Reference Soil and Media Diagnostic Procedures for the Southern Region of the United States

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FORWARD

Over the past several years the Southern Extension and Research Activity Information Exchange Group in Soil Testing and Plant Analysis (SERA-IEG-6) has worked towards developing standard procedures for use in evaluating the nutrient status and acidity level of soils in the southern United States. Standard procedures serve as a reference for those interested in including a new analysis in their program or who wish to employ a more suitable procedure for evaluation of a particular element.

This bulletin contains 15 reference procedures for analyses performed by soil testing laboratories in this region. Procedures were selected based on their accuracy in predicting crop response to applied nutrient as well as their popularity and general acceptance by workers in the soil testing field. Also, they provide a uniform reference for laboratories wishing to exchange samples for evaluation of their soil testing programs.

Future revisions of this bulletin will contain additional reference methods for trace and other elements considered useful in soil nutrient evaluation.

S. J. Donohue
Editor

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Members of the Southern Extension and Research Activity Information Exchange Group in Soil Testing and Plant Analysis (SERA-IEG-6) 1992

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Reference Soil and Media Diagnostic Procedures for the Southern Region of the United States

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C. Owen Plank[1]

1. PRINCIPLE OF THE METHOD

1.1 This method is used to determine the activity of H ions in a soil suspension in the presence of 0.01*M* $CaCl_2$ to approximate a constant ionic strength in soils.

1.2 The use of 0.01*M* $CaCl_2$ in soil pH measurement was proposed by Schofield and Taylor (Schofield and Taylor, 12.1). Peech (12.2) summarized the advantages of using 0.01*M* $CaCl_2$ for measuring soil pH values. Additional merits of determining soil pH at a constant salt level are given by McLean (12.3).

2. RANGE AND SENSITIVITY

2.1 Most commercially available standard pH meters are adequate for measuring soil pH in 0.01*M* $CaCl_2$ through the range 2.5 to 8.0, which would include most soils encountered.

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

3. INTERFERENCES

3.1 Determination of soil pH in 0.01*M* $CaCl_2$ minimizes interferences from variable salt contents and from suspension effects.

4. PRECISION AND ACCURACY

4.1 Temperate and subtropical region soil pH values determined in 0.01*M* $CaCl_2$ are slightly lower in magnitude and less variable than those made in water due to release of H ions from exchange sites by Ca ions.

4.2 Soil pH values determined in 0.01*M* $CaCl_2$ are approximately 0.5 pH unit lower than those measured in water (12.4).

4.3 Random variation of 0.1 to 0.2 pH unit is permissible in replicate determinations, and can be expected from one laboratory to another.

4.4 Scratched glass electrodes will give erratic values. Exercise care to prevent scratching. Reference electrodes with restricted flow of filling solution may also cause unstable readings.

4.5 Dehydrated electrodes give erratic readings. Follow the electrode manufacturer's instructions for proper maintenance.

5. APPARATUS

5.1 No. 10 (2-mm opening) sieve.

5.2 Scoop, 10-cm^3 volumetric.

5.3 Cup, 50 ml (glass, plastic, or waxed paper of similar size).

5.4 Pipette, 10-ml capacity.

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[1] Extension Agronomist, Soil Testing and Plant Analysis, Department of Agronomy, University of Georgia, Athens, Georgia.

5.5 Stirring apparatus (mechanical shaker, stirrer, or glass rod).

5.6 pH meter, line or battery operated, with reproducibility to at least 0.05 pH unit, and glass electrode paired with a calomel reference electrode.

5.7 Glassware and dispensing apparatus for the preparation and dispensing of 0.01*M* $CaCl_2$ and buffer solutions.

5.8 Dropping bottle, 30- or 60-ml capacity (see alternate procedure 7.2 below).

5.9 Analytical balance.

6. REAGENTS

6.1 *0.01M $CaCl_2$* - Weigh 1.47 g calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) into a 1-L volumetric flask and dilute to 1 liter with pure water.

6.2 *Buffer Solutions* - pH 4.0 and pH 7.0 buffers for standardization of pH meter (Donohue, 12.5).

6.3 *(Alternative) 1M $CaCl_2$* - Dissolve 147 g calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in pure water and dilute to 1 L.

7. PROCEDURE

7.1 Scoop 10 cm^3 air-dry < 10 mesh (2-mm) soil into a 50-ml cup (see 5.3). Add 10 ml 0.01*M* $CaCl_2$ solution (see 6.1) and mix thoroughly using a mechanical stirrer or shaker or a glass stirring rod. Allow to stand for 30 minutes. Calibrate the pH meter according to instructions supplied with the meter. Stir the suspension, then lower the electrodes into the 0.01*M* $CaCl_2$ - suspension and record the meter reading as pH in 0.01*M* $CaCl_2$.

7.2 For laboratories desiring soil pH in water and soil pH in 0.01*M* $CaCl_2$, 10 ml of pure water can be substituted for the 10 ml $CaCl_2$ as given in 7.1. After the water pH is determined, add 2 drops of 1*M* $CaCl_2$ (see 6.3) to the soil-water suspension, stir the suspension and allow to stand for 30 minutes. Stir the suspension and then read the pH. The pH is designated pH in 0.01*M* $CaCl_2$.

8. CALIBRATION AND STANDARDS

8.1 The pH meter is calibrated using prepared (see 6.2) or commercially available buffer solutions of pH 7.0 and pH 4.0 according to the instrument instruction manual.

9. CALCULATIONS

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

10. EFFECTS OF STORAGE

10.1 Air-dry soils may be stored several months in closed containers without affecting the pH in 0.01*M* $CaCl_2$ measurement.

10.2 If the pH meter and electrodes are not to be used for extended periods of time, the instructions for storage published by the instrument manufacturer should be followed.

11. INTERPRETATION - See Graham (12.5) or Woodruff (12.6).

12. REFERENCES

12.1 Schofield, R. K. and A. W. Taylor. 1955. The measurement of soil pH. Soil Sci. Soc. Am Proc. 19: 164-167.

12.2 Peech, Michael. 1965. Hydrogen-ion activity. *In* C. A. Black (ed.) Methods of soil analysis. Part 2. Agronomy 9: 914-926. ASA, Madison, WI.

12.3 McLean, E. O. 1973. Testing soils for pH and lime requirement p. 78-95. *In* L. M. Walsh and J. D. Beaton (ed.) Soil testing and plant analysis. Revised edition. SSSA, Madison, WI.

12.4 McLean, E. O. 1982. Soil pH and lime requirement. *In* A. L. Page, R. H. Miller, and D. R. Keeney (ed.) Methods of soil analysis. Part 2. 2nd ed. Agronomy 9:199-224. ASA and SSSA, Madison, WI.

12.5 Donohue, S. J. 1983. Reference soil test methods for the Southern region of the United States. Southern Coop. Ser. Bull. 289, Georgia Agric. Exp. Stn., Athens, GA.

12.6 Graham, E. R. 1959. An explanation of theory and methods of soil testing. Missouri Agric. Exp. Stn. Bull. 734.

12.7 Woodruff, C. M. 1967. Crop response to lime in the Midwestern United States. *In* R. W. Pearson and F. Adams (ed.) Soil acidity and liming. Agronomy 12:207-227. ASA, CSSA, and SSSA, Madison, WI.

DETERMINATION OF SOIL pH IN 1*N* KCl

C. Owen Plank[1]

1. PRINCIPLE OF THE METHOD

1.1 This method is used to determine the H-ion activity in a soil suspension in the presence of 1*N* KCl. Soil pH values determined in 1*N* solution are less influenced by changes in biological and climatic conditions and more closely reflect the inherent characteristic of the soil pH than that of the pH measured in water.

1.2 The use of 1*N* KCl for determining soil pH in the presence of small amounts of salts was proposed by Puri and Asghar (11.3). Additional information on determining soil pH in 1*N* KCl is given by Jackson (11.1) and Peech (11.2).

2. RANGE AND SENSITIVITY

2.1 Most commercially available standard pH meters are adequate for measuring soil pH in 1*N* KCl through the range 2.5 to 8.0, which would include the pH encountered in most soils.

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

3. INTERFERENCES

3.1 The main advantage of the measurement of soil pH in 1*N* KCl is to minimize interferences from variable salt contents and from suspension effects.

4. PRECISION AND ACCURACY

4.1 Temperate and subtropical region soil pH values determined in 1*N* KCl are lower in magnitude and less variable than those made in water due to release of H ions from the exchange sites by K ions.

4.2 Soil pH values determined in 1*N* KCl may be as much as 1.0 to 2.0 pH units lower than those measured in aqueous suspensions using the same soil-to-water ratio.

4.3 Random variation of 0.1 to 0.2 pH unit is permissible in replicate determinations, and can be expected from one laboratory to another.

4.4 Scratched glass electrodes will give erratic values. Exercise care to prevent scratching. Likewise, reference electrodes with restricted flow of filling solution might cause unstable readings.

4.5 Dehydrated electrodes give erratic readings. Follow the electrode manufacturer's instructions in keeping the electrodes hydrated.

5. APPARATUS

5.1 No. 10 (2-mm opening) sieve.

5.2 Scoop, 10-cm^3 volumetric.

5.3 Cup, 50 ml or 100 ml (glass, plastic, or waxed paper of similar size).

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[1] Extension Agronomist, Soil Testing and Plant Analysis, Department of Agronomy, University of Georgia, Athens, Georgia.

5.4 Pipette, 25-ml capacity.

5.5 Stirring apparatus (mechanical shaker, stirrer, or glass rod).

5.6 pH meter with reproducibility to at least 0.05 pH unit, and appropriate electrodes.

5.7 Glassware and dispensing apparatus for the preparation and dispensing of 1*N* KCl and buffer solutions.

5.8 Analytical balance.

6. REAGENTS

6.1 1*N* KCl - Weigh 74.56 g potassium chloride (KCl) into a 1-liter volumetric flask and dilute to 1 liter with pure water.

6.2 *Buffer Solutions* - pH 4.0 and pH 7.0 buffers for standardization of pH meter (Donohue, 11.4).

7. PROCEDURE

7.1 Scoop 10-cm^3 of air-dry, < 10 mesh (2-mm) soil into a 50 or 100-ml cup (see 5.3). Add 25 ml 1*N* KCl solution (see 6.1) and mix thoroughly using a mechanical stirrer or shaker or glass stirring rod. Allow to stand for 30 minutes. Calibrate the pH meter according to instructions supplied with the meter. Stir the suspension, then lower the electrodes into the 1*N* KCl - suspension and record the meter reading as pH in 1*N* KCl.

7.2 If exchangeable acidity and exchangeable Al are to be determined save the suspension and proceed as described in Chapter 13, Section 6.1.

8. CALIBRATION AND STANDARDS

8.1 The pH meter is calibrated using prepared (see 11.4) or commercially available buffer solutions of pH 7.0 and pH 4.0 according to the instrument instruction manual.

9. CALCULATIONS

9.1 The results are reported as pH in 1*N* KCl.

10. EFFECTS OF STORAGE

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

10.2 If the pH meter and electrodes are not to be used for extended periods of time, the instructions for storage published by the instrument manufacturer should be followed.

11. REFERENCES

11.1 Jackson, M. L. 1958. Soil chemical analysis. p. 47. Prentice-Hall, Englewood Cliffs, N.J.

11.2 Peech, Michael. 1965. Hydrogen-ion activity. *In* C. A. Black (ed.) Methods of soil analysis. Part 2. Agronomy 9: 914-926. ASA, Madison, WI.

11.3 Puri, A. N. and Asghar, A. G. 1938. Influence of salts and soil-water ratio on pH values of soils. Soil Sci. 46: 249-257.

11.4 Donohue, S. J. 1983. Reference soil test methods for the Southern region of the United States. Southern Coop. Ser. Bull. 289, Georgia Agric. Exp. Stn., Athens, GA.

DETERMINATION OF PHOSPHORUS BY MEHLICH 3 EXTRACTION

M. R. Tucker[1]

1. PRINCIPLE OF THE METHOD

1.1 The extraction of phosphorus by the Mehlich 3 extraction procedure is designed to be applicable across a wide range of soil properties ranging in reaction from acid to basic. This method correlates well with Bray 1 on acid to neutral soil (r^2 = 0.966). It does not correlate with Bray 1 on calcareous soils. The Mehlich 3 method correlates with the Olsen extractant on calcareous soils (r^2 = 0.918) even though the quantity of Mehlich 3 extractable phosphorus is considerably higher.

