12

[1]y = OM; if organic C was reported, OM was calculated assuming 58 percent C; x = LOI.
[2]OM less than 5 percent (the Gambia).
[3]OM less than 9.9 percent.
[4]Forest floor liter.
[5]OM = -4.72 + 1.40 LOI - 0.0443 $(LOI)^2$.
[6]Mineral soils (Canada).

Schulte et al. (17) studied the effects of heating time, sample size and number of samples ignited at one time on LOI at 360°C. The number of samples ignited at one time in a muffle furnace did not affect LOI. For an organic soil containing 34 percent OM, beaker size (20 or 50 mL) was unimportant, but LOI increased as sample size decreased. Sample size was not significant for a mineral soil (3.6 percent OM). Time of heating, however, was significant for both soils. When the LOI at 360°C for 2 hours of 356 Wisconsin soils was compared with OM determined by Walkley-Black titration, the regression equation was:

$$OM = -0.36 + 1.04\ LOI (R^2 = 0.97).$$

OM in these samples ranged from 0.1 to 54 percent. When only samples containing less than 10 percent OM were included, the regression equation was:

$$OM = -0.33 + 0.973\ LOI (R^2 = 0.90)$$

This confirms the recommendations (6, 9, 17) that separate regression equations be developed for soils differing widely in mineralogy or use.

Soil Organic Matter Methods

Three methods of estimating OM are given in this chapter. The first is the Walkley-Black method (19, 20). This method uses the heat of dilution of concentrated acid to drive the oxidation of C in organic matter to CO_2. The unreduced $Cr_2O_7^{2-}$ is measured by titration. Calcualtion of a percentage OM assumes 77 percent oxidization of organic C and that OM is 58 percent C.

The second method, a modification of the Schollenberger method (14, 15), relies upon outside heat to drive the organic C oxidation by chromic acid. Two digestion alternatives are presented and the amount of Cr reduction is estimated colorimetrically.

The third method of estimating soil OM, loss of weight on ignition, is included because of hazards associated with the use of $Cr_2O_7^{2-}$. This ion in a strong acid medium is a powerful oxidant. It is corrosive to skin, mucous membranes, the respiratory tract and the gastrointestinal tract. It may create a cancer risk. Some municipalities restrict the amount of Cr that can be discharged into the sewage system. For these reasons, alternative procedures not involving $Cr_2O_7^{2-}$ have been sought.

All three methods should be standardized against two check samples differing in OM content based upon total C determined by dry combustion after removal of carbonates. As with the Walkley-Black method, it is assumed that soil OM is 58 percent C. These procedures were developed for surface soils. The assumptions, concerning the percentage of C in OM and that 77 percent of the C is oxidized by chromic acid, may not be valid for subsoils (1).

Walkley-Black Method

Equipment

1. 500 mL Erlenmeyer flasks
2. 10 mL pipette
3. 10 and 20 mL dispensers
4. 50 mL burette
5. Analytical balance
6. Magnetic stirrer
7. Incandescent lamp

Reagents

1. H_3PO_4, 85 percent
2. H_2SO_4, concentrated (96 percent)

3. NaF, solid
4. Standard 0.167 M $K_2Cr_2O_7$: Dissolve 49.04 g of dried (105°C) $K_2Cr_2O_7$ in water and dilute to 1 L.
5. 0.5 M Fe^{2+} Solution: Dissolve 196.1 g of $Fe(NH_4)_2(SO_4)\cdot 6H_2O$ in 800 mL of water containing 20 mL of concentrated H_2SO_4 and dilute to 1 L. The Fe^{2+} in this solution oxidizes slowly on exposure to air so it must be standardized against the dichromate daily.
6. Ferroin Indicator: Dissolve 3.71 g of o-phenanthroline and 1.74 g of $FeSO_4\cdot 7H_2O$ in 250 mL of water.

Procedure

1. Weigh out 0.10 to 2.00 g dried soil (less than 60 mesh) and transfer to a 500 mL Erlenmeyer flask. The sample should contain 10 to 25 mg of organic C (17 to 43 mg OM). For a 1 g sample, this would be 1.2 to 4.3 percent OM. Use up to 2.0 g of sample for light colored soils and 0.1 g for organic soils.
2. Add 10 mL of 0.167 M $K_2Cr_2O_7$ by means of a pipette.
3. Add 200 mL of concentrated H_2SO_4 by means of dispenser and swirl gently to mix. Avoid excessive swirling that would result in organic particles adhering to the sides of the flask out of the solution.
4. Place the flasks on an insulation pad and letstand 30 minutes.
5. Dilute the suspension with about 200 mL of water to provide a clearer suspension for viewing the endpoint.
6. Add 10 mL of 85 percent H_3PO_4, using a suitable dispenser, and 0.2 g of NaF, using the "calibrated spatula" technique. The H_3PO_4 and NaF are added to complex Fe^{3+} which would interfere with the titration endpoint.
7. Add 10 drops of ferroin indicator. The indicator should be added just prior to titration to avoid deactivation by adsorption onto clay surfaces.
8. Titrate with 0.5 M Fe^{2+} to a burgundy endpoint. The color of the solution at the beginning is yellow-orange to dark green, depending on the amount of unreacted $Cr_2O_7^{2-}$ remaining, which shifts to a turbid gray before the endpoint and then changes sharply to a wine red at the endpoint. Use of a magnetic stirrer with an incandescent light makes the endpoint easier to see in the turbid system (fluorescent lighting gives a different endpoint color). Alternatively use a Pt electrode to determine the endpoint after Step 5 above. This will eliminate uncertainty in determining the endpoint by color change. If less than 5 mL of Fe^{2+} solution was required to back-titrate the excess $Cr_2O_7^{2-}$ there was insufficient $Cr_2O_7^{2-}$ present, and the analysis should be repeated either by using a smaller sample size or doubling the amount of $K_2Cr_2O_7$ and H_2SO_4.
9. Run a reagent blank following the above procedure without soil. The reagent blank is used to standardize the Fe^{2+} solution daily.
10. Calculate C and organic matter percentages:
    a. Percentage easily oxidizable organic C:

$$\%\ C = \frac{(B - S) \times M \text{ of } Fe^{2+} \times 12 \times 100}{\text{grams of soil} \times 4{,}000}$$

B = mL of Fe^{2+} solution used to titrate blank.
S = mL of Fe^{2+} solution used to titrate sample.
$^{12}/_{4,000}$ = milliequivalent weight of C in grams.

