Soil Testing

A Guide for Conducting Soil Tests in Missouri

Missouri Cooperative Extension Service
University of Missouri-Lincoln University

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Soil Testing in Missouri

A Guide for Conducting

Soil Tests in Missouri

by
J.R. Brown
R. R. Rodiguez

Preface

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

In 1977, Extension Circular 923, *Soil Testing in Missouri*, was published to replace Station Bulletin 734. Changes in soil testing methods have occurred since 1977 that necessitates revising EC923. This new edition deletes the procedures used in the county labs.

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

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Introduction

Soil testing is a process or group of procedures used to estimate the ability of a soil to supply plant nutrients. The results of tests made on a soil sample should enable testers to evaluate the fertility needs of the soil represented by that sample.

The evaluation of the fertility level of a soil can be used to make recommendations for fertilizer and lime practices. These recommendations should be the most economical combinations of fertilizer and lime needed to reach the crop production goals set for the field. In addition, the soil tests can be used to find excesses of certain nutrients.

An example of the process of soil test evaluation, including an elementary economic evaluation, can be found in Missouri Agricultural Experiment Station Research Bulletin 1007, *Some Considerations Regarding Soil Test Interpretations for Phosphorus and Potassium,* (1974) by T.R. Fisher (2).

The soil testing process consists of

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

Steps in Testing Samples in Missouri Soil Labs


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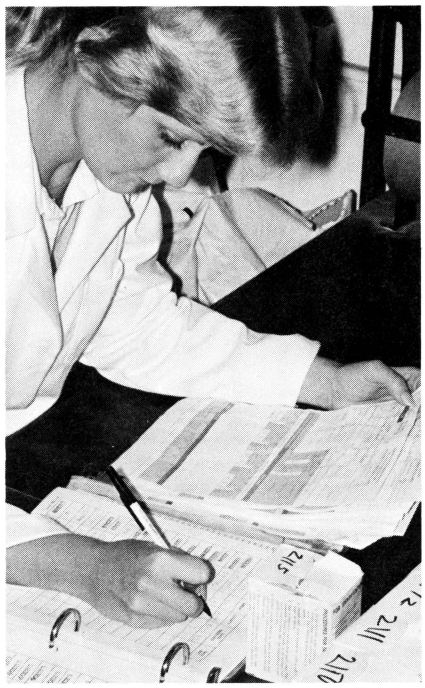
begin when the soil sample arrives at the lab. (1) The soil sample is logged in and assigned a laboratory number on a sheet that accompanies the sample through the lab (right). (2) The sample (above) is transferred to a drying container, then it is placed into an oven for drying.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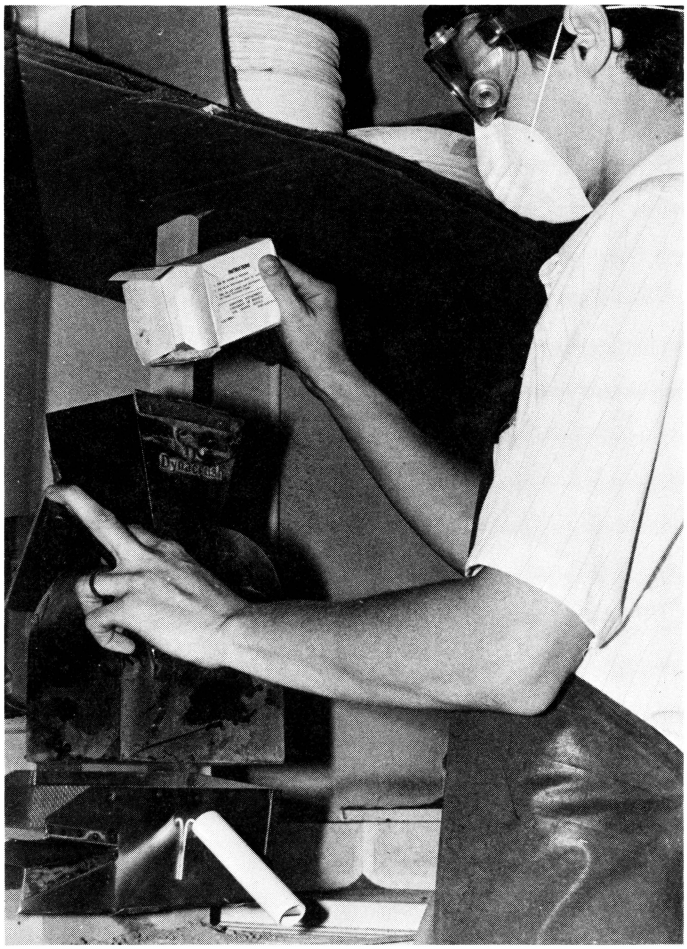
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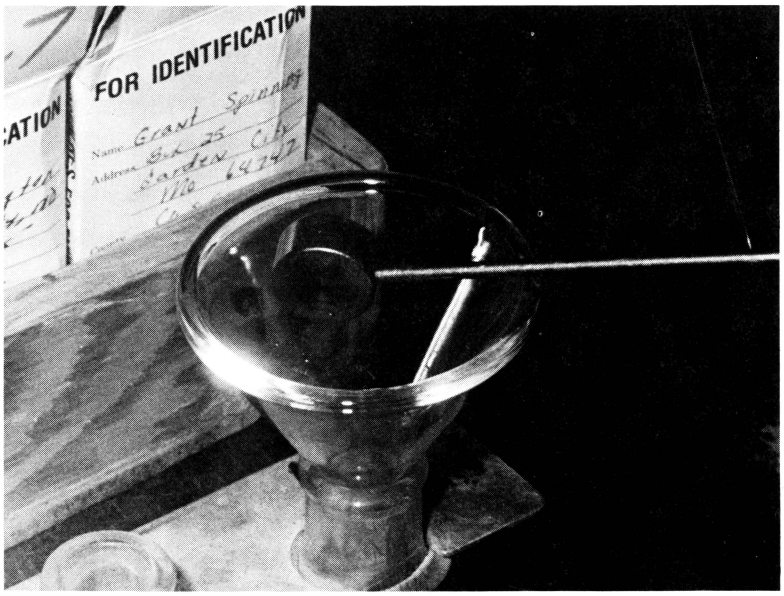

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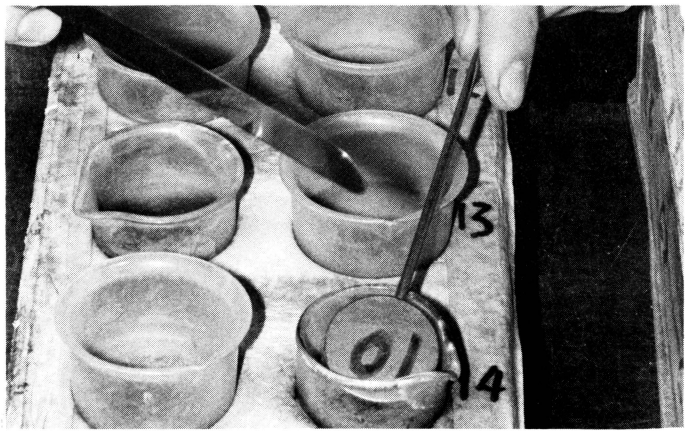
(3) The sample (above) is dried, then ground fine enough to pass through a 10 mesh screen. (4 & 5) The amount of soil required for testing is transferred to appropriate extraction containers.



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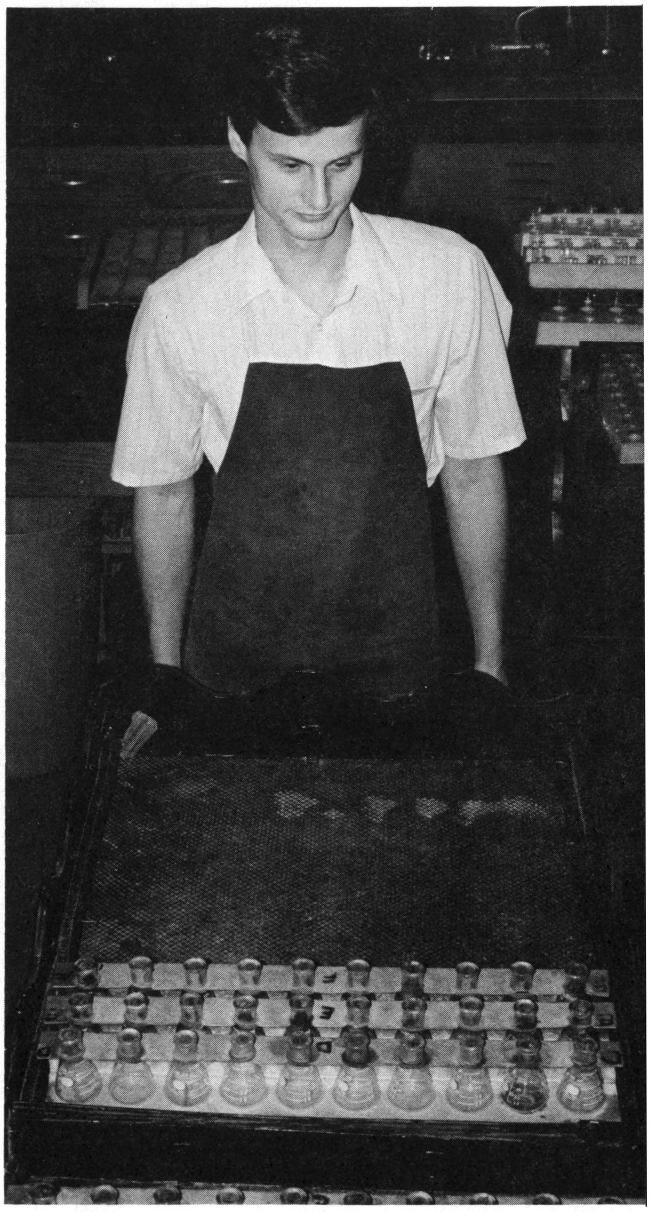
Sampling

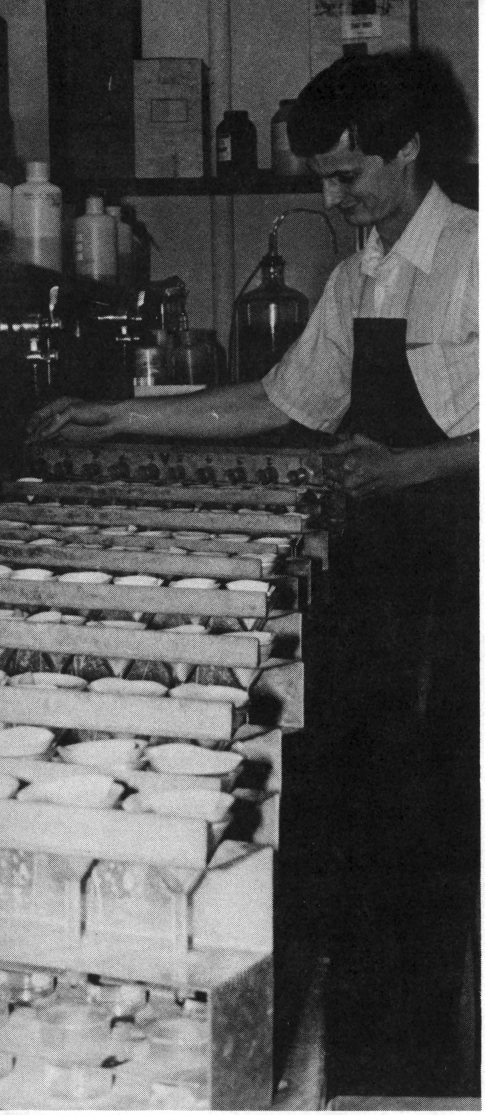
The two weakest links in a soil testing program are sampling and calibration of the test to field response. The first of these weak links is discussed in this section and the second is covered starting on page 14, "Evaluation of Tests".