1.2 This extractant was developed by Dr. Adolf Mehlich in 1981 and described by A. L. Hatfield for the late Dr. Mehlich (10.2). This procedure was developed on a 1:10 soil-solution ratio (2.5 cm^3 soil + 25 cm^3 extractant) for a 5-minute shaking period at 200 4-cm reciprocations/minute.

2. RANGE AND SENSITIVITY

2.1 Phosphorus can be extracted and determined in soil concentrations 2 - 400 kg/ha without dilution using the molybdophosphoric blue color procedure first described by Murphy and Riley (10.3) and modified by Watanabe and Olsen (10.4).

3. PRECISION AND ACCURACY

3.1 Repeated analyses of two standard soil samples for 36 separate extractions by the NCDA Soil Testing Laboratory gave a variance of 6.28 to 6.39%, respectively. Each soil tested 97 and 132 mg P/dm^3, respectively. The variance is most likely related more to the heterogeneity of the samples rather than measurement, extraction, or colorimetric procedures.

4. APPARATUS

4.1 No. 10 (2-mm opening) sieve.

4.2 2.5 cm^3 (volumetric) soil measure and teflon-coated leveling rod.

4.3 100 ml extraction bottles; plastic or glass are suitable.

4.4 Reciprocating shaker, 200 4-cm reciprocations/minute.

4.5 Filter funnels, 11 cm.

4.6 Whatman No. 1 (or equivalent) filter paper, 11 cm.

4.7 Funnel Rack.

4.8 Vials, polystyrene plastic, 25 and 50 ml capacity, for collection of extract and color development, respectively.

4.9 Automatic extractant dispenser, 25 ml capacity. Other dispensers or pipettes could be used depending on preference.

4.10 Dilutor - dispensor apparatus for delivery of sample and color development reagent.

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[1] Chief Agronomist, Soil Testing Laboratory, NCDA Agronomic Division, Raleigh, North Carolina.

4.11 Volumetric flasks and pipettes are required for preparation of reagents and standard solutions. Pipettes could also be used for color development.

4.12 Photometric colorimeter suitable for measurement in the 880 nm range. Colorimeters equipped with moveable fiber optic probe can be used to read samples directly from the color development vials.

5. REAGENTS

5.1 All reagents are ACS analytical grade unless otherwise stated.

5.2 *Extracting reagent (0.2N CH_3COOH; 0.25N NH_4NO_3; 0.015N NH_4F; 0.13N HNO_3; 0.001M EDTA)* - For specific procedure on making up extractant, see Mehlich (10.2).

5.3 *Ascorbic Acid Solution* - Dissolve 176.0 g ascorbic acid ($C_6H_8O_6$) in pure water and dilute to 2 liters with pure water. Store solution in dark glass bottle in a refrigerated compartment.

5.4 *Sulfuric-Molybdate-Tartrate Solution* - Dissolve 100 g ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 500 ml of pure water. Dissolve 2.425 g antimony potassium tartrate [K (SbO) $C_4H_4O_6 \cdot \frac{1}{2}H_2O$] in molybdate solution. Add slowly 1400 ml concentrated H_2SO_4 and mix well. Let cool and dilute to 2 liters with pure water. Store solution in polyethylene or pyrex bottle in a dark, refrigerated compartment.

5.5 *Working Solution* - Dilute 10 ml of the ascorbic acid solution (see 5.3) plus 20 ml of the sulfuric-molybdate-tartrate solution (see 5.4), with extracting reagent (see 5.2) to 1 liter. Allow solution to come to room temperature before using. Prepare fresh daily.

5.6 *Phosphorus Standard (200 µg P/ml)* - Dissolve 0.879 g monopotassium phosphate (KH_2PO_4) in approximately 500 ml of distilled water, bring to 1 liter volume with distilled water. Prepare standards containing 1, 2, 5, 10, 15, and 20 µg P/ml by diluting appropriate aliquots of 200 µg P/ml with distilled water.

6. PROCEDURE

6.1 *Extraction* - Measure 2.5 cm^3 of air-dry, 10-mesh (2-mm) soil into a 100-ml extraction bottle (see 4.3). Add 25 cm^3 of extracting solution (see 5.2) and shake for 5 minutes on reciprocating shaker (see 4.4). Filter and collect the extract. For rationale of using a volume soil measure, see Mehlich (10.1).

6.2 *Color Development* - Using pipette or dilutor dispenser, dilute 1 ml of sample extract (see 6.1) with 27 ml of the working solution (see 5.5). Allow color to develop at least 20 minutes before reading. Read the transmission at 880 nm (2 cm light path probe colorimeter) or at 882 nm for standard cuvette-type colorimeter.

6.3 The color intensity reaches its maximum in approximately 20 minutes and will remain constant for about 6 hours.

7. CALIBRATION AND STANDARDS

7.1 *Working Phosphorus Standards* - After calibration curve is established (see 5.6), the instrument can be calibrated for routine analysis using the extracting solution (see 5.2) as the blank and the 20 µg P/ml standard (see 5.6). The 20 µg P/ml standard should read 10%T following color development at the 1:27 sample-to-working-solution ratio (see 6.2). The blank solution should be diluted at the same 1:27 ratio as the standards. If instrument reading is significantly above or below 10%T, check standard preparation, sample dispensor, or dilution ratio between standard and working solutions. The probe colorimeter technique requires a 1:27 sample - working solution ratio to achieve a 10%T reading at 20 µg P/ml. A linear curve can be obtained by converting %T to optical

density (OD). Other types of colorimeters may require a different sample-to-working-solution ratio.

8. CALCULATIONS

8.1 The results are reported as mg P/dm^3 (μg P/ml of standard or P soil extract multiplied by 10). Multiply mg P/dm^3 by 2 to obtain kg P/ha for a 20 cm depth of soil. If soil extract requires dilution, multiply results by appropriate dilution factor.

8.2 To convert soil test values to other units, see Mehlich (10.1).

9. INTERPRETATION

9.1 Critical phosphorus levels proposed by Mehlich (10.5) are listed below.

Category	mg P/dm^3	KgP/ha	Expected Crop Response
Very low	< 20	< 40	definite
Low	20-30	40-60	probable
Medium	31-50	62-100	less likely
High	> 50	> 100	unlikely

10. REFERENCES

10.1 Mehlich, A. 1972. Uniformity of expressing soil test results on a volume basis. Commun. Soil Sci. Plant Anal. 3(5):417-424.

10.2 Mehlich, A. 1984. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15(12):1409-1416.

10.3 Murphy, J. and J. R. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chem. 27:31-36.

10.4 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. Am. Proc. 29:677-678.

10.5 Mehlich, A. 1978. New extractant for soil test evaluation of phosphorus, potassium, magnesium, calcium, sodium, manganese, and zinc. Commun. Soil Sci. Plant Anal. 9(6):477-492.

DETERMINATION OF POTASSIUM, CALCIUM, MAGNESIUM, AND SODIUM BY MEHLICH 3 EXTRACTION

M. R. Tucker[4]

1. PRINCIPLE OF THE METHOD

1.1 The extraction of calcium, magnesium, potassium, and sodium by this method is designed to be applicable across a wide range of soil properties ranging in reaction from acid to basic. The Mehlich 3 method correlates well with Mehlich 1, Mehlich 2, and ammonium acetate (see 9.1). For specific extraction values and correlation coefficients see Mehlich (9.1, 9.2).

1.2 This extractant was developed by Dr. Adolf Mehlich in 1980-81 and described by A. L. Hatfield for the late Dr. Mehlich (9.2). This procedure was developed on a 1:10 soil-solution ratio (2.5 cm^3 soil + 25 cm^3 extractant) for a 5-minute shaking period at 200 4-cm reciprocations/minutes.

2. RANGE AND SENSITIVITY

2.1 Following a 1:4 dilution of the soil extract with the lithium working solution (see 6.5), soil concentrations of potassium and sodium can be determined up to 1564 and 920 kg/ha respectively. Following a 1:10 dilution of the soil extract with lanthanum solution (see 6.6) soil concentrations of calcium and magnesium can be determined up to 10,020 and 1216 kg/ha, respectively. An atomic absorbtion spectrophotometer equipped with a 3 standard microprocessor is required to obtain linearity at instrument readings above 100. In the absence of microprocessor-equipped instrumentation, extractable calcium and magnesium can be determined in soil concentrations up to 10 and 2 meq/100 cm^3, respectively.

2.2 Sensitivity will vary with type of instrument, wavelength selection, and method of excitation.

2.3 The commonly used methods of analysis for the above elements are flame emission and atomic absorption. For a complete description of these methods see Isaac and Kerber (9.3).

3. INTERFERENCES

3.1 Chemical interferences and compensation for changes in the characteristics of the extract to be analyzed must be acknowledged. The need for internal standards such as lithium and compensating elements such as lanthanum, which are required for most flame methods of excitation, have been shown by Isaac and Kerber (see 9.3).

4. PRECISION AND ACCURACY

4.1 Repeated analyses of the same soil with medium ranges of potassium, calcium, and magnesium will give variances from 5 to 10 percent. The major portion of the variance is related more to the heterogeneity of the soil than to measurement, extraction, or method of analysis.

5. APPARATUS

5.1 No. 10 (2-mm) sieve.

5.2 2.5 cm^3 (volumetric) soil measure and teflon-coated leveling rod.

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[4] Chief Agronomist, Soil Testing Laboratory, NCDA Agronomic Division, Raleigh, North Carolina.

5.3 100 ml extraction bottles, plastic or glass, are suitable.

5.4 Reciprocating shaker (200 4-cm reciprocations/minute).

5.5 Filter funnels, 11 cm.

5.6 Whatman No. 1 (or equivalent) filter paper, 11 cm.

5.7 Funnel rack.

5.8 Vials, polystyrene plastic, 25 ml capacity for collection of extract and sample dilutions.

5.9 Automatic dispenser for extractant, 25 ml capacity.

5.10 Diluter-dispenser mechanism or pipettes, 10 ml capacity.

5.11 Flame emission, atomic absorption spectrophotometer, and/or ICP. A 3-standard microprocessor AA is desirable.

5.12 Volumetric flasks and pipettes as required for preparation of reagents and standard solutions.

5.13 Analytical balance.

6. REAGENTS

6.1 All reagents are ACS analytical grade or standard reference solutions unless otherwise stated.

6.2 *Extracting Reagent (0.2N CH_3COOH; 0.25N NH_4NO_3; 0.015N NH_4F; 0.013N HNO_3; 0.001M EDTA)* - see 6.3 and 6.4 for mixing procedure of extracting reagents.

6.3 *Ammonium Fluoride - EDTA Stock Reagent* - Add approximately 600 ml pure water to a 1 liter volumetric flask, add 138.9 g NH_4F and dissolve, then add 73.05 g EDTA, dissolve mixture, and bring to volume with pure water.

6.4 *Final Extraction Reagent Mixture* - Add approximately 3000 ml of pure water to a 4 liter volumetric flask, add 80 g NH_4NO_3 and dissolve. Then add 16 ml NH_4F-EDTA stock reagent (see 6.3) and mix well. Add 46 ml CH_3COOH and 3.28 ml HNO_3, then bring to volume with pure water and mix thoroughly. The final pH should be 2.5 $\pm$ 0.1. The extractant was made acidic to prevent precipitation of CaF in the soil extract.

6.5 *Lithium Working Solution (18.75 meq Li/L)* - Dilute 12.5 ml of commercial lithium standard (1500 meq Li/L) to 1 liter with pure water. This solution is used as an internal standard for determination of potassium.

6.6 *Lanthanum Compensating Solution (0.55% La)* - Suspend 13 g La_2O_3 in 50 ml pure water in large beaker and dissolve with 28 ml concentrated HNO_3. Allow solution to cool, then pour into a 2-liter volumetric flask and bring to volume with pure water. This solution is used to eliminate chemical interference of phosphorus with calcium.

6.7 *Potassium and Sodium Standard (10 meq K, 10 meq Na/L)* - Dissolve 0.7456 g dried KCl and 0.5844 g NaCl in a liter volumetric flask and bring to volume with extractant (see 6.2). Alternatively, dilute 100 ml of commercial potassium and sodium standard (100 meq K, 100 meq Na) to 1 liter with extractant (see 6.2). Prepare working standards to contain 0, 0.5, 1.0 and 2.0 meq of Na and K/liter by appropriate dilution with extractant (see 6.2).

