Field and Laboratory Procedures Used in a Soil Chronosequence Study

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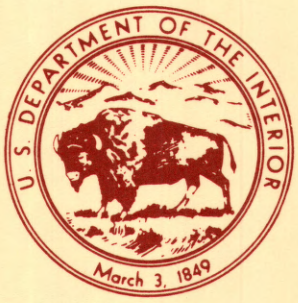

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Michael J. Singer and Peter Janitzky, *Editors*

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Field and Laboratory Procedures Used in a Soil Chronosequence Study[1]

Michael J. Singer *and* Peter Janitzky, *Editors,*
University of California, Davis

INTRODUCTION

In 1978, the late Denis Marchand initiated a research project entitled "Soil Correlation and Dating at the U.S. Geological Survey" to determine the usefulness of soils in solving geologic problems. Marchand proposed to establish soil chronosequences that could be dated independently of soil development by using radiometric and other numeric dating methods. In addition, by comparing dated chronosequences in different environments, rates of soil development could be studied and compared among varying climates and mineralogical conditions. The project was fundamental in documenting the value of soils in studies of mapping, correlating, and dating late Cenozoic deposits and in studying soil genesis. All published reports by members of the project are included in the bibliography.

The project demanded that methods be adapted or developed to ensure comparability over a wide variation in soil types. Emphasis was placed on obtaining professional expertise and on establishing consistent techniques, especially for the field, laboratory, and data-compilation methods. Since 1978, twelve chronosequences have been sampled and analyzed by members of this project, and methods have been established and used consistently for analysis of the samples.

The goals of this report are to:

1. Document the methods used for the study on soil chronosequences,
2. Present the results of tests that were run for precision, accuracy, and effectiveness, and
3. Discuss our modifications to standard procedures.

Many of the methods presented herein are standard and have been reported elsewhere. However, we assume less prior analytical knowledge in our descriptions; thus, the manual should be easy to follow for the inexperienced analyst. Each chapter presents one or more references of the basic principle, an equipment and reagents list, and the detailed procedure. In some chapters this is followed by additional remarks or example calculations.

The flow diagram in figure 1 outlines the step-by-step procedures used to obtain and analyze soil samples for this study. The soils analyzed had a wide range of characteristics (such as clay content, mineralogy, salinity, and acidity). Initially, a major task was to test and select methods that could be applied and interpreted similarly for the various types of soils. Tests were conducted to establish the effectiveness and comparability of analytical techniques, and the data for such tests are included in figures, tables, and discussions. In addition, many replicate analyses of samples have established a "standard error" or "coefficient of variance" which indicates the average reproducibility of each laboratory procedure. These averaged errors are reported as percentage of a given value. For example, in particle-size determination, 3 percent error for 10 percent clay content equals 10 ± 0.3 percent clay. The error sources were examined to determine, for example, if the error in particle-size determination was dependent on clay content. No such biases were found, and data are reported as percent error in the text and in tables of reproducibility.

ACKNOWLEDGMENTS

We thank C. Olson and M.J. Pavich for their reviews of this manuscript and we thank the contributors for their help and patience in compiling this manual. J. Harden was particularly helpful in compiling the statistics for the analyses. The late D.E. Marchand instigated the fieldwork and sample collection that precipitated the need for this manual, and we hope that it meets the needs of the scientists who will continue his work.

[1]This report was prepared under contracts 14-08-0001–20481 and 14-08-0001-21972 from the U.S. Geological Survey.