To convert easily oxidizable organic C to total C, divide by 0.77 (or multiply by 1.30) or other experimentally determined correction factor.

    b. Percentage organic matter (OM):

$$\%\ OM = \frac{\%\ C}{0.58} = \%\ C \times 1.72$$

Routine Colorimetric Determination of Organic Matter

Equipment

1. NCR-13, 1 g scoop
2. Glass marbles[2] having a diameter slightly larger than the mouth of a 50 mL Erlenmeyer flask
3. 50 mL Erlenmeyer flasks
4. Digestion oven, 90°C, with air circulation fan and fume exhaust
5. 10 mL and 25 mL pipettes or dispensers
6. Standard OM samples

Reagents

1. Digestion solution (0.5 M $Na_2Cr_2O_7$ in 5 M H_2SO_4): Dissolve 140 g $Na_2Cr_2O_7\cdot 2H_2O$ in 600 mL of distilled water. Slowly add 278 mL of concentrated H_2SO_4. Allow to cool and dilute to 1 L.

Procedure

1. Scoop 1 g of soil into a 50 mL Erlenmeyer flask, using standard scooping techniques.
2. Add, by means of a pipette or dispenser, 10 mL of

[1]*Marbles (1 inch in diameter) are available from The Peltier Glass Co., Ottawa, IL 61350.*

dichromate-sulfuric acid digestion solution. Include a reagent blank without soil.
3. Cover the Erlenmeyer flasks with glass marbles, which act as reflux condensers, to minimize loss of chromic acid.
4. Place in the digestion oven and heat to 90°C for 90 minutes.
5. Remove samples from the oven, let cool 5 to 10 minutes, remove the glass marble caps, and add 25 mL of water.
6. Mix the suspension thoroughly by blowing air through the suspension via the 25 mL pipettes used to add water or by mechanical shaking.
7. Allow to stand three hours or overnight.
8. Transfer 10 mL (or other suitable volume) of clear supernatant into a colorimeter tube. This can be accomplished conveniently by use of a pipette bank set to dip a suitable distance into the supernatant solution. Care must be taken not to disturb the sediment on the bottom of the flasks.
9. The blue color intensity of the supernatant is read on a colorimeter at 645 nm, with the reagent blank set to give 100 percent transmittance (or 0 absorbance). The instrument is calibrated to read percentage OM (or tons/acre) from a standard curve prepared from soils of known OM content.

Alternate Procedure Involving Heat of Dilution

Reagents

1. 0.5 M $Na_2Cr_2O_7$:
   Dissolve 149 g of $Na_2Cr_2O_7 \cdot 2\ H_2O$ in water and dilute to 1 L.
2. H_2SO_4, concentrated, 96 percent

Procedure

1. Scoop 1 g of soil into a 50 mL Erlenmeyer flask using standard scooping techniques.
2. Add 10 mL of $Na_2Cr_2O_7$ solution by means of dispenser.
3. Add 10 mL of concentrated sulfuric acid using a suitable dispenser. A supply of 2 percent $NaHCO_3$ should be readily available to neutralize spilled acid on skin, clothing or lab bench.
4. Allow to react for 30 minutes.
5. Dilute with 15 mL of water and mix.
6. Proceed with Step 7 immediately above.

A sample exchange involving 25 soil samples among 13 labs in the North Central Region showed that results using the routine colorimetric procedure agreed closely with those of the Walkley-Black Method. However, the standard deviation was somewhat greater with the routine colorimetric procedure, as might be expected (see Table 2). Other modifications of the Walkley-Black Method gave greater amounts of variation among labs. This variation would likely have been lower had the comparisons all been made by the same lab. Nevertheless, the results underscore the need to standardize carefully whatever procedure is followed.

Organic Matter Standard Curve

Analyze standard soils of known OM content (determined by the Walkley-Black Method, above, or by means of a carbon analyzer) in duplicate by the Heat of Dilution Procedure, above, or by means of a carbon analyzer, except read absorbance on the colorimeter. Then plot the known percentage OM (or tons OM/acre) against absorption readings. Calibrate an instrument scale in percentage OM (or tons OM/acre) using values obtained from the graph.

Table 2. Comparison of organic matter determined by different modifications of the Walkley-Black Method.

Comparison	Mean Organic Matter	SD
	––––– Percent –––––	
External Heat Applied:		
Titration (4) vs. Colorimetric (10)		
Titration	2.93	0.16
Colorimetric	2.82	0.65
Heat of Dilution:		
Titration (4) vs. Colorimetric (10)		
Titration	2.93	0.16
Colorimetric	2.58	0.59
Colorimetric Procedures:		
Weight (4) vs. Scoop (6)		
Weight	2.60	0.53
Scoop	2.97	0.70
Filter (3) vs. Settle (6)		
Filter	2.15	0.26
Settle	3.21	0.54
Heat of Dilution (4) vs. External Heat (6)		
Heat of Dilution.	2.58	0.59
External Heat	2.99	0.68

Results are means of 25 samples ranging from 0.3 to 8.1 percent organic matter analyzed by 13 North Central Region soil testing labs in 1979.

Numbers in parentheses indicate number of labs involved in each comparison.

Alternate Procedure: Loss of Weight on Ignition (Adapted from Storer, 1984)

Equipment

1. Oven, capable of heating to 650°C
2. Crucibles – 20 mL

3. Stainless steel crucible rack from local manufacturer
4. Balance sensitive to plus or minus 1 mg in draft-free environment (see Storer (18) for computerized weighing system)

Procedure

1. Scoop 5 to 10 g of dried, ground (10 mesh) soil into tarred crucibles.
2. Dry for 2 hours at 105°C (for gypsiferous and some ion organic matter soils, heat for 2 hours at 150°C)
3. Record weight to plus or minus 0.001 g.
4. Heat at 360°C for two hours (after temperature reaches 360°C).
5. Cool to 150°C.
6. Weigh in a draft-free environment to plus or minus 0.001 g.
7. Calculate percentage loss of weight on ignition:

$$\% \text{ LOI} = \frac{(\text{wt. at } 105°\text{C}) - (\text{wt. at } 360°\text{C}) \times 100}{\text{wt. at } 105°\text{C}}$$

8. Estimate OM.

Estimation of OM from LOI is done by regression analysis. Select soils covering the range in OM expected in your state or area of testing. Determine percent OM by the Walkley-Black Method described above. Regress OM on LOI. The resulting equation is used to convert LOI to percentage OM but should not be used outside the testing area.