A soil sample should be representative of an area. A sample from most Missouri fields should represent no more than 20 acres. Before a soil sample is taken, a field should be divided into uniform areas based upon past management, surface soil color and texture, and slope. Once the field is divided, 10 to 20 cores should be taken at random over the area. These are placed into a clean pail and mixed. The sample or a part of the mixed sample is placed into a clean soil sample bag or box. The sample should be clearly identified by number on the sample container and on a field map.

(6) The extracting reagent is automatically dispensed into the flask.



(7) The soil-extractant mixture is shaken for a specified time.



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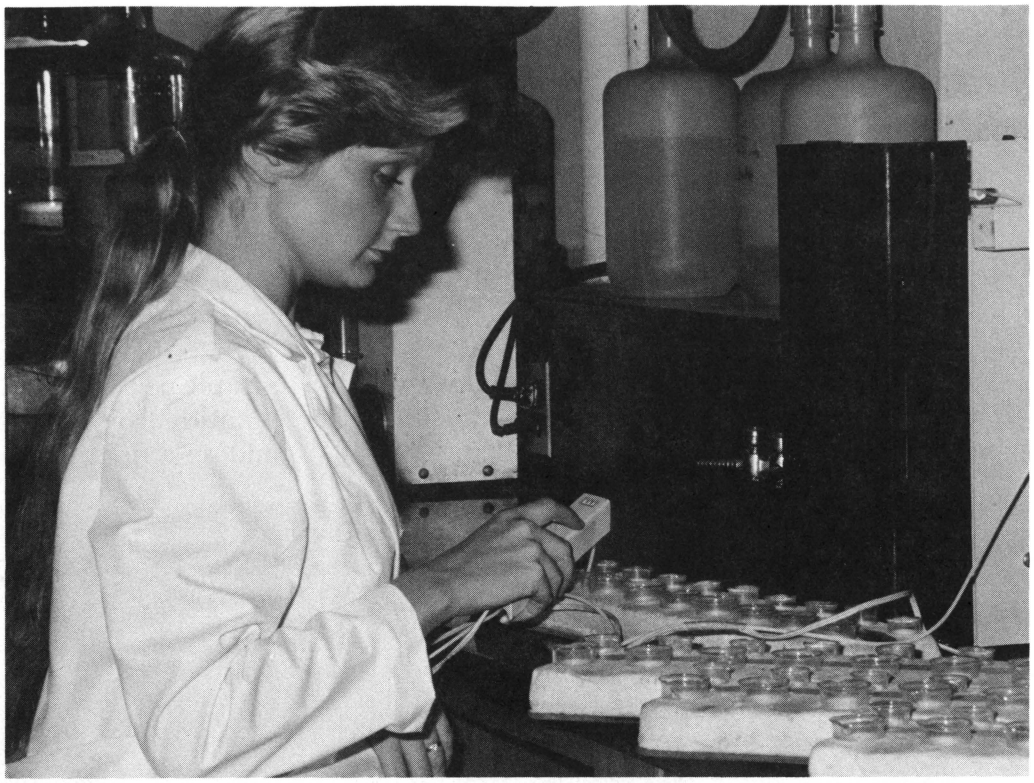

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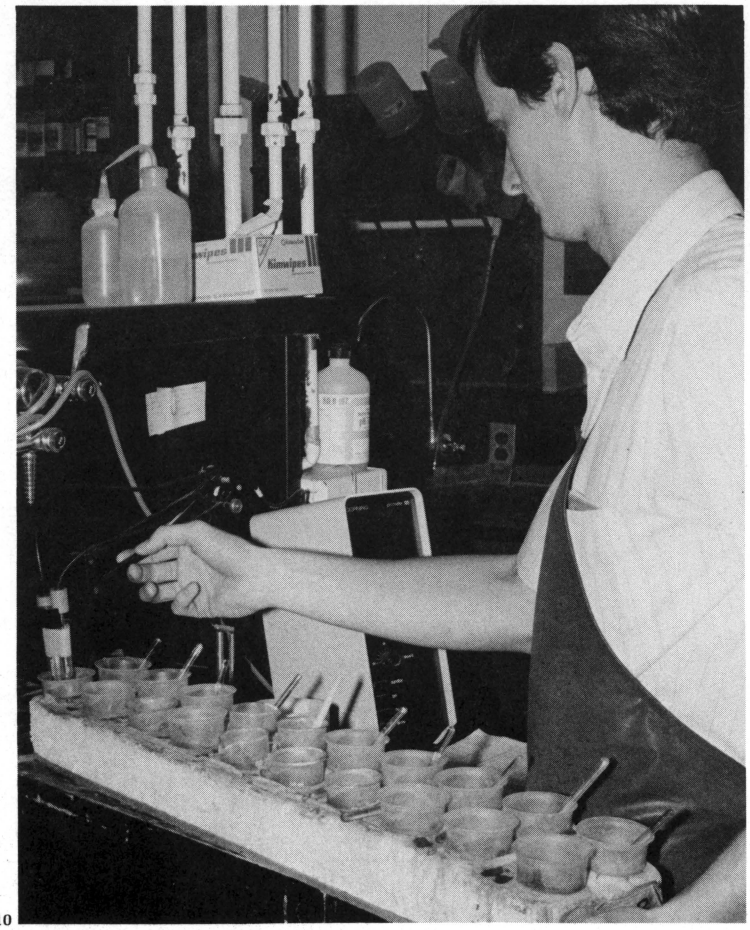
(8) The soil-extractant suspension is filtered. (9) The soil extract is diluted with appropriate reagents to determine the nutrient content. (10) An atomic absorption, flame emission spectrophotometer is used to determine the calcium, magnesium, potassium and micronutrient concentrations in the diluted soil extract.



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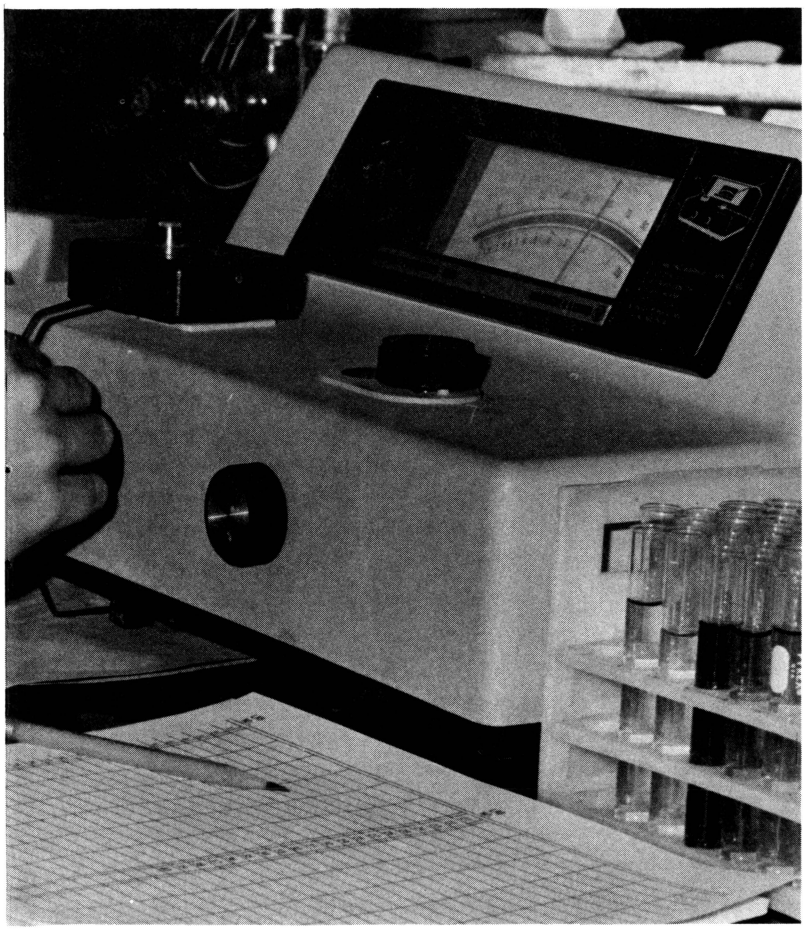
If the sample is not taken to a University of Missouri Extension Center the day it is collected place it in a dust free location and keep the container open to allow the sample to dry while sitting. More details on sampling soils can be obtained from UMC Guide 9075 (3).

Sample Preparation

A representative soil sample and an accurate information sheet are necessary for reliable recommendations of fertilizer practices.

The sample should be taken to a local University of Missouri Extension Center. At the Center, an information sheet is filled out for each sample and a testing fee is collected.

The information sheet can be almost as valuable as the sample. The past management history and the intentions for future crops both enter into the evaluation of the soil test.



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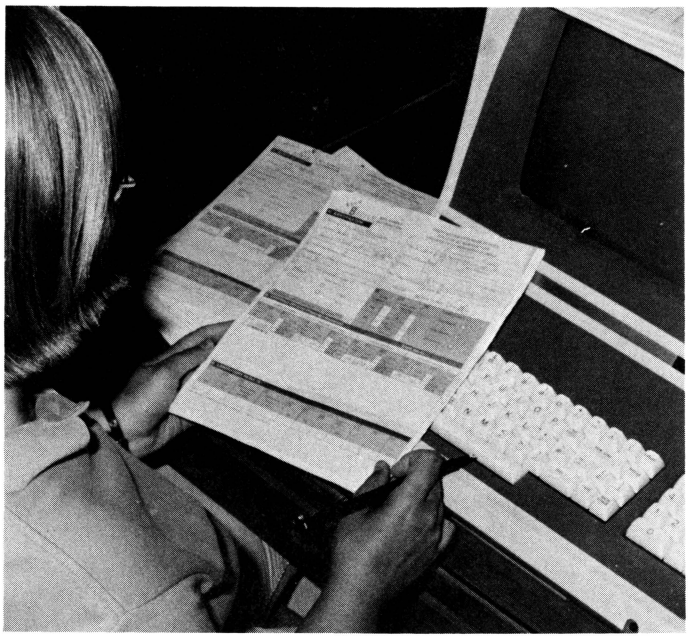
The sample and the information sheet are sent to the soil testing laboratory where the sample is dried at low heat (less than 85° F) and ground to pass through a 10 mesh screen.*

Samples with considerable chert or other stones are handled separately. The soil tests are made on the stone-free soil material.