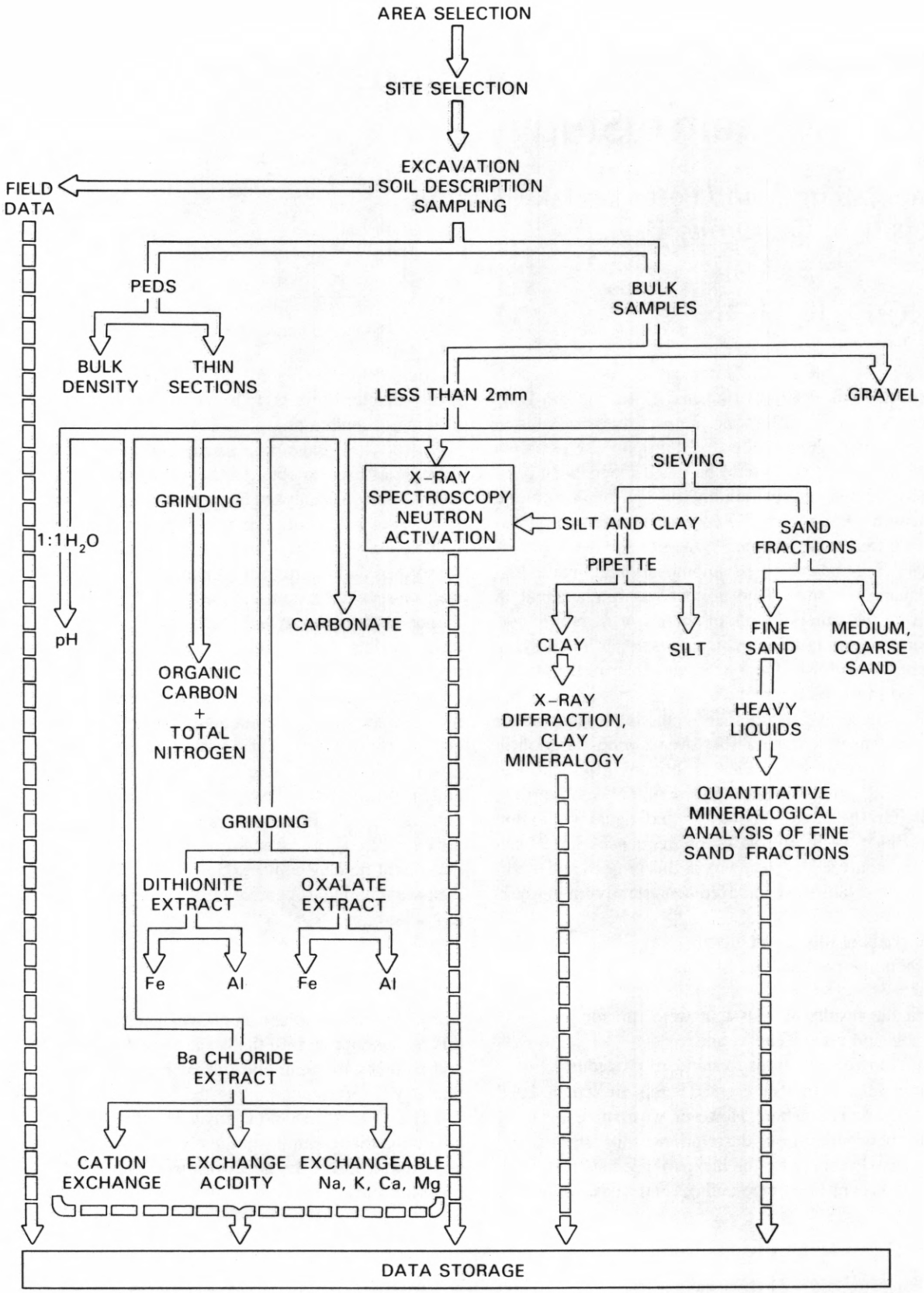

Figure 1. Step-by-step procedures used to analyze soil samples.

FIELD METHODS

By Jennifer Harden, *U.S. Geological Survey*

INTRODUCTION

The soil chronosequence is the basis of our method for studying long-term rates of soil development. By carefully selecting soil sampling sites, we study soils that vary in age, but otherwise developed under similar conditions. The limitations and strengths of our study are determined first in the field and then carried into any analysis of resulting data. This chapter briefly reviews the framework and methodology used in our sampling of soil chronosequences.

BACKGROUND

Chronosequences have been established and studied on deposits that vary in age from a few years to millions of years, and on deposits that include colluvium, stream terrace and fan deposits, coastal terraces, and glacial moraines. Although mapping and stratigraphic problems are unique to each deposit, the common problems of spatial separation, correlation, and age control of geologic units are of particular concern to soil-chronosequence studies.

The age of the deposits and soils must be determined independently of soil development in order to study soil development as a function of time. Correlation tools (other than soils) that help to distinguish the age of different units include: (1) elevation gradients of reconstructed stream deposits (fig. 2), (2) mineralogy or depositional patterns that are unique to particular units, (3) quantitative and semiquantitative dating methods that can be used on materials within the units, (4) cut-and-fill or other crosscutting relationships used in relation to other, more recognizable units, and (5) degree of dissection or other postdepositional erosion and surface alteration.

Recent advances have established techniques for dating different deposits of varying ages. For example, the uranium-trend method of Rosholt (1980) is applied directly to samples of soil horizons; carbonate accumulation methods (Backman and Machette, 1977; Arkley, 1963, 1981) determine the sum of pedogenic carbonate that has accumulated in soil since it first formed; thermal luminescence of soil carbonates and primary quartz grains (May and Machette, 1983; D. Norton and D. R. Harden, 1982, oral commun.) is also used to determine the time since soil formation started. Conventional radiocarbon and potassium-argon methods are often not useful when applied to materials that may significantly predate or postdate the formation of a soil. Sometimes these methods are valuable where appropriate age materials are found. Dating methods that have been used by this project include radiocarbon, potassium-argon, tephrochronology, open-system uranium series on bone and shell, uranium trend, amino acid racemization, rate of pedogenic carbonate accumulation, thermal luminescence of pedogenic carbonate, and paleomagnetic stratigraphy.

Chronology of a deposit is best understood when both numeric ages and genetic models of erosion and sedimentation are used to estimate the age. Also, the relative order of units constrains ages, especially if buried soils separate the deposits. The interdependence of age constraints and sedimentation models is unavoidable, and the best chronology is one that considers the strengths and weaknesses of both methods (see Birkeland and others, 1976; Lajoie and others, 1982; M.C. Reheis, written commun., 1985; and J.W. Harden, written commun., 1985)

SOIL SITE SELECTION

Where stratigraphy and chronology are well defined, sampling sites are selected on the basis of soil-forming factors other than time. As a result, because the primary difference among the soil sites is age (of the surface and soil), pedogenic trends are inferred from the differences in successively older soils. Covariance of a factor with time in a group of pedons can introduce significant bias to the age trends.[2]

Other important considerations for selecting sites include slope position, present vegetation, and cultivation practices. For this project, we generally sampled 0-5 percent slopes, and if the deposit had considerable relief, we sampled on topographic highs. We also chose uncultivated areas and tried to sample areas with similar vegetation.

SOIL DESCRIPTION AND SAMPLING

References

Soil Survey Staff, 1951, 1975, 1981.

Principle

Soils are composed of horizontal layers (horizons) of material related to the accumulation and movement of chemical, biological, and mineralogical constituents. The thickness and character of soil horizons vary according to many environmental factors. The objective of soil studies is to recognize and describe soil horizons in the field and to sample (or subsample) the horizons for analysis in the laboratory.

Because soil descriptions help to identify soil horizons, they are fundamental to analyses and interpretations that

[2]If such covariance of a factor (such as climate) with age is unavoidable, then soil development must be defined as a function of age as well as climate. Quantification of climate then becomes paramount for discriminating age as an independent variable.

follow. This section briefly describes the information collected for each profile sampled in our project. The measurements and observations necessary for a proper soil description are described by the Soil Survey Staff (1951, 1975).

Site descriptions should include the series name from the U.S. Department of Agriculture (USDA), Soil Conservation Service, and the most recent classification according to Soil Taxonomy (Soil Survey Staff, 1975). The sampling location should include the quarter sections and specific distance to nearest reference point, and the location on the U.S. Geological Survey topographic sheet at the smallest scale available (1:25,000 if possible). A formal formation name or working name at time of investigation should be given for the geologic unit, and a description of the nature and texture of the deposit is useful. The type of erosional or constructional surface and the internal drainage of the profile are important. We use well-, imperfectly, and poorly drained classes rather than six classes as recommended by USDA (Soil Survey Staff, 1951).

In addition, depth to ground water, elevation, erosion class, slope, aspect, mean annual temperature and precipitation, and natural and present vegetative cover are noted (fig. 3).