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Chapter13

Soil Salinity

D. A. Whitney

All soils contain some water soluble salts which include essential nutrients for plant growth. When the level of water soluble salts exceeds a certain level, harmful effects on plant growth occur. A soil with excess total soluble salts is referred to as a saline soil. Saline soil is the most common type of salt-affected soil and usually the easiest type to reclaim (2, 5).

Another type of salt-affected soil is termed a sodic or alkali soil. They have a low total soluble salt content, a high pH (usually 8.5 or higher) and exchangeable sodium in excess of 15 percent of the cation exchange capacity. These soils usually are dispersed due to the excessive sodium (2, 5). Salt-affected soils often result from the lateral or artesian flow of salty water onto an area. In other cases it is caused by an impermeable layer in the soil resulting in a high water table or side-hill seeps. In well-drained, irrigated soils the application of poor quality water in amounts insufficient to leach the soluble salts from the surface horizons will result in a salt accumulation. They may also result from saltwater spills associated with oil field activity and from high rates of manure or sludge.

The influence that a certain level of soluble salt will have on crop growth depends upon several factors, such as climatic conditions, soil texture, distribution of salt in the profile, salt composition and plant species (5). The areal extent and depth of a salt problem is usually irregular. Soil sampling on a grid system may be necessary to map the extent of the problem.

Soluble salts are most commonly detected by measuring the soil solution's ability to conduct an electrical current, referred to as electrical conductivity (EC). The common unit of measurement for EC has been mmhos/cm. The official international unit of measurement is seimen/m (S/m). One mmhos/cm is equal to 0.1 S/m or 1.0 dS/m.

There are several detection methods for assessing soluble salt content of a soil. The type of information needed in a particular situation will determine which method is used.

If a rapid in situ measurement of the apparent electrical conductivity is desired showing the extent of a saline area, the noncontacting terrain conductivity meters, such as the EM31 and EM38 made by Geonics Limited (3), can be used. If a more accurate reading is needed, measurement of electrical conductivity on a 1:1 soil-to-water suspension in the laboratory is best. Once a salt problem is identified by one of these methods, the more detailed information needed to correct the situation should be obtained from an electrical conductivity measurement made on a saturated paste extract. Some laboratories use chloride content as an indication of salt content. This is not an acceptable method because many salt-affected soils are low in chlorides but high in sulfates.

Soil Salinity Methods

Noncontacting Terrain Conductivity Meters

Soil electrical conductivity can be obtained from above-ground electromagnetic measurements by relating electromagnetic conductivity to electrical conductivity (1). This method is very fast and accurate once the meter is calibrated for a particular set of conditions. Several soil factors in addition to salinity, such as soil porosity, moisture and amount and type of clay, influence the readings (3); therefore, a single calibration can only be used on similar soils. Refer to the instrument instruction manual for details.

1:1 Soil-to-Water Method

The electrical conductivity value obtained by the 1:1 Soil-to-Water Method is not as easily interpreted as that for the Saturated Paste Method. With the 1:1 method, the relationship between conductivity and crop growth varies with soil texture. (Table 1).

Equipment

1. Standard NCR-13, 10 g scoop
2. Dip-type conductivity cell
3. Conductivity meter

Reagents

1. Distilled water
2. Calibration solution (0.01 M KCl solution): Dissolve 0.7456g KCl in 1 L of water. This solution has a conductivity of 1.41 mmhos/cm or dS/m at 25°C.

Procedure

1. Scoop 20 g of soil into a large test tube or paper portion cup.
2. Add 20 mL of distilled water. Periodically stir the suspension and allow it to equilibrate for 15 to 20 minutes. This sample could also be used for a pH measurement after (not before) taking the conductivity measurement.
3. Insert the conductivity cell calibrated with the 0.01 M KCl into the suspension and read the conductivity in mmhos/cm.

Saturated Paste Method

The Saturated Paste Method has long been the recommended method for assessing soil salinity in relation to plant growth. The advantage of this method is that the saturation moisture percentage is directly related to the field moisture range. Conductivity by this method relates directly to plant response for all soils without adjustment for texture (6) as with the 1:1 method. The disadvantage of this method is more expense and time.

Equipment

1. Conductivity meter
2. Conductivity cell
3. 250 mL containers (such as plastic cups)
4. Buchner funnels

Reagents

1. Distilled water
2. 0.01 M KCl solution: Dissolve 0.7456g KCl in 1 L of water. This solution has a conductivity of 1.41 mmhos/cm at 25°C.

Procedure

1. The amount of soil used will depend on the number of measurements that will be made on the extract. A 250 g sample provides sufficient extract for most purposes.
2. Add distilled water to the soil while stirring it with a spatula. At saturation, the soil paste will glisten as it reflects light, flow slightly when the container is tipped, and the paste slides freely and cleanly off the spatula for all soils except clays.
3. After mixing, allow the sample to stand for at least 1 hour and then recheck for saturation. Free water should not collect on the soil surface. If the paste stiffens or loses its glisten, add more water and remix. If free water exists on the surface after standing, add more soil and remix.
4. Transfer the saturated paste to the filter funnel and apply vaccum.
5. Determine conductivity and/or other measurements on extract.

Calibration

The 1:1 method is meant to be used as a screening method to determine if there is a possible salinity problem. Unlike the Saturated Paste Method, the degree of salinity for the 1:1 method is related to soil texture (Table 1). Once it is determined that a salt problem exists, the Saturated Paste Method is used to determine the kind and amount of salt in order to plan a corrective program (6).

Table 1. The relationship between conductivity and degree of salinity for the 1:1 Method and the Saturated Paste Method.

	————Degree of Salinity————				
Texture	Non-Saline	Slightly Saline	Mod. Saline	Strongly Saline	Very Strongly Saline
1:1 Method	--------mmhos/cm or dS/m--------				
Coarse to Loamy Sand	0-1.1	1.2--2.4	2.5-4.4	4.5-8.9	9.0+
Loamy Fine Sand to Loam	0-1.2	1.3-2.4	2.5-4.7	4.8-9.4	9.5+
Silt Loam to Clay Loam	0-1.31	1.4-2.5	2.6-5.0	5.1-10.0	10.1
Silty Clay Loam to Clay	0-1.4	1.5-2.8	2.9-5.7	5.8-11.4	11.5+
Saturated Paste Method	––––mmhos/cm or dS/m——				
All Textures	0-2.0	2.1-4.0	4.1-8.0	8.1-16.0	16.1+

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Chapter 14

Greenhouse Root Media

D. Warncke

Root media used for production of plants in greenhouses and nurseries are composed of lightweight, natural and processed material such as peat, perlite, vermiculite, sand, bark, coconut fiber (coir), compost and similar materials. These are mixed together in various combinations to provide the actual root media. These lightweight mixes are easy to handle and provide good aeration and moisture-holding properties, but provide little nutrient-holding capability. Soil systems provide plant available nutrients in the soil solution (intensity factor) and have a reserve nutrient supplying capacity with exchangeable cations, "fixed" nutrients and insoluble complexes (capacity factor). Most prepared root media contain only small amounts of soil, if any, and therefore have a limited nutrient reserve (capacity factor). Hence, the availability of nutrients in most prepared root media is dependent on the intensity factor.

