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Four Reference Soil and Rock Samples for Measuring Element Availability in the Western Energy Regions

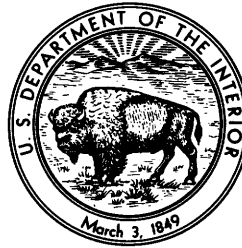
Four Reference Soil and Rock Samples for Measuring Element Availability in the Western Energy Regions

By J. G. Crock and R. C. Severson

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ABSTRACT

Attaining acceptable precision in extractable element determinations is more difficult than in total element determinations. In total element determinations, dissolution of the sample is qualitatively checked by the clarity of the solution and the absence of residues. These criteria cannot be used for extracts. Possibilities for error are introduced in virtually every step in soil extractions. Therefore, the use of reference materials whose homogeneity and element content are reasonably well known is essential for determination of extractable elements. In this report, estimates of homogeneity and element content are presented for four reference samples. Bulk samples of about 100 kilograms of each sample were ground to pass an 80-mesh sieve. The samples were homogenized and split using a Jones-type splitter. Fourteen splits of each reference sample were analyzed for total content of Ca, Co, Cu, Fe, K, Mg, Mn, Na, and Zn; DTPA-extractable Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn; exchangeable Ca, Mg, K, and Na; cation exchange capacity; water-saturation-extractable Ca, Mg, K, Na, Cl, and SO_4 ; soil pH; and hot-water-extractable boron. Error measured between splits was small, indicating that the samples were homogenized adequately and that the laboratory procedure provided reproducible results.

INTRODUCTION

Measures of extractable or "available" elements in soils have historically been more useful for estimating plant element composition than measures of total element content (Bear, 1964). At the present time, there is much concern for monitoring and predicting changes in the natural soil-plant environment resulting from energy-related developments (for example, Wali, 1979; Schaller and Sutton, 1978). Measures of extractable elements in soils are preferred to measures of total element content for such evaluations; however, many different extraction techniques have been used for a single element (for example, Andersson, 1975). Therefore, in selecting methods to use in performing such analyses, we considered those that would possibly be used by regulatory agencies to write guidelines and those that

appear to have the greatest potential for providing an estimate of element utilization by plants in the West. The methods are taken from the literature and are ones currently in use and generally accepted (Black, 1965; Sandoval and Power, 1977; Lindsay and Norvell, 1969, 1978). However, some of the steps in sample preparation and analysis have been modified to increase efficiency and reduce operator error. Because many variables exist in sample preparation, extraction, and analysis that affect the actual amount of an element extracted (for example; Jacober and Sandoval, 1971; Severson and others, 1979; and Soltanpour and others, 1976), reference samples have been prepared to determine the precision of analyses made using these laboratory procedures. This report discusses the preparation of four such reference materials and describes the samples, the analytical procedures, and the results of repeated analysis.

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SAMPLE DESCRIPTIONS

Four reference samples are described in this report. Two of the samples are of Tertiary rocks: one from a roadcut in New Mexico (Sample A), and the other from the headwall of the Decker Coal Mine (Sample B), operated by the Decker Coal Company and the State of Montana. The other two samples are soils from the San Juan Basin of New Mexico (Sample C and Sample D).

Sample A consists of a buff-colored, clayey siltstone of Tertiary age (formation unknown), collected from a roadcut in San Juan County, N. Mex. The approximate sampling location was in sec. 9, T. 23 N., R. 8 W. (about lat 36,15' N. and long 107,40' W).

Sample B consists of a gray, massive sandy siltstone of Tertiary age (formation unknown), collected from the headwall of the Decker Mine. The sample was collected about 21 m stratigraphically above the coal, on the lower part of the upper overburden bench. The mine is located in secs. 15, 16, T. 95 S., R. 40 E., Bighorn County, Mont. (about lat 45,08' N. and long 106,49' W).

Sample C consists of the A1 horizon (sampled between the depths of 5 and 50 cm) of a soil classified at the series level as Manzano (Cumulic Haplustoll, fine-loamy, mixed, mesic). The sample was collected from McKinley County, N. Mex., from sec. 22, T. 20 N., R. 5 W. (about lat 35,57'35" N. and long 107,21'10" W).

Sample D consists of the B2 horizon (sampled between the depths of 20 and 45 cm) of a soil classified at the series level as Doak (Typic Haplargid, fine-loamy, mixed, mesic). The sample was collected in San Juan County, N. Mex., from sec. 32, T. 23 N., R. 8 W. (about lat 36,21'15" N. and long 107,50'10" W).

SAMPLE PREPARATION

The samples were homogenized in the following sequence: The rock samples were initially crushed to less than 5 mm in diameter by passing them through a motor-driven jaw crusher. The soil samples did not require this treatment. After initially crushing the rock samples, all four samples were treated similarly. Each sample was mixed by successive passes through a large-capacity Jones-type splitter. A single pass was not used: opposite quarters of samples already split were recombined and resplit. Splitting and recombining were repeated several times to assure adequate homogenization. The 100-kg samples were then split into 16 parts and stored in gallon cartons. Each of the 16 gallons of material obtained from the splitting was further ground in a ceramic mill to pass an 80-mesh sieve. The 16 gallons of finely ground material were then recombined and split again using the quartering and recombining procedure described above. Each resulting gallon (or partial gallon) of sample was further split into eight parts by again following the same procedure of quartering and recombining opposite quarters; however, a much smaller Jones-type splitter was used. Each of the eight subsamples was labeled to indicate its splitting history. A total of 128 splits was obtained for each reference sample, each split containing about 500 g of material.

LABORATORY METHODS

Total Element Content

The sample is totally dissolved using a low-temperature, low-pressure, multi-acid digestion procedure modified from that described by Swanson and Huffman (1976). In this procedure the sample is digested in a mixture of concentrated hydrofluoric,

nitric, and perchloric acids in a platinum dish on a hotplate. After evaporating to dryness, the remaining salts are dissolved in 5 percent hydrochloric acid and brought to a given volume. Flame atomic absorption spectrometry (A.A.S.) is used to determine the total element content of the resulting solution.

Procedure:

- 1) Weigh 1.000 g of the air-dried soil into a 100-mL, flat-bottomed, platinum Blair-form dish. Wet the sample with a minimal amount of demineralized water.
- 2) Add 10 mL concentrated nitric acid, 10 mL of concentrated perchloric acid, and 10 mL of concentrated (42 percent) hydrofluoric acid.
- 3) Cover with a teflon watch glass and let stand overnight in a well-ventilated hood.
- 4) Place the covered dish on a steam bath and heat for 1 hour.
- 5) Place on a hotplate pre-set to about 110°C and remove the teflon cover. Heat gently until fumes of perchloric acid are visible. Slowly bring the temperature to about 200°C over a time period of 2 hours. Evaporate to dryness.
- 6) Cool. Wet the salts with about 10 mL of demineralized water. Add 5 mL of perchloric acid, swirling to mix. Repeat step 5.
- 7) Cool and add 25 mL of demineralized water, 5 mL of concentrated hydrochloric acid, and about 1 mL of 30 percent hydrogen peroxide.
- 8) Cover with a glass watch glass. Return to the steam bath for about 30 minutes to insure that all of the salts are dissolved and that the excess peroxide is destroyed.
- 9) Cool and bring to volume in a 100-mL volumetric flask using demineralized water.

Analysis:

All elements were determined using a Perkin-Elmer 5000 A.A. spectrophotometer or a Perkin-Elmer 603 A.A. spectrophotometer. Cobalt was first extracted into methyl-iso-butyl ketone (Mountjoy, 1970). Zinc, copper, and manganese were determined directly, whereas calcium, magnesium, potassium, and sodium were determined by on-line dilutions using a peristaltic pump with an appropriate diluent. The sample and diluent tubes are connected before the nebulizer by a small glass "h" interface. The diluent tube is usually connected to the top, straight section, because the pump tube is usually of larger radius and its flow remains unbroken in the introduction of sample.

Notes:

- 1) Digestion can easily be done in 150-mL teflon beakers. The digestion and evaporation steps are slower because care must be taken not to overheat and melt the beakers.
- 2) The addition of the hydrogen peroxide is important to insure complete dissolution of the manganese oxides that may form if appreciable manganese is present.

DTPA-Extractable Metals

The DTPA (diethylene triamine pentaacetic acid) extraction procedure has been modified from Lindsay and Norvell (1969, 1978). The extracting solution is 0.005 M DTPA, 0.01 M calcium chloride, and 0.1 M triethanolamine at a pH of 7.30.

Solution:

- 1) To a 2-L volumetric flask, add 3.9335 g DTPA, 3.90 g calcium chloride, and 29.84 g triethanolamine. (See Note 3.) Bring to about 1950 mL using demineralized water. Mix well and adjust the pH to 7.30 using concentrated ammonium hydroxide or concentrated nitric acid. Bring to volume using demineralized water.

Procedure:

Weigh 15.00 g of air-dried soil into a 125-mL polyethylene Erlenmeyer flask. Add 30.0 mL of the DTPA solution. Cap tightly with a polyethylene thimble. Shake on a reciprocating shaker at 240 cycles/minute for 2 hours. Decant into a 50-mL polyethylene centrifuge tube, and centrifuge for 5-6 minutes at 2000 rpm. Decant and filter through an 11-cm Whatman 41 filter paper into a 2-oz polyethylene bottle. Acidify with four drops of concentrated nitric acid.

Analysis:

Eight metals are determined from this sample preparation: Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn. A Perkin-Elmer 5000 A.A. spectrophotometer and a Perkin-Elmer AS50 auto-sampler with peristaltic pump for on-line dilutions were used for all analyses. Instrument settings, pump-tube sizes, and standard preparations are given in table 1.