Field Description of Soil Characteristics

The Soil Survey Staff (1951, 1975) includes a detailed discussion on describing soil morphology, which we followed. Soil colors are measured using the Munsell Soil Color Chart (1954) or the Japanese Soil Color book (Fujihira Industry Co., 1985). We record all colors of the matrix, pedfaces, and clay films in the natural exposure of the soil and indicate the approximate abundance of the colors if not noted

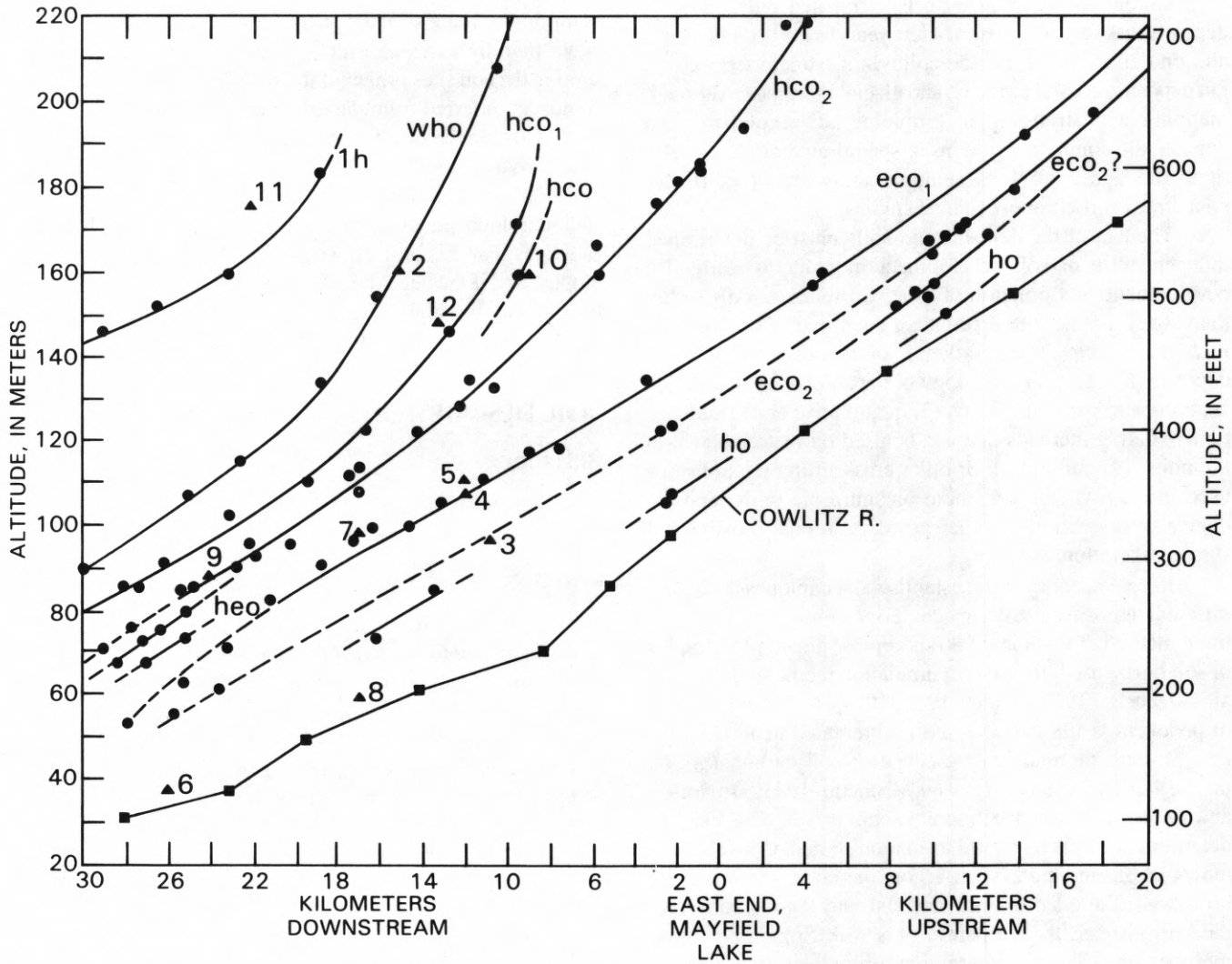

Figure 2. Profiles of Pleistocene and Holocene terraces developed along the Cowlitz River near Toledo, Washington. Numbered triangle, soil-sampling locations; square, altitude of modern stream bed; circle, altitude of surfaces of stream terrace; dashed line, uncertainty of profile. (Modified from Dethier and Bethel, 1981.)

SOIL DESCRIPTION SHEET

Described by: Harden Sampled by: Harden Sample No.: CH1

Date: Dec. 1, 1976 Date: Dec. 2, 1976

Soil Series Corning, acid variant Soil Taxonomy

Location NE¼NW¼ sec. 2, T. 6 S., R. 14 E. Quadrangle Yosemite Lake 7-½', Calif.

Geologic Unit China Hat Gravel Member, Laguna Fm. Provenance granitic, metamorphic

Nature, texture of deposit gravel unit with sand matrix

Geomorphic surface fan or terrace of the Merced River

Internal drainage well-drained Ground water greater than 10 meters (gully exp.)

Erosion + gully Elevation 198 m Slope about 5% Aspect SW

Climate about 35 cm MAP 17.5 d. C

Natural cover grassland Present cover annual and perennial grasses & forbs

Remarks Profound mimamound-hogwallow topography, 1-2 m in relief. Sampled on topographic high; filling of burrows in B horizons is of several age groups; B21 and below are continuous below mounds and hogwallows.

Profile sketch	Color	Texture	Structure	Consistence	Reaction	Misc.: Roots, pores, clay films, concretions
A11 g,w 12 cm	7.5YR6/6 dry 10YR5/4 moist	gr. SiL	1 fi sbk	d- sh m- - w- ss, ps	6.0	pores- 2 med & co tub roots- 2 med & fi grav.- 20%
B1 a,w 53 cm	7.5YR6/6 dry 7.5YR4/4 moist burrows from below: 2.5YR4/4 D & M	gr. SiCL	1 fi sbk	d- sh m- w- ss, ps	4.9	pores- 3 med & co roots- 2 fi & med grav.- 20% clay films- 2 n po 2 n coats
IIB21$_t$ g,w 140 cm	5YR4/8, ---5/6 dry 2.5YR3/6 ---4/6 moist cl.films 10R3/6m & 4/8m	gr. SiCL	2 m sbk	d- ex h m- w- vs,pv	4.4	pores- 2 m tub roots- 1 m clay films- 3 k po 3 k br 3 k pf

Figure 3. Example of a soil-description sheet used in this project. (From Soil Survey Staff, 1951.) For remainder of description, see Harden, 1982a.

elsewhere. In addition to matrix color measurements (Soil Survey Staff, 1981, p. 4-66), mottling is described in terms of quantity, size, and contrast.