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(11) Soil acidity and lime requirement are determined with a pH meter. (12) Concentration of phosphorus and the organic matter in the soil extract is determined colorimetrically on a spectrophotometer. (13) Results are recorded and sent to a computer center. Data are evaluated by computer. Field information, soil test results and lime and fertilizer recommendations are printed on a report form and sent to the grower.

*Drying the sample is for convenience in handling. Soil scientists agree that tests of field-moist samples should give a better reflection of the true nature of the soil fertility level.

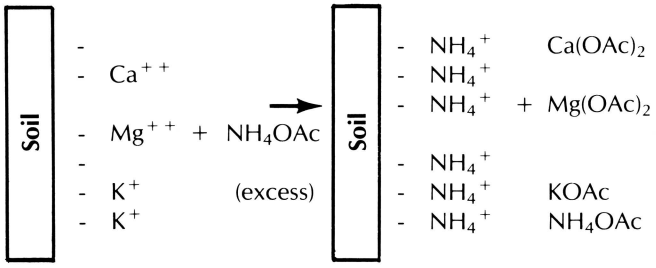
Extraction

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

Phosphorus exists in the soil in the orthophosphate form as $H_2PO^-_4$, HPO^{-2}_4 or PO^{-3}_4. The first two phosphate anions dominate in most soils unless a soil is extremely acid. An acid ammonium fluoride extractant is used to extract from the soil acid soluble phosphate as well as that which is water soluble. The fluoride ion in the solution tends to tie up calcium to prevent reprecipitation of calcium phosphate.

The concentration of phosphorus in the soil extract is determined by colorimetry. The extract is treated with an acidic molybdate solution to form a blue phosphomolybdate complex. The intensity of the blue color which develops is proportional to the amount of phosphorus extracted from the soil. A set of standards of known phosphorus concentration is used for comparison. The intensity of the blue color is determined on a spectrophotometer by measuring the transmittancy for light of a specific wave length. The transmittancies (or optical density) of the standards are plotted on graph paper against the phosphorus concentration to form a standard curve. The transmittancy of each soil extract is then compared to the standard curve to determine the phosphorus concentration in the soil extract. Then, by calculation, the estimate of available phosphorus, in pounds of P or of P_2O_5 per acre, is made.

An ammonium acetate extracting solution is used to remove exchangeable potassium (K), calcium (Ca) and magnesium (Mg) from the soil samples as shown schematically in the following equation:



The ammonium ions exchange for ions such as calcium ions, held on the soil particles. The replaced ions go into solution as the acetate.

The potassium concentration in the ammonium acetate soil extract is determined by flame emission (or in some cases by atomic absorption). The extract sample is placed in a flame which excites the potassium atoms. When the potassium atoms leave the flame they loose excitation energy and this energy is emitted in a wave length of light characteristic of potassium. The amount of light emitted is measured by an instrument. This emission is proportional to the amount of potassium in the sample. Standards of known potassium concentration are used to relate the light emitted to concentration by means of a standard curve.

Calcium and magnesium in the soil extract are determined by atomic absorption. This technique uses a flame to place the calcium and magnesium atoms in the proper chemical form and position. A beam of light is passed through the flame. This beam of light is of a preselected wave length (monochromatic). Calcium and magnesium atoms each absorb light of a specific wave length. The amount of light absorbed, measured by the instrument, is directly proportional to the quantity of calcium or magnesium atoms present in the flame. Standards of known concentration are used to relate the amount of absorption to the ion concentration. Calcium, magnesium, and potassium are reported in pounds per acre.

pH and Acidity Determination

The degree of acidity of a soil has great impact on the availability of nutrients, both those already in the soil and those applied in fertilizer. Most soil testing systems include a determination of soil acidity.

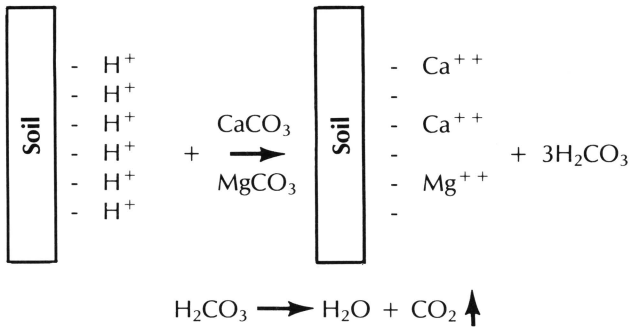
In the Missouri testing program the soil pH is determined in 0.01 M $CaCl_2$ solution. It is assumed that fertilizer will be used on the soil. Most fertilizers are salts that go into solution when applied to the soil. Plants growing on that soil will contact the dilute salt solution, hence it is logical to estimate the acidity plants will contact, rather than an estimate of pH using distilled water and soil. An additional argument for using salt pH is that natural biological activity causes seasonal shifts in soil pH when measured in water. The 0.01 M $CaCl_2$ masks these shifts, giving a fertile soil pH.

The pH determination (salt pH or pH_s) is a measure of the activity of hydrogen in the soil solution. Formally defined,

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

where a_H is the activity of H in soil solution. In strongly acid soils (pH_s<4.5) aluminum affects the system and becomes detrimental to crop root development as the pH decreases. For a detailed discussion of soil pH see the book edited by Pearson and Adams (4).

The pH measurement refers only to the *active acidity* (soil solution acidity). To neutralize the acidity of an acid soil, the *reserve acidity* as well as the active acidity must be neutralized. Reserve acidity is that acidity held on the soil particles and it may be removed by the calcium and magnesium in limestone. The acidity (hydrogen) is then removed from the soil. The classical "liming reactions" are:



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

A sample of soil is placed in a container with the specified quantity of 0.01 M $CaCl_2$. A given quantity of the Woodruff buffer is added. After a period of equilibration the pH is measured. The buffer, when added, is at pH 7.0. As it reacts with the acid soil the pH drops to a stable value which is measured as pH_B. Each 0.1 unit drop is equivalent to 1 me H per 100 grams of soil if the soil solution ratio is not altered from that given in the detailed procedures (page 29). That is:

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

Evaluation of Tests

Tests for plant nutrients are estimates of the ability of the soil to provide nutrients for a growing crop. For soil tests to be useful, they must be calibrated to field response.

This calibration is done through field experiments and statistical evaluation of the resulting data. Plots are selected with different soil test levels. The plots are subdivided and several rates of a plant nutrient are applied. Study crops are grown and yields are determined. The data obtained will give yields at a soil test level without fertilizer and the amount of yield increases (or decreases) for each rate of fertilizer. The degree to which the fertilizer changes the soil test also is measured. The more data of this type that are collected, the more reliable the soil test becomes as a basis for fertilizer recommendations.

Field research and data collection are continuing processes. Each new soil test goes through this calibration process for it to be a useful basis for making fertilizer recommendations. The calibration must be done on soils with some degree of deficiency in the nutrient being studied.

The calibration data are evaluated and a set of fertilizer response equations is developed. The equations form the basis of the computer program used to make the recommendations printed on the Soil Test Report Form.

Procedures

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

Most of the procedures listed were evaluated by T. R. Fisher and J. Garrett prior to incorporation, in 1968, into the Delta Area Regional Soil Testing Laboratory. Modifications have been made in the analysis. Based upon recent work, the DTPA soil test for micronutrients has been added. Some procedures differ slightly from reference or standard procedures (6, 7).

Soil testing has evolved over time, and the tests have been calibrated against field and greenhouse results. Before a modified test is adopted, that modification is evaluated and calibrated using field results.

In this bulletin, there is a reference section at the end of the description of each procedure. These references will not be included in the

general literature cited section (page 43).

Some procedures in this section are not used in routine soil testing in Missouri but are used in research, or may be used routinely in the future.

The following are routine procedures:

- Readily Oxidizable Soil Organic Matter
- Extractable Soil Phosphorus (Bray I method)
- Ammonium Acetate Extractable Calcium, Magnesium and Potassium
- Soil pH in Salt Solution (pH_s)
- Determination of Neutralizable Acidity (NA)—New Woodruff Buffer Method

Readily Oxidizable Soil Organic Matter

Principle of Method

1.1 The procedure estimates the organic matter of a soil by indirect measurement of carbon oxidized:

$$2H_2Cr_2O_7 + 3C \rightarrow 2H_2Cr_2O_4 + 3CO_2\uparrow$$

Orange Green

The quantity of chromic acid reduced to chromous acid is estimated colorimetrically. The amount of reduction is calibrated to known standards. The method utilizes oven heat to speed the reaction.

1.2 Several methods of wet oxidation are discussed in the references (12.1-12.6). The method described in this section is one developed by DeBolt (12.1) for a large volume of samples. It is designed to process large numbers of samples with a minimum expenditure of chemicals and time.

Range and Sensitivity

2.1 The method is useful for soils up to about 8% organic matter with a sensitivity of 0.1 to 0.2% organic matter.

Interferences

3.1 No detailed determination of interferences has been recorded. The organic matter is incompletely oxidized, hence must be related to standards made from soils of this region.

3.2 The procedure is not recommended for very high organic matter soils or for precise determinations of organic carbon.

Precision and Accuracy

4.1 The method is indirect and is based on comparison to standards of known carbon content as determined by combustion (12.3). A factor of 1.79 x %C is used to provide a percentage organic matter for each standard.

4.2 The digestion reaction is carried at 85°C in an oven. The digestion bottles should be spaced to allow free uniform movement of air in the oven chamber. "Hotspots" in the chamber will affect the results.

4.3 Repeated determination should give a coefficient of variation of less than 10%.

Equipment

5.1 Balance or 1g scoop (NCR-13)

5.2 30 ml bottle, wide mouth.

5.3 Reagent dispenser, 10 ml.

5.4 Automatic dilutor (0.5 ml diluted to 5.5 ml).

5.5 Timer.

5.6 Oven @ 85°C, forced draft.

5.7 Spectrophotometer.

5.8 Spectrophotometer tubes or automatic flow-thru device.

Reagents

6.1 **Digestion Mixture** (0.5M $Na_2Cr_2O_7$ in 11.5N H_2SO_4).

Dissolve 149 g $Na_2Cr_2O_7$ $2H_2O$ in 580 ml distilled water. Add 166 ml of concentrated H_2SO_4 with stirring. Allow to cool and add an additional 154 ml of concentrated H_2SO_4 with stirring. Allow to cool and bring to a volume of 1 liter with distilled water.

6.2 Organic Matter Standards
Two standards are needed. One standard should be from 1.5 to 2.2% organic matter and the other from 4.2 to 5.2% organic matter. Determine the organic carbon content by dry combustion (12.3). Multiply the percentage carbon by 1.79 to obtain the percentage organic matter.

Procedure

7.1 Weigh or scoop 1 g of < 10 mesh soil into a 30 ml bottle. Add 10 ml of the Digestion Mixture (6.1), swirl and place in a preheated oven at 85° C. After 90 minutes remove the heated bottles without stirring and allow to cool for 10 to 15 minutes.

7.2 Dilute 0.5 ml of the supernatant in each bottle with 5 ml of water and dispense into a spectrophotometer tube.

7.3 Read the percentage transmittancy on a spectrometer at 620 nm adjusted to 100% transmittancy with diluted Digestion Reagent.