Table 1.--Preparation of standard solutions and instrumental settings for determining DTPA-extractable metals

[Dilute to volume using the DTPA reagent solution. N.A., not applicable]

Metal	Standard solutions ¹			Flow rates (mL/min)	Wavelength (nm)	Slit (nm)
	S1	S2	S3			
Fe	2.0	5.0	10.0	22.6 31.0	248.3	0.2
Mn	2.0	5.0	10.0	22.6 31.0	279.5	.2
Zn	1.0	2.0	5.0	22.6 31.0	213.9	.7
Cu	1.0	2.0	5.0	N.A.	324.7	.7
Co	1.0	2.0	0	N.A.	240.7	.2
Ni	1.0	2.0	0	N.A.	232.0	.7
Pb	1.0	2.0	0	N.A.	4283.3	.7
Cd	1.0	2.0	0	N.A.	4228.8	.7

¹All metal concentrations in parts per million (ppm).

²Sample.

³Demineralized water.

⁴With background correction.

Notes:

- 1) All the variables in this extraction will affect the amount of metal extracted. Care must be taken to follow the procedure exactly to obtain precise data. A good description of the effect of the variables is given by Soltanpour and others (1976) and Severson and others (1979).

- 2) Compressed air was blown over the motor of the reciprocating shaker to prevent overheating and to maintain the DTPA solution at room temperature.
- 3) Use a 50-mL beaker when weighing the triethanolamine.
- 4) Extraction of the DTPA solution might be necessary if low-level measurements of Co, Ni, and Pb are required. Initial investigations have shown that the DTPA complex will have to be destroyed before successful extraction/concentration can be done. Elimination of as many major elements as possible is essential in order to use flameless A.A.S. to determine low-level Co, Ni, and Pb (Govett and Whitehead (1973), Mubarak and others (1978), and Yamasaki and others (1975)).
- 5) Soltanpour and Schwab (1977) have reported success with a new extracting solution for both micronutrients and macronutrients of soils. They use a 0.005 M DTPA and 1.0 M ammonium bicarbonate (NH_4HCO_3) solution at a pH of 7.6. The results are reported to correlate well with the DTPA extraction procedure.

Cation Exchange Capacity and Exchangeable Cations

In this extraction, the readily soluble and readily exchangeable cations are measured. The major cations determined are Ca, K, Mg, and Na. The extraction procedure used has been modified from that of Chapman (1965). Atomic absorption spectrometry with on-line dilution is the method of analysis for all determinations.

Solutions Needed:

- 1) 100 meq Ca/L: Weigh 5.004 g calcium carbonate (primary standard grade) into a 1.00-L volumetric flask. Add about 100 mL of demineralized water. Add dropwise a minimum amount of concentrated hydrochloric acid until the solid is dissolved. Then add 10 mL in excess. Dilute to volume.
- 2) 100 meq Na/L: Weigh 5.844 g sodium chloride (primary standard grade) into a 1.00-L volumetric flask. Dissolve and dilute to volume with demineralized water.
- 3) 100 meq K/L: Weigh 7.455 g potassium chloride into a 1.00-L flask. Dissolve and dilute to volume with demineralized water.
- 4) 100 meq Mg/L: Dissolve 1.216 g magnesium metal ribbon in a minimum of 50 percent hydrochloric acid in a 1.00-L volumetric flask. Dilute to volume with 1 percent hydrochloric acid.
- 5) 5 percent lanthanum buffer: Weigh 234.4 g reagent grade lanthanum oxide (La_2O_3) into a large beaker (2 L or larger). Wet the solid with about 200 mL demineralized water. Place the beaker in an ice bath in a hood. Add very slowly a total of 500 mL concentrated hydrochloric acid while

- stirring constantly with a glass rod. When addition of the acid has caused complete dissolution, dilute to 4.00 L with demineralized water. (See Note 1.)
- 6) 0.1 percent Na buffer: Dissolve 2.542 g of sodium chloride in 1.00 L of demineralized water.
 - 7) 0.1 percent K buffer: Dissolve 1.907 g of potassium chloride in 1.00 L of demineralized water.
 - 8) 1.0 N sodium acetate: Dissolve 136 g sodium acetate trihydrate in water to just less than volume in a 1.00-L volumetric flask. Adjust the pH to 8.2 with acetic acid or sodium hydroxide. Dilute to volume with demineralized water.
 - 9) 1.0 N ammonium acetate: Dilute 114 mL of glacial acetic acid with demineralized water to about 1 L in a 2.00-L volumetric flask. Slowly add 138 mL of concentrated ammonium hydroxide. Dilute with demineralized water to about 1980 mL. Adjust the pH to 7 with concentrated acetic acid or concentrated ammonium hydroxide. Dilute to a 2-L volume with demineralized water.
 - 10) Isopropyl alcohol 99 percent, reagent grade.
 - 11) 0.1 percent sodium hexametaphosphate: Weigh 0.50 g sodium hexametaphosphate, $(\text{NaPO}_3)_6$, into a 500-mL volumetric flask. Dissolve and dilute to volume with demineralized water.

Procedure:

- 1) Weigh 4.00 g of air-dried soil into a 65-mL culture tube (20 mm X 225 mm). Add 33 mL of 1.0 N ammonium acetate solution. Place the tube horizontally on a reciprocating shaker and shake for 3 minutes at 240 cycles per minute. Centrifuge at 2000 rpm for 5 minutes. (See Note 2.) Decant the solution through a 6.5-cm funnel containing 11-cm Whatman 41 filter paper into a 100-mL volumetric flask. Repeat the ammonium acetate wash procedure two additional times, making sure that the soil plug is broken up before using the reciprocating shaker. Add four drops of the 0.1 percent sodium hexametaphosphate solution. Bring to volume with 1.0 N ammonium acetate. This solution will be analyzed for exchangeable Ca, Mg, Na, and K. The amount of sodium added as the hexametaphosphate is negligible when compared to the sodium present as exchangeable sodium.
- 2) To the residual soil-plug residue, add 25 mL of 1.0 N sodium acetate solution. Break up the plug and shake on the reciprocating shaker for 3 minutes at 240 cycles per minute; centrifuge at 2000 rpm for 5 minutes; decant and discard the solution. Repeat Step 2 three additional times.
- 3) To the soil plug from Step 2, add 20 mL of isopropanol. Break up the plug; shake on the reciprocating shaker for 3 minutes at 240

cycles per minute; centrifuge at 2000 rpm for 5 minutes; decant and discard the solution. Repeat Step 3 three additional times.

- 4) To the above soil plug, add 33 mL of 1.0 N ammonium acetate solution. Break up the plug and then shake on the reciprocating shaker for 3 minutes at 240 cycles/minute. Decant and filter through 11-cm Whatman 41 filter paper into a 100-mL volumetric flask. Repeat Step 4 two additional times, combining the washes. Bring to volume with the ammonium acetate solution. This solution will be analyzed for Na as a measure of total cation exchange capacity (C.E.C.) of the soil.

Analysis:

A Perkin-Elmer 5000 A.A. spectrophotometer and a Perkin-Elmer AS-50 autosampler were used for automated, sequential A.A.S. analysis of all five elements. On-line dilution of the samples using a peristaltic pump and rotation of the burner head allows for direct measurement of all five elements. (See Notes 3-5.)

Consult table 2 for preparation of the standards used for determining Ca, Mg, K, and Na in the first solution. The standards for determining total C.E.C. as Na are made by pipetting 7.5 mL, 12.5 mL, and 25.0 mL of the stock Na solution into a 100 mL volumetric flask and diluting to volume with ammonium acetate. This results in solutions of 7.5, 12.5, and 25.0 meq/L, respectively.

Table 3 lists the instrumental conditions. All elements were determined using the 10-cm single-slot burner. Three 3-second integrations were taken in the concentration mode and automatically averaged.

There is a multiplication factor of 2.5 if the results are reported as meq/100 g.

Notes:

- 1) When preparing the lanthanum buffer, the operator should wear rubber gloves and eye protection.
- 2) A slightly longer centrifuging time, as much as 10 minutes, might be required for the clay-rich soils.
- 3) If the peristaltic pump and burner rotation are not employed to effect the proper dilution of the samples, then dilute the samples for exchangeable Ca, Mg, Na, and K with appropriate buffer to give a 1:50 dilution. For the total C.E.C. measurement, at least a 1:100 dilution should be made. Also dilute the standards accordingly.

Table 2.--Instrumental parameters for the determination of Na, K, Ca, Mg, and cation exchange capacity (C.E.C.)