Soil carbonates may appear to be alike, but with closer observation, they have a wide range of hues, chromas, and values. With the detailed records of soil colors recorded by Gile and Grossman (1979), we were able to devise a quantification scheme for color lightening (increase in value) and color paling (decrease in hue and chroma) (Harden and Taylor, 1983). Therefore, the color of carbonate filaments, nodules, and other structures should be measured aside from those of the matrix.

Soil texture of the less-than-2-mm fraction is determined by feel, but the amount of greater-than-2-mm material is important for determining discontinuities and source areas for the deposit, and for calculating water-holding capacities and volumes of soil constituents in the profile. Stiffness, cohesiveness, and grittiness of the sample help to determine amounts of clay, silt, and sand. Although most samples will receive an accurate determination of texture in a laboratory, field textures are important for distinguishing soil horizons.

Consistence in the dry, moist, and wet states is important to both horizon determination and studies of the degree of soil development. It is important to measure consistence at the proper moisture state. We found that wetting a dry soil for moist consistence was not a reliable method because of the variable degree of induced wetness. If the soil is in a moist field state, we recommend measuring consistence at that state and describing it as such.

Structure becomes more pronounced as the soil dries and planes of weakness open. If possible, sample pits should be left open to allow drying. This is often impossible or impractical, and structure must be described under the circumstances at hand. We describe primary and secondary structures including their grade (strength in place), class (size of peds), and type (shape and arrangement of peds).

Clay films, as well as organic, manganese, and silt coatings, are described according to their abundance, thickness, and location (Soil Survey Staff, 1981). Harden (1982a) defined a class of films as a set of films with a given abundance, location, and thickness. In a single horizon, there may be several classes of films, such as thick films on pedfaces, thin films on pedfaces, and thin films as grain bridges.

The recognition and accurate description of clay films require practice on different soil types as well as instruction from an experienced pedologist. Description of clay films can be standardized, and, where clay films are present, accurate descriptions result in a useful index of soil development when quantified by the Soil Development Index (Harden, 1982a).

To determine the pH in the field, any one of a variety of pH kits may be used. We conducted a test on field kits to determine which kit gave results that best corresponded to laboratory-determined pH. Acid, alkali, saline, clay-rich, and sandy soils were analyzed in the lab by the 1:1 soil-to-water method using a pH electrode (see chapter on "Determination of Soil pH") and by four field kits: Hellige-Truog, La Motte, a kit from California Polytechnic State University, and a kit from University of California, Berkeley. Results from the La Motte kit have the closest agreement with 1:1 pH, but the results from the Hellige-Truog kit also correspond closely to 1:1 pH (correlation coefficients are high, slopes are close to 1.0, and intercepts are close to zero) (fig. 4). The kit from the University of California has a slope of 0.915, indicating a good correspondence of kit pH to 1:1 pH, but the correlation coefficient is lower than La Motte and Hellige-Truog, suggesting that reproducibility or precision is lower. The kit from the California Polytechnic State University produces a slope of 0.432 against 1:1 pH and has a correlation coefficient of 0.669, indicating lower precision and accuracy than the other three methods.

Gile and Grossman (1979, p. 139-191) developed a scheme for describing carbonate morphology. They recognized filaments, coatings, veins, nodules, cylindroids, concretions, clusters, and plates. Subsequently, Bachman and Machette (1977) have modified the scheme to include a stage V morphology. Carbonate-development stages I through IV are based on the occurrences, orientation, and to some extent the abundance of such carbonate forms. We recommend that for each soil horizon, the pedologist describe the abundance and size of the various forms in each horizon. Other precipitates, such as gypsum, silica, or salts, may also occur in different forms (Reheis, 1985; E.M. Taylor, oral commun., 1985), and should be described according to size and abundance.

Other characteristics described for each horizon are roots (abundance and size), pores (abundance, size, and orientation), concretions (size and abundance), and soil-horizon boundaries (distinctness and topography), as well as fluidity, smeariness, and animal traces. Enough emphasis cannot be placed on measuring, describing, and noting all characteristics in the soil profile, for these are the data upon which are based sampling, data analysis, conclusions, and future work.

Sampling Procedures

For each horizon, peds and bulk samples should be collected for bulk density, thin sections, and laboratory analysis. (We generally collected three to five 200- to 250-g peds from different depths within a soil horizon.) If thin sections are to be prepared, the orientation of each ped must be marked before sampling.

The purpose of collecting bulk samples for analysis is to provide data that will accurately represent the depth variation of different soil characteristics. Regular sampling increments will suffice if increments are small enough to avoid homogenizing distinctly different horizons. In most instances, however, 5- or 10-cm intervals require that hundreds of samples be collected and analyzed, making the cost of further replicate sampling prohibitive. As an alternative, sampling can be done according to soil horizons.

For horizon samples, we recommend channel sampling along a continuous vertical section throughout the horizon. It is critical that samples of different horizons not be combined because such combining could remove or obscure important flexures in the depth function.

Subsamples can be taken within horizons if horizons appear too thick for the calculation of accurate depth functions. For example, in figure 5, clay-depth curves are plotted for horizon samples and for subsamples within the horizons. (For this test of stratified Holocene soils from the Merced River, California, chronosequence, we sampled by soil horizons and at 15- to 20-cm intervals within any horizon thicker than about 20 cm.) The sampling test indicates that when sampling thick soil horizons without subsampling, important flexures in the depth curves can be missed, especially when differences in clay (or other field properties) are too subtle to notice in the field. When total amounts of clay of each sampling technique are compared, the volume or unit of clay is quite similar for both.

Indelible markers should be used to label sample bags with the profile or site number, soil horizon, and depth increment. It is important to include depth increments in case the soil horizons are renamed later. We also recommend inserting a separate pencil-labeled card into the sample bag. For transferring and packing ped samples, we often cushion peds in a bed of grass or leaves. If the peds are moist, lids should be removed from the cartons so that the samples can dry in one piece rather than crumble in the moist container.