Calibration and Standards

8.1 The standards (6.2) are to be included in each day's run or whenever reagents are changed, whichever is more frequent. The percent transmittancy of each standard is plotted on the log scale of semi-log graph paper against percentage organic matter to develop a standard curve.

Calculations

9.1 Percentage organic matter is read directly from the standard curve.

9.2 Estimates of organic carbon can be made by: (0.56 x % organic matter).

Storage Effects

10.1 Storage of air dry soil for several months will not affect the organic matter content of soil.

Interpretation

11.1 Interpretations will depend upon the purpose of the analysis. The organic matter contents of soil are used for nitrogen and herbicide recommendations. Appropriate Extension Service and industry guides should be consulted.

11.2 Graham (12.5) discusses one interpretation. The organic matter of a Missouri silt loam soil is about 5% nitrogen. Of this total nitrogen, about 2% will become active in a growing season. Thus, assuming an acre furrow slice (6⅔") weighs 2 million pounds, 1% organic matter may contribute 20 lbs of active nitrogen to a crop.

References

12.1 DeBolt, D. C. 1974. A High Sample Volume Procedure for the Colorimetric Determination of Soil Organic Matter. Comm. in Soil Sci. and Plant Analysis 5:131-137.

12.2 Allison, L. E. 1965. Organic Carbon, Ch 90 *In* Methods of Soil Analysis. C. A. Black, ed. Agronomy No. 9., Part 2. Amer. Soc. Agron., Madison, WI.

12.3 Allison, L. E., W. B. Ballew and C. D. Moodie. 1956. Total Carbon, Ch 89 *In* Methods of Soil Analysis. C. A. Black, ed. Agronomy No. 9, Part 2. Amer. Soc. of Agron., Madison, WI.

12.4 Fisher, T. R. 1968. Procedures for Determining Organic Matter. Univ. of Mo. Dept. of Agron. Mimeo.

12.5 Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. Mo. Agric. Exp. Stn. Bul. 734.

12.6 Council on Soil Testing and Plant Analysis. 1980. Handbook on Reference Methods for Soil Analysis.

Ammonium Acetate Extractable Calcium, Magnesium, Potassium and Sodium

Principle of the Method

1.1 This method utilizes 1N ammonium acetate at pH 7.0 to extract basic cations from the soil. The quantity of extracted basic cations is equivalent to the quantity considered exchangeable. The ammonium ion replaces the basic cations by cation exchange. Ammonium is selected as a replacing ion because of the relatively low levels of exchangeable ammonium in most arable soils, and because the quantity of cations extracted by ammonium acetate reaches a relatively stable quantity after a short period of time. The acetate in suspensions of acid soils tends to buffer the suspension near a desirable level of acidity for most crops, hence the basic cations are determined in such a system.

1.2 See references 12.1, 12.2, and 12.3 for detailed discussions of the method.

Range and Sensitivity

2.1 The procedure described here has a range of 0 to 12,000 lbs Ca/A, 0 to 1200 lbs Mg/A, and 0 to 600 lbs K/A. The range can be extended by dilution of the soil extract.

2.2 The sensitivity will depend on the instrument used and extraction parameters.

Interferences

3.1 If free carbonates of Ca and Mg are present, the extracting reagent may dissolve some of the carbonates. If calcareous soils are extracted, the basic cations in the extract would be termed exchangeable plus soluble or extractable. (12.4.)

3.2 Lanthanum diluent for the atomic absorption spectrophotometer is used to suppress interfering substances in the soil extracts.

Precision and Accuracy

4.1 Extraction aliquots of the same soil sample should give coefficients of variation less than 10%. Samples testing near the upper end of the range will have more variability than those in the mid-to-low end of the range.

4.2 Sample drying tends to change the level of extractable K (usually an increase). However, the physical problems associated with routine testing of moist samples have caused most soil testing facilities to use dried samples.

Apparatus

5.1 Balance or 2 g scoop (NCR-13).

5.2 50 ml Erlenmeyer extraction flask.

5.3 Extracting solution dispenser (20 ml).

5.4 Mechanical shaker, 180 or more oscillations per minute.

5.5 Filter funnel (45 mm top ID).

5.6 Funnel rack.

5.7 Filter paper, Whatman # 2 or equivalent, 9 cm.

5.8 Receiving beakers, 10 to 30 ml.

5.9 Diluter.

5.10 Atomic absorption spectrophotometer.

5.11 Flame photometer (if preferred for K analysis).

Reagents

6.1 Extracting Solution (1N NH_4OAc @ pH 7.0).
Pour 58 ml of acetic acid ($HC_2H_3O_2$), 95.5%, 1.05 sp. gr. into about 500 ml of demineralized water. Add 70 ml of ammonium hydroxide, 0.9 sp. gr., (NH_4OH) and mix. Dilute to a total of about 950 ml and cool. Adjust the pH to 7.0 ± 0.05 with acetic acid or ammonium hydroxide. Dilute to 1 liter with demineralized water.

6.2 Lanthanum Diluent (0.105% La).
Place 1.2314 g lanthanum oxide (La_2O_3), low calcium grade, in a one liter volumetric flask. Add 4 ml of 6 N HCl to dissolve the La_2O_3 and then dilute to one liter with demineralized water.

6.3 Calcium Standards.
The recipe given below is designed to give standards to be used with the diluter to accompany soil extracts.

One liter volumetric flasks are used and the solutions are brought to volume with 1N NH_4OAc. The dilution is 0.5 ml of solution plus 9.5 ml of lanthanum diluent.

Concentration		Ca AA	Mg AA	Equivalent
Final	Stock	Stock 10,000ppm	Stock 10,000ppm	Soil Ca
ppm	*ppm*	*ml/l*	*ml/l*	*lbs/A*
0	0	0	1	0
5	100	10	1	2000
10	200	20	1	4000
15	300	30	1	6000
20	400	40	1	8000
30*	600	60	1	12000

*Not normally used in routine runs.

6.4 Magnesium Standards.
The recipe given below is designed to give standards to be used with the diluter to accompany soil extracts. One liter volumetric flasks are used and the solutions are brought to volume with 1N NH_4OAc. The dilution is 0.5 ml of solution and 9.5 ml of lanthanum diluent.

Concentration		Mg AA	Ca AA	Equivalent
Final	Stock	Stock 10,000ppm	Stock 10,000ppm	Soil Mg
ppm	*ppm*	*ml/l*	*ml/l*	*lbs/A*
0	0	0	20	0
0.5	10	1	20	200
1.0	20	2	20	400
1.5	30	3	20	600
2.0	40	4	20	800
3.0*	60	6	20	1200

*Not normally used in routine runs.

6.5 K Stock Solution (1000 ppm).
Dissolve 1.906 g KCl in demineralized water and dilute to one liter.

6.6 K Standards (flame photometer).
The recipe given below is designed to give standards to be used with soil extracts in a 1:1 dilution of soil extract or standard and lithium solution. A final Li internal standard concentration of 15 milliequivalent (meq) per liter for flame photometers which require internal standards is needed.

One liter volumetric flasks are used and the solutions are brought to volume with 1N NH_4OAc.

Concentration			Equivalent
Final	Stock	Stock	Soil K
ppm	*ppm*	*ml/l*	*lbs/A*
0	0	0	0
2.5	5	5	100
5	10	10	200
7.5	15	15	300
10	20	20	400
15	30	30	600

6.7 Na Stock Solution (1000 ppm Na).
Dissolve 3.6971 g $NaNO_3$ in demineralized water and dilute to one liter.

6.8 Na Standards.
Follow the recipe for K standards but substitute Na Stock Solution for the K stock solution.

Procedure

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

7.2 Potassium Determination

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

7.22 Flame emission spectrometers may be used for determination of potassium directly in the extract. In such cases where no internal standard is used; potassium standards of 0, 5, 10, 15, and 20 ppm K in 1N ammonium acetate are used.

7.3 Alternate Potassium Determination
Transfer 5 ml of the extract into a beaker. Add 5 ml of Lithium Diluent (6.8) as an internal standard and determine on a flame photometer.

7.4 Sodium Determination
Sodium may be determined on the extracts used for potassium determination (7.2 or 7.3). Sodium standards must be used (6.8).

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

Calibration and Standards

8.1 The standards are described in paragraphs 6.3 (Ca), 6.4 (Mg), and 6.6 (K). The standards are diluted by the same procedure as the soil extracts.

8.2 Calibration of the instruments must be done according to the appropriate instrument operating procedures given in the manual.

Calculations

9.1 In Missouri, cation results are reported in pounds/acre assuming 2 million lbs in a 6 ⅔-inch furrow slice.

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

Storage

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

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

Interpretation

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

References

12.1 Chapman, H. D. 1965. Total Exchangeable Bases. Ch. 58. *In* C. A. Black (ed.). Methods of Soil Analysis, Part 2. Soil Sci. Soc. of Amer., Madison, WI.

12.2 Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, N.J.

12.3 Carson, P. L. 1980. Recommended Potassium Test. Ch. 7. *In* Recommended Chemical Soil Test Procedures for the North Central Region, N.C. Reg. Pub. 221 (Revised). (No. Dak. Agric. Exp. Stn. Bul. 499).

12.4 Council on Soil Testing and Plant Analysis. 1980. Handbook on Reference Methods for Soil Testing. Athens, GA.

Extractable Soil Phosphorus

Bray I and Bray II Methods

Principle of the Method

1.1 This soil test procedure for P is a modification of the procedure originally developed in Illinois by Roger Bray and co-workers S. R. Dickman and Touby Kurtz (12.1). Over the years the procedure has been evaluated and modified (12.2, 12.3, 12.4). The ascorbic acid method of developing the color has been adapted for use with soil extracts (12.5, 12.6). The tests used in the Missouri county soil testing laboratories and at the Delta Center laboratory have been outlined by Graham and Fisher (12.7, 12.8). In recent years attempts have been made to eliminate procedural variability between states (12.9). The procedure given here is the one proposed as standard for the North Central States with modification to include the Bray II test (12.10).

1.2 The HCl in the Bray extractants tends to extract a portion of the acid soluble P in soils. The Bray I (weak, 0.025N HCl) is less reactive than the Bray II (strong, 0.1N HCl). In Missouri, the Bray II method had been used in the past because it tends to separate soils which had received rock phosphate from those which had not. Now, the Bray I method is used routinely. In states such as Iowa very little rock phosphate has been used, hence the Bray I test has been preferred. The F^- ion in the extractant tends to suppress the activity of Al and Ca. These two cations (Al and Ca) tend to combine with orthophosphate anions ($H_2PO_4^-$, $H_2PO_4^{2-}$, PO_4^{3-}), thus the F^- ion action helps maintain phosphates in solution during extraction.
The Bray extractants should not be used on alkaline soils because (1) the acid will tend to be neutralized and/or (2) excessive calcium phosphates may be extracted, giving a false, high test for available P.

Range and Sensitivity

2.1 The Fiske-Subbarrow standard curve is essentially linear up to 10 ppm P in the extract. The Ascorbic Acid variation is linear up to about 7 ppm P in the extract.

2.2 The test is sensitive to about 0.1 ppm P in the extract or 2 pounds P/A if the ascorbic acid variation is used.

Interferences

3.1 Arsenic
Normal field soils would generally not have sufficient arsenic to be a problem. Arsenic in orchard soils may be sufficiently high to be additive to the P test (12.6). Jackson outlines steps to remove arsenic interference (12.11).