[For all determination, rotate the burner 30° from parallel]

Element	Wavelength (nm)	Slit (nm)	Buffer (percent)	Sample flow rate (mL/min)	Buffer flow rate (mL/min)
Na-----	589.6	1.4	0.1 K	1.0	6.4
K-----	766.7	1.4	.1 Na	1.0	6.4
Ca-----	422.7	1.4	1.0 La	1.0	6.4
Mg-----	285.2	.7	1.0 La	1.0	6.4
Total C.E.C.	589.6	1.4	.1 K	.6	10.9

Table 3.--Preparation of standard solutions for cation exchange capacity measurements and for measurements of exchangeable Ca, K, Mg, and Na

[After mixing, dilute each standard to 500 mL using the ammonium acetate solution. Store in 16-oz plastic bottles]

Parameter	Standard solutions		
	S1	S2	S3
Amount of 100 meq/L Na stock solution (in mL)	3.00	5.00	10.0
Concentration of Na in meq/L-----	.6	1.0	2.0
Amount of 100 meq/L K stock solution (in mL)	3.0	5.00	10.0
Concentration of K in meq/L-----	.6	1.0	2.0
Amount of 100 meq/L Ca stock solution (in mL)	25.0	75.0	125.0
Concentration of Ca in meq/L-----	5.0	15.0	25.0
Amount of 100 meq/L Mg stock solution (in mL)	5.0	10.0	15.0
Concentration of Mg in meq/L-----	1.0	2.0	3.0
Drops of sodium hexametaphosphate solution-----	20	20	20

- 4) The elements Na and K could also be easily measured, using the A.A. spectrophotometer in the emission mode or a flame photometer.
- 5) Let the solution settle overnight to eliminate the fine material that might pass through the filter paper.
- 6) The total C.E.C. measurement may be smaller or large than the sum of Ca+K+Mg+Na, depending on the type of soil. For example, in an alkaline soil, free halite, gypsum, calcite, or other salts may cause a higher cation sum than the determined total C.E.C. In some cases where these constituents are very small, subtracting the water-soluble constituents measured in the water-saturation extract from the exchangeable cations measured will result in better estimates of exchangeable amounts. However, when the amounts of these constituents are large, the data for Ca and Mg should be disregarded because some of these minerals are less soluble in a water extract than in an acetate extract. An estimate of Ca+Mg can be obtained by subtracting exchangeable K+Na from the C.E.C. value. Correcting exchangeable cations for water-soluble cations can be done by using the following formula:

$$X C_c = X C_u - \frac{(XS) (SI)}{1000},$$

where $X C_c$ is the corrected exchangeable cation value (meq/100 g), $X C_u$ is the uncorrected exchangeable cation value (meq/100 g), XS is the amount of the cation measured in the saturation extract (meq/L),

and SI is the saturation index (percent). If the sample contains appreciable cations not analyzed, such as Al, Ba, Fe, H, Li, Mn, or Sr, the total C.E.C. can be larger than the cation sum, especially if the pH of the soil is less than 7.

- 7) The soil plug is easily broken up by gently rapping the culture tube on a foam pad. Do not use a glass rod to break it up.
- 8) Extracts should be refrigerated to avoid bacterial growth which might alter the concentrations.

Water-Saturation Extract

A saturation paste of a soil is made to estimate the amount of water-soluble salts that a plant would be exposed to under field conditions. This extract has been described by Bower and Wilcox (1965) and is the method presented here.

Solutions:

- A) 0.01 N potassium chloride: Weigh 0.7456 g of potassium chloride into a 1.00-L volumetric flask. Dissolve with demineralized water and dilute to volume. This solution at 25°C has an electrical conductivity of 1.412 mmhos/cm.
- B) Concentrated standards, buffers, and sodium hexametaphosphate solution used also in the C.E.C. determination.

Procedure:

- 1) Weigh and record weight of an 800-mL beaker and plastic spatula.
- 2) Weigh 200.0-500.0 g of sample into the beaker. The sample weight depends on the clay content of the sample. Usually, the larger the amount of clay, the more sample is needed. Record the weight of soil taken.
- 3) Mixing with the spatula, add demineralized water until a saturated paste is reached. The saturation criteria are when the paste glistens, flows freely off of the spatula (Note 3), and has no free water standing.
- 4) Cover the beaker and let stand for 1 hour. Recheck for the saturation criteria. (See Note 4.) Add more water if too dry or a known weight of soil if water is standing on the surface. Mix after each addition.
- 5) Re-cover and wait for 3 hours. Check again for the saturation criteria. Reweigh to obtain the total weight of the soil and water mixture.
- 6) Transfer paste to a Buchner funnel containing a Whatman 41 filter paper. Filter under low vacuum, about 20 to 30 torr, until the paste cracks and draws air (See Notes 6-10).

Analysis:

- 1) Calibrate the Beckman Solu-Bridge Conductivity Bridge, Model SD-26 with the 0.01 N potassium chloride, thereby compensating for room temperature.
- 2) Measure the conductivity of the extract.
- 3) Centrifuge for 5-6 minutes at 2000 rpm.

- 4) Filter through a Whatman 41 filter paper into a 2-oz plastic bottle. Add two drops of concentrated nitric acid and one drop of the sodium hexametaphosphate solution per 25 mL of extract.
 - 5) Using demineralized water and a Lab Industries Repipet, make 10.0 mL of a 1:50 dilution of the extract and place it directly into the sample tubes of the Perkin-Elmer AS-50 auto sampler's carousel. Determine Na, K, Ca, and Mg using a Perkin-Elmer 5000 A.A. spectrophotometer and the conditions given in table 4. Also see table 4 for preparing the standards for determining Ca, Mg, Na, and K in solution. Report the values as meq/L. A multiplication factor of 50 is linked to the dilution.
 - 6) Chloride and sulfate are determined simultaneously using standard Technicon Auto Analyzer II equipment. (See Note 12.) Chloride is determined using an ion-selective electrode and Technicon's Industrial Method No. 441-76 WE. After a 1:10 sample-dilution loop, sulfate is determined colorimetrically using Technicon's Industrial Method No. 118-71 W/B.
- Notes:
- 1) For this study, plastic disposable 800-mL beakers and plastic spatulas were used. The plastic beakers were found to be more advantageous than glass because the paste will flow more freely from them. They also proved to be cheaper than glass, because they can be washed and reused and will not break as readily.
 - 2) For convenience, use one spatula per beaker and do not remove while weighing.
 - 3) Many clay-rich soils will not flow freely off the spatula, and sometimes they tend to swell two to three times in volume.
 - 4) The endpoint for the saturation paste is most easily recognized when water is just starting to stand on the surface. A very small amount of water can be detected. Tip the beaker on its side to help notice standing water.
 - 5) Care must be exercised when preparing sandy soils. Substantially smaller amounts of water are needed to reach saturation.
 - 6) When filtering the paste, an easy-to-clean, two-piece, plastic, 9.0-cm Buchner funnel was used. This size funnel holds about 150 mL total volume and is large enough to hold the paste from 300 g of most soils.
 - 7) Filtering was done directly into a 50-mL plastic centrifuge tube supported in a 500-mL vacuum flask by a styrofoam pad.
 - 8) Care must be taken not to have too low of a vacuum or the extracts will boil, causing a concentration of the extract.
 - 9) When applying vacuum to very clay-rich soils, a layer of impermeable clay will form, preventing the complete cracking of the paste. In this case, the paste was filtered for a maximum of 1 hour, or until no additional filtrate was noticed for about 15 minutes.
 - 10) A plastic, 40-mesh screen was placed between the funnel and the filter paper to assist in the filtering. This prevents the filter paper from being pulled into and therefore clogging the holes of the funnel.
 - 11) A 1:50 dilution of the extract could also be done using a volumetric flask. Using an auto-diluter can save a large amount of time.
 - 12) When determining the chloride, the low standard was 5 or 10 meq/L chloride, and the full-scale, high standard was 50 meq/L. Combined chloride and sulfate standards of 10, 25, and 50 meq/L provide a good working range.
 - 13) Do not let the solutions stand in the plastic sample tubes used in the Perkin-Elmer AS-50 carousel for any length of time. Adsorption of the metals onto their surfaces may be a problem.
 - 14) The sample weight was routinely 250 g. About 15-25 mL of extract was recovered, depending on the clay content of the soil.
 - 15) The extraction procedure should be followed closely, because extracting time, vacuum applied, and particle size will affect the salt content of the extract (Jacobson and Sandoval, 1971).

Hot-Water-Soluble Boron

Boron is an essential element, but can commonly occur at either deficient or toxic levels in soils. The method used is modified from that given by Wear (1965). The sample is refluxed in a plastic bottle in a boiling water bath instead of in a condensor. This helps eliminate contamination due to the boron found in glassware.

Procedure:

1. Weigh 20.0 g of air-dried soil into a 4-oz polyethylene bottle.
2. Add 20.0 mL of distilled water and 0.5 mL of 10 percent barium chloride aqueous solution.
3. Manually shake to mix.

Table 4.--Preparation of standard solutions and pump arrangements for determining cations in a water saturation extract

[For S1, S2, and S3, use four drops of sodium hexametaphosphate per 100 mL. See table 2 for the analytical wavelength slit for each element]

Element	Standard solutions			Buffer	Sample flow rate (mL/min)	Buffer flow rate (mL/min)
	S1 (meq/L)	S2 (meq/L)	S3 (meq/L)			
Ca	0.10	0.30	0.60	1.0 pct La	3.2	3.2
Mg	.10	.30	.60	1.0 pct La	1.0	6.4
Na	.04	.06	.10	0.1 pct K	3.2	3.2
K	.04	.06	.10	.1 pct Na	3.2	3.2

4. Immerse into a boiling water bath for 30 minutes. The boiling water should keep the solution mixed.
5. Remove and cool to room temperature with the bottle upright.
6. Decant and filter through a Whatman 41 filter paper in a polyethylene funnel into a 2-oz polyethylene bottle. Acidify with two to three drops of concentrated nitric acid.
7. Determine boron with a d.c. argon plasma at 249.7 nm with internal background correction. See Ball and others (1978) for more details of the instrumental setup.

Note:

- 1) Care must be taken not to contaminate the sample with boron coming from contact with regular laboratory glassware. A very high (commonly over 2 ppm) boron blank can be encountered if this procedure is performed in pyrex glass.

Soil pH

Measuring the pH, or the negative logarithm of the hydrogen ion activity, is one of the most important tests performed on a soil. The pH is not only a characteristic of the soil, but also a cause and control of many reactions in the soil (McLean, 1973). The soil is mixed with an equal weight of water and the quasi-equilibrium pH determined using a combination pH electrode. This 1:1 extract has been described by Peech (1965).

Procedure:

1. Weigh 20.0 g air-dried soil into 50-mL beaker.
2. Add 20.0 mL water.
3. Mix well using a glass stirring rod. Repeat the stirring every 10 minutes for the next 30 minutes. Let stand covered for 1 hour.
4. Immerse a combination glass electrode into the solution standing above the soil and measure the pH. A 3-minute waiting time was used for the electrode to approach equilibrium. The pH meter was standardized using a pH 7.0 buffer.