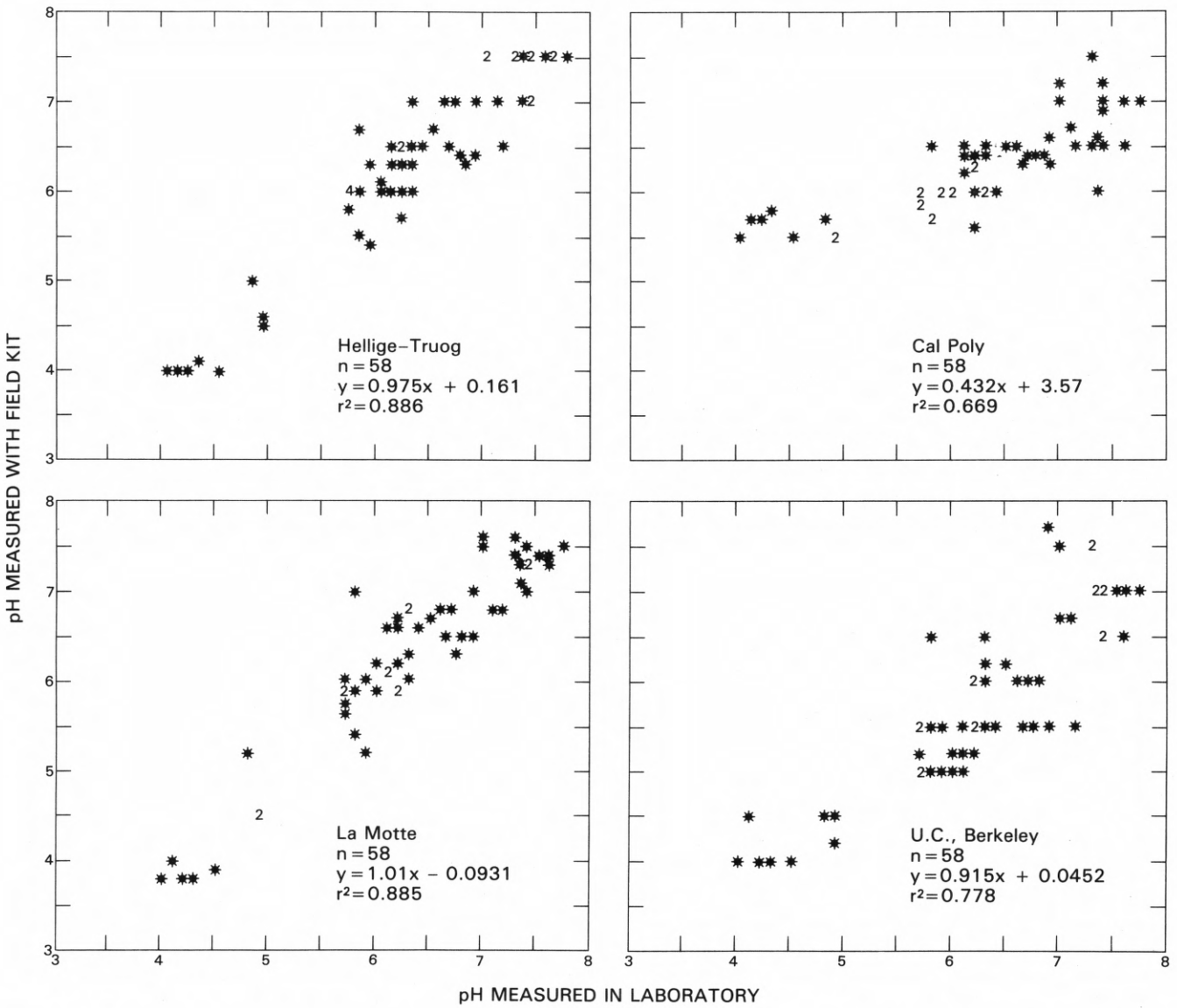

Figure 4. Determination of pH by four different field kits versus laboratory 1:1 soil-to-water method using calomel electrode. Numbers in plot indicate points at that position. Regression equations and correlation coefficients included for each kit. n indicates number of samples.

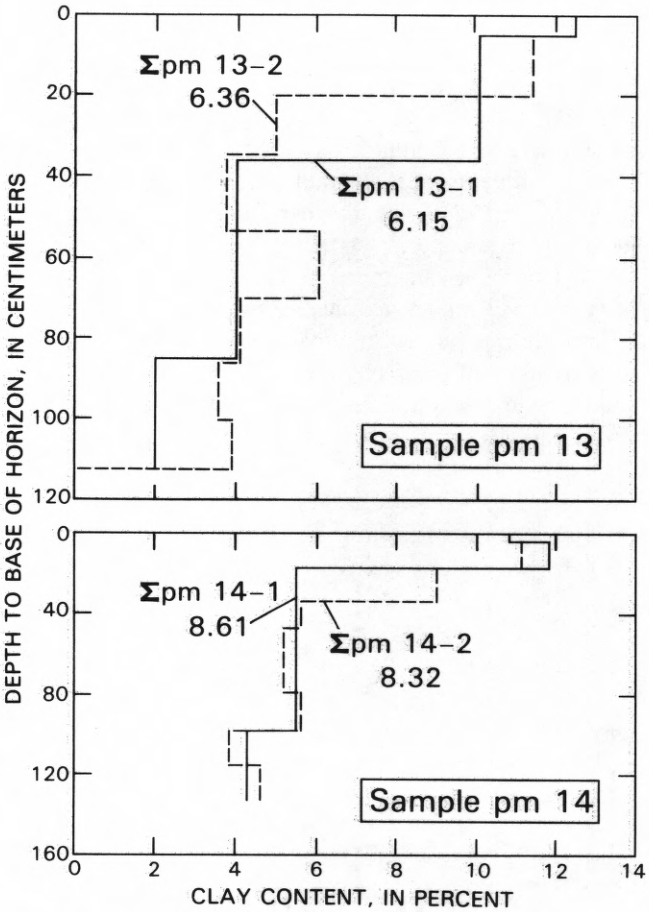

Figure 5. Percent <2-micrometer-clay versus depth for horizon samples (solid line) and subsamples (dashed line) for two samples from the Merced chronosequence (Harden, 1982a). Area to the left of clay-depth curves is indicated by figures and is calculated as Σ(percentage clay × horizontal thickness) for horizons in profile.