6.8 *Calcium and Magnesium Standard (25 meq Ca, 5 meq Mg)* - Dissolve 2.5 g dried $CaCO_3$ and 10.14 g $MgSO_4 \cdot 7H_2O$ in approximately 500 ml extractant (see 6.2) and

10 ml of concentrated HNO_3; bring to 1 liter volume with extractant (see 6.2). Alternatively, dilute 500 ml commercial Ca reference standard (1 ml = 1 mg Ca) and 60.75 ml commercial Mg reference standard (1 ml = 1 mg Mg) to 1 liter with extractant (see 6.2). Dilute with extractant (see 6.2) to obtain 5, 10, 15, 20 and 25 meq Ca and 1, 2, 3 and 5 meq Mg/liter. The latter dilutions compose the working standards.

7. PROCEDURE

7.1 *Extraction* - Measure 2.5 cm^3 of air-dry, 10 mesh (2-mm) soil into a 100-ml extraction bottle (see 5.3). Add 25 cm^3 of extracting solution (see 6.2) and shake for 5 minutes on a reciprocating shaker (see 5.4). Filter and collect the extract in 25 cm^3 plastic vials (see 5.8).

7.2 *Determination of Potassium and Sodium* - Using a diluter-dispenser (see 5.10) or pipette, transfer 2 ml of soil extract (see 7.1) or potassium-sodium working standards (see 6.7) and 8 ml of lithium working solution (see 6.5) into plastic vials (see 5.8). Set instrument reading at 100 using the 1 meq K-Na working standard. Atomize soil extract and record instrument reading. For final calculations for a 20 cm depth of soil to meq/100 cm^3, mg/dm^3, kg/ha, and lbs/acre of K and Na (see 7.4).

7.3 *Instrument Calibration* - Proper precautions should be taken to follow manufacturer's recommendations in the operation and calibration of the instrument. Linearity between concentration of K and Na can be ascertained by running a series of appropriate standards (see 6.7). If the instrument reading exceeds 200, dilute equal portions of the soil extract - lithium sample mixture with zero standard (see 7.2) and multiply the results by 2.

7.4 *Calculations (Potassium and Sodium)* - With the 1 meq K-Na standard (see 6.7) set at 100, the instrument reading = 0.01 meq K or Na/100 cm^3 soil. Alternatively, the instrument reading x 3.91 = mg K/dm^3 and the instrument reading x 2.3 = mg Na/dm^3 of soil. For conversion of mg K and Na/dm^3 to kg/ha multiply by 2. Multiply mg K or Na/dm^3 by 1.78 to obtain lbs/acre to a depth of 20 cm. All the above calculations are based on the volume of soil (see 5.2) that is employed in these soil test procedures (see 9.5).

7.5 *Determination of Calcium and Magnesium* - Using a diluter-dispenser (see 5.10) or pipette, transfer 1 ml of Ca-Mg standard (see 6.8) or soil extract (see 7.1) and 9 ml of lanthanum compensating solution (see 6.6) into plastic vials (see 5.8). Adjust instrument to zero with a blank composed of 1 ml extractant (see 6.4) and 9 ml of La compensating solution (see 6.6). Standardize instrument with Ca-Mg standards (see 6.8) [by setting the 10 meq Ca - 2 meq Mg working standard (see 6.8) at 100 and the 25 meq Ca - 5 meq Mg working standard at the 250 instrument reading,] respectively. An instrument equipped with a 3-standard microporcessor is required, to obtain linearity above an instrument reading of 100.

7.6 *Instrument Calibration* - Proper precautions should be taken to follow manufacturer's recommendations in the operation and calibration of the instrument. Linearity between concentration of Ca and Mg can be ascertained by running a series of appropriate standards (see 6.8). Calcium and magnesium concentrations are linear up to 10 meq Ca and 2 meq Mg at a corresponding instrument reading of 100. By use of a 3-standard microprocessor, linearity can be obtained up to 25 meq Ca and 5 meq Mg with a corresponding instrument reading of 250. If scale expansion above 100 instrument reading is not available and the unknown readings exceed 100, dilute known aliquot of soil extract - La mixture with zero standard (see 7.5) and multiply by the dilution factor.

7.7 *Calculations (Calcium and Magnesium)* - With the 10 meq Ca - 2 meq Mg and 25 meq Ca - 5 meq Mg standards (see 6.8) set at an instrument reading (IR) of 100 and 250 respectively; the corresponding concentrations on a volume soil basis are: IR x 0.1 = meq Ca/100 cm^3 and IR x 0.02 = meq Mg/100 cm^3. Alternatively, to convert IR to mg Ca

and Mg/dm^3, multiply by 20.04 and 2.432, respectively. To obtain kg Ca and Mg/ha, multiply mg/dm^3 by 2. Then kg/ha of Ca and Mg multiplied by 0.891 = lbs/acre.

8. INTERPRETATION

8.1 Evaluation of the analytical results and the corresponding fertilizer recommendations must be based on field response data conducted under local soil-climate crop conditions (see 9.6). Dr. A. Mehlich proposed critical levels of P, K, Mg, Mn, Zn, and Cu for the Mehlich III extractant (9.2) as well as interpretive guidelines for evaluating percent calcium and base saturation (9.1).

9. REFERENCES

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DETERMINATION OF SULFATE SULFUR BY MONOCALCIUM PHOSPHATE EXTRACTION

G. V. Johnson[1]

1. PRINCIPLE OF THE METHOD

1.1 Available soil S exists in both organic and inorganic forms. However, since inorganic forms usually provide the major supply and plants absorb soil-available S as $SO_4^=$, measures of SO_4-S in soil have generally provided the best relationship to plant uptake.

1.2 Several extraction solutions have been used for measuring SO_4-S in soils (11.2). The most common utilize monocalcium phosphate either in water or 2N acetic acid (11.3). In either extractant the concentration of monocalcium phosphate is 500 ppm P. The phosphate anion promotes desorption of sulfate through exchange reactions.

1.3 In acid solutions sulfate reacts with barium to form an insoluble fine crystaline precipitate. This reaction is the basis for turbidometric quantitative analysis of sulfate. Satisfactory analysis can also be performed by vacuum ICP.

2. RANGE AND SENSITIVITY

2.1 The procedure is sensitive to 1 lb/A of SO_4-S and response is linear to 25 lbs S/A.

3. INTERFERENCES

3.1 Any colloidal matter or color in the extract will cause error. Care must be taken during filtering to assure a clear filtrate from the extraction. Charcoal is used to adsorb dissolved soil organic matter which might otherwise cause a positive error in determinations.

4. PRECISION AND ACCURACY

4.1 Repeated analysis of the same sample will yield results within ± 1 to 2 lbs S/A when care has been taken to standarize technique throughout the procedure. The turbidometric analysis is the source of most variability.

5. APPARATUS

5.1 No. 10 (2-mm opening) sieve.

5.2 Scoops: 8.5 - cm^3 (10 g); two 1/4 teaspoon.

5.3 Extraction/filtrate flasks, 50-ml Erlenmeyer (test tubes may be used as an alternative to filtrate flasks).

5.4 Reciprocating shaker, 180 oscillations per min.

5.5 Filter funnel, 11-cm.

5.6 Filter paper, Whatman No. 42, 11-cm.

5.7 Magnetic stirrer and 1/2" stirring bars (vortex shaker may be used as an alternative).

5.8 Spectrophotometer or colorimeter with a 420 nm filter.

5.9 Analytical balance and assorted glassware for preparing and dispensing solutions.

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6. REAGENTS

6.1 *Extracting Reagent* - Dissolve 2.0 g of $Ca(H_2PO_4)_2 \cdot H_2O$ in deionized water and bring to 1.0 liter volume.

6.2 *Seed Solution* - Dissolve 0.1087 g of K_2SO_4 in 500 ml of deionized H_2O and add 500 ml of concentrated HCl. Slowly add 2 g of powdered gum acacia while stirring. Keep refrigerated.

6.3 *Barium Chloride Crystals* - Use 20-30 mesh $BaCl_2 \cdot 2\ H_2O$.

6.4 *Charcoal* - Wash Darco G-60 activated carbon with extracting solution until it is free of measureable S, rinse with deionized H_2O and oven dry. Store in a closed container.

6.5 *S Standards* - Prepare a 50 ppm S primary standard by dissolving 0.2685 g of $CaSO_4 \cdot 2\ H_2O$ in extracting solution. Bring to one liter volume using extracting solution. Using the table below, prepare working standards by pipeting the indicated volume of primary standard into a 100 ml volumetric flask and bringing to volume with extracting solution.

Primary Standard ml	SO_4-S in Solution ppm	SO_4-S in Soil lbs/A
0	0	0
4	2	10
10	5	25
20	10	50

7. PROCEDURE

7.1 Measure 10 g of dry, sieved soil into an extraction flask, dispense 25 ml of the extracting solution to the flask, and shake for 30 minutes. Add ¼ teaspoon (about 0.15 g) of powdered charcoal and shake an additional 3 minutes. Filter and transfer a 10 ml aliquot to another flask. Add 1 ml of seed solution and immediately swirl the contents. Place flask on magnetic stirrer and add ¼ teaspoon (0.3 g) of $BaCl_2 \cdot 2H_2O$ crystals. Stir for about 1 minute and then read absorbance or concentration (on instruments which provide a proportional concentration output) at 420 nm.

8. CALIBRATION AND STANDARDIZATION

8.1 The spectrophotometer or colorimeter must be calibrated each day. It is also very important to standardize operational techniques and conditions since the size and development of $BaSO_4$ crystals is influenced by reaction time and temperature.

9. CALCULATIONS

9.1 As indicated by the table in Section 6.5, a factor of 5 is used to convert from ppm S in solution to lbs S/A. This conversion factor takes into account the 1:2.5 dilution by extraction and the conventional ppm to lb/A conversion (2X).

10. INTERPRETATION

10.1 A "first approach" to interpretation may be achieved by estimating the sulfur requirement from existing crop-yield goal and nitrogen-requirement relationships assuming a N:S ra-

tio of 20:1 (11.2). Accordingly, a soil test of 4 lbs available S/A would be adequate for 50 bushels of wheat, 70 bushels of corn, 1 1/2 bales of cotton, or 1 1/2 tons of alfalfa (11.4). As in the case of available-N tests, a subsoil test is necessary for a complete assessment of available S.

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DETERMINATION OF ZINC, MANGANESE, COPPER, AND IRON BY DTPA EXTRACTION

G. V. Johnson[6]

1. PRINCIPLE OF THE METHOD

1.1 The theory of this method has as its foundation the favorable formation constants (12.2) for the synthetic chelate DTPA (Diethylenetriaminepentaacetic acid: $C_{14}H_{23}O_{10}N_3$) and the metal ions of Zn, Mn, Cu, and Fe at an equilibrium pH of 7.3. The chelate has a relatively weak affinity for Ca at pH 7.3 that allows satisfactory extraction of these elements in calcareous soils. The formation constants are sufficiently great to complex significant amounts of the elements in the presence of natural chelates and insoluble inorganic compounds common in soils. An excess of chelate eliminates metal competition for ligands, and TEA (triethanolamine) buffer assures pH stability. The presence of $CaCl_2$ in the extraction solution suppresses dissolution of calcium carbonate and release of occluded micronutrients. The soil sources extracted by the chelate are believed to be at least partially responsible for providing these nutrient elements to plants.

1.2 The procedure was first developed and reported by Lindsay and Norvell (12.1) and calibrated for use with Colorado soils (12.3).

2. RANGE AND SENSITIVITY

2.1 Extractable iron and manganese levels will range from a fraction of one ppm from alkaline soils low in organic matter to as much as 100 ppm from strongly acid soils. Zinc and copper levels will generally range a factor of 10 lower and be strongly influenced by soil organic matter level.

2.2 The sensitivity will depend upon the analytical instrumentation and techniques used. Because of the established critical levels used for detecting deficiencies, detection limits should be at least 0.05 ppm for Zn, Mn, and Cu and 0.1 ppm for Fe. Analysis by AA or ICP easily meets these requirements.