Geraldson (2) developed an "intensity and balance" testing system for poorly buffered sandy soil systems using the saturation/extraction approach adopted by the U.S. Salinity Laboratory (9). Lucas et al. (4, 5) found that saturation extracts of greenhouse root media gave a reliable measure of plant available nutrients. Researchers in the Netherlands (6, 7) have also reported saturation extract results to be a dependable measure of the available nutrient status of peat-based mixes. In summarizing test results over a 2-year period, Whipker et al. (16) demonstrated that root media analysis by saturation extraction is a valuable tool for evaluating greenhouse nutrition problems.

Saturation extraction methodology provides several advantages over previous procedures (11, 12, 14). For many years, soil testing laboratories have handled prepared soilless root media samples in a manner similar to that for field soil samples. Analytical procedures used have been modifications of the Spurway (8) test procedures. These worked well for testing greenhouse soil mixes when soil was the base material. However, as the composition of greenhouse root media has changed to include peat and processed materials, the field soil testing procedures have become inadequate. The major shortcomings in treating greenhouse root media in the same way as field soils are related to handling and diagnostic sample size. Drying, grinding and sieving of greenhouse samples result in significant alteration of the sample properties. Trying to measure out a uniform, small sample (2.0 or 1.7 cc) from a heterogenous mix of materials is difficult. Interpretation of the results must take into account the bulk density which may range from 0.2 to 1.2 g/cc. The Saturated Media Extract (SME) approach has been shown to successfully eliminate these handling, sampling and interpretation problems (11, 12, 14). This procedure can also be used to evaluate the suitability of composts for use in growing plants.

With the saturation procedure a large sample of the root media (400 cc), just as the grower uses it, is extracted and analyzed, reducing sampling error. With no preliminary handling necessary, samples can be processed and analyzed quickly. The water holding characteristics of the various root media tend to be related to the bulk density. This acts as an automatic compensator for differences in bulk densities which affect interpretation of results from saturation extracts. As demonstrated by Geraldson (3), nutrient balance is very important in weakly buffered systems such as exist with many greenhouse root media. With the SME approach, nutrient balance information is readily calculated. Root media which contain slow-release fertilizer can be extracted by the saturation extract method with very little inflation of the tests results (13). With other handling and extraction procedures, test values are greatly inflated due to excessive solubilization of the slow-release fertilizer.

Available micronutrient levels in plant growth media are important for the growth of container grown plants. In peat and bark based root media, the basic micronutrients are complexed by organic compounds (10). Hence, the concentrations of these micronutrients in a water saturation extract are quite low. Zinc and manganese concentrations rarely exceed 0.8 mg/L and iron rarely exceeds 4.0 mg/L. Therefore, it is difficult to distinguish between deficient and adequate levels.

In evaluating 15 extractants, Berghage et al. (1) found that extractable levels of iron, manganese and zinc could be increased greatly by using weak solutions of various salts, acids or chelates in the saturating solution with the saturation extract procedure.

Saturation with a 0.005 M DTPA solution was found to most consistently increase extractable micronutrient levels while having only a minor effect on the other key test parameters: total soluble salts and extractable levels of nitrate, phosphorus, potassium, calcium, magnesium, sodium and chloride.

Saturated Media Extract Method

The Saturated Media Extract Method (SME) was developed at Michigan State University and has been routinely used in their soil testing lab. It allows extraction of moist samples just as they come from greenhouses. Drying of samples is unnecessary and undesirable. Storage of prepared root media in either the dry or moist state will influence the soluble nitrate-nitrogen (N) and soluble salt levels. If samples will not be extracted within two hours of receipt, store them in a refrigerated area.

Equipment

1. 600 mL plastic beaker
2. Spatula
3. Buchner funnel, 11 cm
4. Filter paper (Whatman No. 1) 11 cm
5. Vacuum flask, 500 mL
6. Vacuum pump
7. Vial, snap-cap 100 mL
8. Conductivity meter, (Solu-bridge 31 or equivalent)
9. Dipping type conductivity cell wtih cell constant equaling 1.0
10. Thermometer
11. pH meter with expanded scale or specific ion meter
12. pH glass electrode with a paired calomel reference electrode
13. Nitrate electrode with paired reference electrode
14. Colorimeter
15. Flame emission, atomic absorption and/or plasma emission spectrophotometer
16. Volumetric flasks and pipettes as required for preparation of reagents and standard solutions

Reagents

1. Distilled or deionized water
2. 0.01 M potassium chloride (for standardizing solu-bridge)
3. Reagents for determining pH, nitrate-N, phosphorus, potassium, calcium, magnesium and micronutrients of interest

Procedure

1. Fill a 600 mL beaker about two-thirds full with the root medium. Gradually add distilled water while mixing until the sample is just 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 distilled water. Then allow to equilibrate for an additional 30 minutes.
2. Determine the pH of the saturated sample by carefully inserting the electrodes. Wiggle the electrodes gently to attain good solution contact.
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. Spread the sample out with a spatula and tap the funnel to eliminate entrapped air and to insure good contact between the saturated sample and the filter. Continue 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.
4. Soluble Salts: (See Chapter 13.) Use 0.01 M KCl to calibrate the solu-bridge. Prepare a 0.01 M KCl solution by dissolving 0.7456 g KCl in about 800 mL of distilled or deionized water. Then bring it to 1 L volume with distilled or deionized water. With the temperature adjustment properly made, a 0.01 M KCl solution should have an electrical conductivity of 1.418 dS per m (mS per cm). *Note:* For those with older solu-bridges:

   $$1.0\ dS\ m^{-1} = 1.0\ mmho\ cm^{-1}.$$

   To determine the electrical conductivity of the extract solution, check its temperature and adjust the temperature dial on the solu-bridge. Rinse the electrode and dip the conductivity cell into the extract solution and record the reading in dS m^{-1} (mS cm^{-1}).
5. Nitrate-N and Ammonium-N: (See Chapter 5.) Nitrate and ammonium can be determined with the appropriate specific ion electrode or by cadmium reduction (nitrate) and Nesslerization (ammonium) through an autoanalyzer unit. With the high concentrations of nitrate usually present, use of a nitrate electrode is preferred. After establishing the standard curve, determine the nitrate-N content with a nitrate electrode. Record the millivolt reading on an expanded scale pH meter or specific ion meter, and obtain the concentration of nitrate from a standard curve of Emf vs. nitrate concentration plotted on semi-logarithmic graph paper.