Notes:

- 1) Some of the very clay-rich samples may need an additional 20 mL of water in order to obtain a water layer deep enough to read the pH. Owing to dilution, this should normally increase the measured pH.
- 2) The 1-hour waiting time is not critical. A longer time may be used. Usually a batch of 20 samples was run at a given time. Therefore, the last sample sat for about 2.5 hours. At the end, the first samples were reread with no significant difference between the pH readings.
- 3) For this study disposable plastic beakers and stirring rods were used to eliminate dishwashing. Fifty-mL glass beakers could also be used.

ERROR DUE TO SAMPLE SPLITTING

For each reference sample, 14 of the 128 splits were selected for chemical analysis using the methods described above. In addition, 4 of the 14 samples were further divided in half to provide an estimate of analytical error. The 72 samples (4 reference materials times 14 samples plus 4 splits) were placed in random order and analyzed in this sequence to effectively convert any systematic bias to a random error. The nested analysis-of-variance design used to estimate variance components between and within splits and to estimate analytical error is shown in table 5. The data resulting from the analysis of variance are shown in tables 6-9.

Because only a few samples of each reference material were analyzed, the form of the frequency distribution could not accurately be determined (for example, see figs. 1 and 2). Elements occurring in trace quantities in natural materials commonly exhibit positively skewed frequency distributions. Therefore, data for all parameters (except pH, which is reported as a logarithm) were transformed to their common logarithm prior to statistical analysis. Log-transformed data should more closely resemble a frequency distribution with a Gaussian form than should nontransformed data, and the geometric mean should be a better measure of central tendency than the arithmetic mean. As more splits of each reference sample are analyzed, it will become possible to test the validity of this transformation for each parameter measured on each reference material.

The variance components for splitting estimate errors in the physical process of mixing the samples, splitting the samples, and putting them into their individual containers. The variance component labeled analytical estimates all remaining errors, which are due to subsampling, preparing the sample by whatever method is necessary to obtain an appropriate solution for chemical analysis, the actual analysis, any calculations, and transcribing the data and transmitting it to the person requesting the analysis.

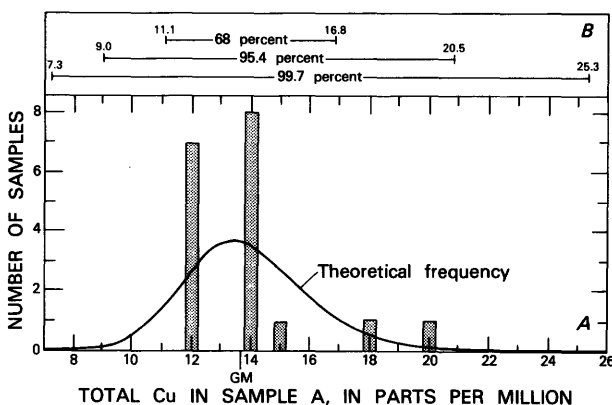


Figure 1.—A, actual (bars) and theoretical (line) frequency distribution for total copper in Sample A. Geometric mean (GM), 13.7. B, expected range of total copper at the probability level indicated.

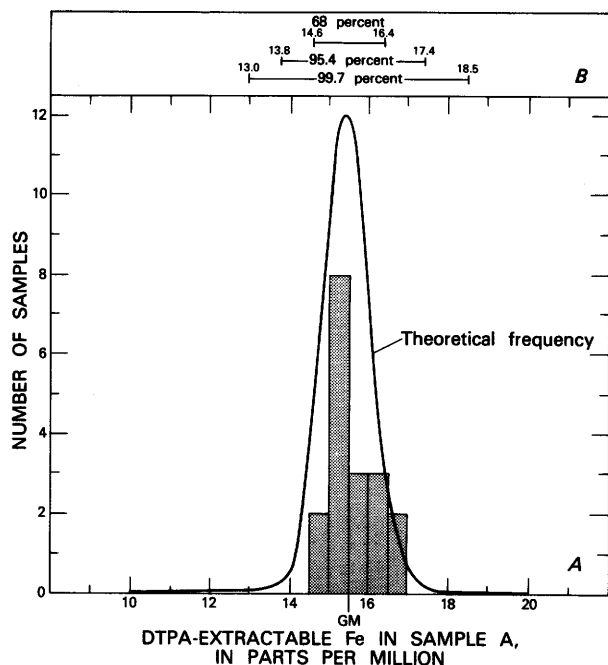


Figure 2.—A, actual (bars) and theoretical (line) frequency distribution for DTPA-extractable iron in sample A. Geometric mean (GM), 15.5. B, expected range of DTPA-extractable iron at the probability level indicated.

The statistical design used here only gives an estimate of each error component, splitting and analytical. In order to insure that an analytical error was not

interpreted as a splitting error, each individual sample would need to be analyzed in the laboratory at least twice.

In tables 6-9, the data for total element content provide the best information on how well the samples were homogenized, because a determination of total element content is not subject to the many laboratory variables that may affect a determination of extractable element content. Many extractions are nonequilibrium reactions and may be affected by such factors as sample preparation, extraction technique, extraction time, and the element being determined. If homogeneity of samples is indicated by the data for total element content, then this homogeneity can be assumed when interpreting the extractable element data.

Interpretation of the variance components in tables 6-9 can be made relative to the following hypothetical statements: If the sample-splitting process contained no significant error, then the total variance should reflect only analytical imprecision. If the various steps in chemical analysis contained no significant error, then the analytical error variance would be zero and any error would be distributed among the levels of the statistical design reflecting only splitting errors. If those splitting errors were constant, then error variance at each level of the statistical design would be equally distributed.

Total content of any element at any single level of the statistical design shows no consistent significant variance component (tables 6-9). Significance is determined by the conventional F-ratio at the 0.05 probability level. The random distribution of significant variance components among levels of the statistical design indicates that both splitting and analytical errors are probably not systematic, but tend to be random. Therefore, adequate homogenization of all four reference samples can be assumed.

Table 5.—Unbalanced, nested, analysis-of-variance design used to estimate splitting and analytical error

Source of variation	Degrees of freedom	Mean-square estimates	F-ratio ¹	Variance component
a--8-gallon splits--	1	$MS_1 = s_h^2 + 1.4 s_g^2 + 1.9 s_f^2 + 2.8 s_e^2 + 4.3 s_d^2 + 5.6 s_c^2 + 7.1 s_b^2 + 8.9 s_a^2$	MS_1/MS_2	$s_a^2 = \frac{MS_1 - MS_2}{8.9} = \sigma_a^2$
b--4-gallon splits--	2	$MS_2 = s_h^2 + 1.1 s_g^2 + 1.1 s_f^2 + 1.2 s_e^2 + 1.4 s_d^2 + 1.6 s_c^2 + 1.8 s_b^2$	MS_2/MS_3	$s_b^2 = \frac{MS_2 - MS_3}{1.8} = \sigma_b^2$
c--2-gallon splits--	2	$MS_3 = s_h^2 + 1.1 s_g^2 + 1.1 s_f^2 + 1.3 s_e^2 + 1.5 s_d^2 + 1.7 s_c^2$	MS_3/MS_4	$s_c^2 = \frac{MS_3 - MS_4}{1.7} = \sigma_c^2$
d--1-gallon splits--	2	$MS_4 = s_h^2 + 1.1 s_g^2 + 1.2 s_f^2 + 1.4 s_e^2 + 1.7 s_d^2$	MS_4/MS_5	$s_d^2 = \frac{MS_4 - MS_5}{1.7} = \sigma_d^2$
e--1/2-gallon splits	2	$MS_5 = s_h^2 + 1.5 s_g^2 + 1.7 s_f^2 + 2.2 s_e^2$	MS_5/MS_6	$s_e^2 = \frac{MS_5 - MS_6}{2.2} = \sigma_e^2$
f--1/4-gallon splits	2	$MS_6 = s_h^2 + 1.5 s_g^2 + 2.0 s_f^2$	MS_6/MS_7	$s_f^2 = \frac{MS_6 - MS_7}{2.0} = \sigma_f^2$
g--1/8-gallon splits	2	$MS_7 = s_h^2 + 1.3 s_g^2$	MS_7/MS_8	$s_g^2 = \frac{MS_7 - MS_8}{1.3} = \sigma_g^2$
h--Analytical-----	4	$MS_8 = s_h^2$	---	$s_h^2 = \sigma_h^2$

¹Leaders (---), no F-ratio exists.