3. INTERFERENCES

3.1 The procedure is essentially free of interferences. There is a sufficiently large excess (est. 10X) DTPA to assure that the micronutrient metals will not be competing for the chelate. Other metal elements which might also be complexed are not normally present in agricultural soils at competing (interfering) levels. Analysis of these metals by AA or ICP is free of significant interference.

3.2 The greatest chance for erroneous soil test values arises from sample contamination during sampling or sample preparation. Special precaution should be taken to avoid the use of galvanized sampling tools or screens. Plastic, wood, or stainless steel materials should be used whenever soil comes in contact with sampling or preparation equipment.

4. PRECISION AND ACCURACY

4.1 Repeated analysis of the same soil for these metals should yield coefficients of variability of about 10%. Much of this variability will be associated with soil heterogeneity.

5. APPARATUS

5.1 No. 10 (2-mm opening) sieve.

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5.2 Scoop, 8.5-cm^3.

5.3 Extraction flask, 50 ml Erlenmeyer.

5.4 Reciprocating shaker, 180 oscillations per minute.

5.5 Filter funnel, 11-cm.

5.6 Whatman No.42 ashless filter paper (or equivalent), 11-cm.

5.7 AA or ICP instrument.

5.8 Analytical balance, pH meter with electrodes, and assorted glassware for preparation of standards and dispensing solutions.

6. REAGENTS

6.1 *Triethanolamine (TEA).*

6.2 *Diethylenetriaminepentaacetic acid (DTPA).*

6.3 $CaCl_2 \cdot 2H_2O$.

6.4 *Hydrochloric acid, 6N.*

6.5 *Extracting Reagent* - Combine 14.92 g TEA, 1.97 g DTPA, and about 100 mls of water. After the DTPA is in solution, add 1.47 g $CaCl_2$ and bring to one liter volume with water while adjusting pH to 7.3 using the 6N HCl. This solution is stable for several months.

6.6 *Metal Standards* - Working standards in the range of 0 to 10 ppm for Fe and Mn and 0 to 2.5 ppm for Cu and Zn will be suitable for either AA or ICP analysis. These may be conveniently prepared using the extracting reagent to dilute commercially available 1000 ppm certified stock solutions.

7. PROCEDURE

7.1 Measure 10 g or 8.5 cm^3 of air-dry, sieved soil into an extraction flask. Add 20 ml of extracting reagent and shake for 2 hours. Filter and analyze directly by AA or ICP.

8. CALIBRATION AND WORKING STANDARDS

8.1 *Working Standards* - These solutions should be prepared as indicated in Section 6. If element concentrations are found above the high standard, there is generally no need to dilute the sample and reanalyze since there is obviously an adequate supply of the nutrient for crop production. When toxic levels are of interest, samples can be diluted and analyzed again.

8.2 *Calibration* - Calibration procedures will vary with instrument. Instruments should be calibrated according to manufacturer's specifications, taking care that the critical level (see Section 1) is about midway in the calibration range or at a point of optimum precision and accuracy.

9. CALCULATIONS

9.1 The ppm concentration of metal in soil extracts should be multiplied by a factor of 2 to convert to ppm of soil (solution:soil ratio is 2:1). Interpretations are made using initial levels established as metal extracted on a ppm soil basis (see Section 11).

10. EFFECTS OF STORAGE

10.1 Drying of soils may increase extractable Fe levels by as much as 2X and Mn by as much as 10 fold. Once dried, extractable levels are relatively stable except for Mn, which may continue to slowly increase, especially if the initial drying was incomplete or at only slightly higher than room temperature.

11. INTERPRETATION

11.1 Calibration of test values is often difficult due to a lack of soils with deficiencies of these micronutrients. As a first approach, the critical levels reported initially by Lindsay and Norvell (12.3) of Zn = 0.8 ppm, Fe = 4.5 ppm, Mn = 1 ppm, and Cu = 0.2 ppm are sometimes used. These calibrations were used in Oklahoma but subsequent research and observation showed a Zn level of 0.3 ppm was adequate except for corn (0.8 ppm) and pecans (2.0 ppm). Wheat was found to be adequately supplied even with Zn levels of 0.1 ppm (12.4). Copper and manganese deficiencies have yet to be identified in Oklahoma.

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DETERMINATION OF ZINC, MANGANESE, AND COPPER BY MEHLICH 3 EXTRACTION

M. R. Tucker[7]

1. PRINCIPLE OF THE METHOD

1.1 The extraction and determination of manganese, zinc, and copper by this procedure is designed to be applicable across a wide range of soil properties ranging in reaction from acid to basic. Although the method was correlated with established extractants from several regions and critical levels established, the specific critical levels should be based on local soil, crop, and climatic conditions. Good correlations were obtained between Mehlich 2 and Mehlich 3 for Mn and Zn (9.2) even though the mean values were not the same. Mehlich 3 correlated well with the Mehlich-Bowling extractant for Cu (9.5). For critical levels for the Mehlich 3 extractant, see 9.2.

2. RANGE AND SENSITIVITY

2.1 Managanese, zinc and copper can be extracted and determined without dilution in soil concentrations of 20, 4.0 and 4.0 mg/dm^3 respectively. These equate to 40, 8.0 and 8.0 kg/ha for Mn, Zn, and Cu respectively. Higher concentrations can be determined with appropriate dilutions or by using instrumentation equipped with a 3-standard microprocessor. The method was developed using atomic absorption spectrophotometry at a 1:10 soil to sulution ratio (9.2).

2.2 Sensitivity will vary with type of instrument, wavelength selection, and method of excitation. For a complete description of these parameters see Issac and Kerber (9.8).

3. PRECISION AND ACCURACY

3.1 Repeated analyses of an internal check sample from 20 extractions by the NCDA Soil Testing laboratory gave variances of 9.69, 10.82, and 9.44% for Mn, Zn, and Cu, respectively. The mean values were 5.42, 2.29, and 1.71 mg/dm^3 of Mn, Zn, and Cu. The variance is essentially a factor related to sample heterogeneity rather than measurement, extraction, or method of analysis.

4. INTERFERENCES AND CONTAMINATION

4.1 There are no known interferences.

4.2 The potential of contamination between samples or from external sources (extraction vials, filter funnels, and washing apparatus) should be recognized. Precautions should be taken to avoid the use of extraction vials which contain micronutrient impurities. Certain plastic bottles are also charged and can retain copper and zinc from previous extractions. Consequently, all laboratory apparatus must be washed with a reagent capable of displacing adsorbed micronutrients. The rinsing solution used in this procedure is described below (see 7.0).

5. APPARATUS

5.1 No. 10 (2-mm) stainless steel sieve.

5.2 2.5 cm^3 (volumetric) soil measure and teflon-coated leveling rod.

5.3 100-ml extraction bottles, preferably plastic.

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5.4 Reciprocating shaker (200 4-cm reciprocations/minute).

5.5 Plastic filter funnels, 11 cm.

5.6 Whatman No 1 (or equivalent) filter paper, 11 cm.

5.7 Funnel rack.

5.8 Vials, polystyrene plastic, 25 ml capacity for sample collection.

5.9 Automatic dispenser for extractant, 25 ml capacity.

5.10 Atomic absorption spectrophotometer and/or ICP. A 3-standard microprocessor AA is desirable.

5.11 Volumetric flasks and pipettes as required for preparation of reagents and standard solution.

5.12 Analytical balance.

6. REAGENTS

6.1 All reagents are ACS analytical grade or standard reference solutions unless otherwise stated.

6.2 *Extracting Reagent (0.2N CH_3COOH; 0.25N NH_4NO_3; 0.015N NH_4F; 0.013N HNO_3; 0.001M EDTA)* - see 6.3 and 6.4 for mixing procedure of extraction reagents.

6.3 *Ammonium Fluoride - EDTA Stock Reagent* - Add approximately 600 ml pure water to a 1-liter volumetric flask; add 138.9 g NH_4F and dissolve, then add 73.05 g EDTA, dissolve mixture and bring to volume with pure water.

6.4 *Final Extraction Reagent Mixture* - Add approximately 3000 ml of pure water to a 4-liter volumetric flask, add 80 g NH_4NO_3 and dissolve; add 16 ml NH_4F-EDTA stock reagent (see 6.3) and mix well. Add 46 ml CH_3COOH and 3.28 ml conc. HNO_3, then bring to volume with pure water and mix thoroughly. The final pH should read 2.5 ± 0.1.

6.5 *Manganese Standard (20 µg Mn/ml)* - Dilute 20 ml of commercial Mn reference standard (1 ml = 1 mg Mn) to 1 liter with extractant (see 6.4).

6.6 *Manganese Working Standards* - Dilute 25, 50, 75 and 100 ml of manganese standard (see 6.5) to 1 liter with extractant (see 6.4), corresponding to 0.5, 1.0, 1.5, and 2.0 µg Mn/ml. Following manufacturer's guidelines, set instrument at zero with extractant (see 6.4). Using the 2.0 µg Mn/ml standard, set instrument reading to 100. Intermediate standards can be used to check linearity. Higher concentration ranges can be used with a 3-standard microprocessor-equipped atomic absorption spectrophotometer.

6.7 *Procedure and Calculations* - With the 2.0 µg Mn/ml set at the 100 instrument reading, soil extracts can be read directly with appropriate dilutions when instrument readings exceed 100. Instrument readout x 0.2 = mg Mn/dm^3 of soil. The mg Mn/dm^3 x 2 = kg Mn/ha and kg Mn/ha x 0.891 = lbs Mn/acre. These calculations are based on a volume of soil to a depth of 20 cm. For rationale see 9.4, 9.7.

6.8 *Zinc and Copper Standards (4 µg Zn, Cu/ml)* - Dilute 100 ml of commercial reference standard (1 ml = 1 mg Zn, 1 mg Cu/ml) to 1 liter with extractant (see 6.4). From this mixture, dilute 40 ml to 1 liter with extractant (see 6.4) for corresponding concentrations of 4 µg Zn and Cu/ml. These standards can be prepared separately or in combination, depending on preference.

6.9 *Zinc and Copper Working Standards* - Dilute 5 and 10 ml of zinc and copper standard (4 μg Zn, Cu/ml) to 1 liter with extractant corresponding to 0.2 and 0.4 μg Zn, Cu/ml. Following manufacturer's guidelines, adjust instrument to zero with extractant (see 6.4). Atomize the 0.4 μg Zn, Cu/ml standard and adjust instrument reading to 100. Intermediate standards can be prepared to check for linearity. Higher concentrations can be used on instruments equipped with a 3-standard microprocessor.

6.10 *Procedure and Calculations* - With the 0.4 μg Zn, Cu/ml standard set at the 100 instrument reading, soil extracts can be read directly with appropriate dilutions when the instrument reading exceeds 100. Instrument reading x .04 = mg Zn, Cu/dm^3 of soil. Alternately, instrument reading x 0.08 = kg Zn, Cu/ha. To convert kg Zn, Cu/ha to lbs/acre multiply by 0.891. These calculations are based on a volume of soil to a depth of 20 cm. For rationale see 9.4, 9.7.

7. DECONTAMINATION SOLUTION (0.2% $AlCl_3 \cdot 6H_2O$)

7.1 Dissolve 20 g $AlCl_3$ in about 2 liters of pure water and make to 10 liters with pure water. This solution volume can vary with the number of samples involved.

7.2 *Procedure* - Wash extraction bottles (see 5.3), extraction vials (see 5.8), and funnels (see 5.7) with hot tap water, rinse with 0.2% $AlCl_3 \cdot 6H_2O$, then rinse with distilled water. After placement of filter paper into funnels, rinse paper with 0.2% $AlCl_3 \cdot 6H_2O$ followed with distilled water and allow to drain. All washing apparatus should be constructed from stainless steel or plastic.

8. INTERPRETATION

8.1 *Manganese* - Calibration of the Mn soil test with this extractant is based on extractable Mn and soil pH (see 9.1). Equations predicting the manganese availability index (MnAI) for soybeans and corn are as follows:

Soybean MnAI = 101.2 + 0.6 (MnI) - 15.2 (pH).

Corn MnAI = 108.2 + 0.6 (MnI) - 15.2 (pH).

The critical soil test MnI = 4 mg Mn/dm^3, which is equal to a 25 soil text index. Due to limited soil test calibration for other crops, calculation of the MnAI is based on their sensitivity to Mn as compared with corn or soybeans. For example, the soybean MnAI is used to predict Mn needs for small grains since their sensitivity is closely related to soybeans.