3.2 Fluoride
Fluoride may interfere with color develop-

ment. Boric Acid is added to some reagents to prevent such interference.

Precision and Accuracy

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

Equipment

5.1 Balance or 2 g scoop(NCR-13).

5.2 Erlenmeyer extraction flask, 50 ml.

5.3 Rack for extraction flasks.

5.4 Automatic dispensers and diluters (kind and quantity dependent upon laboratory arrangement and volume).

5.5 Shaker (> 180 oscillations per minute).

5.6 Funnel (45 mm x 50 mm stem).

5.7 Funnel rack.

5.8 Filter paper (Whatman No. 2, or equivalent, 9 cm).

5.9 Receiving beaker.

5.10 Spectrophotometer tubes (or automatic flow-thru cell).

5.11 Spectrophotometer.

Reagents

6.1 Bray I Extracting Reagent
Dissolve 11.11 g of reagent grade ammonium fluoride (NH_4F) in about 9000 ml of distilled water. Add 21.6 ml of hydrochloric acid (sp. gr. 1.19, 37.5%). Dilute to 10 liters and mix. Store in a polyethlene container. This solution should be 0.03N NH_4F in 0.025N HCl.

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

6.3 Color development reagents - Fiske-Subbarrow Variation.

6.31 *Acid Molybdate Solution*
Dissolve 75.25 g ammonium molybdate—$(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$—in 490 ml warm (60°C) distilled water. Cool. Add 1500 ml HCl (sp. gr. 1.19, 37.5%) and mix. Cool and dilute to 2 liters with distilled water. Store in a glass stoppered brown bottle to which 100 g boric acid has been added.

6.32 *Dry Reducing Powder*
Mix 5 g 1-amino-4-sulfonic acid and 10 g sodium sulfite (Na_2SO_3) with 292.5 g of sodium pyrosulfite ($Na_2S_2O_5$). Grind the mixture to a fine powder. Store in a brown bottle in a dark, cool place. Shelf life approximately 1 year if properly stored.

6.33 *Dilute Reducing Solution*
Dissolve 16 g of the dry reducing solution in 100 ml of warm (60°C) distilled water. Cool and store in a brown bottle. Maximum shelf life of 3 weeks.

6.4 Color Development Reagents—Ascorbic Acid Variation

6.41. *Acid Molybdate Stock*
Dissolve 60 g of ammonium molybdate in 200 ml of warm (60°C) distilled water. Cool. Dissolve 1.455 g antimony potassium tartrate in the aqueous molybdate solution. Slowly add 700 ml of concentrated sulfuric acid. Cool and dilute to 1 liter. Store in a dark refrigerated compartment. This solution may be blue but will clear when diluted for use.

6.42 *Ascorbic Acid Stock*
Dissolve 132 g ascorbic acid in distilled water and dilute to a final volume of 1 liter. Store in the dark under refrigeration.

6.43 Working Solution
Add 25 ml of acid molybdate stock to 800 ml distilled water. Add 10 ml of ascorbic acid stock. Dilute to 1 liter with distilled water. MAKE FRESH DAILY.

Procedure

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

7.2 Filtration
Filter into the receiving vessel. Refilter if filtrate is not clear.

7.3 Color Development.

7.31 *Fiske-Subbarrow Method.*

7.311 Transfer a 5 ml aliquot to a test tube.

7.312 Add 0.25 ml acid molybdate solution.

7.313 Add 0.25 ml dilute reducing solution. Shake.

7.314 Read percent transmittancy (or optical density) on a spectrophotometer set at 660 nm between 15 and 45 minutes after addition of dilute reducing solution. Use a blank (O ppm P standard) which has been diluted with acid molybdate and dilute reducing solutions to set 100% transmittancy.

7.32 *Ascorbic Acid Variation.*

7.321 Transfer 2 ml aliquot to a test tube.

7.322 Add 8 ml of working solution in a manner to insure mixing in the test tube.

7.323 Allow 20 minutes for color development. Read percent transmittancy (or optical density) on a spectrophotometer set at 660 nm with a blank (0 ppm P standard) which has been diluted with the working solution giving 100% transmittancy. The color is relatively stable for at least 2 hours.

Calibration and Standards

8.1 Standard Stock Solution—1000 ppm P
Dissolve 4.3936 g of reagent grade potassium dihydrogen phosphate (KH_2PO_4), which has been oven dried in a minimum quantity of distilled water. Dilute to 1 liter with the appropriate extracting reagent (Bray I or Bray II). Storage life indefinite in a stoppered polyethylene container.

8.2 Working Stock Solution—10 ppm P
Dilute 10 ml of the standard stock solution to 1000 ml with extracting reagent in a volumetric flask.

8.3 Operating Standards
Use the following table to make the appropriate standards. Use transfer pipets and volumetric glassware. Fill to volume with the appropriate extracting solution.

Volume of 10 ppm Working Solution	Final Volume	Working Concentration	Equivalent Concentration in the soil			
			Ascorbic Acid		Fiske-Subbarrow	
		P	*P*	P_2O_5	*P*	P_2O_5
ml	*ml*	*ppm*	*ppm*	*lbs/A*	*ppm*	*lbs/A*
10	200	0.5	5	23	5	23
10	100	1	10	46	10	46
25	100	2.5	25	114	25	114
50	100	5	50	229	50	229
75	100	7.5	--	---	75	344

8.4 Standard Curve
Prepare a standard curve by starting the procedure at paragraph 7.3 using the operating standards instead of soil extracts. Read the percent transmittancy or optical density in the same way as for the soil extracts. Plot percent transmittancy on the logarithmic axis of semi-log graph paper and concentration on the linear axis. (If optical density is used ordinary linear graph paper should be used to develop the standard curve). If all reagents are operating properly a straight line should result (except perhaps with the most concentrated standard).

Calculations

9.1 The results may be reported as ppm P, lbs P/A or lbs P_2O_5/A as desired (see paragraph 8.3). This procedure assumes a weight relationship of 2 million pounds of soil per acre furrow slice of 6 ⅔ to 7 inches.

Effects of Storage

10.1 Soil samples may be stored for several months with no change in extractable P.

10.2 Soil extracts should be stored no longer than 24 hours if in an air tight container. Once the color has been developed follow the time directions in paragraph 7.31 or 7.32.

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

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

Interpretation

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

Literature Cited

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

(a) Bray, R. H. 1929. A Test for Available Phosphorus in Soils. Univ. of IL., Bul. 337.

(b) Dickman, S. R. and R. H. Bray. 1941. Replacement of Absorbed Phosphate from Kaolinite by Fluoride. Soil Sci. 52:263-273.

(c) Bray, R. H. and S. R. Dickman. 1942. Tentative Fluoride Extraction Methods for Soil Phosphorus. Univ. of IL., Agric. Exp. Stn. Mimeo AG 1006.

(d) Bray, R. H. 1942. Rapid Tests for Measuring and Differentiating Between the Absorbed and Acid-Soluble Forms of Phosphate in Soils. Univ. of IL., Agron. Mimeo.

(e) Bray, R. H. and L. T. Kurtz. 1945. Determination of Total, Organic, and Available Forms of Phosphorus in Soil. Soil. Sci. 59:39-45.

(f) Bray, R. H. 1948. Correlation of Soil Tests With Crop Response to Added Fertilizers and With Fertilizer Requirement. Ch. II *in* Diagnostic Techniques for Soils and Crops. H. B. Kitchen, ed., Amer. Potash Institute, Washington, D.C.

12.2 Arnold, C. Y. and Touby Kurtz. 1946. Photometer Method for Determining Available Phosphorus in Soils. Univ. of IL., Agron. Dept. Mimeo AG1306.

12.3 Laverty, J. C. 1963. The Illinois Method for Determining Available Phosphorus in Soils. Univ. of IL., Agron. Dept. Mimeo AG1861.

12.4 Laverty, J. C. 1963. A Modified Procedure for the Determination of Phosphorus in Soil Extracts. Soil Sci. Soc. Amer. Proc. 27:360-361.

12.5 Murphy, J. and J. R. Riley. 1962. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. Anal. Chem. Acta 27:31-36.

12.6 Watanabe, F. S. and S. R. Olsen. 1965. Test of an Ascorbic Acid Method for Determining Phosphorus in Water and $NaHCO_3$ Extracts from Soil. Soil Sci. Soc. Amer. Proc. 29:677-678.

12.7 Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. Univ. of MO. Agric. Exp. Stn. Bul. 734.

12.8 Fisher, T. R. 1969. Soil Testing Laboratory Improvements in Missouri. Univ. of MO. Agron. Dept. Unpublished Mimeo.

12.9 Council on Soil Testing and Plant Analysis. 1980. Handbook on Reference Methods for Soil Testing. The Council on Soil Testing and Plant Analysis. Athens, GA, 30601.

12.10 Knudsen, D. 1980. Recommended Phosphorus Soil Tests. p. 14-16 *In* Recommended Chemical Soil Test Procedures for the North Central Region. N. C. Reg. Pub. 221 (Revised) (No. Dak. Agric. Exp. Stn. Bul. 499).

12.11 Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall, Inc. Englewood Cliffs, N. J.

Soil pH in Water (pH_w)

Principle

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

1.2 This procedure is a modification of the procedure given in Reference 12.2

Range and Sensitivity

2.1 A range of pH of 3.2 to 8.5 can be obtained with most commercial pH meters and will be adequate for the majority of soils.

2.2 In routine soil testing, it is necessary to read pH_w only to 0.1 unit. This requirement is easily met by most commercial pH meters if the glass and calomel electrodes are in good condition.

Interferences

3.1 Most interferences are discussed in reference 12.1 This reference should be consulted to obtain a working knowledge of problems inherent in determining pH_w. Scratched glass electrodes and plugged reference electrodes cause most of the problems in the determination of pH_w.

3.2 In alkaline soils, atmospheric CO_2 may have an appreciable effect on soil pH.

Precision and Accuracy

4.1 Random variation of 0.1 to 0.2 pH unit can be expected in replicates of the same sample or in exchanges of the same sample between laboratories.

Apparatus

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

5.2 Cup, 50 ml capacity (glass, plastic or paper).

5.3 Dispenser, 10 ml.

5.4 Stirrer, shaker or glass rod.

5.5 pH meter, line or battery operated, with a glass electrode and a calomel reference electrode (or a combination electrode).

Reagents

6.1 pH 7.0 Buffer solution—commercially available.

6.2 pH 4.0 Buffer solution—commercially available.

Procedure

7.1 Weigh or scoop 10g of air-dry, <10 mesh soil into a cup (see 5.3). Add 10 ml of distilled water. Shake for 30 minutes or stir intermit-

tently several times over a 30 minute period. Lower the electrodes into the soil-water suspension. Read the pH_w to the nearest 0.1 unit.