6. Phosphorus, potassium, calcium, magnesium: Determine phosphorus on a aliquot of the extract by one of the accepted colorimetric procedures (See Chapter 6). Determine potassium, calcium and magnesium on an aliquot of the extract by flame emission or atomic adsorption spectroscopy (See Chapter 7). All of these elements may also be determined with an Inductively Coupled Plasma Emission Spectrograph (ICP).
7. Micronutrients: Most micronutrients of interest can be determined with an ICP. For methods of analysis, refer to Chapter 9.

Modified (DTPA) Saturated Media Extract Method

By using 0.005 M DTPA as the primary saturating solution, extraction of the basic micronutrients (zinc, manganese and iron) can be greatly enhanced. For each liter of DTPA solution to be prepared, transfer exactly 1.97 g dry DTPA (diethylenetriaminepenta-acetic acid) into a 1 L volumetric flask and add about 800 mL of distilled or deionized water. Heating the water to 50°C and stirring facilitates dissolution of the DTPA. After the solution has cooled, make to volume with distilled or deionized water. The modified SME method involves a change in the procedure used to saturate the growth media and in the measurement of pH.

DTPA Saturation Extract Preparation

1. Place 400 cc of growth media into a 600 mL beaker.
2. Add 100 mL of 0.005 M DTPA.
3. While mixing gradually, add pure water to bring the media just to the point of saturation.

From this point on, proceed as indicated under the original SME Method, except for pH determination. Since the DTPA solution affects the media pH, use one part of the media by volume and two parts of deionized water by volume for a separate determination of the media pH.

Calculations

Soluble salt levels are reported as dS m^{-1} or mS cm^{-1}. The electrical conductivity (dS m^{-1} or mS cm^{-1}) can theoretically be converted to ppm (mg/L) by multiplying by 640. However, empirically, 700 seems to provide more practical information. Results for nitrate-N, phosphorus, potassium, calcium and magnesium are reported as mg/L of extract. Nutrient balance is determined by calculating the percent of total soluble salts for each nutrient as follows:

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

$$= \frac{(\text{mg/L})\,(100)}{(\text{mg/L})}$$

$$\text{Total soluble salt conc.} = \text{electrical conductivity} \times 700$$

Interpretation

Desirable pH, soluble salt and nutrient levels vary with the greenhouse or nursery crop being grown and management practices. The general guidelines given in Table 1 can be used in making a preliminary judgment of the results obtained with either the water or DTPA saturation extracts. When using the DTPA Extraction Method, the generally adequate ranges for key micronutrients are: boron, 0.7 to 2.5 mg/L; iron, 15 to 40 mg/L; manganese, 5 to 30 mg/L; and zinc, 5 to 30 mg/L. The specific desirable levels vary with the crop being grown.

Table 1. General interpretation guidelines* for greenhouse growth media analyzed by the Saturated Media Extract Method.

Analysis	Low	Acceptable	Optimum	High	Very High
Soluble salt, dS/m	0-.75	.75-2.0	2.0-3.5	3.5-5	5.0+
Nitrate-N mg/L	0-39	40-99	100-199	200-299	300+
Phosphorus mg/L	0-2	3-5	6-10	11-18	19+
Potassium mg/L	0-59	60-149	150-249	250-349	350+
Calcium mg/L	0-79	80-199	200+	-	-
Magnesium mg/L	0-29	30-69	70+	-	-

*These guidelines are suitable for use with results obtained by either water or DTPA extraction.

Desired nutrient balance is to have 8 to 10 percent of the total soluble salt be nitrate-N, less than 3 percent ammonium-N, 11 to 13 percent potassium, 14 to 16 percent calcium and 4 to 6 percent magnesium. If chloride and sodium are determined, their percentage should each be less than 10 percent.

Adjustments in available nutrient levels can be made by the following additions (12, 13, 15); 75 g calcium nitrate (15-0-0) per cubic meter (2 oz./yard^3) to increase the test level 10 ppm N; 600 g (0-46-0) per cubic meter (1 lb./yard^3) to increase the test level 5 ppm phosphorous; and 55 grams potassium nitrate per cubic meter (1.5/yard^3) to increase the test level 10 ppm K.

Modified Spurway Procedure

Modified Spurway Procedures can be used to analyze greenhouse root media if care is taken in the handling process. Care must be taken not to alter the growth medium composition through grinding and/or sieving. Diagnostic sample size should be adequate to minimize error due to sample variability. A minimum size sample is 5 cc. A larger size sample is desirable, but becomes more difficult to extract. Before analysis, the root media is allowed to air dry.

A Typical Spurway Procedure

Extract 5 cc (1 tsp) sample with 25 mL of 0.018 M acetic acid (Spurway active extraction solution). Shake the sample for 1 minute and filter. Analyze this extract using suitable methods and standards. Some labs have modified this approach by using extractants similar to those used for field soils. Sample-to-solution ratio and shaking time have also been adjusted by some labs. Each modification necessitates a change in interpretation guidelines.

Determine pH using one part growth medium to one part distilled water on a volume-to-volume basis. Determine soluble salt content on a volume-to-volume basis using a 1:2 or 1:5 root medium-to-water ratio.

Bulk density must be determined to aid in interpretation of the results. When expressed in mg/kg, the acceptable test levels are higher for growth media of low bulk density. Determine bulk density by filling a 100 mL graduate cylinder with the growth media and tapping the cylinder firmly on the bench top five times. The volume is recorded and the sample weighed. Bulk density equals weight divided by volume and is expressed in g/cm^3.