8.2 *Copper* - The critical copper soil test level was established with the Mehlich-Bowling (9.5) and the Mehlich 3 extractants (9.6). The critical level is 0.5 mg Cu/dm^3, which equates to a soil test index of 25.

8.3 *Zinc* - The critical zinc soil test level by this procedure is 1.0 mg Zn/dm^3, which equates to a soil test index of 25. A zinc availability index (ZnAI) has been established for mineral, mineral organic, and organic soils based on the relationship between extractable zinc and soil pH (9.9). These values are as follows:

ZnAI (mineral soils) = Zn I x 1.0

ZnAI (mineral-organic soils) = ZnI x 1.25

ZnAI (organic soils) = ZnI x 1.66

9. REFERENCES

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DETERMINATION OF BORON BY HOT WATER EXTRACTION

R. A. Isaac[6]

1. PRINCIPLE OF THE METHOD

1.1 This method is based on a modification of the method published by Berger and Truog (11.1).

1.2 Since water extracts of low CEC soils often produce colloidal suspensions, colorimetric analysis using the azomethine method is unsuitable. However, the curcumin colorimetric method would be applicable because measurement of the extracted boron in an alcohol solution eliminates the effect of colloidal suspensions.

2. RANGE

2.1 The range of the method is 0.10 to 3.00 kg/ha.

3. INTERFERENCES

3.1 There are no significant interferences.

4. APPARATUS

4.1 ICP emission spectrograph.

4.2 Shaking hot water bath.

4.3 Analytical balance.

4.4 Scoop, 5 cm^3 volumetric.

4.5 125 ml plastic erlenmeyer flasks.

4.6 Plastic filter funnels, 7 cm.

4.7 Plastic auto self-zeroing buret, 50 ml.

4.8 Whatman No. 5 filter paper or equivalent, 11 cm.

4.9 No. 10 (2-mm opening) sieve.

5. REAGENTS

5.1 *Boron Standard (100 ppm)* - weigh 0.5716 g boric acid (H_3BO_3) into a 1 L volumetric flask and dilute to volume with deionized water. Store in a plastic bottle.

5.2 *Boron Standard (10 ppm)* - pipet 10 ml of the 100 ppm boron standard (see 5.1) into a 100 ml volumetric flask and dilute to volume with dionized water. Store in a plastic bottle.

5.3 *Deionized Water.*

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6. PROCEDURE

6.1 Scoop 5.0 cm^3 of air-dry < 10 mesh (2-mm) soil into a 125 ml plastic erlenmeyer flask. Add 25 ml deionized water and shake for 30 minutes on a hot water shaking bath at 80 C. Filter through Whatman No. 5 filter paper into a 125 ml plastic erlenmeyer flask. Prepare 2 sample blanks for each 40 samples analyzed. Analyze the filtrate for boron using an ICP emission spectrograph. Colorimetric procedures such as azomethine-H (11.2) and the curcumin method (11.3) may also be employed. However, note comments in 1.2.

7. CALIBRATION AND STANDARDS

7.1 *Working Standards* - prepare working standards containing 0.10 and 0.30 µg boron/ml by diluting aliquots of the 10 ppm boron stock solution standard (see 5.2) with deionized water. Store in plastic bottles.

7.2 *Calibration* - use deionized water (0.0 µg/ml boron/ml) and the 0.30 µg boron working standard for 2 point calibration. The 0.10 µg/ml working standard is used to check the linearity of the 2-point calibration curve. The curve should be linear within ±5%.

8. CALCULATIONS

8.1 The results are reported as kg/ha for a 20 cm depth of soil. Kg of boron/ha = (µg/ml of boron in extraction filtrate - µg of boron in blank) x 10. If extraction filtrate is diluted, the dilution factor must be applied.

9. EFFECTS OF STORAGE

9.1 After extraction, the boron-containing filtrate should not be stored any longer than 24 hours unless refrigerated or treated to prevent bacterial growth.

10. INTERPRETATION

10.1 Evaluation of the analytical results to crop response must be based on correlation data from field and greenhouse tests under local soil-climate-crop conditions.

11. REFERENCES

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DETERMINATION OF NITRATE-NITROGEN BY SPECIFIC-ION ELECTRODE

G. V. Johnson[9]

1. PRINCIPLE OF THE METHOD

1.1 This procedure describes the determination of available (soluble) nitrate-nitrogen (NO_3-N) using a digital pH/mV meter and a specific ion (NO_3) electrode with a double junction reference electrode. The technique and principles of the procedure are similar to that of measuring pH with a glass electrode. The NO_3 is measured in a suspension of soil with water or a dilute salt such as $(NH_4)_2SO_4$ or $CaSO_4$ and is usually reported as NO_3-N. Nitrogen so measured is often called "residual" or "carryover" N and is subtracted from the total crop N requirement as a final step in determining fertilizer N requirement. This measurement is probably most useful in cropping systems where the soil is not highly leached. However, even in leached soils the measurement can be useful when samplings are properly timed and include a subsoil sample (12.1).

1.2 The use of this method and general interest in NO_3-N soil testing occurred in about the late '60s (12.1). Early research demonstrated the procedure to be relatively free of interference from other ions commonly found in soils (12.1, 12.3). A major disadvantage of the early electrodes was the high requirement for skill and dexterity in replacing the membrane and reassembling the electrode every three weeks. The newer electrodes have a screw-on module that eliminates this problem.

2. RANGE AND SENSITIVITY

2.1 The electrode operates linearly in the range of about 1 to 1,000 ppm NO_3-N.

2.2 Sensitivity of the electrode procedure in soil testing is a function of the soil-to-solution ratio. However, even for crops with only moderate nitrogen requirements (e.g., cotton), a soil-to-solution ratio of 1:2.5 will allow measurement of levels as low as 5 lb/A.

3. INTERFERENCES

3.1 Chloride, carbonate, and bicarbonate are the ions most common to soil extracts which may cause interference. However, even these ions have only negligible effect. At concentrations of up to 400 ppm these ions will cause less than a 10% error in analysis of 10 ppm NO_3-N. Specific details of interferences as well as electrode principles and operational procedures are usually provided with electrode purchase (12.4).

4. PRECISION AND ACCURACY

4.1 Repeated analysis of different control samples used over several months in the Oklahoma State University Agronomic Services Laboratory has demonstrated a reproducibility of ± 2 to 3 lbs/A of the mean value of samples containing 10 to 50 lbs/A of NO_3-N. Requests for rerun of the test, even on soils containing over 100 lbs/A of NO_3-N, usually repeat within ± 10 % of the initial test value.

5. APPARATUS

5.1 No. 10 (2-mm opening) sieve.

5.2 Scoop, 8.5 cm^3 volumetric (10 g).

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5.3 *Extraction container, 100 ml.* Disposable, 3.5 oz. plastic Solo cups, fitted into a styrofoam base, are inexpensive and work very well.

5.4 A digital pH/mV meter.

5.5 *A double junction reference electrode.* Use the calcium sulfate extraction solution (see 6.1) as the outer-chamber filling solution instead of the filling solution shipped with the reference electrode. Replace the solution in the outer chamber daily.

5.6 A nitrate ion-sensitive electrode.

5.7 A magnetic stir bar and plate (or other suitable means for gently suspending soil in small samples).

6. REAGENTS

6.1 *Extracting Reagent* - Dissolve 2.0 g of calcium sulfate or 2.53 g of calcium sulfate dihydrate in pure water and bring to 1.0 liter with pure water.

6.2 *Primary Standard Solution* - Weigh 7.220 g of dry potassium nitrate into a 1 liter volumetric flask. Dissolve the potassium nitrate and bring to 1 liter volume with calcium sulfate extracting solution. Label 1000 ug/ml N as potassium nitrate.

6.3 *Working Standard* - Prepare a 100 ug/ml working standard solution by transferring 100 ml of the primary standard (see 6.2) to a 1 liter volumetric flask and bringing to volume with extracting solution. Both the primary standard and the working standard solutions should be stored in the refrigerator.

6.4 *Calibration standards* - Prepare calibration standards using the working standard solution (6.3) according to the following table. Bring to 500 ml volume using extracting reagent.

MLS Working standard	Actual ppm NO_3-N	Reading in lbs N/A
0	0	0
25	5	25
50	10	50
100	20	100

7. PROCEDURE

7.1 Measure 10 g of air-dry, sieved soil into the extraction container. Add 25 ml of extracting solution and shake for 30 minutes on a rotary shaker at 150 rotations/minute.

7.2 Measure NO_3-N in soil/extraction solution suspension by immersing electrode directly into the suspension while it is being stirred. Analyze a standard solution every 10 samples and restandardize if necessary.

8. CALIBRATION AND STANDARDS

8.1 *Working standards.* Working standards should be prepared as described in section 6.4. These solutions may be prepared in sufficient volume to satisfy the needs for one week when stored in a refrigerator.

8.2 Standardize the instrument using the 100 lbs N/A solution for the high standard and the 25 lbs N/A solution for the low standard with a two-point standardization. Solutions should be stirred while readings are being taken, and the electrode rinsed with distilled water and blotted after each determination. Verify reliable (linear) standardization by analysis of the remaining calibration solutions (see 6.4).

9. CALCULATIONS

9.1 The results are reported as lbs. NO_3-N per acre furrow slice (6 2/3 inch depth). The same testing procedure is used to measure available NO^3-N in the subsoil. The surface and subsoil values may be combined after adjustments to the subsoil value have been made to account for the difference in soil depth sampled.

10. EFFECTS OF STORAGE

10.1 Soils may be stored in an air-dry condition for several months with no effects on the available NO_3-N content.

10.2 After extraction the suspensions should be analyzed as soon as possible. Results are unlikely to change significantly within 12 hours after extraction.

11. INTERPRETATION

11.1 Evaluation of the results with respect to adequacy of nitrogen for crop production is possible when the nitrogen requirement of different crop yield goals has been established. In the simplest, most direct interpretation, N fertilizer requirement is calculated by subtracting the soil test N value from the N requirement estimated from crop yield goal (12.5).

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DETERMINATION OF pH, SOLUBLE SALTS, NITRATE, PHOSPHORUS, POTASSIUM, CALCIUM, MAGNESIUM, SODIUM, AND CHLORIDE IN POTTING MEDIA (NON-SOIL MIXES) BY SATURATION EXTRACTION

G. Kidder[10]

1. PRINCIPLE OF THE METHOD

1.1 Potting media (non-soil mixes) used for production of plants in pots or similar containers generally have relatively low nutrient-holding capacity. The primary source of nutrients for plant growth are those in the soil solution. Saturation extract of the media gives a good indication of the available nutrient status. In this method, the media sample is saturated without grinding or sieving; thus possible segregation of the mix components is eliminated and analysis of the actual growth media being used by the client is assured. Soluble salt and nutrient concentrations in the saturation extract are related to the moisture-holding capacity of the media. This method eliminates the need to consider bulk density and enables one set of guidelines for all mixes (12.5).

1.2 Saturation extraction for measuring salt content of soil was adopted by the U.S. Salinity Laboratory (12.4). In a study of the saturated soil extract method for analyzing greenhouse growth media, Lucas, Rieke, and Doll (12.2) found it provided more meaningful results and was more advantageous than the Spurway method (12.3). Warneke and Krauskopf (12.5) discussed the saturation extract method and presented the interpretations used by the Michigan State University Soil Testing Laboratory.

2. RANGE AND SENSITIVITY

2.1 The method is adapted to potting media (soil-less mixes and sand) that have low nutrient-holding capability. The method is less accurate for soils or mixes that have appreciable nutrient-holding capacity.

2.2 Sensitivity of analysis is dependent upon the instrumentation used. Dilution may be necessary for samples having high soluble salt levels.

3. INTERFERENCES

3.1 High soluble salt levels may confound pH measurements.

3.2 Mixes containing slow-release fertilizers may give inconsistent results.

3.3 Interferences relevant to individual analytical procedures (soluble salt, pH, NO_3-N, P, K, Ca, Mg, Na, and Cl) apply.

4. PRECISION AND ACCURACY

4.1 Reproducibility of results is dependent upon wetting the sample just to the point of complete saturation. When properly saturated, pH, soluble salt, and nutrient levels are reproduced with good agreement.