7.2 Save the sample if a buffer pH determination is desired.

Calibration and Standards

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

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

Calculation

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

Storage Effects

10.1 Storage of air-dry samples for several months in closed containers will not affect the pH_w.

10.2 Instructions for storage of the pH meter and the electrodes published by the manufacturer(s) should be followed.

Interpretation

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

References

12.1 Coleman, N. T. and G. W. Thomas. 1967. The Basic Chemistry of Soil Acidity. Ch 1 *in* Soil Acidity and Liming, R. W. Pearson and F. Adams, ed. Agronomy No. 12. Amer. Soc. of Agron., Madison, WI.

12.2 Council on Soil Testing and Plant Analysis. 1980. Handbook on Reference Methods for Soil Testing. Athen, GA.

Soil pH in Salt Solution (pH_s)

Principle of the Method

1.1 This method estimates the activity of H ions in a soil suspension in the presence of 0.01M $CaCl_2$ to approximate a constant ionic strength for all soils regardless of past management, mineralogical composition, and fertility level.

1.2 The use of 0.01M $CaCl_2$ in soil pH measurement was proposed by Schofield and Taylor (12.4). Peech (12.3) summarized the advantages of using 0.01M $CaCl_2$ for measuring soil pH values. Additional discussions of the merits of determining soil pH in a constant salt level are given by McLean (12.2) and Woodruff (12.6).

Range and Sensitivity

2.1 Commercially available standard pH meters have an adequate range to measure the pH in 0.01M $CaCl_2$ of acid soils (pH_s 2.5 to 7.0).

2.2 The sensitivity will depend on the instrument. In routine soil testing it is necessary to read pH only to the 0.1 unit.

2.3 The pH in 0.01M $CaCl_2$ may be estimated with a brom cresol purple solution (12.5).

Interferences

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

Precision and Accuracy

4.1 Measurements of soil pH in 0.01M $CaCl_2$ are more precise than those made in water due to elimination of interferences (3.1).

Apparatus

5.1 Balance or 10 g scoop (NCR-13)

5.2 Cup, 50 ml capacity (glass, plastic or paper).

5.3 Dispenser, 10 ml.

5.4 Stirrer, shaker, or glass rod.

5.5 pH meter, line or battery operated, with a glass electrode and a calomel reference electrode (or a combination electrode).

Reagents

6.1 0.01M $CaCl_2$—dissolve 1.47 of calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in good quality distilled water and dilute to one liter.

6.2 pH 7.0 Buffer solution—commercially available.

6.3 pH 4.0 Buffer solution—commercially available.

6.4 (alternative) 1M $CaCl_2$—dissolve 147 g of calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in good quality distilled water and dilute to one liter.

Procedure

7.1 Weigh or scoop 10 g of < 10 mesh soil into a 50 ml beaker (or comparable container—5.3). Add 10 ml of 0.01 M $CaCl_2$ solution and stir for 30 min. on a mechanical stirrer or shaker (or periodically with a glass rod for a period of 30 min.). Calibrate the pH meter according to instructions supplied with the specific meter. Lower the electrodes into the 0.01 M $CaCl_2$-soil suspension and record the meter reading as pH_s (or pH in 0.01M $CaCl_2$).

7.2 In laboratories desiring both a soil pH in water and a soil pH in 0.01M $CaCl_2$, the 10 ml of distilled water can be substituted for the 10 ml of 0.01M $CaCl_2$ in 7.1. After the pH_w is determined (pH_w or pH in water), two drops of 1M $CaCl_2$ can be placed in the soil-water suspension, the suspension stirred for 30 minutes, and the pH read; the pH is designated pH_s or pH in 0.01M $CaCl_2$.

7.3 In laboratories using the Woodruff Buffer method of determining neutralizable acidity, the Woodruff Buffer may be added to the samples after pH_s is determined.

7.4 Alterations in quantities of soil and solution will not affect the results if the ratio given in paragraph 7.1 is maintained.

Calibration and Standards

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

Calculations

9.1 The results are reported as pH_s or pH in 0.01M $CaCl_2$.

Effects of Storage

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

10.2 If the pH meter and electrodes will not be used for extended periods, the instructions for storage published by the manufacturers should be followed.

Interpretation See 12.1 or 12.6

References

12.1 Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. MO. Agric. Exp. Stn. Bul. 734.

12.2 McLean, E. O. 1973. Testing Soils for pH and Lime Requirement. Ch. 7 *In* Walsh, L. M. and J. D. Beaton, ed. Soil Testing and Plant Analysis Rev. Ed. Soil Sci. Soc. of Amer. Madison, WI.

12.3 Peech, M. 1965. Hydrogen—Ion Activity. Ch. 60 *In* Black, C. A., ed. Methods of Soil Analysis Part 2. Chemical and Microbiological Properties. Amer. Soc. Agron. Madison, WI.

12.4 Schofield, R. K. and A. W. Taylor. 1955. The Measurement of Soil pH. Soil Sci. Soc. Amer. Proc. 19:164-167.

12.5 Woodruff, C. M. 1961. Brom Cresol Purple as an Indicator of Soil pH. Soil Sci. 91:272.

12.6 Woodruff, C. M. 1967. Crop Response to Lime in the Midwestern United States. Ch. 5 *In* Pearson, R. W. and F. Adams ed. Soil Acidity and Liming. Amer. Soc. of Agron. Madison, WI.

Determination of Neutralizable Acidity (NA)

New Woodruff Buffer Method

Principle of the Method

1.1 This procedure describes the estimation of the lime requirement of a soil by the new Woodruff buffer method. This is a modification of the original Woodruff buffer method (12.1, 12.2, 12.3). The lime requirement, in practical terms, is the quantity of agricultural limestone required to raise the pH level of a soil to a desired level. The desired level depends upon the soil and the crops to be grown. This procedure was evaluated by Cisco (12.4) by comparison with the older Woodruff method (12.2) and the "SMP" method (12.5). In addition, the data were related to soil pH changes due to application of $CaCO_3$. In all cases, the New Woodruff method gave the best correlation with the true lime requirement.

1.2 A buffer solution is added to an acid soil sample at an initial pH. After mixing the buffer and the acid soil sample, the pH of the suspension will be lower than the original buffer pH. This depression in buffer pH is due to neutralizable acidity, the same acidity which agricultural limestone will neutralize. The new Woodruff buffer is designed so that 0.1 pH depression equals 1 milliequivalent (meq) neutralizable acidity per 100 g of soil if the ratio of soil to buffer given in paragraph 7.1 is maintained.

Range and Sensitivity

2.1 This procedure is useful for soils with neutralizable acidity $\leq$ 10 meq per 100 g. If the pH depression exceeds 1 pH unit, rerun the procedure with one-half the designated quantity of soil and double the results.

2.2 Neutralizable acidity (NA) should be determined to the nearest 1 meq per 100 g.

Interferences

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

Precision and Accuracy

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

Apparatus

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

5.2 Cup or beaker, 50 ml capacity (glass, plastic or paper).

5.3 Dispensers, 10 ml (2).

5.4 Shaker, stirrer or glass rod.

5.5 pH meter, line or battery operated, with a glass electrode and a calomel reference electrode (or a combination electrode).

Reagents

6.1 0.01M $CaCl_2$.

6.2 **Woodruff Buffer Solution** (New).
Dissolve 10 g calcium acetate ($Ca(C_2H_3O_2)_2$)

and 4.0 g calcium hydroxide ($Ca(OH)_2$) in 500 ml cool distilled water. Heat (70°C) 200 ml distilled water and dissolve 12.0 g para-nitrophenol in the hot water. Add 10.0 g salicylic acid ($C_7H_6O_3$) to the acetate-hydroxide solution and mix vigorously for a minute or two. Pour in the para-nitrophenol solution and mix. (Delay in adding the para-nitrophenol solution will cause undesirable side reactions.) Bring the resulting solution to 1 liter and adjust the pH to 7.0 ± 0.05 with 6N NaOH or 6N HCl.

6.3 pH 7.0 Buffer solution—commercially available.

6.4 pH 4.0 Buffer solution—commercially available.

Procedure

7.1 Weigh or scoop 10 g of <10 mesh soil into a 50 ml container. Add 10 ml of 0.01M $CaCl_2$ solution. (If pH_s is desired determine it on the stirred sample after 30 minutes). Add 10 ml of the Woodruff Buffer Solution (6.2), stir intermittantly over a 30-minute period and determine pH_B on a pH meter set at pH 7.00 with the Woodruff Buffer Solution.

7.2 Five grams of soil can be used with 5 ml 0.01M $CaCl_2$ and 5 ml of Woodruff Buffer Solution without affecting the results.

Calibration

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

Calculation

9.1 The buffer solution is at pH 7.0 when added to the soil. pH 7.0 - pH_B = pH depression.

9.2 10 x pH depression = neutralizable acidity (NA) in meq per 100 g soil.

Effects of Storage

10.1 Air dry soil may be stored in closed containers for several months with no effect on pH_B.

10.2 The electrodes should be stored according to the manufacturer's instructions.

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

Interpretation

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

References

12.1 Woodruff, C. M. 1948. Determination of the Exchangeable Hydrogen and Lime Requirement of the Soil by Means of the Glass Electrode and a Buffered Solution. Soil Sci. Soc. Amer. Proc. 12:141-142.

12.2 Woodruff, C. M. 1948. Testing Soils for Lime Requirement by Means of a Buffered Solution and the Glass Electrode. Soil Sci. 66:53-63.

12.3 Graham, E. R. 1959. An Explanation of Theory and Methods of Soil Testing. Mo. Agric. Exp. Stn. Bul. 734.

12.4 Cisco, J. R. 1981. Estimating the Lime Requirements of Missouri Soils. Unpublished M.S. Thesis. Library, University of Missouri-Columbia.

12.5 Dahnke, W. C., ed. 1980. Recommended Chemical Soil Test Procedures for the North Central Region. North Central Reg. Publ. 221 (Revised). (No. Dak. Bul. 499).

Micronutrients DTPA Extraction

Iron, Manganese, Zinc, Copper

Principle of the Method

1.1 This method was developed as a nonequilibrium extraction by Lindsay and Norvell (13.3). DTPA (diethylenetriaminepenta-acetic acid) will chelate iron (Fe), manganese (Mn), zinc (Zn) and copper (Cu), hence it serves as an effective extracting agent. In the two-hour shaking time provided in the procedure, equilibrium is not attained and, as pointed out by Whitney (13.2), conditions such as pH, shaking time, and laboratory temperature will affect the results. As a result, any modifications of the procedure "must be carefully monitored to adjust the interpretation levels" (13.2).

1.2 Kennedy (13.4) evaluated this procedure and found the results for zinc in Missouri soils could be interpreted for DTPA extracts as described by Soltanpour *et al.* (13.5).

Range and Sensitivity

2.1 Zn, Fe, Mn, and Cu can be extracted and determined in soil concentrations of 0.1 ppm to 10 ppm Zn, 0.1 ppm to 10 ppm Fe, 0.1 ppm to 10 ppm Mn, 0.1 to 10 ppm Cu without dilution. The range and upper limits may be extracted by diluting the extracting filtrate prior to analysis.

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

Interferences

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

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

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

Precision and Accuracy

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

Apparatus

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

5.2 50 ml Erlenmeyer extraction flask.