Table 6.--Variance components attributed to splitting and analyses of Sample A

[*, variance component significantly different from zero at the 0.05 probability level; level, source of variation as indicated in table 5]

Parameter	Total	Percentage of total variance							
	log ₁₀ variance	Level h, 8-gallon splits	Level g, 4-gallon splits	Level f, 2-gallon splits	Level e, 1-gallon splits	Level d, 1/2-gallon splits	Level c, 1/4-gallon splits	Level b, 1/8-gallon splits	Level a, analytical error
Based on total content									
Ca-----	0.00185	4.6	6.9	0	26.6	0	0	28.8	33.1
Co-----	.00641	10.0	0	0	0	0	0	0	90.0
Cu-----	.01046	0	0	0	*70.3	0	7.8	0	21.9
Fe-----	.00045	0	8.0	5.4	11.0	0	0	56.4	19.3
K-----	.00010	16.1	0	0	19.6	19.6	0	0	44.7
Mg-----	.00011	0	31.9	0	15.5	0	0	18.7	33.9
Mn-----	.00041	0	18.5	0	0	0	0	46.4	35.1
Na-----	.00009	15.8	0	33.5	3.6	16.2	0	0	30.9
Zn-----	.00035	0	*29.1	0	13.0	0	10.4	2.9	44.6
Based on DTPA extract									
Cu-----	0.00200	8.1	0	0	37.8	12.1	0	0	42.0
Fe-----	.00068	22.5	0	8.8	0	29.8	*22.1	10.7	6.1
Mn-----	.00097	11.2	0	0	53.6	0	4.0	31.2	0
Pb-----	.01733	5.9	.9	0	14.3	1.4	0	0	77.5
Zn-----	.00184	8.7	0	0	*91.3	0	0	0	0
Based on exchangeable cations									
C.E.C. ¹ ---	0.00024	11.2	0	0	25.1	0	0	0	63.7
Ca-----	.00209	9.1	0	1.6	14.2	0	*40.9	0	34.2
K-----	.04296	5.3	0	8.8	.5	0	0	*82.6	2.8
Na-----	.00045	0	24.8	0	42.4	0	*22.1	5.6	5.1
Mg-----	.00020	0	33.8	*46.7	0	0	0	0	19.5
Based on saturation extract									
S.C. ² ----	0.00086	7.1	12.5	0	12.3	0	0.6	24.0	43.5
Ca-----	.00182	0	24.3	0	*8.1	0	22.8	0	44.8
Cl-----	0	0	0	0	0	0	0	0	0
K-----	.03414	9.4	0	*45.5	0	0	20.7	0	24.4
Na-----	.00209	*16.0	10.1	0	17.7	0	15.7	0	40.5
Mg-----	.00509	19.5	0	0	20.3	0	20.4	0	39.8
SO ₄ -----	.00308	18.0	0	0	11.9	0	20.7	21.3	28.1
Measured by specific-ion electrode									
pH ³ -----	0.08953	0	27.2	19.0	0	3.2	0	38.1	12.5
Based on water-saturation extract									
S.I. ⁴ ----	0.00146	*18.2	11.2	0	4.0	0	13.4	0	53.2

¹Cation exchange capacity.

²Specific conductance at 25°C.

³Variance is arithmetic.

⁴Saturation index.

Table 7.--Variance components attributed to splitting and analyses of Sample B

[*, variance component significantly different from zero at the 0.05 probability level; level, source of variation as indicated in table 5]

Parameter	Total	Percentage of total variance							
	log ₁₀ variance	Level h, 8-gallon splits	Level g, 4-gallon splits	Level f, 2-gallon splits	Level e, 1-gallon splits	Level d, 1/2-gallon splits	Level c, 1/4-gallon splits	Level b, 1/8-gallon splits	Level a, analytical error
Based on total content									
Ca-----	0.00031	7.7	0	0	0	0	33.1	0	59.2
Co-----	.03044	0	*62.8	2.2	0	0	1.2	1.4	32.4
Cu-----	.00082	0	9.8	0	25.5	6.5	13.3	0	44.9
Fe-----	.00026	4.2	.8	0	13.1	35.7	0	0	46.2
K-----	.00010	5.4	0	0	25.9	28.5	0	0	40.2
Mg-----	.00018	0	6.7	0	7.0	0	26.1	0	60.2
Mn-----	.00025	0	0	16.7	0	3.0	0	*72.8	7.5
Na-----	.00016	80	0	0	0	26.8	17.5	0	47.7
Zn-----	.00028	0	*74.9	0	0	*14.9	4.3	0	5.9
Based on DTPA extract									
Cd-----	0.00996	0.8	0	*71.8	0	0	0	0	27.4
Cu-----	.00095	0	*60.6	0	0	0	4.0	2.9	32.5
Fe-----	.00600	0	24.4	8.1	0	.4	0	0	67.1
Mn-----	.00263	0	7.6	8.7	0	1.7	8.2	0	73.8
Pb-----	.03014	16.5	0	3.3	0	17.4	0.2	0	62.6
Zn-----	.00122	0	*82.5	4.6	0	3.6	.9	0	8.4
Based on exchangeable cations									
C.E.C. ¹ ---	0.10253	0	*38.9	*6.0	0	0	0	*52.3	2.8
Ca-----	.02903	1.7	*16.0	0	10.2	0	29.4	0	42.7
K-----	.01343	0	27.5	0	0	0	0	23.5	49.0
Na-----	.00040	20.8	2.5	0	0	0	0	58.0	18.7
Mg-----	.00155	12.0	4.3	0	22.6	0	19.8	.1	41.2
Based on saturation extract									
S.C. ² ----	0.00491	0	0	17.3	0	15.2	17.2	0	50.3
Ca-----	.40922	25.2	0	0	*44.9	3.7	14.8	0	11.4
Cl-----	0	0	0	0	0	0	0	0	0
K-----	.11574	7.5	*11.8	0	34.7	0	*35.3	3.2	7.5
Na-----	.01020	0	0	10.6	0	23.3	*13.1	0	53.0
Mg-----	.21665	25.0	0	0	*46.6	5.5	1.5	10.8	10.6
SO ₄ -----	.00603	.9	0	*68.3	0	7.2	3.1	0	20.5
Measured by specific-ion electrode									
pH ³ -----	0.04194	0	*45.1	6.8	0	0	0	*45.1	3.0
Based on water-saturation extract									
S.I. ⁴ -----	0.00272	0	39.1	*29.8	0	0	*12.1	0	19.0

¹Cation exchange capacity.

²Specific conductance at 25° C.

³Variance is arithmetic.

⁴Saturation index.

Table 8.--Variance components attributed to splitting and analyses of Sample C

[*, variance component significantly different from zero at the 0.05 probability level; level, source of variation as indicated in table 5]

Parameter	Total	Percentage of total variance							
	log ₁₀ variance	Level h, 8-gallon splits	Level g, 4-gallon splits	Level f, 2-gallon splits	Level e, 1-gallon splits	Level d, 1/2-gallon splits	Level c, 1/4-gallon splits	Level b, 1/8-gallon splits	Level a, analytical error
Based on total content									
Ca-----	0.00079	0	*63.3	0	0	16.9	0	0	19.8
Co-----	.02438	3.2	0	36.3	0	*15.1	0	32.6	12.8
Cu-----	.00589	0	*58.7	2.5	0	10.2	4.4	0	24.2
Fe-----	.00193	0	0	21.5	0.5	4.6	0	43.3	30.1
K-----	.00021	3.2	0	10.5	0	21.8	0	26.8	37.7
Mg-----	.00162	2.8	0	*18.0	0	23.5	0	*47.1	8.6
Mn-----	.00073	1.1	0	*51.1	0	19.6	0	7.1	21.1
Na-----	.00009	.2	10.4	0	41.3	4.5	0	0	43.6
Zn-----	.01434	12.3	0	0	0	0	0	0	87.7
Based on DTPA extract									
Cd-----	0.02399	*38.0	0	0	0	7.3	0	*48.2	6.5
Cu-----	.00326	9.3	0	0	0	58.7	0	32.0	0
Fe-----	.00097	.8	7.0	3.1	0	*47.8	10.2	0	31.1
Mn-----	.00211	0	*47.6	0	0	18.4	1.0	14.1	18.9
Pb-----	.07567	0	20.7	0	24.0	3.0	0	0	52.3
Zn-----	.00237	.5	0	7.4	0	28.9	0	15.8	47.4
Based on exchangeable cations									
C.E.C. ¹ --	0.02195	11.8	0	1.7	0	0	0	0	86.5
Ca-----	.00044	28.6	0	0	0	39.6	31.8	0	0
K-----	.03212	11.0	0	*52.7	0	5.7	0	11.4	19.2
Na-----	.02500	13.4	0	*75.7	.9	0	.7	0	9.3
Mg-----	.00120	16.3	0	*47.4	0	1.7	0	19.9	14.7
Based on saturation extract									
S.C. ² ----	0.00380	17.3	0	3.2	0	35.9	3.8	0	39.8
Ca-----	.00151	11.5	6.0	0	8.6	0	*19.8	0	54.1
Cl-----	0	0	0	0	0	0	0	0	0
K-----	.00852	0	*67.5	0	*19.1	.3	.4	0	12.7
Na-----	.00555	0	0	15.7	6.9	0	38.6	0	38.8
Mg-----	.00146	9.6	12.7	0	11.8	0	1.0	0	64.9
Measured by specific-ion electrode									
pH ³ -----	0.05785	13.4	0	43.1	3.9	0	1.5	27.4	10.7
Based on water-saturation extract									
S.I. ⁴ ----	0.00058	*35.3	5.2	0	12.7	0	0	15.3	31.5

¹Cation exchange capacity.

²Specific conductance at 25°C.

³Variance is arithmetic.

⁴Saturation index.