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Chapter 15

Laboratory Quality Assurance Program

B. Hoskins and A. Wolf

A quality assurance (QA) program is necessary at some level in all laboratories to document analytical uncertainty and to promote confidence in analytical results. QA can be divided into two parts: quality control and quality assessment. Quality control (QC) is comprised of those lab practices which are undertaken specifically to achieve accurate and reliable analytical results. Quality assessment is comprised of those processes undertaken to monitor and document the effectiveness of the QC program. A regular assessment of QC will document both accuracy (closeness to the known or expected value) and precision (agreement or repeatability of multiple results for the same sample) (2). Accuracy and precision, together, characterize analytical uncertainty.

A QA program will add additional time, effort and cost to any lab operation. This additional overhead should be more than offset by an improved ability to pinpoint problems early, resulting in a streamlining of operations. An effective QA program will also improve customer satisfaction with analytical results. The relative cost-to-benefit ratio of individual QC components or techniques should be considered when implementing or modifying a QA program (2).

The scale of a QA program should be in proportion to the scale of the lab operation and to the end-use of the analytical results. It is not the purpose of this chapter to delineate QA standards for all laboratories. Specific QA program components and guidelines should be determined internally within each lab operation, with input from and participation by all lab personnel.

The purpose of any soil testing laboratory is to provide a consistent index of soil fertility and to identify soil properties which may affect plant growth or potentially harm the environment. The end-use for this information may not be the same in all cases. The accuracy and precision needed to generate consistent lime and fertilizer recommendations may be different than that needed for the purpose of regulating trace element application from municipal sludge, for example. In any case, there should always be a concerted effort to provide the best quality analytical results possible from the lab resources available.

Components of a Quality Control Program

A good QC program includes documentation, training, and implementation of good laboratory practices (GLP) and procedures. Many of the QC procedures suggested here may already be in use or require only slight alterations of existing processes used in most laboratories. This chapter does not include a complete listing of GLP or QC program components, but is intended to address common operational problems and practices affecting analytical accuracy and precision.

First of all, a complete listing of standard operating procedures (SOP) is always a good practice. As cited in Chapter 1 on soil sample preparation, slight alterations in soil testing procedures can cause surprisingly large differences in the final results. A detailed description of all steps in sample preparation, extraction, calibration, solution preparation, and instrument setup/operation/maintenance, down to minor details, can help minimize analytical uncertainty. Quality assessment methods and expectations can also be included within SOP, spelling out what types of reference samples are to be run, at what frequency, and with general guidelines for allowable ranges of results. Numbers and frequency of reagent blanks (see below) should be specified within applicable SOP. Documentation of SOP is also required by many contractors, as well as by most laboratory certification agencies.

Sample preparation and, where applicable, solution analysis procedures within SOP should be referenced wherever possible to published standard methods to demonstrate method conformity and to inform customers of the exact methodology in use. One of the purposes of this bulletin is to provide a methodology reference for all soil testing laboratories in the North Central Region.

A second useful QC technique, which can especially benefit new employees, is a written summary of known sources of error in the lab operation. These include, but are certainly not limited to, the examples listed in Table 1.

Table 1. Known sources of error in soil testing labs.

Example Source of Error	Corrective Action
Segregation or stratification of soils in storage.	Rehomogenize before sub-sampling for analysis.
Sample or equip. contamination by lab environment.	Store samples, reagents, equipment separately.
Sample carryover on extraction vessels or apparatus.	Rinse with cleaning solution between samples.
Samples weighed,processed or analyzed out of order.	Run known reference sample at regular interval.
Inaccurate concentrations in calibration solutions.	Check new standards against old before use.
Sample or calibration solution matrix mismatch.	Make up standards in extracting solution used for soil samples.
Drift in instrument response	Use frequent calibration/QC checks.
Poor instrument sensitivity or high detection limits.	Optimize all operating parameters.
Faulty data handling or human transcription errors.	Proofread input, automate data transfer.

Keeping a log of known errors encountered over time, some of which may be peculiar to a specific apparatus or process, can be an invaluable tool when troubleshooting laboratory problems. An error log also promotes continuity within a group or succession of technicians/operators, as well as more consistent operation over time for any individual technician.

A third laboratory practice, often overlooked, is the inclusion of process or reagent blanks. One or more empty sample containers are carried through the entire preparation process, with all extractants or other reagents added. The final solution is analyzed in the same manner and for the same analytes as prepared solutions from actual samples. Blanks can be run at regular intervals or only on occasion, depending on whether the blank concentrations are significant (or even above detection limits). Blanks are more likely to be significant for those analytes present at relatively low concentrations, as in micronutrient or trace element analysis.

The blank(s) will quantify the contribution of containers, reagents and the laboratory environment to the elemental concentrations of the final solutions. Any significant and consistent blank values are subtracted from the solution concentration values for each of the analytes in samples run in association with the blank(s). Blank subtraction is meant to be used to correct for systematic sources of contamination, not random ones. Groups of process or reagent blanks can also be used to calculate effective detection limit, defined as three times the standard deviation of the blank values for each analyte (3). Blanks should be run at regular intervals until valid mean and standard deviation statistics can be generated and a determination made as to whether blank values are significant and constant. Blank values should be rechecked after any major change in procedures or reagents.

Quality Assessment

The second part of a QA program is quality assessment. Quality assessment checks the effectiveness of the QC practices used in the laboratory, and is used to determine if an analytical process is meeting QA guidelines. Quality assessment is achieved through systematic documentation of accuracy and precision.

Documenting Accuracy

Accuracy of analytical results can be documented by analyzing reference samples of known content. A reference sample is a bulk, homogenized sample which is as similar as possible to the routine samples being tested. Several standard reference materials (SRM) can be purchased from commercial or government sources, such as the National Institute of Standards and Technology (Standard Reference Materials Catalog, NIST Special Publication 260, Gaithersburg, MD 20899-0001). SRMs typically have a certified analysis (with a range of uncertainty) of the elemental content for several analytes. Analysis of an SRM is considered the most unbiased way to document accuracy in a laboratory QA program (1). There are several drawbacks, however. SRMs are quite expensive and typically of limited volume. Many analytes of interest will not be reported or are reported, but not certified. SRMs usually do not list extractable or "available" content based on soil fertility testing methodology. Those reference soils which are available are typically guaranteed for total content only.