5.3 Mechanical reciprocating shaker, 180 oscillations per minute.

5.4 Filter funnel.

5.5 Whatman No. 2 ashless filter paper (or equivalent).

5.6 Atomic Absorption Spectrophotometer.

Reagents

6.1 Extracting Reagent (DTPA-diethylenetriaminepenta-acetic acid) -
Weigh 1.96 g DTPA* into a 1 liter volumetric flask. Add 14.92 g TEA (Triethanolamine). Bring volume to approximately 950 ml with pure water. Add 1.47 g calcium chloride ($CaCl_2 \cdot 2H_2O$). Bring to 1 liter with pure water while adjusting the pH to exactly 7.3 with redistilled

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

6N HCl. The final concentration will be 0.005M DTPA, 0.1M TEA, and 0.1M $CaCl_2$.

6.2 Zinc Standard (1000 ppm)
Dissolve 1.00 g pure zinc metal in 5-10 ml conc HCl. Evaporate almost to dryness and dilute to 1 liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the stock solution standard with extracting reagent (see 6.1) to cover the anticipated range in concentration found in the soil extraction filtrate. Working standards from 0.1 to 10 ppm Zn should be sufficient for most soils.

6.3 Iron Standard (1000 ppm)
Dissolve 1.000 g pure iron wire in 5-10 ml conc HCl. Evaporate almost to dryness and dilute to 1 liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the stock solution standard with extracting reagent to cover the anticipated range in concentration in the soil filtrate. Working standards from 0.1 to 10 ppm Fe should be sufficient for most soils.

6.4 Manganese Standard (1000 ppm)
Dissolve 1.582 g manganese oxide (MnO_2) in 5 ml conc HCl. Evaporate almost to dryness and dilute to 1 liter with extracting reagent (see 6.1) Prepare working standards by diluting aliquots of the stock solution standard with extracting reagent to cover the anticipated range in concentration in the soil filtrate. Working standards from 0.1 to 10 ppm Mn should be sufficient for most soils.

6.5 Copper Standard (1000 ppm)
Dissolve 1.000 g pure copper metal in minimum amount conc HNO_3 and add 5 ml conc HCl. Evaporate almost to dryness and dilute to 1 liter with extracting reagent (see 6.1). Prepare working standards by diluting aliquots of the stock solution with extracting reagent to cover the anticipated range in concentration in the soil filtrate. Working standards from 0.1 to 10 ppm Cu should be sufficient for most soils.

Procedure

7.1 Extraction
Weigh or scoop 10 g of air-dry <10 mesh (2 mm) soil into a 50 ml extraction flask (see 5.3). Add 20 ml extracting reagent (see 6.1) and shake on a reciprocating shaker for 2 hours. Samples shaken longer than 2 hours will give high results because a final equilibrium of the metal and soil is not reached in 2 hours. Filter and collect the filtrate.

7.2 Analysis
The elements Zn, Mn, Fe, and Cu in the filtrate can be determined by atomic absorption spectroscopy. Because instruments vary in their operating conditions, no specific details are given. It is recommended that the procedure described by Isaac and Kerber (see 13.6) be followed.

Calibration and Standards

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

8.2 Calibration
Calibration procedures vary with instrument techniques and type of instrument. Every precaution should be taken to ensure that the proper procedures are taken and manufacturer recommendations followed in the operation and calibration of the instrument used.

Calculations

9.1 For expressing the results in ppm of soil use the following formula:

ppm in soil = ppm in solution x 2

Effects of Storage

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

Interpretation

11.1 Accurate micronutrient fertilizer recommendations are based on soil test results, field response for each crop and local field conditions. Interpretative data for critical levels established by Viets and Lindsay for Colorado soil are available (see 13.7). Boawn did work with DTPA for Zn on Washington soil (see 13.8) and Kennedy evaluated DTPA for Missouri soils (see 13.4).

Comments

12.1 Grinding can change the amount of DTPA-extractable micronutrients, especially iron (Fe). Therefore, it is imperative that grinding procedures be standardized along with extraction procedures. Grinding should be equivalent to

using a wooden roller to crush the soil aggregates (see 13.9).

References

13.1 Council on Soil Testing and Plant Analysis. 1980. Handbook on Reference Methods for Soil Testing. Athens, GA.

13.2 Whitney, D. A. 1980. Micronutrient Soil Tests - Zinc, Iron, Manganese and Copper. Ch. 8 *in* W. C. Dahnke ed. Recommended Chemical Soil Test Procedures for the North Central Region. No. Dak. Agric. Exp. Stn. Bul. 499 Revised (NCR Publication 221-revised).

13.3 Lindsay, W. L. and W. A. Norvell. 1969. Development of a DTPA micronutrient soil test. Agron. Abstracts, p. 84. Equilibrium relationships of Zn^{2+}, Fe^{3+}, Ca^{2+}, and H^{+} with EDTA and DTPA in soil. Soil Sci. Soc. Amer. Proc. 33:62-68.

13.4 Kennedy, Ann C. 1979. Evaluation of Three Zinc Soil Tests for Missouri Soils. Unpublished M.S. Thesis, Library, University of Missouri-Columbia.

13.5 Soltanpour, P. N. and A. P. Schwab. 1977. A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils. Comm. in Soil Sci. and Plant Analysis. 8:195-207.

13.6 Isaac, R. A. and J. D. Kerber. 1972. Atomic Adsorption and flame photometry: techniques and uses in soil, plant, and water analysis. p. 17-24. *In* L. M. Walsh, (ed), Instrumental Methods for Analysis in Soils and Plant Tissue, revised edition. Soil Sci. Soc. Amer., Madison, WI.

13.7 Viets, Jr., F. G. and W. L. Lindsay. 1973. Testing soils for zinc, copper, manganese, and iron. p. 153-172. *In* L. M. Walsh and J. D. Beaton (ed), Soil Testing and Plant Analysis, revised edition. Soil Sci. Soc. Amer., Madison, WI.

13.8 Boawn, L. C. 1971. Evaluation of DTPA extractable zinc as a zinc soil test for Washington soils. Proc. 22nd Annual Pac. N. W. Fert. Conf. Bozeman, Mont., Pacific NW Plant Food Assoc., p. 143-147.

13.9 Soltanpour, P. N., A. Khan, and W. L. Lindsay. 1976. Factors affecting DTPA-extractable Zn, Fe, Mn and Cu. Comm. Soil Sci. Plant Anal. 7:797-821.

Determination of Extractable Soil Zinc with 0.1 N HCL

Principle of the Method

1.1 This method is primarily for determining extractable zinc in acid soils (pH_s less than 6.8). The method is not suitable for alkaline soils unless additional measures are taken (see 12.2, 12.3, and 12.5).

1.2 The procedure was derived from methods of acid extraction of soils. The present procedure is a modification of a method used by Wear and Evans (12.7) with calibration work by Gilroy (12.1). Many variations of the method have been used. Differences between methods include shaking time and soil: extractant ratios.

1.3 The procedure is based upon the assumption that all or a portion of the soil zinc which will become available for plant uptake during a growing season is acid soluble. The quantity of acid soluble zinc serves as an index of availability (see 12.4).

Range and Sensitivity

2.1 The range of the test could be modified as a result of experience with a certain group of soils. The test is designed to divide soil samples into two groups, i.e. those which probably need zinc soil treatments and those which probably will not benefit from zinc fertilizer.

2.2 The sensitivity of the analytical procedure used to determine the concentration of zinc in the extract will depend upon the atomic absorption instrument used and its flame characteristics.

Interferences

3.1 In the usual range of zinc concentrations there are no interferences. The comment in 1.1 was necessary because the acid extractant can be neutralized by free carbonates and rendered ineffective.

3.2 All apparatus that will come in direct contact with the extractant, soil, or extraction filtrate must be thoroughly washed and rinsed in dilute redistilled HCl and zinc-free demineralized water before use. Plastic or glass containers and plastic tubing must be used where possible.

Precision and Accuracy

4.1 Repeated extractions of soils in the range of 2 to 10 ppm Zn have given coefficents of variation of less than 10%. As with most soil tests the major source of variation lies with sam-

pling rather than with the analytical techniques.

4.2 It is necessary to prevent contact of the soil sample, extractant, and filtrate with zinc containing materials such as rubber and metals.

Apparatus

5.1 No. 10 (2mm) sieve (Stainless steel).

5.2 Balance or scoop, NCR-13 5 g stainless steel scoop (.85 cc/g).

5.3 Extraction vessels, 50 ml Erlenmeyer flasks.

5.4 Automatic buret to deliver 20 ml (must be so constructed to minimize contact between the extractant and metal or rubber parts).

5.5 Mechanical shaker (180 to 200 oscillations per min.).

5.6 Filter funnel, 55 mm top ID.

5.7 Filter paper, Whatman No. 2, 9 cm.

5.8 Beaker, polypropylene, 30 ml capacity.

5.9 Funnel racks.

5.10 Atomic absorption spectrophotometer with supporting materials including fuel, oxidant, and Zn hollow cathode lamp.

5.11 Volumetric flasks, and pipettes for reagent and standard preparation.

5.12 Storage vessel for extractant (one to 16 liter capacity depending upon number of samples analyzed).

5.13 HCl acid redistillation apparatus.

5.14 Mixed bed demineralizer.

Reagents

6.1 Zinc free demineralized water.

6.2 Redistilled 6N HCl (1:1 demineralized water: commercial 12.1N concentrated HCl mixture distilled in a Pyrex still).

6.3 **Zinc standard (1000 ppm)**
Commercially available atomic absorption reference standard. Prepare working standards by diluting aliquots of the stock (1000 ppm) solution with the extracting solution to cover the working range. Working standards of 0, 0.1, 0.5, 1.0, and 2.0 ppm will be adequate.

6.4 **Extracting reagent (0.1N HCl)**
Dilute 16.7 ml redistilled 6N HCl to 1 liter. Titrate an aliquot with standard base to the phenolphthalein endpoint. Adjust the solution to 0.1N with 6N HCl or demineralized water.

Procedure

7.1 **Extraction**
Weigh or scoop 5 g of air dry, <10 mesh soil into a 50 ml extraction flask. Add 20 ml of the extracting reagent with an automatic buret. Place the flask on the platform of an orbital shaker for 30 minutes at 180 to 200 oscillations per minute. Filter through extractant washed filter paper into the reception beaker. A blank should be carried through the entire procedure with each run.

7.2 **Analysis**
The zinc concentration in the filtrate can be determined by atomic absorption spectroscopy. The instrument manufacturer's instructions should be followed.

Calibration and Standards

8.1 **Working Standards**
Working standards are prepared as in 6.3. If the zinc concentration exceeds that of the highest standard used either dilute the unknown or report the sample as being in excess of 8 ppm Zn.

Calculations

9.1 The results are reported as ppm Zn in the soil to the depth of sampling. Ppm Zn in the soil = ppm Zn in the filtrate x 4. If the extraction filtrate is diluted the dilution factor should be applied.

9.2 Convert to other units by calculation.

Storage Effects

10.1 Storage of soil in the air-dry condition in a closed container for several weeks should not affect the extractable zinc.

10.2 Extraction filtrate should not be stored for more than a few hours.

Interpretation

11.1 An evaluation of the results as well as accurate fertilizer recommendations must be based upon field response data obtained under local soil-climate-crop conditions. (See 12.6.)