Table 9.--Variance components attributed to splitting and analyses of Sample D

[*, variance component significantly different from zero at the 0.05 probability level; level, source of variation as indicated in table 5]

Parameter	Total	Percentage of total variance							
	log ₁₀ variance	Level h, 8-gallon splits	Level g, 4-gallon splits	Level f, 2-gallon splits	Level e, 1-gallon splits	Level d, 1/2-gallon splits	Level c, 1/4-gallon splits	Level b, 1/8-gallon splits	Level a, analytical error
Based on total content									
Ca-----	0.00089	12.0	0	54.5	0	*22.9	2.3	0	8.3
Co-----	.01210	0	36.9	11.6	0	0	0	0	51.5
Cu-----	.00754	9.7	0	*23.7	0	23.6	0	0	43.0
Fe-----	.00039	0	1.6	0	15.4	7.2	18.0	0	57.8
K-----	.00008	10.4	0	43.9	0	0	0	14.8	30.9
Mg-----	.00103	6.6	16.4	0	9.0	0	*18.2	0	49.8
Mn-----	.00070	7.7	0	0	17.5	*28.0	0	20.9	25.9
Na-----	.00039	5.2	1.5	0	0	0	26.8	0	66.5
Zn-----	.00026	0	45.7	0	12.6	0	5.1	9.7	26.9
Based on DPTA extract									
Cd-----	0.01588	9.2	0	0	90.8	0	0	0	0
Cu-----	0	0	0	0	0	0	0	0	0
Fe-----	.00119	0	18.0	0	0	.6	0	0	81.4
Mn-----	.00440	0	23.0	0	0	0	.6	0	76.4
Pb-----	.0192	0	18.3	0	5.2	0	20.4	0	56.1
Zn-----	.00654	17.5	6.0	0	22.2	0	0	54.3	0
Based on exchangeable cations									
C.E.C. ¹ ---	0.00086	3.1	0	5.8	0	12.0	6.0	0	73.1
Ca-----	.00074	15.8	0	0	33.3	0	0	2.7	48.2
K-----	.02666	0	24.8	6.9	0	0	*29.3	0	39.0
Na-----	.00454	8.9	0	0	2.3	0	17.3	0	71.5
Mg-----	.00044	1.3	7.5	0	36.4	10.2	*5.3	0	39.3
Based on saturation extract									
S.C. ² ----	0.00043	17.4	0	*46.1	0	0	0	4.3	32.2
Ca-----	.00080	0	0	36.1	0	0	0	19.4	44.5
Cl-----	0	0	0	0	0	0	0	0	0
K-----	.01270	11.5	0	0	0	2.8	11.1	0	74.6
Na-----	.00436	17.7	0	0	5.6	5.7	.5	0	70.5
Mg-----	.00159	0	15.7	0	0	0	0	30.0	54.3
Measured by specific-ion electrode									
pH ³ -----	0.12433	7.2	0	0	15.4	0	18.1	0	59.3
Based on water-saturation extract									
S.I. ⁴ -----	0.00063	11.1	0	8.6	0	0	0	17.2	63.1

¹Cation exchange capacity.

²Specific conductance at 25°C.

³Variance is arithmetic.

⁴Saturation index.

ERROR DUE TO LABORATORY ANALYSIS

Tables 10-13 give statistics that summarize the total and extractable element composition of each of the four reference samples. For total content of most elements and for all four samples, the observed ranges in tables 10-13 are generally within the accepted relative standard deviation for flame A.A.S. of 5

Table 10.--Statistical summary for repeated analyses of Sample A

[Ratio, number of samples in which the parameter was found in measurable concentrations relative to the number of samples analyzed; means and deviations are geometric, except as indicated; <, less than; leaders (---), no data available]

Parameter ¹	Ratio	Geometric mean	Geometric deviation	Geometric error	Observed range
Based on total content					
Ca, pct-----	18:18	0.31	1.104	1.059	0.30 - 0.35
Co, ppm-----	18:18	6.6	1.202	1.191	5.0 - 8.0
Cu, ppm-----	18:18	13.7	1.266	1.117	12 - 20
Fe, pct-----	18:18	1.94	1.050	1.022	1.85 - 2.02
K, pct-----	18:18	1.91	1.023	1.016	1.86 - 1.94
Mg, pct-----	18:18	.40	1.024	1.014	.39 - .41
Mn, ppm-----	18:18	202	1.048	1.028	190 - 210
Na, pct-----	18:18	1.49	1.022	1.012	1.45 - 1.53
Zn, ppm-----	18:18	42	1.044	1.029	41 - 45
Based on DTPA extract					
Cd, ppm-----	2:18	---	---	---	<0.05 - 0.05
Cu, ppm-----	18:18	.73	1.109	1.069	.7 - .8
Fe, ppm-----	18:18	15.5	1.062	1.015	14.6 - 16.7
Mn, ppm-----	18:18	1.2	1.074	1.000	1.1 - 1.3
Pb, ppm-----	18:18	1.1	1.354	1.306	.8 - 1.6
Zn, ppm-----	18:18	.72	1.104	1.000	.7 - .8
Based on exchangeable cations					
C.E.C. ² , meq/100 g	18:18	22.0	1.037	1.029	21.3 - 23.1
Ca ³ , meq/100 g----	18:18	7.6	1.111	1.064	6.8 - 8.6
Ca ⁴ , meq/100 g----	18:18	6.4	1.141	1.073	5.7 - 7.5
K ³ , meq/100 g----	18:18	.40	1.612	1.083	.29 - .61
K ⁴ , meq/100 g----	18:18	.35	1.676	1.102	.25 - .57
Na ³ , meq/100 g----	18:18	32.5	1.050	1.011	31 - 34
Na ⁴ , meq/100 g----	18:18	13.9	1.223	1.021	11 - 16
Mg ³ , meq/100 g----	18:18	2.5	1.033	1.015	2.4 - 2.6
Mg ⁴ , meq/100 g----	18:18	1.8	1.074	1.037	1.6 - 1.9
Based on water-saturation extract					
S.C. ⁵ , mmhos/cm----	18:18	40.1	1.070	1.045	38.2 - 43.7
Ca, meq/L-----	18:18	23.8	1.103	1.068	21.8 - 27.4
K, meq/L-----	18:18	.86	1.530	1.234	.7 - 1.4
Na, meq/L-----	18:18	375	1.111	1.069	350 - 430
Mg, meq/L-----	18:18	14.2	1.178	1.109	12.5 - 17.4
SO ₄ , meq/L-----	18:18	348	1.136	1.070	310 - 410
Cl, meq/L-----	18:18	.5	1.000	1.000	.5 - .5
Based on hot-water extract					
B, ppm-----	0:18	<0.5	---	---	<0.5 - <0.5
Measured by specific-ion electrode					
pH ⁶ -----	18:18	7.5	0.292	0.106	7.2 - 7.9
Based on calculated parameter					
S.I. ⁷ , pct-----	18:18	49.4	1.092	1.066	44.9 - 57.2

¹pct, percent; ppm, parts per million; meq/100 g, milliequivalents per 100 grams; mmhos/cm, reciprocal milliohms per centimeter at 25 degrees

²Celsius; meq/L, milliequivalents per liter.

³Cation exchange capacity.

⁴Values uncorrected for the fraction soluble in water.

⁵Values corrected for amounts measured in the water-saturation extract.

⁶Specific conductance.

⁷Mean, deviation, and error are arithmetic.

⁸Saturation index.

percent. This narrow observed range would also indicate that adequate homogenization of each sample was achieved and that any splitting errors are within acceptable limits. Therefore, the reasons for less precision in the determination of extractable elements must be related to the character of the samples and to the factors in the laboratory procedure that may influence the amount of the element extracted.

Table 11.--Statistical summary for repeated analyses of Sample B

[Ratio, number of samples in which the parameter was found in measurable concentrations relative to the number of samples analyzed; means and deviations are geometric, except as indicated; <, less than; leaders (---), no data available]

Parameter ¹	Ratio	Geometric mean	Geometric deviation	Geometric error	Observed range
Based on total content					
Ca, pct-----	18:18	2.76	1.041	1.032	2.57 - 2.79
Co, ppm-----	18:18	9.6	1.494	1.257	5 - 12
Cu, ppm-----	18:18	24.8	1.068	1.045	23 - 27
Fe, pct-----	18:18	2.02	1.038	1.026	1.94 - 2.09
K, pct-----	18:18	1.72	1.024	1.015	1.68 - 1.75
Mg, pct-----	18:18	1.42	1.031	1.024	1.32 - 1.45
Mn, ppm-----	18:18	358	1.037	1.010	350 - 370
Na, pct-----	18:18	1.03	1.029	1.020	1.00 - 1.06
Zn, ppm-----	18:18	75.7	1.039	1.009	73 - 79
Based on DTPA extract					
Cd, ppm-----	18:18	0.11	1.258	1.128	0.09 - 0.14
Cu, ppm-----	18:18	2.3	1.074	1.041	2.1 - 2.5
Fe, ppm-----	18:18	84.0	1.195	1.157	72.6 - 99.4
Mn, ppm-----	18:18	4.6	1.125	1.107	4.2 - 5.2
Pb, ppm-----	18:18	2.4	1.491	1.372	1.1 - 3.1
Zn, ppm-----	18:18	7.8	1.084	1.024	7.5 - 8.9
Based on exchangeable cations					
C.E.C. ² , meq/100 g	18:18	23.0	2.090	1.132	8.6 - 53
Ca ³ , meq/100 g----	18:18	13.8	1.483	1.292	9.2 - 19.5
Ca ⁴ , meq/100 g----	18:18	13.1	1.510	1.297	8.9 - 19.3
K ³ , meq/100 g----	18:18	.54	1.306	1.205	.41 - .74
K ⁴ , meq/100 g----	18:18	.46	1.449	1.214	.28 - .69
Na ³ , meq/100 g----	18:18	9.7	1.047	1.020	9.0 - 10.2
Na ⁴ , meq/100 g----	18:18	7.0	1.107	1.077	6.2 - 7.8
Mg ³ , meq/100 g----	18:18	3.8	1.095	1.060	3.4 - 4.1
Mg ⁴ , meq/100 g----	18:18	3.3	1.259	1.069	2.2 - 3.9
Based on water-saturation extract					
S.C. ⁵ , mmhos/cm----	18:18	1.5	1.175	1.121	1.3 - 1.8
Ca, meq/L-----	18:18	2.7	4.362	1.644	1.0 - 15.5
K, meq/L-----	18:18	.45	2.189	1.237	.27 - 1.3
Na, meq/L-----	18:18	16.4	1.262	1.185	13.6 - 19.6
Mg, meq/L-----	18:18	2.4	2.920	1.418	1.2 - 9.4
SO ₄ , meq/L-----	18:18	7.7	1.196	1.084	6.5 - 10.0
Cl, meq/L-----	0:18	<.5	---	---	<.5 - <.5
Based on hot-water extract					
B, ppm-----	0:18	<0.5	---	---	<0.5 - <0.5
Measured by specific-ion electrode					
pH ⁶ -----	18:18	9.0	0.025	0.035	8.8 - 9.3
Based on calculated parameter					
S.I. ⁷ , pct-----	18:18	164.1	1.128	1.054	141.6 - 178.4

¹pct, percent; ppm, parts per million; meq/100 g, milliequivalents per 100 grams; mmhos/cm, reciprocal milliohms per centimeter at 25 degrees

²Celsius; meq/L, milliequivalents per liter.