An alternative to purchasing a reference sample is to become enrolled in one or more proficiency testing or sample exchange programs. In these programs, subsamples of bulk, homogenized soils are sent to all cooperating laboratories, which analyze them by specified methods and protocols. Analytical results for soil fertility testing methods which are not typically reported for purchased SRMs can be obtained in this way. Mean (or median) values and standard deviations (or mean absolute deviations) are determined and reported for each analyte and for each method, based on the data returned by participating labs. While this does not constitute a certified or guaranteed analysis, the mean values obtained from several laboratory sources can be considered closer to the "true" values than results derived solely from one lab-

oratory. Similarly, the relative accuracy of a laboratory's own internal reference sample can be evaluated by having subsamples analyzed by other laboratories using the same methodology. Proficiency testing programs are available through the Soil and Plant Analysis Council (Georgia University Station, P.O. Box 2007, Athens, GA 30612-0007) and through the International Soil Exchange Program (P.O. Box 8005, 6700 EC Wageningen, The Netherlands) at a reasonable cost.

Many smaller sample exchange programs occur within soil testing work groups, regions or states. However, small scale exchanges can suffer from poor statistical control due to the relatively small number of contributing laboratories.

Documenting Precision

Precision of analytical results can be documented through replicate testing of routine samples or by routine analysis of internal reference samples. Replicate analysis typically involves two or more analyses of routine sample unknowns at some specified frequency, such as every fifth or every 10th sample. The frequency of replication should be determined by balancing the additional time/effort/expense incurred with an adequate ongoing documentation of precision. A relatively high frequency of replication should be used initially. Replication frequency can be reduced after the minimum number of replicates has been generated to produce valid statistics (see R-Chart section) and once QA precision standards for the method are being met. Replicate analysis is especially useful where appropriate reference samples are unavailable (2). Since actual sample unknowns are being used, the final solution matrix and the concentration ranges of each analyte will automatically match those of the samples being run. Matrix and concentration range mismatch can be a concern when running internal or external reference samples (1). Since all analytical results are generated internally, no determination of accuracy is provided by the use of sample replication.

An alternative or supplement to replicate analysis is to run internal reference sample(s). An internal reference is typically a bulk, homogenized sample, subsamples of which are run at regular or irregular intervals in the routine sample stream. Bulk samples can be prepared relatively easily and with minimal expense. It is important that the bulk sample be sieved and thoroughly homogenized before use and remixed at regular intervals (ie.,weekly) to prevent sample stratification. Internal reference samples are usually the first line, daily QC check in most laboratories. Since all analytical results are derived internally, an internal check sample can only legitimately be used as a precision check.

General Considerations

Quality assessment samples can be run with the full knowledge of the technical staff or as single or double blind samples. Check samples of known composition run at known intervals can be used by technicians to monitor the quality of analytical results as they are being produced. A blind sample is known to the technical staff as a check sample, but the composition is unknown. A double blind sample is completely unknown to the technical staff and eliminates the possibility of bias in results from knowing the location or composition of the check sample. Blind and double blind samples are best reserved for formal QC appraisals (3).

By consistently running internal check samples and occasionally running an SRM and/or sets of exchange samples, statistical control of both precision and accuracy can be adequately documented at the least cost (1).

Statistical Control

Descriptive statistics used to quantify a laboratory QA program can be presented in a variety of ways, not all of which will be described here. Accuracy is measured in terms of the deviation or relative deviation of a measured value from the known or certified value. Precision is presented in terms of standard deviation (SD) or relative standard deviation (RSD) from the mean of repeated measurements on the same sample. Together, accuracy and precision document the systematic and random errors which reflect the analytical uncertainty in laboratory results.

Besides documenting uncertainty, descriptive statistics from an established QA program can be used for other purposes. Accuracy and precision statistics are the performance criteria used to determine if a methodology is in "statistical control" (that is, whether quality assurance standards are being met over the long term). Check sample statistics can also be used by technicians and managers as daily decision-making tools during sample analysis to determine if expected results are being generated and if the analytical system is functioning properly at any given time. Determining that a problem exists at the time it is happening can save a great deal of lost time in running samples over again at a later date (1).

X-Charts

Quality assessment statistics can be presented graphically through control charts for ease of interpretation. X-charts can be used to present both accuracy and precision data. Repeated measurements of external or internal reference samples are graphed on a time line. A minimum of seven measurements is

needed, though 15 are recommended for valid statistical calculations (3). Superimposed on the individual results is the cumulative mean (in the case of an internal reference sample) or the known value (in the case of an external SRM or exchange sample). Control levels which typically represent plus or minus 2 SD (upper and lower warning limits, UWL & LWL) and plus or minus 3 SD (upper and lower control limits, UCL & LCL) from the mean are also superimposed (see Figure 1). In a normally distributed sample population, plus or minus 2 SD represents a 95 percent confidence interval (CI) and plus or minus 3 SD corresponds to a 99 percent CI.

An individual value between UWL and UCL or LWL and LCL is considered acceptable, though two or more in a row are unacceptable. A single value outside UCL or LCL is considered unacceptable. If statistical control is considered unacceptable based on either standard, all routine sample unknowns between the unacceptable check sample(s) and the last check sample which was in control should be rerun. Check sample results which fall within the warning limits, but which are exhibiting a trend toward the UWL or LWL, can signal a potential problem in the process which needs to be addressed (1). X-charts are especially useful as a day-to-day tool to monitor for ongoing or emerging problems. It should be recognized that the above control limits are guidelines based only on statistical analysis of a normally distributed sample population. Depending on the required or desired accuracy for the specific analysis, the analyst may want to vary these accordingly.

R-Charts

Another graphical display is the R-chart or range chart. When two or more replicate analyses are run on a routine sample or a reference sample, the difference between the lowest and highest values in a set of replicates (or just the difference between replicates when there are only two) is called the replicate range. The R-chart maps individual replicate ranges for a given analyte over time. The replicated samples should ideally be within an acceptable total range of concentration for the same analytical process or methodology (1). A cumulative mean range is calculated and superimposed on the individual range values. Warning and control limits are calculated as 2.512 times (95 percent CI) and 3.267 times (99 percent CI) the mean range (3). Since replicate ranges are all positive values, only one warning and control limit are displayed (see Figure 2). Since R-chart data consist solely of replicate ranges, they can only be used to document precision. A minimum of 15 replicated samples is recommended for producing an R-Chart (3)

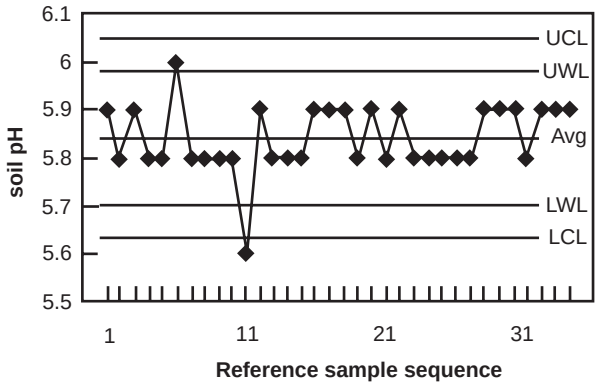

Figure 1. Typical X-chart used in a QA/QC program.