11.2 This procedure is a routine soil test used by the Missouri Regional Soil Testing Laboratories. Field studies have shown that soils with <2 ppm 0.1NHCl extractable Zn will probably need zinc soil treatments to obtain optimum zinc levels for maize and grain sorghum.

References

12.1 Gilroy, T. E. 1969. Relationship between extractable soil zinc and zinc concentration in corn leaves. Unpublished M.S. Thesis, University of Missouri-Columbia Library.

12.2 Nebraska Soil Testing Service. 1967. HCl extractable soil test for zinc. Mimeo.

12.3 Nelson, J. L., L. C. Broawn and F. G. Viets, Jr. 1959. A method for assessing zinc status of soils using acid extractable zinc and "titratable alkalinity" values. Soil Sci. 88:275-283.

12.4 Tucker, T. C. and L. T. Kurtz. 1955. A comparison of several chemical methods with the bio-assay procedure for extracting zinc from soils. Soil Sci. Soc. Amer. Proc. 19:477-481.

12.5 Viets, F. G., Jr. and L. C. Boawn. 1965. Zinc. *In* C. A. Black et al. (ed.). Methods of Soil Analysis, Part 2. Amer. Soc. Agron., Agronomy 9:1090-1101. Madison, WI.

12.6 Viets, F. G., Jr. and W. L. Lindsay. 1973. Testing soils for zinc, copper, manganese and iron. Ch. 11 *In* L. M. Walsh and J. D. Beaton (ed). Soil Testing and Plant Analysis Revised Edition, Soil Sci. Soc. Amer. Inc. Madison, WI.

12.7 Wear, J. I. and C. E. Evans. 1968. Relationship of zinc uptake by corn and sorghum to soil zinc measured by three extractants. Soil Sci. Soc. Amer. Proc. 32:543-546.

Electrical Conductivity

Principle of the Method

1.1 This method estimates the salt concentration in a soil:water extract. Ideally, the salinity of the soil solution should be monitored in the field moisture range. This is best accomplished in the laboratory by using a water saturated soil paste (saturation extract) as recommended by the U.S. Salinity Lab (11.4). However, for ease of measurement and reproducibility of results, a 1:1 (weight:volume) ratio of soil to water is used by many labs.

1.2 Electrical conductivity (EC) is measured using a modified Wheatstone bridge with alternating currents. Pipet- or dip-type conductivity cell with platinized electrodes should be used. The cell should be approximately 1.0 reciprocal centimeter. For instructions on replatinizing electrodes see reference 11.4.

1.3 This method is a rapid and reasonably precise determination that does not alter or consume the sample.

Range and Sensitivity

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

Interferences

3.1 Only deionized water from which salts have been removed should be used to make extracts.

3.2 Clean and well-platinized electrodes are essential for reproducible results.

3.3 As temperature of the extract rises, the conductivity measurement will also rise. If the temperature of the sample extract and the standard are different, correct all readings to 25°C (see table 8.3).

Precision and Accuracy

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

Apparatus

5.1 Balance or 10 g scoop (NCR-13)

5.2 125 ml Erlenmeyer flask with stopper

5.3 Mechanical shaker

5.4 Buchner funnel

5.5 Filter paper, Whatman #2 or equivalent

5.6 500 ml filtering flask

5.7 Test tube, 25 mm x 150 mm

5.8 Vacuum pump or aspirator

5.9 Appropriate size tubing

5.10 Thermometer

Reagent

6.1 Potassium Chloride Standard
Dissolve 0.7456 g anhydrous KCl in freshly boiled and cooled deionized water and dilute to 1 liter. At 25°C, this solution has an electrical conductivity of 1.413 mmho/cm. Store in glass stoppered pyrex bottle.

Procedure

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

7.2 Measure the temperature of the sample extract and the standard.

7.3 Measure conductivity of the sample extract and standard according to the operating instructions of the particular conductivity bridge used. Rinse electrode with deionized water between each sample. Then rinse electrode with part of sample before each reading.

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

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

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

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

Calculations

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

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

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

Storage

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

Interpretations

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

References

11.1 Bower, C. A. and L. V. Wilcox. 1965. Soluble Salts. Ch. 62. *In* C. A. Black (ed.). Methods of Soil Analysis, Part 2. Soil Science Society of America, Madison, WI.

11.2 Council on Soil Testing and Plant Analysis. 1980. Handbook on Reference Methods for Soil Testing. Athens, GA.

11.3 Jurinak, J. J. 1978. Salt-Affected Soils (unpublished class text). Department of Soil Science and Biometerology, Utah State University, Logan, UT.

11.4 United States Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. U.S.D.A. Handbook No. 60.

Extractable Sulfate Sulfur

Principle of the Method

1.1 Hoeft *et al.* reviewed the work on extractants of soil sulfur (12.1). Their study concluded that the best available sulfate sulfur (SO_4-S) extractant for soils was 2N acetic acid containing 500 μg P/ml as $Ca(H_2PO_4)\cdot H_2O$. The phosphate is present as an anion which can replace adsorbed sulfate sulfur. Because phosphate is adsorbed more strongly than sulfate, the replaced sulfate tends to remain in solution. The acid system tends to prevent reprecipitation of the sulfate from the extract. Thom (12.2) evaluated ammonium acetate based extractants and concluded that the phosphate was essential for sulfate extraction. Hanson (12.3) and Barton (12.4) used a procedure modified from that published by Hoeft *et al.*

1.2 The procedure reported in this manual varies from the standard reference procedure proposed for the North Central Region (12.5). The procedure is based upon the Hoeft *et al.* method as modified by Hanson (12.3).

Range and Sensitivity

2.1 Hoeft *et al.* (12.1) reported ranges in soil sulfate sulfur up to 18 ppm. Eik (12.5) indicated the need "for improvement in the precision of the SO_4-S determinations".

Interferences

3.1 Most soil testing laboratories use a turbidimetric method of analyzing the soil extract for sulfate sulfur. In these methods, a suspension of $BaSO_4$ is developed by adding an excess of barium chloride to the acid soil extract. A stabilizing agent such as gum arabic is used. The speed of $BaSO_4$ formation, suspension stability and optical properties of the suspension are affected by many factors including temperature, acidity of the solution, size and quantity of $BaCl_2\cdot 2H_2O$ crystals and the presence of foreign materials (12.5). Time is always a factor with which to contend.

Precision and Accuracy

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

Apparatus

5.1 Balance or 10 g scoop (NCR-13)

5.2 Extraction flask (50 or 125 ml)

5.3 Mechanical shaker (180 or more oscillations per minute)

5.4 Dispenser for extracting solution

5.5 Filter funnel

5.6 Filter paper (Whatman No. 2 or equivalent)

5.7 Aliquoter or pipette - 10 ml

5.8 Folin-Wu or similar tubes (50 ml capacity)

5.9 Spectrophotometer or nephelometer with 420 nm wavelength setting with cuvets or sampling cell.

Reagents

6.1 **Extracting solution** (500 ppm - P in 2*N* Acetic Acid)
Dissolve 2.03 g of $Ca(H_2PO_4)_2\cdot H_2O$ in about 800 ml of deionized water. To this, add 115 ml of glacial acetic acid and dilute to 1 liter.

6.2 Buffer and $BaCl_2$ solution (Gum arabic - $BaCl_2$ - Acetic Acid)
Dissolve 5 g of gum arabic in about 500 ml of hot, deionized water and filter if cloudy. Add 50 g of $BaCl_2 \cdot 2H_2O$ and 450 ml of glacial acetic acid and dilute to 1 liter.

6.3 Standard Solutions

6.31 *Standard Sulfur (S) solution* (100 ppm - S)
Dissolve 0.544 g of oven dried (105°C) K_2SO_4 in about 500 ml of deionized water, add 10 ml of acetic acid as a preservative, and dilute to 1 liter with deionized water.

6.32 *Working Sulfur standards* (0, 2, 4, 6, 8, and 10 ppm - S)
Transfer 0, 2, 4, 6, 8, and 10 ml of the 100 ppm sulfur standard to 100 ml volumetric flasks. Add 25 ml of a 2000 ppm - P and 8N acetic acid solution, (8.12 g of $Ca(H_2PO_4)_2 \cdot H_2O$ plus 460 ml of glacial acetic acid diluted to 1 liter) and dilute to 100 ml.

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

Procedure

7.1 Weigh or scoop 10 g of < 10 mesh soil into an extraction flask.

7.2 Add 25 ml of the extracting solution (6.1) and 0.1 g of the activated charcoal (6.4).

7.3 Shake the suspension for 15 minutes and filter through Whatman No. 2 (or equivalent) filter paper previously washed with diluted acetic acid and dried to remove sulfate-sulfur impurities.

7.4 A 10 ml aliquot of filtrate is transferred to a 50 ml Folin Wu tube or other suitable container. Add 10 ml of the gum arabic - $BaCl_2$ - acetic acid solution (6.2) and shake for 10 minutes.

7.5 Transfer the solution to a cuvet or cell of a spectrophotometer or nephelometer and read %T at a wavelength of 420 nanometers.

7.6 If dilutions are needed, dilute the original filtrate with the extracting solution and proceed with the addition of gum arabic - $BaCl_2$ - acetic acid solution.

Calibration and Standards

8.1 A standard curve is determined with each run of samples.

8.2 A 10 ml aliquot of each working standard is treated the same as described for the soil extracts. The instrument is adjusted to read 0% T with the zero sulfur standard.

Calculations

9.1 $$\text{ppm } SO_4\text{-S in soil} = \text{ppm S in extract} \times \frac{25}{10 \text{ g}}$$

9.2 $$\text{lbs } So_4\text{-S in soil} = \text{ppm S in extract} \times \frac{25}{10 \text{ g}} \times 2$$

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

Storage

10.1 Air-dry soil samples may be stored for several months without significant changes in SO_4-S.

10.2 Once extraction is complete, the determination of the concentration of sulfate sulfur in the extract should be made with a minimum delay.

Interpretations

11.1 The test must be calibrated to field response. Current extension service guides should be consulted.

References

12.1 Hoeft, R. G., L. M. Walsh and D. R. Keeney. 1973. Evaluation of various extractants for available soil sulfur. Soil Sci. Soc. Amer. Proc. 37:401-404.

12.2 Thom, W. O. 1972. Estimating plant available sulfur in selected soils of the Southeastern Missouri Delta region. M.S. Thesis, Library, University of Missouri-Columbia.

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12.4 Barton, M. J. 1982. A study of sulfur effect on cotton growth and nutrient status on two southeast Missouri soils. M.S. Thesis, Library, University of Missouri-Columbia.

12.5 Eik, K. 1980. Recommended chemical soil test procedures for the North Central Region. Ch. 10 *In* W. C. Dahnke, ed., North Central Region Publ. 221 (revised). (No. Dak. Agric. Exp. Stn. Bul. 499-revised).

Calculated Cation Exchange Capacity

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

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

meq Ca/100 g = lbs Ca/A ÷ 400 lbs/meq
meq Mg/100 g = lbs Mg/A ÷ 240 lbs/meq
meq K/100 g = lbs K/A ÷ 780 lbs/meq

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

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