³Cation exchange capacity.

⁴Values uncorrected for the fraction soluble in water.

⁵Values corrected for amounts measured in the water-saturation extract.

⁶Specific conductance.

⁷Mean, deviation, and error are arithmetic.

⁸Saturation index.

The observed range for all elements, except Pb, extracted by DTPA from Sample A (table 10) is narrow, indicating that acceptable analytical precision was achieved. For Sample B, the wider observed range in DTPA-extractable elements (table 11) indicates that less analytical precision was achieved with this sample. Several factors may account for this drop in precision. A very fine clay-sized suspension was persistent in Sample B, even after centrifuging. The

Table 12.--Statistical summary for repeated analyses of Sample C

[Ratio, number of samples in which the parameter was found in measurable concentrations relative to the number of samples analyzed; means and deviations are geometric, except as indicated; <, less than; leaders (---), no data available]

Parameter ¹	Ratio	Geometric mean	Geometric deviation	Geometric error	Observed range
Based on total content					
Ca, pct-----	18:18	.61	1.067	1.029	0.55 - 0.65
Co, ppm-----	18:18	3.5	1.433	1.137	3 - 5
Cu, ppm-----	18:18	10.3	1.193	1.091	8 - 11
Fe, pct-----	18:18	.80	1.107	1.057	.71 - .85
K, pct-----	18:18	2.65	1.034	1.021	2.57 - 2.74
Mg, pct-----	18:18	.16	1.097	1.028	.15 - .17
Mn, ppm-----	18:18	265	1.064	1.029	250 - 285
Na, pct-----	18:18	1.50	1.023	1.015	1.45 - 1.54
Zn, ppm-----	18:18	29.8	1.317	1.295	27 - 56
Based on DTPA extract					
Cd, ppm-----	11:18	0.051	1.429	1.095	<0.05 - 0.06
Cu, ppm-----	18:18	.57	1.141	1.000	.5 - .6
Fe, ppm-----	18:18	22.1	1.074	1.041	20.5 - 23.6
Mn, ppm-----	18:18	21.5	1.111	1.047	19.9 - 24.7
Pb, ppm-----	18:18	.48	1.884	1.581	.3 - 1.0
Zn, ppm-----	18:18	.65	1.119	1.080	.6 - .7
Based on exchangeable cations					
C.E.C. ² , meq/100 g	18:18	9.5	1.407	1.373	8.2 - 21.2
Ca ³ , meq/100 g----	18:18	6.4	1.050	1.000	6.2 - 6.8
Ca ⁴ , meq/100 g----	18:18	6.3	1.050	1.001	6.1 - 6.7
K ³ , meq/100 g----	18:18	.43	1.511	1.199	.33 - .85
K ⁴ , meq/100 g----	18:18	.41	1.524	1.206	.31 - .86
Na ³ , meq/100 g----	18:18	1.07	1.439	1.118	.89 - 2.1
Na ⁴ , meq/100 g----	18:18	1.06	1.442	1.119	.88 - 2.1
Mg ³ , meq/100 g----	18:18	1.1	1.083	1.031	1.0 - 1.2
Mg ⁴ , meq/100 g----	18:18	1.1	1.086	1.031	1.0 - 1.2
Based on water-saturation extract					
S.C. ⁵ , mmhos/cm--	18:18	0.59	1.152	1.094	0.50 - 0.66
Ca, meq/L-----	18:18	5.0	1.093	1.068	4.5 - 5.4
K, meq/L-----	18:18	.63	1.237	1.079	.56 - .86
Na, meq/L-----	18:18	.28	1.187	1.113	.23 - .35
Mg, meq/L-----	18:18	1.37	1.092	1.073	1.2 - 1.5
SO ₄ , meq/L-----	0:18	<1.0	---	---	<1.0 - <1.0
Cl, meq/L-----	18:18	1.0	1.000	1.000	1.0 - 1.0
Based on hot-water extract					
B, ppm-----	0:18	<0.5	---	---	<0.5 - <0.5
Measured by specific-ion electrode					
pH ⁶ -----	18:18	7.2	0.241	0.079	6.9 - 7.5
Based on calculated parameter					
S.I. ⁷ , pct-----	18:18	23.7	1.057	1.032	22.3 - 25.5

¹pct, percent; ppm, parts per million; meq/100 g, milliequivalents per 100 grams; mmhos/cm, reciprocal milliohms per centimeter at 25 degrees Celsius; meq/L, milliequivalents per liter.
²Cation exchange capacity.
³Values uncorrected for the fraction soluble in water.
⁴Values corrected for amounts measured in the water-saturation extract.
⁵Specific conductance.
⁶Mean, deviation, and error are arithmetic.
⁷Saturation index.

pH of this sample was about 9.0, and the DTPA extractant was buffered at pH 7.3. Perhaps significant dissolution of iron oxy-hydroxide coatings occurred differentially from sample to sample. This could also account for the wide observed range in other metals, because oxy-hydroxides are good scavengers of trace metals (Jenne, 1968). For Sample C (table 12), the observed range for DTPA-extractable elements suggests that adequate analytical precision was

Table 13.--Statistical summary for repeated analyses of Sample D

[Ratio, number of samples in which the parameter was found in measurable concentrations relative to the number of samples analyzed; means and deviations are geometric, except as indicated; <, less than; leaders (---), no data available]

Parameter ¹	Ratio	Geometric mean	Geometric deviation	Geometric error	Observed range
Based on total content					
Ca, ppm-----	18:18	0.54	1.071	1.020	0.50 - 0.60
Co, ppm-----	18:18	4.3	1.288	1.199	3 - 6
Cu, ppm-----	18:18	14.3	1.221	1.140	12 - 20
Fe, pct-----	18:18	1.45	1.046	1.035	1.40 - 1.52
K, pct-----	18:18	2.05	1.021	1.012	2.00 - 2.10
Mg, pct-----	18:18	.33	1.077	1.053	.32 - .36
Mn, ppm-----	18:18	392	1.063	1.032	360 - 420
Na, pct-----	18:18	.92	1.046	1.038	.88 - .95
Zn, ppm-----	18:18	36.3	1.038	1.019	35 - 38
Based on DTPA extract					
Cd, ppm-----	2:18	---	---	---	<0.05 - 0.06
Cu, ppm-----	18:18	.8	1.000	1.000	.8 - .8
Fe, ppm-----	18:18	12.9	1.083	1.074	12 - 14
Mn, ppm-----	18:18	19.9	1.165	1.143	17.2 - 23.4
Pb, ppm-----	18:18	1.0	1.375	1.270	.7 - 1.5
Zn, ppm-----	18:18	.55	1.205	1.000	.5 - .7
Based on exchangeable cations					
C.E.C. ² , meq/100 g	18:18	18.5	1.070	1.060	17.2 - 20.8
Ca ³ , meq/100 g----	18:18	13.1	1.065	1.044	12.0 - 14.2
Ca ⁴ , meq/100 g----	18:18	12.9	1.065	1.045	11.9 - 14.1
K ³ , meq/100 g----	18:18	.50	1.456	1.265	.37 - .70
K ⁴ , meq/100 g----	18:18	.50	1.462	1.268	.36 - .69
Na ³ , meq/100 g----	18:18	1.05	1.168	1.140	.94 - 1.2
Na ⁴ , meq/100 g----	18:18	1.05	1.169	1.141	.93 - 1.2
Mg ³ , meq/100 g----	18:18	2.6	1.050	1.031	2.5 - 2.8
Mg ⁴ , meq/100 g----	18:18	2.6	1.050	1.031	2.5 - 2.8
Based on water-saturation extract					
S.C. ⁵ , mmhos/cm--	18:18	0.50	1.049	1.027	0.48 - 0.53
Ca, meq/L-----	18:18	4.3	1.067	1.044	4.0 - 4.6
K, meq/L-----	18:18	.23	1.296	1.251	.19 - .32
Na, meq/L-----	18:18	.30	1.164	1.136	.25 - .37
Mg, meq/L-----	18:18	1.05	1.096	1.070	.97 - 1.2
SO ₄ , meq/L-----	0:18	<1.0	---	---	<1.0 - 1.0
Cl, meq/L-----	18:18	1.0	1.000	1.000	1.0 - 1.0
Based on hot-water extract					
B, ppm-----	0:18	<0.5	---	---	<0.5 - <0.5
Measured by specific-ion electrode					
pH ⁶ -----	18:18	7.7	0.353	0.272	7.2 - 8.1
Based on calculated parameter					
S.I. ⁷ , pct-----	18:18	29.2	1.060	1.047	26.9 - 31.5

¹pct, percent; ppm, parts per million; meq/100 g, milliequivalents per 100 grams; mmhos/cm, reciprocal milliohms per centimeter at 25 degrees Celsius; meq/L, milliequivalents per liter.
²Cation exchange capacity.
³Values uncorrected for the fraction soluble in water.
⁴Values corrected for amounts measured in the water-saturation extract.
⁵Specific conductance.
⁶Mean, deviation, and error are arithmetic.
⁷Saturation index.

achieved and that factors affecting the amount of an element extracted were constant. In table 13, the observed range in DTPA-extractable metals for Sample D also indicates adequate analytical precision, except for Mn. In general, for the DTPA extraction, when the natural soil pH is much different from that of the buffered extracting solution (as in Sample B), analytical precision is affected, especially for Fe. In all four reference samples, however, the observed range was greatest for Pb, probably because the amounts determined were near the lower detection limit. Much care must be taken to standardize the laboratory procedure for this extraction because it is a nonequilibrium extraction and will be influenced by many aspects of the extraction technique. Also, the amounts of the various metals present may affect the amounts of any single metal extracted, because DTPA is a generalized chelating agent.