5. APPARATUS

5.1 600-ml plastic beaker.

5.2 Spatula.

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5.3 Filter paper (Whatman No. 1), 11-cm.

5.4 Vacuum flask, 250-ml.

5.5 Buchner funnel, 11-cm.

5.6 Vacuum pump.

5.7 Vial, snap-cap, 100 ml.

5.8 Conductivity bridge with 0 to 1 million ohm range.

5.9 Conductivity cell, dipping type, (cell constant of 1.0).

5.10 Thermometer.

5.11 pH meter with paired glass and calomel reference electrodes.

5.12 pH meter with expanded scale or specific ion meter.

5.13 Nitrate electrode with paired reference electrode.

5.14 Chloride electrode with paired reference electrode.

5.15 Colorimeter.

5.16 Flame emission and/or atomic absorption spectrophotometer.

5.17 Volumetric flasks and pipettes as required for preparation of reagents and standard solutions.

6. REAGENTS

6.1 *Pure Water* - for saturation of samples.

6.2 *0.01N Potassium Chloride (KCl)* - for standardizing conductivity bridge.

6.3 *Buffer Solutions* - pH 4.00 and 7.00 buffers for standardizing pH meter.

6.4 *Nitrate-Nitrogen Standard (1000 ppm)* - Weight 7.218 g dry KNO_3 into a 1-liter volumetric flask and bring to volume with pure water. Prepare standards containing 1, 5, 10, 50, 100 and 200 ppm nitrate-nitrogen by diluting appropriate aliquots of the 1000 ppm standard with pure water.

6.5 *Chloride Standard (1000 ppm)* - Weigh 2.103 g dry KCl into a 1-liter volumetric flask and bring to volume with pure water. Prepare standards containing 1, 5, 10, 50, 100 and 200 ppm chloride by diluting appropriate aliquots of the 1000 ppm standard with pure water.

6.6 *Phosphorus Reagents* - see Chapter 3, Section 6.2 for phosphorus color development.

6.7 *Potassium Reagents* - see Chapter 4, Section 7.2 for potassium determination.

6.8 *Calcium Reagents* - see Chapter 4, Section 7.5 for calcium determination.

6.9 *Magnesium Reagents* - see Chapter 4, Section 7.5 for magnesium determination.

6.10 *Sodium Reagents* - see Chapter 4, Section 7.2 for sodium determination.

7. PROCEDURE

7.1 Fill a 600-ml beaker about 2/3 full with the potting media sample as received from the client. Gradually add pure water (see 6.1) while mixing until the sample is just saturated. At saturation the sample will flow slightly when the container is tipped and will be easy to work with a spatula. Depending on the mix's composition, the saturated sample may glisten as it reflects light. After mixing, allow the sample to equilibrate for one hour and then check 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 more media or pure water. Then allow to equilibrate for an additional half hour.

7.2 Determine pH on the saturated sample by carefully inserting the electrodes directly into the saturated media. Transfer the saturated sample to a Buchner funnel lined with a filter paper. Be sure there is good contact between the saturated sample and the filter. Eliminate entrapped air. Apply a vacuum and collect the extract in the flask. Transfer the extract to a snap-cap vial.

7.3 Check the temperature of the extract and adjust the temperature dial on the conductivity bridge. Rinse the electrode, then dip the conductivity cell into the extract. Determine the electrical conductance of the extract and record in decisemens per meter (dS/m, equivalent to mmhos per cm).

7.4 After establishing the standard curve, determine the nitrate-nitrogen content with a nitrate electrode. Record millivolt reading on an expanded scale pH meter or specific ion meter and compare with the standard curve plotted on semilogarithmic graph paper (12.1).

7.5 After establishing the standard curve, determine the chloride content with a chloride electrode. Record millivolt reading on an expanded scale pH meter or specific ion meter and compare with the standard curve plotted on semilogarithmic graph paper.

7.6 Determine phosphorus on an aliquot of the extract using an accepted colorimetric procedure (see Chapter 3).

7.7 Determine potassium, calcium, magnesium, and sodium on an aliquot of the extract by flame emission or atomic absorption spectroscopy (see Chapter 4).

8. CALIBRATION AND STANDARDS

8.1 *Working Standards* - Working standards should be prepared as indicated in section 6. If the element concentrations are outside the range of the instrument or standards, prepare a suitable dilution. Dilute only as necessary to minimize magnification of error introduced by diluting.

8.2 *Calibration Procedures* - Calibration procedures vary with instrument techniques and type of instrument. Take every precaution to ensure that the proper procedures and manufacturer recommendations are followed in the operation and calibration of the instruments used.

9. CALCULATIONS

9.1 Report soluble salt levels as decisemens per meter (dS/m). Convert the electrical conductance (dS/m) to ppm (mg/l) by multiplying by the empirically derived factor of 700.

9.2 Report results for nitrate-nitrogen, phosphorus, potassium, calcium, and magnesium as mg/l of extract.

9.3 Determine nutrient balance by calculating for each nutrient element its percentage of the total soluble salts, as follows:

$$Element, \% = \frac{(Element\ conc)\ (100)}{Total\ soluble\ salt\ conc} = \frac{(mg/l)\ (100)}{(mg/l)}$$

10. EFFECT OF STORAGE

10.1 This procedure allows extraction of moist samples just as they are received from the client. Drying of potting media samples is unnecessary and undesirable. Storage of samples in either the dry or moist state will influence primarily the soluble nitrate-nitrogen level.

11. INTERPRETATION

11.1 Desirable pH, soluble salt, and nutrient levels vary with the crop being grown, the growth stage of the plants, and management practices. The following general guidelines can be used in making preliminary judgement of the results. Clients should be urged to observe plant growth and develop interpretations of test results particularly suited to their crop, media, and management situations.

Annuals (12.5)

	Rating Category				
Analysis	Low	Acceptable	Optimum	High	Very High
pH	< 5.3	5.3- 5.6	5.6-5.8	5.8-6.5	> 6.5
Soluble Salts (dS/m)	< 0.8	0.8-2.0	2.0-3.5	3.5-5.0	> 5.0
Nitrate-N (mg/l)	< 40	40-100	100-200	200-300	> 300
Phosphorus (mg/l)	< 3	3- 5	6- 10	11- 18	> 18
Potassium (mg/l)	< 60	60-150	150-250	250-350	> 350
Calcium (mg/l)	< 80	80-200	200-400	> 400	
Magnesium (mg/l)	< 30	30- 70	70-140	> 140	

Woody Ornamentals*
Adapted from Yeager and Ingram (12.6)

Analysis	Rating Category				
	Low	Acceptable	Optimum	High	Very High
pH	< 5.0	5.0-5.5	5.5-5.8	5.8-6.5	> 6.5
Soluble Salts (dS/m)	< 0.7	0.7-1.0	1.0-1.5	1.5-3.0	> 3.0
Nitrate-N (mg/l)	< 40	40-80	80-100	100-200	> 200
Phosphorus (mg/l)	< 3	3- 8	8- 12	12- 18	> 18
Potassium (mg/l)	< 10	10-20	20- 40	40- 80	> 80
Calcium (mg/l)	< 10	10-20	20- 40	40-100	> 100
Magnesium (mg/l)	< 10	10-15	15- 20	20- 60	> 60

*Plants of the Ericaceae family (e.g., azaleas) require lower levels of nutrients than those shown in this table.

11.2 Desired nutrient balance as percent of the total soluble salts is: 8 to 10% nitrate-nitrogen, 11 to 13% potassium, 14 to 16% calcium, and 4 to 6% magnesium. If chloride and sodium are determined, their percentages should each be less than 10%.

12. REFERENCES

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STRIP-MINE TESTING PROCEDURE FOR MAXIMUM POTENTIAL ACIDITY AND ALKALINITY DETERMINATION

W. O. Thom[1]

A. TOTAL POTENTIAL ACIDITY

1. PRINCIPLE OF THE METHOD

1.1 The total potential acidity is a total of the potential acidity plus the free acidity of the soil or spoil material. The free acidity is the acidity of the soil or spoil as measured with the buffer pH method. The potential acidity is the acidity of the soil or spoil after oxidation of the sulfides has occurred.

1.2 Developmental work on the total potential acidity test was done to obtain reliable and reproducible values on a routine basis. The test meets this requirement except that, when calcium carbonate is present in the material, an erroneously low value for potential acidity will be obtained.

1.3 An effervescence test for calcium carbonate is included to aid in judgement for determining the alkalinity or neutralization potential of the soil or spoil sample (Part B).

1.4 The major source of sulfides found in strip mine areas is iron pyrite (FeS_2). Its oxidation with H_2O_2 is as follows:

$$2FeS_2 + 15H_2O_2 \rightarrow Fe_2O_3 + 4SO_4^{-2} + 11H_2O + 8H^+$$

For every equivalent of FeS_2 present, 4 equivalents of H^+ are produced.

2. RANGE AND SENSITIVITY

2.1 Due to the small quantities of iron pyrite needed to generate a final recommendation of several tons of lime (20 mg FeS_2 = 10 tons $CaCO_3$), it is important that great care be given to sample collection and handling, especially in the grinding and mixing of the sample.

2.2 If the lime ($CaCO_3$) requirement is greater than 20 tons per acre with a 5 g sample, the procedure should be repeated with a 1 g sample in duplicate, or 0.2 g sample in duplicate.

3. INTERFERENCES

3.1 Free $CaCO_3$ or lime reduces measured potential acidity.

4. APPARATUS

4.1 Jaw crusher-grinder.

4.2 Pulverizing grinder.

4.3 Hot water bath.

4.4 Hot plate.

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4.5 18 liter bottle with ascarite column.

4.6 4.5 cc scoop.

4.7 50 ml beaker.

4.8 Glass stirring rod.

4.9 500 ml beaker.

4.10 Ribbed cover glasses for 500 ml beaker.

4.11 pH meter with expanded scale.

4.12 Titration buret.

4.13 Separating riffle.

5. REAGENTS

5.1 *Hydrogen peroxide, 30%.* Keep refrigerated.

5.2 *Potassium hydrogen phthalate ($KHC_8H_4O_4$).*

5.3 *Sodium hydroxide, 0.02 to 0.05N* - Add 30 ml 1:1 NaOH to 18 liters of boiled, deionized water. Standardize with $KHC_8H_4O_4$ and store in stoppered bottle with ascarite column.

5.4 *Standard pH 4.0 buffer.*

5.5 *Standard pH 7.0 buffer.*

5.6 *6N hydrochloric acid.*

6. PROCEDURE

6.1 The well-mixed sample is crushed into particles 1/4 inches or less using the jaw-crusher grinder. The sample is then ground through the pulverizing grinder until all the sample passes a 10-mesh screen. *No part of the sample is discarded.*

6.2 The whole sample is riffled into two sub-samples. One sub-sample is replaced in the original container for storage and the other sub-sample is ground through a pulverizing grinder until all the sub-sample passes an 80-mesh screen. A micromill may be used to finish grinding what the pulverizing grinder does not finish. *No part is discarded.*

6.3 A preliminary effervescence test is carried out prior to measuring potential acidity. Measure 4.5 cc of dry 80-mesh sample into a 50-ml beaker, add 10-ml deionized water and stir with a glass rod to remove bubbles. Add 4-6 ml of 6N HCl and stir with glass rod. Immediately observe surface for bubbling (effervescence). Effervescence is rated as 0, +, + +, or + + + indicating carbonates as none, few numerous, or very numerous. Samples rated + + or + + + should have total alkalinity measured (Part B) for neutralizing credit from potential neutralizing bases.

6.4 Weigh 5.00 g of dry 80-mesh sample into a 500 ml beaker and cover with ribbed cover glass (Use balance with 0.01 g sensitivity).

6.5 Place beaker with sample into hot water bath at 50 C.

6.6 Add 10 ml H_2O_2 to sample and wait until reaction stops. Continue to add H_2O_2 by 10 ml increments until 120 ml of H_2O_2 has been added (This procedure may require 3 to 4 hours).

6.7 Keep reaction at 50°C for about 8 hours, turn off heat in hot water bath and allow reaction to continue until the next morning.