LABORATORY METHODS

Sample Preparation

By Michael J. Singer,
University of California, Davis

PRINCIPLE

Sample preparation is used to (l) separate the fine (<2 mm) from the coarse (>2 mm) fraction, (2) homogenize the sample so that "representative" subsamples can be obtained from the bulk sample, and (3) increase the efficiency of extraction. Sample preparation normally involves four steps: Step 1, drying; step 2, crushing; step 3, sieving; step 4, grinding.

There is some concern among soil scientists that air-drying samples changes soil properties. Changes in microbiological activity, loss of volatile constituents, changes in chemistry (for example, pH), and changes in some physical properties (for example, aggregate stability) probably occur upon drying and rewetting of samples. However, it is most convenient and economical to store dry samples rather than field samples in various moisture conditions.

EQUIPMENT

1–quart cardboard containers and tops
indelible marking pen
wooden mallet or rolling pin
2-mm-opening mesh sieve (#10)
180-μm, 80-mesh (Tyler) sieve
dust masks (disposable)
"butcher" paper (60 cm wide) (optional)
spatula
motor-driven mortar (optional)
agate mortar and pestle
20-mL sample container with cup

PROCEDURE

Each sample is given a laboratory number and both the field label and laboratory number are entered into a logbook. If bulk density or other fabric-related analyses are to be done, an undisturbed sample is removed from the bulk sample. Most often, undisturbed samples are collected separately and are not "prepared" for further analysis.

Samples are removed from their containers and are placed on white butcher paper (optional) or in trays in an open area for drying. Each day, (or in hot weather, several times each day) the sample is mixed to ensure rapid and even drying. Samples high in clay are checked frequently so they can be crushed at an appropriate moisture content. The appropriate moisture content is below the liquid limit, but above the point at which the sample is rock hard. The appropriate moisture content is different for each sample, and choosing it is a matter of experience.

When the sample is dry, it is gently (if possible) crushed using a wooden mallet or similar tool. The goal of the procedure is to break soil aggregates without breaking any rock or gravel fragments or individual mineral grains. This is particularly difficult on some soil samples that contain large quantities of soft or brittle gravel or rock fragments.

All of the sample is sieved, crushed, and resieved until the <2-mm and >2-mm materials are separated. The two fractions may be weighed to determine the weight percentage of >2-mm fraction. If sampling was on a volumetric basis, this number can be meaningful, but if coarse fragments were avoided during sampling, the number will have little meaning.

Each dry sample is placed into labeled containers for

storage. If excess sample has been prepared, the remainder is discarded. (In this project excess material was stored in Menlo Park at the USGS.) If many samples are to be prepared, the field sample may be split and a fraction crushed and sieved.

Stored samples are subsampled for further processing as needed. Standard grinding procedures are described here. Special preparation such as that required for X-ray diffraction and X-ray fluorescence analyses are described in other sections of this report.

The <2-mm fraction is subsampled for grinding using a spatula (see p. 15 for discussion on sample splitters versus spoon). Approximately 10 g is sufficient for those analyses described here. The sample is ground with an agate pestle in an agate mortar until the entire >2-mm fraction sample passes an 80-mesh sieve. For the oxalate extraction of iron oxides, excess mineral crushing can be minimized by frequently sieving the sample between grinding (see page 41). Grinding can be accelerated by using a mechanical grinder if one is available. The ground sample is stored in a labeled, capped vial of appropriate size.

Ultrasonic Dispersion Pretreatment

By Alan J. Busacca,
University of California, Davis[1]

REFERENCES

Edwards and Bremner, 1967.
Watson, 1971.
Genrich and Bremner, 1972.
Busacca, 1982.
Busacca, Aniku, and Singer, 1984.

PRINCIPLE

A noncontaminating physical means of dispersing soil samples was developed for the separation of particle sizes. Common dispersing agents such as Calgon (sodium hexametaphosphate) introduce large amounts of phosphorus and sodium into soil samples. Probe-type ultrasonic devices shed significant quantities of Ti, Al, and V into solution as a result of probe-tip pitting. The cup horn allows complete dispersal of the sample with absolutely no contamination of the soil.

A soil sample is pretreated with H_2O_2 and is then dispersed using sonic energy. Measurement of particle-size distribution or separation of samples into different size fractions follows.

[1]Present address: Department of Agronomy and Soils, Washington State University, Pullman, WA.

EQUIPMENT

Heat Systems-Ultrasonics Cup Horn model 431A
Heat Systems-Ultrasonics model W-220 F sonicator, or equivalent model
air- or motor-driven stirrer
soundproof housing for sonicator and sample
Tygon tubing
Kimax 250-mL tall-form beakers
balance (0-120 g)
filter candle apparatus
hot plate (optional)
wash bottle
watchglass
desiccator
oven
Tiltapet (5 mL) (optional)

REAGENTS

30 percent H_2O_2 (optional)
pH 9.5 Na_2CO_3 solution (~1.5 g/15 L)
distilled water
isobutyl alcohol

PROCEDURE

Pretreatment—This procedure is for a group of six soil samples. First, dry the samples in an oven at 95-97 °C for 24 hours, so that weights can be expressed on the dry basis. (Higher temperatures may affect the clays.) Next, cool the samples in a desiccator. Weigh 20 g of each dry sample into a Kimax 250-mL tall-form beaker. (The shape of the bottom of the beakers and material affects sonication efficiency.) If particle-size separation is to follow the sonication, mark each beaker with a 7-cm line and a 110-mL volume mark.

Use a few milliliters of Na_2CO_3 to wet samples in the tall-form beaker. Put samples onto a cold hot plate, carefully add 5 mL of 30 percent H_2O_2, to each and cover each with a watchglass. Mix the peroxide with the samples. Use a drop or two of isobutyl alcohol to control foaming. After the initial reaction has subsided, add an additional 5 mL of H_2O_2 to each. If foaming is not violent, heat samples to 50-70 °C. Continue adding H_2O_2 (as much as 30 mL) until the organic matter has been destroyed (usually 1.5-2 hours of heating).