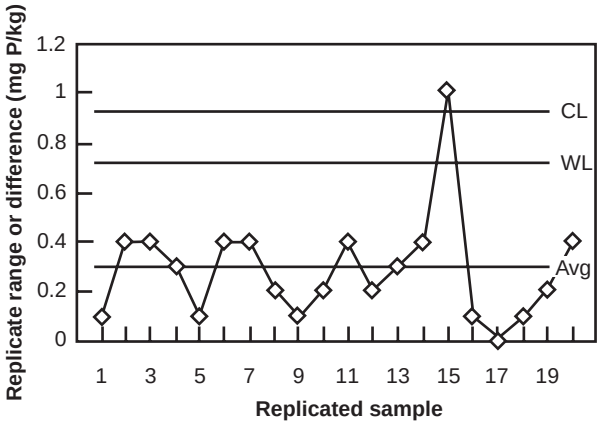

Figure 2. Typical R-chart used in a QA/QC progarm.

QA Statistical Standards

Since warning and control limits are calculated from cumulative statistical data, new quality assessment data are always viewed relative to past performance. Cumulative statistics effectively characterize the inherent capability of a laboratory operation to execute a given methodology. The purpose of quality assurance is not to enforce acceptable precision as much as to delineate attainable precision (3)

For instance, accuracy and precision are expected to be relatively poor in those cases where the level of an analyte is close to the detection limit for the instrumentation available. Realistic QA standards for accuracy and precision in any lab must take this inherent capability into account. Once attainable standards are determined, they should be used to maintain consistent analytical quality. QA standards should be re-evaluated when methodologies are changed or modified and as analytical capabilities are improved.

Recommended Reading

For a more thorough coverage of QA/QC, including statistical analysis, planning, documentation and control charting, the books by Garfield (1991) and Taylor(1992) are highly recommended.

References

1. Delavalle, N. B. 1992. Handbook on reference methods for soil analysis. Quality assurance plans for agricultural testing laboratories: p. 18 - 32. Soil and Plant Analysis Council, Inc. Athens, Ga.
2. Garfield, F. M. 1991. Quality Assurance Principles for Analytical Laboratories. Association of Official Analytical Chemists. Arlington, Va.
3. Taylor, J. K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Inc. Chelsea, Mich.

Glossary of Terms

A

Acid Soil – A soil with a pH below 7.0. The degree of acidity increases as the pH decreases.

Alkaline Soil – A soil having a basic reaction with a pH above 7.0

Anion – A negatively charged atom or combination of atoms; e.g., Cl^-, CO_3^{2-}, NO_3-, SO_4^{2-}

Available Soil Nutrients – Soil nutrients in chemical forms accessible to plant roots or compounds likely to be convertible to such forms during the growing season.

C

Calcareous Soil – A soil having a pH above 7.0 that effervesces when a drop of 6 M HCl is placed on it.

Cation – A positively charged atom or combination of atoms; e.g., Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+, H^+, Mn^{2+}, Zn^{2+}.

Cation Exchange Capacity – The capacity of a soil to adsorb cations on the negatively charged colloids of the soil expressed in milliequivalents per 100 grams or cmol+ charge per kilogram.

Chemical Extractant – An aqueous solution of one or more chemicals used to extract plant available nutrients from soil.

Composite Soil Sample – A soil sample consisting of several single core samples taken to a specified depth that, mixed together, represents a given area to that specified depth.

E

Extractable Soil Nutrients – Plant nutrients that can be removed from the soil by a specified chemical extractant.

L

Lime Requirement – The quantity of liming material required to increase the pH of a specified depth or volume of soil to a desired level to eliminate the adverse effects of soil acidity on plant growth.

N

Nutrient Soil Test – A procedure used to extract one or more nutrients from soil to estimate the level of plant available nutrients in a soil sample using a chemical extractant.

P

Parts Per Million (ppm) – Indicates the number of units of an element or compound contained in a million units of soil.

S

Saline Soil – A soil containing enough soluble salts to impair plant growth, usually greater than 4 dS/m of electrical conductivity in a saturation extract.

Saline/Sodic Soil – A soil containing a sufficiently high combination of both salts and sodium to impair plant growth.

Saturated Soil Paste – Soil containing sufficient water to saturate the sample without the presence of any free water on the surface of the soil/water mixture. A saturated soil paste will glisten in light and flow slightly when tipped.

Saturation Extract – Solution drawn by vacuum from a saturated soil paste.

Sodic Soil – A soil containing enough exchangeable sodium to affect its properties and impair plant growth, usually greater than 15 percent of the exchangeable cations.

Soil Buffer Capacity – Relative ability of a soil to resist change, usually in pH when acidic or basic materials are added.

Soil pH – A measure of the hydronium ion (H_3O^+) or, more commonly, the hydrogen ion (H^+) activity in the soil solution.

Soil Sampling– The procedure of collecting a portion of soil from a field that is representative of an area and to the same depth used in calibration of a soil test.

Soil Test Calibration – A two stage process to: 1) determine the agronomic meaning of a soil test index value in terms of a particular crop response, and 2) establish the amount of nutrient element required for specific crops within each test category to achieve optimum yield.

Soil Test Correlation – The process of determining the relationship between plant nutrient uptake or yield and the amount of nutrient extracted by a nutrient soil test. This procedure is used to select a suitable chemical extractant.

Soil Test Interpretation Category – An interval of soil test values associated with the corresponding probabilities of response by specific crops to nutrient applications.

Soil Test Critical Level – The concentration of an extractable nutrient above which a yield response to added fertilizer would be unlikely for a particular soil test method.

Soil Test Interpretation – The process of developing nutrient application recommendations from soil test levels and other soil, crop and climatic conditions.

Soil Test Value – The amount of a nutrient extracted with a given soil test procedure and expressed as a concentration or index. Its relative level is determined through the process of soil test calibration.

T

Total Soluble Salts – Total soluble anions and cations in a soil, usually measured by conductivity in a soil/water suspension or extract.

W

Working Standard Solutions – A set of solutions of known elemental concentration used for calibrating an instrument to determine the element concentration in unknown soil extract solutions.

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