6.8 Remove beakers from water bath the next morning and place on hot plate at 95°C. Boil with ribbed cover glass in place until all effervescence has stopped. Add deionized water when volume drops to 50 ml. *Do not allow samples to boil dry.*

6.9 Remove samples from hot plate, cool to room temperature, and add deionized water until total volume is 150 ml. Use some of the deionized water to rinse adhered material from the sides of the beaker.

6.10 Titrate the sample with standardized NaOH to pH 7.0 using a standardized pH meter. Fill and empty the titration buret before titrating the sample.

6.11 A preliminary calculation should be made to determine if the procedure should be repeated with a smaller sample size:

$$ml\ NaOH\ x\ normality\ x\ 15\ =\ Est.\ Tons/A$$

If the answer is greater than 20, then repeat steps 6.4 through 6.10 with duplicate samples using 1.0000 g samples (Use balance with 0.01 mg sensitivity).

6.12 If the procedure using 1.0000 g samples is followed, a second calculation should be used to determine if the sample size should be further reduced:

$$ml\ NaOH\ x\ normality\ x\ 75\ =\ Est.\ Tons/A$$

If the answer is greater than 100, then repeat steps 6.4 through 6.10 with duplicate samples using 0.2000 g samples.

7.0 CALCULATIONS

7.1 Standardization of the NaOH requires the following calculation:

$$NaOH\ normality\ =\ \frac{(g\ KHC_8H_4O_4)\ (1000)}{(204.228)\ (ml\ NaOH)}$$

7.2 Determine total requirement of $CaCO_3$ to neutralize potential acidity as measured by this procedure:

$$Tons\ CaCO_3/1000\ tons\ material\ =\ \frac{(ml\ NaOH)\ (normality)\ (50)}{(sample\ size,\ g)}$$

7.3 The amount of agricultural lime recommended per 1000 tons of material will depend on the effective neutralizing capability of the lime and the conversion factors developed through research studies.

7.4 The bulk density may be greater from a surface disturbed by mining than from an agricultural soil. Therefore, the calculated amount of lime needed should not be recommended on a per acre basis until the bulk density of the reconstructed surface is determined.

B. NEUTRALIZATION POTENTIAL (ALKALINITY)

1. PRINCIPLE OF THE METHOD

1.1 This procedure was developed to measure bases that may be present in the surface following strip mining, or from unreacted liming materials applied prior to sampling that will contribute to reducing the lime requirement for neutralizing potential acidity.

1.2 The amount of neutralizing bases, including carbonates, present in the surface material is determined by treating the sample with a known excess of standardized hydrochloric acid and then measuring the unreacted acid by titration with standardized sodium hydroxide. The sample and acid are heated to insure that the reaction goes to completion.

1.3 The effervescence rating from the potential acidity determination is used to insure the addition of sufficient acid to react with carbonates and other bases present.

2. INTERFERENCES

2.1 Run a blank for each volume of acid used or for each normality of acid added to the sample in order to correct for any environmental and glassware influences on the sample results.

3. APPARATUS

3.1 Flask, Erlenmeyer, 250 ml (4 required).

3.2 Burets, 100 ml (one for acid and one for base).

3.3 Hot plate (steam bath can be substituted).

3.4 pH meter with expanded scale and combination electrode.

3.5 Balance, sensitivity of 0.0001 g.

3.6 1-liter bottles equipped with ascarite columns (4 needed).

4. REAGENTS

4.1 *CO_2-free water.*

4.2 *Hydrochloric acid (HCl), approx. 0.5N* - Dilute 42 ml of concentrated HCl to a volume of 1 liter with CO_2-free water. Protect with ascarite columns. Standardize with approx. 0.5N NaOH after it is standardized.

4.3 *Hydrochloric acid (HCl), approx. 0.1N* - Dilute 200 ml of the 0.5N HCl to 1 liter with CO_2-free water. Protect with ascarite column. Standardize with approx. 0.1N NaOH after the NaOH is standardized.

4.4. *Sodium hydroxide (NaOH), approx. 0.5N* - Dissolve 20.00 g of NaOH pellets in CO_2-free water and dilute to 1 liter with CO_2 free water. Protect with ascarite column. Standardize with $KHC_8H_4O_4$.

4.5 *Sodium hydroxide (NaOH), approx. 0.1N* - Dilute 200 ml of 0.5N NaOH to a volume of 1 liter with CO_2-free water. Protect with ascarite column. Standardize with $KHC_8H_4O_4$.

4.6 *Potassium hydrogen phthalate ($KHC_8H_4O_4$).*

5. PROCEDURE

5.1 Weigh 2.000 g of dry 80-mesh sample into each of two 250 ml Erlenmeyer flasks.

5.2 Carefully add HCl in the amount and normality indicated by the following table into 1 flask. In the second flask, carefully dispense the amount and normality for the next higher rating in the table.

Volume and normality of HCl used, by effervescence rating.

Effervesence Rating	HCl	
	ml	Normality
0	20	0.1
+	40	0.1
+ +	40	0.5
+ + +	80	0.5
--	100	0.5

5.3 Heat the flask and hot plate to near boiling, swirling the flask at least every 5 minutes, until the reaction is complete. *Do not boil the sample.* If boiling occurs, discard the sample and rerun.

5.4 The reaction is complete when gas evolution has stopped and the remaining sample particles will settle evenly over the bottom of the flask.

5.5 Add CO_2-free water to make a total volume in the sample flask of 125 ml.

5.6 Place sample on hot plate and boil for 1 minute. Remove sample from hot plate and cool to 30 C. Cover tightly and cool to room temperature. Do not place stopper in the hot flask as it may implode upon cooling.

5.7 Place pH electrode in flask and titrate with standardized NaOH of either approximately 0.1N or 0.5N, whichever is closest to the normality of the HCl added before digestion in step 5.2. Titrate until a constant reading of 7.00 remains on the pH meter for at least 30 seconds.

5.8 If less than 3 ml of NaOH is required to obtain a pH of 7.00, it is likely that the HCl added in the first flask was not sufficient. The duplicate sample should then be titrated and used for calculations.

5.9 A blank should be run starting at step 5.2 for each volume and normality of HCl used (2 needed for each sample). The blank titrated should match the one used for calculation.

6. CALCULATIONS

6.1 Standardization of the NaOH requires the following calculations using potassium hydrogen phthalate ($KHC_8H_4O_4$):

$$NaOH\ normality = \frac{(g\ KHC_8H_4O_4)\ (1000)}{(204.228)\ (ml\ NaOH)}$$

6.2 Normality of the HCl is determined after standardization of the NaOH:

$$HCl\ normality = \frac{(NaOH\ normality)\ (ml\ NaOH)}{(ml\ HCl)}$$

6.3 A constant (C) is calculated from titration of the appropriate blank:

$$C = \frac{(ml\ HCl\ in\ blank)}{(ml\ NaOH\ in\ blank)}$$

6.4 Amount of acid consumed by the sample:

$$ml\ HCl\ consumed = (ml\ HCl\ added) - [\ (ml\ NaOH)\ (C)\ ]$$

6.5 The calcium carbonate equivalent of the bases is calculated per 1000 tons of material:

$$Tons\ CaCO_3/1000\ tons\ material = (ml\ HCl\ consumed)\ (HCl\ normality)\ (25.023)$$

6.6 The bulk density may be greater from a surface disturbed by mining than from an agricultural soil. Therefore, the calculated amount of $CaCO_3$ available for neutralizing on an acre basis should be corrected after the bulk density of the reconstructed surface is determined.

DETERMINATION OF EXCHANGEABLE ACIDITY USING $BaCl_2$-TEA BUFFER

M. E. Sumner[12]

1. PRINCIPLE OF THE METHOD

1.1 This method measures the acidity that is exchangeable by the $BaCl_2$-TEA extractant that is buffered at pH 8.2. Thus the exchangeable acidity measured is comprised of exchangeable Al and any H that will dissociate when the soil is brought to a pH of 8.2 (potential acidity). It is also a measure of the variable charge developed between the soil pH and pH 8.2.

1.2 This method was developed by Mehlich (9.2), and is a modification of a previous Mehlich method (9.1).

2. RANGE AND SENSITIVITY

2.1 By varying the quantity of soil used, this method can be used on all soils to measure exchangeable acidity.

2.2 Because the endpoint is determined colorimetrically, some variation between operators can be expected.

3. INTERFERENCES

3.1 Few problems are experienced.

4. PRECISION AND ACCURACY

4.1 Exchangeable acidity can be determined within 0.1 meq/100g.

5. APPARATUS

5.1 Beakers, 100 ml glass.

5.2 Buchner funnel (5.5 cm) and vacuum flask.

5.3 Whatman No. 42 filter paper, 5.5 cm.

6. REAGENTS

6.1 *Buffer solution* - Adjust 0.5N barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), 61.07 g/liter, and 0.2N triethanolamine [$N(CH_2CH_2OH)_3$], 29.8 g/liter, to pH 8.2 with hydrochloric acid (HCl). Protect from CO_2 contamination by attaching a tube containing soda lime to the air intake.

6.2 *Replacing solution* - Combine 0.5N barium chloride ($BaCl_2$) (61.07 g of $BaCl_2 \cdot 2H_2O$/liter) with 0.4 ml of the above buffer solution per liter. Protect from CO_2 as with the buffer solution.

6.3 *Hydrochloric acid (HCl)* - Approximately 0.2N, standardized.

6.4 *Bromocresol green* - 0.1% aqueous solution.

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6.5 *Mixed indicator* - Dissolve 1.250 g of methyl red and 0.825 g methylene blue in 1 liter of 90% ethanol.

7. PROCEDURE

7.1 Scoop 10 cm^3 air dry < 10 mesh soil into 100 ml beaker (use 5 cm^3 for very acid soils). Add 25 ml of buffer solution, mix well and allow to stand for 1 hour. Transfer mixture to Buchner filtration system and add a further three aliquots (25 ml) of buffer solution. Continue with 100 ml of replacing solution for a total of 200 ml.

7.2 Mix 100 ml of buffer solution with 100 ml of replacing solution to serve as a blank. Add 2 drops bromocresol green and 10 drops mixed indicator. Titrate with HCl to a green to purple endpoint. Follow same method for soil filtrates.

8. CALCULATIONS

$$\frac{\textit{Exchangeable acidity}}{(meq/100\,g)} = \frac{(ml\,HCl\,for\,blank - ml\,HCl\,for\,soil\,filtrate)}{sample, g}$$

9. REFERENCES

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DETERMINATION OF EXCHANGEABLE ACIDITY AND EXCHANGEABLE Al USING 1*N* KCl

M. E. Sumner[1]

1. PRINCIPLE OF THE METHOD

1.1 The acidity measured by the $BaCl_2$-TEA method bears very little relationship to that to which plant roots react. The N KCl method extracts the acidity exchangeable at the existing soil pH and consists primarily of Al and some H. It is termed the "active" acidity in soil and determines to a substantial extent whether or not roots will grow in an acid soil.

2. RANGE AND SENSITIVITY

2.1 This is a reliable and convenient method that is quite accurate. Exchangeable acidity as little as 0.05 meq/100 g is readily determined.

3. INTERFERENCES

3.1 There are no interferences.

4. APPARATUS

4.1 Beakers, 100 ml glass.

4.2 Buchner funnel (5.5 cm) and vacuum flask.

4.3 Whatman No 42 filter paper, 5.5 cm.

4.4 Buret, 50 ml.

5. REAGENTS

5.1 *Replacing solution (1N potassium chloride)* - 74.56 g of KCl/liter.

5.2 *Aluminum complexing solution (1N potassium fluoride)* - Titrate 58.1 g of KF/liter to a phenolphathalein endpoint with sodium hydroxide (NaOH).

5.3 *Hydrochloric acid* - approximately 0.1N, standardized.

5.4 *Sodium hydroxide* - approximately 0.1N, standardized.

5.5 *Phenolphthalein solution* - 1 g of phenolphthalein/100 ml of ethanol.

6. PROCEDURE

6.1 Scoop 10 cm^3 air dry < 10 mesh soil into 100 ml beaker, add 25 ml of N KCl, mix and allow to stand for 30 min. Transfer mixture to Buchner filtration system and add 5x25 ml aliquots of N KCl to give a total volume of 150 ml.

6.2 Titrate filtrate, after adding 4 to 5 drops of phenolphthalein with 0.1 N NaOH to the first permanent pink endpoint. This titre gives exchangeable acidity.