After the samples cool, add 150-180 mL of Na_2CO_3 and wash all the sample to the bottom of the beaker. Use filter candles to reduce volume to near dryness. Use Na_2CO_3 in a wash bottle to clean filter candles and fill beakers to 110-mL mark. This gives a soil solution ratio of 1:5.

Sonication—Place beaker in soundproof box and adjust so that it is held exactly 1.5 mm above the flat cup-horn radiating face. Clamp the beaker firmly in place centered directly over the cup horn. The centering and distance above the horn are critical to efficient dispersion.

Insert stirrer into the sample. (There is insufficient sonic energy to keep all the soil in suspension.) The propeller of the stirrer should be submerged 10-20 mm. Adjust the stirrer so that it creates a wash zone 10-25 mm up the sides of the beaker from the suspension rest position.

Adjust the water flow to the cooling jacket until there is a slow steady flow from the overflow outlet (fig. 6).

Close the soundproof box and begin sonication. The power setting and time of sonication necessary for dispersion will depend on the instrument. The cup horn attached to the Heat Systems W-220 F was operated at ~130 watts for 15 minutes. With a Bronwill Biosonic IV unit, ~200 watts for 25 minutes were required for complete dispersion.

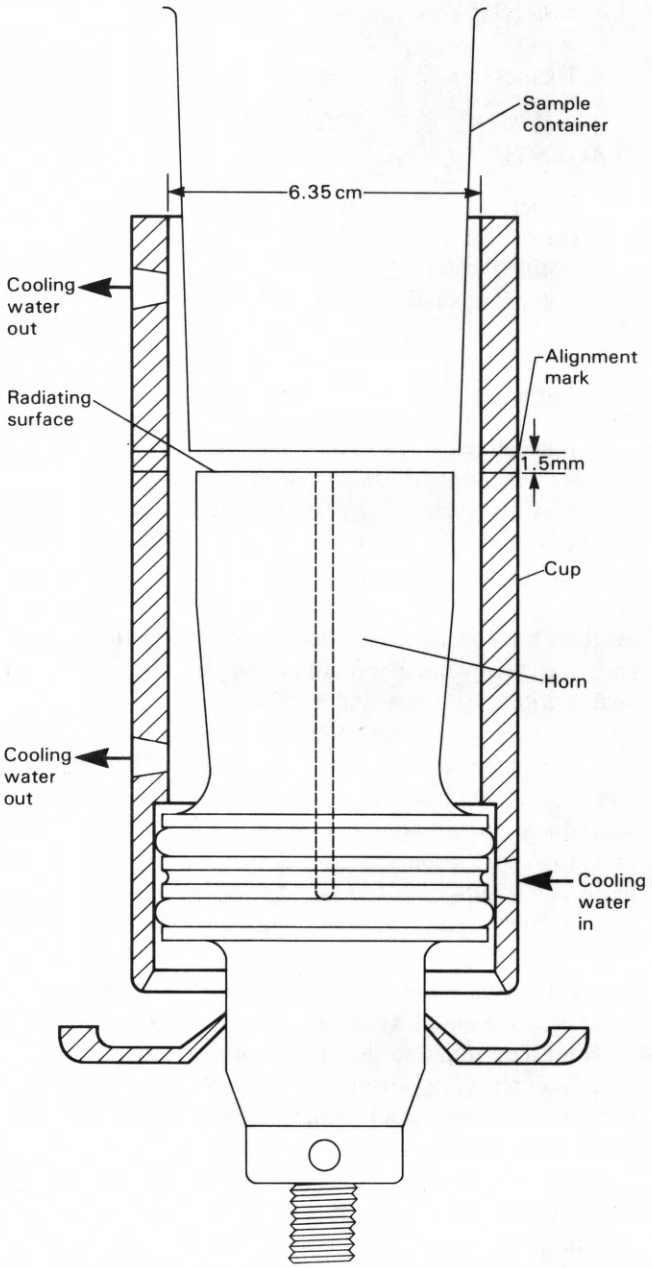

Figure 6. View of sample in proper position over cup horn.

Turn off the sonicator, cooling water, and stirrer; remove the stirrer from the beaker and wash any particles from it into the beaker with Na_2CO_3 from a wash bottle.

The Biosonic required a cooling period between samples, while the Heat Systems unit did not. All samples were treated the same.

Additional Remarks

Table 1 presents a comparison between dispersion using the cup horn and Biosonic IV and standard Calgon-pipette-particle-size analysis. Percentage of clay (<2μm) released by the two methods is quite comparable for samples of A, B, and C horizons that have from 15 percent to almost 50 percent clay. Only sample 1206 falls as much as 4 percent below comparable Calgon results. This is a B2t horizon from a 1.6-m.y.-old soil formed on the lower part of the Laguna Formation. It has more than 5 percent dithionite extractable iron, kaolinitic mineralogy, and was the only test sample to form a thixotropic mixture during sonication.

The viscosity of the mixture may be responsible for the lower clay yield. Samples that yield less clay by sonic treatment than by Calgon treatment have correspondingly higher silt contents, suggesting that some clays remained aggregated in silt-size particles after sonication. Samples that have clay yields similar to those measured after Calgon treatment have silt contents more nearly equal to those yielded by Calgon. Total percent sand does not demonstrate a consistent difference among samples, whether dispersed by Calgon or ultrasonic energy. Percent very fine sand is invariably higher using sonic dispersion (with a maximum increase of 3.5 percent in sample 1029) with a corresponding decrease in very coarse, coarse, and medium sand fractions. This suggests that some coarser sands are fractured into fine sands in response to ultrasonic energy, or from particle abrasion. This is at variance with results reported by Edwards and Bremner (1967), who found that in most cases overnight shaking in Calgon solution caused more particle damage than did ultrasonic treatment. They also demonstrated that all soil dispersion pretreatment methods lead to some change in the original particle-size distribution.