Cation exchange capacity and exchangeable-cation determinations for Sample A (table 10) exhibit narrow ranges, indicating adequate analytical precision. However, the large difference between C.E.C. and the uncorrected sum of the exchangeable cations indicates a need to correct for soluble cations. Exchangeable Na appears to be much too high. This probably reflects a sodium salt of sulfate or bicarbonate that was partially dissolved by the exchanging solution. When corrected for soluble cations, the sum of exchangeable cations is in good agreement with C.E.C. The large observed range for C.E.C. and for exchangeable cations for Sample B indicates that a serious problem exists when using these methods on this sample. In Sample B, problems in removing a very fine clay-sized suspension existed. This could explain the lack of precision. An ultracentrifuge would be necessary to remove this fine clay from suspension. For Sample C, the observed range in C.E.C. is quite large; however, when corrected for water-soluble cations the exchangeable-cation determinations seem to be reasonably precise. The most precise results for C.E.C. and exchangeable cations were for Sample D. In general, C.E.C. and exchangeable-cation determinations, using the method proposed, result in precision that is lower than desired for reference samples. The data for these samples also show that correcting the exchangeable-cation determinations for water-soluble constituents is essential.

Parameters measured in the water-saturation extract for Sample A and Sample B (tables 10 and 11) exhibit wider observed ranges than those for Sample C and Sample D (tables 12 and 13); however, relative to the absolute amounts of the parameters measured, the precision seems similar for Samples A, C and D. Sample B is an exception, and it also presented the greatest difficulties in the laboratory in determining when saturation criteria had been met. Perhaps, the data for Samples A, C, and D represent the maximum precision that can be expected for this method because of the subjective nature of the steps performed to produce a solution to analyze.

Measurements of soil pH for all samples show an observed range that is probably typical for this standard method of determination.

Hot-water-extractable boron was not detected in any of the reference samples and, therefore, the precision of the method could not be evaluated. However, analysis of an in-house standard used at the Wooster Agricultural Research Center, Wooster, Ohio (M. E. Watson, written commun., August 25, 1978) indicates that this method will probably provide acceptable precision and accuracy.

SAMPLE-HOMOGENEITY ESTIMATES

Total variation given for each parameter in tables 6-9 contains two components: variation due to splitting (sample homogeneity, levels b-h) and variation due to the procedures necessary to obtain a measurement in the laboratory (analytical error, level a). The geometric deviation reported for each parameter in tables 10-13 estimates the sum of this variation due to sample inhomogeneity and analytical error, while the geometric error is an estimate of only analytical error. Parameter variability resulting from only sample inhomogeneity can be estimated in the following way: First, analytical error is removed from the geometric deviation by using the following equation:

$$GD_n = \text{antilog} \left[(\log GD)^2 - (\log GE)^2 \right]^{1/2}$$

where GD_n is the geometric deviation with analytical error removed and GD and GE are, respectively, the geometric deviations and geometric errors reported in tables 10-13. Then, 68.3 percent of the time an analysis of a sample for any parameter should range from GM/GD_n to $GM \cdot GD_n$ on the basis of this estimate of sample inhomogeneity. This range in parameter values reflects an estimate of sample inhomogeneity. Similarly, 95.4 and 99.7 percent of the time the range is estimated by GM/GD_n^2 to $GM \cdot GD_n^2$, and GM/GD_n^3 to $GM \cdot GD_n^3$, respectively. For example, the 68 percent range for total Cu in Sample A (table 10) is from 11.1 to 16.8 with analytical error removed, the 95.4 percent range is from 9.0 to 20.8, and the 99.7 percent range is from 7.3 to 25.3. For DTPA-extractable Fe in this sample, the 68 percent range is from 14.6 to 16.4, the 95.4 percent range is from 13.8 to 17.4, and the 99.7 percent range is from 13.0 to 18.5. Figures 1 and 2, each containing the same area under the curve, illustrate the differences in inhomogeneity of these two elements for the same reference sample. From a comparison of these two figures, the reference sample is clearly more homogeneous for DTPA-extractable Fe than for total Cu. From these figures Sample A is concluded to be a much better reference material for DTPA-extractable Fe than it is for total Cu on the basis of the estimates of homogeneity. Similar plots could be made for each parameter measured for each reference material by using the data in tables 10-13. These two parameters were chosen because, while they have about the same average content, they differ in homogeneity. The two figures also illustrate that the actual data tend to resemble a log-normal distribution but that not enough samples have been analyzed to graph the distribution accurately.

REFERENCES

- Andersson, Arne, 1975, Relative efficiency of nine different soil extracts: *Swedish Journal of Agricultural Research*, v. 5, p. 125-135.
- Ball, J. W., Thompson, J. M., and Jenne, E. A., 1978, Determination of dissolved boron in fresh, estuarine, and geothermal waters by d.c. argon-plasma emission spectrometry: *Analytica et Chimica Acta*, v. 98, p. 67-75.
- Bear, F. E., 1964, Introduction, in *Chemistry of the soil*: New York, Van Nostrand Reinhold Co., American Chemical Society Monograph Series 160, p. xix-xxii.
- Black, C. A., ed., 1965, Chemical and microbiological properties, pt. 2 of *Methods of soil analysis*: Madison, Wisc., American Society of Agronomy, p. 771-1569.
- Bower, C. A., and Wilcox, L. V., 1965, Soluble salts, in *Chemical and microbiological properties*, pt. 2 of *Methods of soil analysis*: Madison, Wisc., American Society of Agronomy, p. 899-900.
- Chapman, H. D., 1965, Cation-exchange capacity, in *Methods of soil analysis*, pt. 2, Chemical and microbiological properties: Madison, Wisconsin, American Society of Agronomy, p. 899-900.
- Govett, G. J. S., and Whitehead, R. E., 1973, Errors in atomic absorption spectrophotometric determinations of Pb, Zn, Ni, and Co in geologic materials: *Journal of Geochemical Exploration*, v. 2, p. 121-131.
- Jacober, F. M., and Sandoval, F., 1971, Effect of soil grinding, suction, and extraction time on salt concentration of saturation extracts: *Soil Science*, v. 112, no. 4, p. 263-266.
- Jenne, E. A., 1968, Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water—The significant role of hydrous Mn and Fe oxides, in *Trace inorganics in water*: Washington, D.C., American Chemical Society Advances in Chemistry Series 73, p. 337-387.
- Lindsay, W. L., and Norvell, W. A., 1969, Development of a DTPA micronutrient soil test: Madison, Wisc., American Society of Agronomy, Agronomy Abstract, p. 84.
- _____, 1978, Development of a DTPA soil test for Zn, Fe, Mn, and Cu: *Soil Science Society of America Journal*, v. 42, p. 421-428.
- McLean, E. O., 1973, Testing soils for pH and lime requirement, in *Soil testing and plant analysis*: Madison, Wisc., Soil Science Society of America, Inc., p. 77-95.
- Mountjoy, Wayne, 1970, Determination of cobalt in geologic materials by solvent extraction and atomic absorption spectrometry, in *Geological Survey research 1970*: U.S. Geological Survey Professional Paper 700-B, p. B174-B176.
- Mubarak, A., Hageman, L., Howald, R. A., and Woodriff, R., 1978, Serious interferences in the determination of trace metals in soils by flame and flameless atomic absorption spectrophotometry: *Soil Science Society of America Journal*, v. 42, p. 889-891.
- Peech, Michael, 1965, Hydrogen-ion activity, in *Chemical and microbiological properties*; pt. 2, of *Methods of soil analysis*: Madison, Wisc., American Society of Agronomy, p. 922-923.
- Sandoval, F. M., and Power, J. F., 1977, Laboratory methods recommended for chemical analysis of mined-land spoils and overburden in Western United States: U.S. Department of Agriculture, Agriculture Handbook 525, 31 p.
- Schaller, F. W., and Sutton, Paul, eds., 1978, Reclamation of drastically disturbed land: Madison, Wisc., American Society of Agronomy, 742 p.
- Severson, R. C., McNeal, J. M., and Dickson, J. J., 1979, Effects of soil preparation on DTPA-extractable elements in soils of the Northern Great Plains: *Soil Science*, v. 128, p. 70-79.
- Soltanpour, P. N., Khan, A., and Lindsay, W. L., 1976, Factors affecting DTPA-extractable Zn, Fe, Mn, and Cu from soils: *Communications in Soil Science and Plant Analysis*, v. 7, no. 9, p. 797-821.
- Soltanpour, P. N., and Schwab, A. P., 1977, A new soil test for simultaneous extraction of macro and micro-nutrients in alkaline soils: *Communications in Soil Science and Plant Analysis*, v. 8, no. 3, p. 195-207.
- Swanson, V. E., and Huffman, Claude, Jr., 1976, Guidelines for sample collecting and analytical methods used in the U.S. Geological Survey for determining chemical composition of coal: U.S. Geological Survey Circular 735, 11 p.
- Wali, M. K., ed., 1979, Ecology and coal resource development, v. 1 and 2: New York, Pergamon Press, 1091 p.
- Wear, J. I., 1965, Boron, in *Chemical and microbiological properties*, pt. 2 of *Methods of soil analysis*: Madison, Wisc., American Society of Agronomy, p. 1059-1063.
- Yamasaki, Shin-ichi, Yoshino, Akio, and Kishita, Akira, 1975, The determination of sub-microgram amounts of elements in soil solution by flameless atomic absorption spectrophotometry with a heated graphite atomizer: *Soil Science Plant Nutrition*, v. 21, no. 1, p. 63-72.