6.3 Add 10 ml of 1N KF and titrate with 0.1 N HCl until pink color disappears. Wait 30 min. and add additional HCl to a clear endpoint. This titre gives exchangeable Al.

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[1] Professor of Soil Fertility, University of Georgia, Athens, Georgia.

7. CALCULATIONS

$$meq\ KCl\ acidity = \frac{(ml\ NaOH\ sample - ml\ NaOH\ blank) \times N \times 100}{sample,\ g}$$

$$meq\ KCl\ exchangeable\ Al = \frac{ml\ HCl \times N \times 100}{sample,\ g}$$

$$meq\ H = KCl\ exchangeable\ acidity - KCl\ exchangeable\ Al$$

8. REFERENCES

8.1 Thomas, G. W. 1982. Exchangeable cations. *In* A. L. Page, R. H. Miller, and D. R. Keeney (ed.) Methods of soil analysis. Part 2. 2nd ed. Agronomy 9:159-165. ASA and SSSA, Madison, WI.

COLORIMETRIC DETERMINATION OF HUMIC MATTER WITH 0.2*N* NaOH EXTRACTION

M. R. Tucker[14]

1. PRINCIPLE OF THE METHOD

1.1 This extraction method is designed to determine the sodium hydroxide-soluble humic matter that consists of humic and fulvic acids. These components comprise approximately 85 to 90 percent of the soil humus and are responsible for the cation and anion exchange properties exhibited by the soil organic fraction.

The method is based on the concept that humic matter compounds are soluble in dilute alkali solutions (6.1, 6.2, 6.5). Acidic organic compounds are converted to ions with subsequent formation of a physical solution of these ions in water (6.5). The reaction of a dilute alkali with the humic matter results in a colored solution that is proportional to the soluble humic matter content within the soil. The color varies from shades of brown to black depending on the type of soil from which the sample originates. Colorimetric determination of the humic matter content of soils by this method is based upon the color intensity of the solution following extraction with a dilute alkali extractant. The alkali used in the method was NaOH, which serves as the humic acid solvent; DTPA aids in the dispersion of some of the large molecular Ca-humate compounds and ethanol aids in the solubility of hydrophobic lipid components of soil organic matter. Calibration data were generated from a standard humic matter source (4.5).

This method was designed to accomplish two major objectives: (1) to estimate the chemically reactive portion of the soil organic fraction for better prediction of herbicide rate requirements and (2) to remove chromium from the effluent of municipal waste sytems. Experimental evidence has shown that this method can be used to predict herbicide rates (6.3, 6.4, 6.7).

2. RANGE AND SENSITIVITY

2.1 The humic matter content of soils by this method can be determined up to 10 percent. Higher levels could be determined with a wider extraction ratio (6.6). The method as described will encompass a majority of mineral soils. Saturation by this method is encountered on the organic and mineral organic soils where total organic matter is high. There are cases, however, of organic soils in which the humic matter content is low even though the percent combustible organic content may be in excess of 90 percent.

The sensitivity of this method would depend on quality and homogeneity of the field sample.

3. APPARATUS

3.1 No. 10 (2-mm opening) sieve.

3.2 1.0 cm^3 (volumetric) soil measure and teflon-coated leveling rod.

3.3 55 ml polystyrene extraction vials. (35 mm D x 75 mm H).

3.4 Automatic dispenser for extractant, 20 ml capacity.

3.5 Diluter-dispenser, 5:35 ml capacity.

3.6 Analytical balance.

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3.7 Photometric colorimeter suitable for measuring in the 650 nm range. Colorimeters equipped with moveable fiber optic probes can be used to read samples directly from diluted sample vials.

4. REAGENTS

4.1 All reagents are ACS analytical grade unless otherwise stated.

4.2 *Sodium hydroxide (NaOH).*

4.3 *DTPA (Diethylenetriaminepenta acetic acid, pentasodium salt)* - Technical grade (40 ± 1% in H_2O), fw = 503.26. Density = 1.26.

4.4 *Ethyl alcohol, denatured (C_2H_5OH).*

4.5 *Standard humic acid* (Aldrich Chemical Co., 940 W. St. Paul Ave., Milwaukee, WI 53233).

4.6 *Extracting Solution, 0.2N NaOH - 0.0032M DTPA - 2% Alcohol.* Using a 4-liter volumetric flask, add about 1000 ml of pure water, 32 g NaOH (see 4.2), and dissolve. Then add 16 ml of DTPA (see 4.3) and 80 ml of ethanol (see 4.4). Make to volume with pure water and mix thoroughly. Larger volumes of the extractant can be prepared depending on the number of samples to be analyzed.

5. PROCEDURE

5.1 *Standard Humic Matter Calibration.* Dry the humic acid standard (see 4.5) at 105 C for approximately 4 hours. Loss on ignition at 550 C shows this humic matter standard contains 87% organic matter. For calibration weigh 0.115 g of standard humic acid (0.1 ÷0.87 = 0.115) and place into 55-ml polystyrene vials (see 3.3). Add 20 ml of extractant (see 4.6) with sufficient force to mix sample. Allow sample to sit for 1 hour, then add an additional 20 ml of extractant (see 4.6) with sufficient force to mix well. The two 20-ml portions of extractant are added separately to enhance dissolution of the humic matter. Let sample sit overnight (16-18 hours minimum), then pipette 5 ml of the supernatant and 35 ml of water into 55-ml polystryene vials (see 3.3). Caution should be taken not to pipette colloidal precipitation from bottom of vials.

The final dilution of the sample is a 1:8 ratio (5 ml sample + 35 ml water) which is required at this extraction dilution to get within the instrument reading range. Set instrument at 100% T with 5 ml of extractant and 35 ml water. Read standard at 650 nm. Using a Brinkman probe colorimeter with a 2-cm light path, the standard humic acid standard should read 10% T. This equates to 10 g/100 cm^3 humic matter equivalent. A standard curve can be developed by sequential 1:1 dilutions of the 10% humic acid standard. To develop the factor for converting the instrument reading to g HM/100 cm^3, convert %T to absorbance, then divide g HM/100 cm^3 by absorbance. Assuming linearity of the standard, the ratio of g HM/absorbance should be a constant.

If a larger volume of humic acid standard is required for calibration, multiple quantities of standard humic acid and extractant can be used.

5.2 *Soil Sample Extraction and Analysis.* Measure 1 cm^3 soil (screened-2mm) into 55 ml polystyrene vials (see 3.3) and add 20 ml of alkali extractant (see 4.6) with sufficient force to mix well. After 1 hour, add another 20 ml of extractant with mixing force and allow samples to sit overnight. In addition to allowing adequate reaction time for humic matter to react with extractant, setting allows soil particles to settle out leaving a clear supernatant. Transfer 5 ml of undisturbed supernatant and 35 ml water into 55-ml polystyrene vials. Set instrument to read 100% T with blank (5 ml extractant + 35 ml water). Read samples at 650 nm and record %T. A check sample whose humic matter content has been previously determined should be analyzed routinely with unknown

samples. Samples which exceed 10% HM can be diluted with water and the appropriate dilution factor employed.

5.3 *Calculations*

The humic matter (HM) content of a soil can be determined from a standard curve or by converting %T to Abs and multiplying by the factor developed in the calibration procedure (see Section 5.1). For this method the factor is 10; therefore Abs x 10 = gm HM equiv/100 cm^3 of soil. If the percent HM on a weight basis is desired, divide HM (g/100 cm^3) by the W/V (weight/volume in g/cm^3) of each soil. For specific values in development of this procedure, see 5.4.

5.4 *Calibration Procedure.* The values shown below were developed for determination of HM up to 10%, using an extraction ratio of 1:40 (1 cm^3 soil + 40 ml extractant (see 5.1), with 0.115 g of humic acid standard (87% organic matter).

HM Equiv[1] g/100 cm^3	Abs	HM equiv/Abs	Factor[3]
10.000	-	-	-
5.000	-	-	-
2.500	-	-	-
1.250[2]	1.000	1.25	10
0.625	0.509	1.23	-
0.313	0.206	1.21	-
0.156	0.131	1.19	-
0.078	0.061	1.28	-
0.036	0.027	1.33	-
		Avg 1.25 x 8 =	10

1. Standard HA sample diluted sequentially (1:1) with H_2O for development of standard curve.
2. Standard HA sample diluted 1:8 (5 cm^3 sample extract + 35 ml H_2O), read at 650 nm = 10% T or 1.0% Abs. Unknown samples diluted in same manner.
3. Factor determined by taking average of HM/Abs multiplied by 8 (d.f.).

6. REFERENCES

6.1 Hayes, M.H.B., R. S. Swift, R. E. Wardle, and J. K. Brown. 1975. Humic materials from an organic soil: a comparison of extractants and properties of extracts. Geoderma 13:231-245.

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TESTING METHOD FOR WASTE-AMENDED SOILS

G. V. Johnson and S. J. Donohue[15]

1. RATIONALE

1.1 Soils are often used as a disposal medium for waste materials, such as municipal sewage effluent or sludge, and industrial wastes. State and federal regulations often provide guidance on the quantity and manner for disposal of these substances based on criteria developed for, or extrapolated from, water quality concerns. For lack of standard procedures, hazardous metals in soil may be examined (as part of a monitoring program) by procedures ranging from water extraction and analysis to total analysis after HF dissolution. Because many of these elements have soil-chemical properties similar to plant nutrient elements, soil scientists (especially those involved in soil testing procedures) are in a position to provide insight and expertise in how soils should be tested for these elements.

2. CONSIDERATIONS

2.1 The most dominant chemical species of these elements in soil solutions are likely to be Cd^{2+}, CrO_4^{2-}, Ni^{2+}, Pb^{2+}, $H_2AsO_4^-$ and $HAsO_4^{2-}$. The chemistry of Cd is similar to that of Zn and Ca, Ni^{2+} is similar to Cu^{2+}, and $HAsO_4^{2-}$ is like HPO_4^{2-}. Procedures used for extracting Zn and Cu should be appropriate first approaches for Cd and Ni. Likewise, procedures which are successful for extracting available phosphate would be good candidates for extraction of "plant available" arsenic. Similarities between familiar plant nutrient elements and either Pb or Cr are less obvious. However, Pb may be expected to react in a manner similar to Ni and Cu.

Given the gaining popularity of the Mehlich 3 extraction procedure for "available" soil phosphorus, this procedure should have support for extracting some level of As meaningfully related to plant uptake. Since the cationic metals (especially those in the transition series) are easily chelated and often exist in this form in soil, the DTPA extraction procedure commonly used for Fe, Mn, Cu and Zn should provide a reasonable extraction of Cd, Cr, Pb and Ni levels that could be associated with uptake by plants. Maximum soil extraction levels should be in the order of Ni = 100 ppm, Cd = 1 ppm, Pb = 20 ppm and Cr = 100 ppm. Log formation constants (M + L ---> ML) with DTPA are Ni = 21.3, Cd = 20.1, and Zn = 19.7; such constants indicate successful chelation and extraction. The 0.005M DTPA is concentrated enough to complex twice the expected maximums of these or other metal elements.

3. INTERPRETATION

3.1 Limited work has been done on evaluation of soil test methods for sludge-amended soils. Rappaport et al. (5.1, 5.2) reported that the DTPA method correlated well with metals applied in sludge but found generally poor correlations with plant uptake. More research is needed in this area, particularly with sensitive crops.

4. RECOMMENDATIONS

4.1 Use Mehlich 3 extraction for As (see Chapter 3).

4.2 Use DTPA extraction for Cd, Cr, Ni, Pb, Zn, Cu (see Chapter 6).

4.3 Use ICAP or other reliable analytical procedure for measuring amounts extracted.

4.4 Use control (non-amended) soil as measure of "normal" metal concentration.

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[15] Professors, Oklahoma State University, Stillwater, Oklahoma, and Virginia Polytechnic Institute and State University, Blacksburg, Virginia, respectively.

4.5 Share experiences and develop data base to establish critical values.

4.6 Measure soil pH.

5. REFERENCES

5.1 Rappaport, B. D., J. D. Scott, D. C. Martens, R. B. Reneau, Jr., and T. W. Simpson. 1987. Availability and distribution of heavy metals, nitrogen, and phosphorus from sewage sludge in the plant-soil-water continuum. VPI-VWRRC-BULL 154 5C. Virginia Water Resources Research Center, Blacksburg, VA.

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