A sand and silt destruction test was performed using replicate samples of medium to very coarse sand (250-2000 μm), fine plus very fine sand (45-250 μm), and coarse silt (20-47 μm) (table 2). These were wet- and dry-sieved before and after sonication to record changes in particle-size distribution. The coarse fraction lost about 7 percent of its original weight, the middle fraction about 11 percent, and the fine fraction about 6 percent. However, X-ray diffraction analysis of the newly released silt and clay showed that a part of the weight loss is actually additional dispersion of 2:1 phyllosilicate minerals and not only shattered primary minerals. The shift in the coarse sand fractions is the result of primary mineral breakage. The sand and silt used in this test

Table 1. Comparison of cup horn ultrasonic soil dispersion, in weight percent, with Calgon soil dispersion for soils from the Honcut Creek chronosequence

[All trials are averages of three replicates. From Busacca, 1982]

Sample	Treatment	Sand						Silt	<2 μm clay
		Very coarse	Coarse	Medium	Fine	Very fine	Total		
1021	Sonic -------	0.0	0.0	0.2	9.2	26.1	35.5	50.2	14.3
	Calgon -------	.1	.2	.5	12.7	23.8	37.3	46.9	15.8
1029	Sonic -------	.2	.5	.7	4.6	16.0	22.0	54.1	23.9
	Calgon -------	.1	.8	1.2	6.1	12.5	20.7	55.4	23.9
1102	Sonic -------	3.2	6.9	5.0	12.6	13.0	40.7	42.7	16.6
	Calgon -------	4.2	7.6	5.9	12.6	12.0	42.3	40.9	16.8
1106	Sonic -------	.6	1.6	.8	2.1	11.6	16.7	50.5	32.8
	Calgon -------	.6	2.3	1.0	2.9	9.9	16.7	49.3	34.0
1206	Sonic -------	2.8	8.3	6.3	9.4	5.4	32.2	24.1	43.7
	Calgon -------	3.3	9.2	6.8	8.8	5.1	33.2	18.8	48.0

Table 2. Sand and silt destruction, in weight percent, during ultrasonic treatment

[From Busacca, 1982]

Sample	Treatment	Sand						Silt	<2 μm clay
		Very coarse	Coarse	Medium	Fine	Very fine	Total		
Sand	Before ---	18.1	48.2	33.7			100.0	4.9	1.7
	After ----	15.8	43.1	30.3	3.4	0.8	93.4		
Sand	Before ----------				46.6	53.4	100.0		
	After ----------				38.8	51.0	89.3	8.1	2.6

		Coarse silt (20–47 μm)	Fine silt (2–20 μm)	Clay (<2 μm)
Coarse Silt	Before ----------	100.0		
	After ----------	94.3	4.2	1.5

were collected from samples that had been dispersed by standard Calgon. This suggests that sonication removes clay minerals that adhere to sand and silt more completely than does the Calgon treatment, although there is also some fracturing of primary grains. The sand and silt is visibly more neutral in color (less brown) after sonication.

In summary, the cup horn sonication method effectively disperses soil samples and gives results comparable to standard dispersion treatments. Dispersion is achieved without chemical dispersing agents, and there is neither Ti nor Al contamination as in probe-type sonication. Use of the cup horn, linked to the Heat Systems W-220 F sonicator, results in reduced sonication time and energy, when compared to the Biosonic system (comparison data for W-220 F not shown). This, in turn, results in less abrasion and fracturing and lower levels of primary mineral destruction than that shown for the cup horn and Biosonic.

Particle-Size Analysis

By Peter Janitzky, *University of California, Davis*

REFERENCES

Day, 1965.
Jackson, 1969.

PRINCIPLE

Samples are treated to remove organic matter and soluble salts. The samples are then dispersed in a sodium solution. Sands are removed by wet sieving, and the silts and clays are washed into sedimentation cylinders. The amount of silt or clay remaining in a predetermined volume of liquid in

the cylinders over time is used as a measure of the percentage of silt and clay in the sample. The basic tenet of the analysis is that spherical particles will settle in fluid at a rate proportional to their radius (Stokes' law).

The method described here is known as the "pipette method" because of the procedure used to obtain samples. The advantages over the well-known hydrometer method are (1) it is more accurate, and (2) it allows subsampling for clay or silt mineralogy. The major disadvantage is that it requires more time than the hydrometer method. Because particle-size analysis is commonly determined, it is discussed in detail. We were interested in determining reproducibility, as well as determining the effects of sample pretreatments on results.

EQUIPMENT

250-mL beaker
balance (analytical)
watchglass
tweezers
eyedropper
hot plate
filter candle apparatus
rubber policeman
teflon policeman
stirring rod
wash bottle
oven
desiccator
repipette (optional)
shaker bottle
mechanical shaker for sieves
nest of sieves (1.0, 0.5, 0.25, 0.177, 0.105 mm)
reciprocating shaker
size 6½ rubber stopper
sedimentation cylinders
Whittig-type wash bottle (optional)
glass funnel
300-mesh sieve (47μm)
large rubber stopper
weighing jar and lid
Kimwipes (optional)
plunger
thermometer
clock with sweep second hand
25-mL pipette

REAGENTS

distilled water
hydrogen peroxide 30 percent or sodium hypochlorite 5 percent isopropyl alcohol
hexametaphosphate dispersing solution (7.94 g Na_2CO_3 + 35.7 g $(NaPO_3)_6$ per liter of distilled H_2O

PROCEDURE

Preparation of Samples

1. Label 250-mL beakers with laboratory sample numbers. Weigh the empty beakers to 0.01-g accuracy. Check frequently to be certain that the balance is zeroed.
2. Add approximately 10 g of <2-mm soil to the appropriate beaker and cover with a watchglass.

Organic Matter Oxidation

1. Remove visible, undecomposed organic matter (roots, woody particles, and so forth) with tweezers. In B or C horizons this is rapidly accomplished because those horizons generally contain little organic matter. The A horizons, however, may contain large quantities of roots and fibers that must be removed. To extract most of the undecomposed particles 30-45 minutes may be necessary.
2. Wet each sample with distilled H_2O, add a few milliliters of 30 percent H_2O_2, and re-cover with the watchglass. Every 5-10 minutes add 3-5 mL of H_2O_2 and stir gently by slowly swirling the beaker. Use distilled H_2O to rinse the beaker sides of foam. If it is necessary to rapidly reduce foaming because the sample is about to overflow, add a drop or two of isopropyl alcohol directly to the foam.
3. After most foaming subsides, heat to about 70 °C and continue H_2O_2 additions for about one hour. Samples low in organic matter may be heated soon after the first addition of H_2O_2. With samples high in organic matter, however, it is preferable to allow the reaction to occur overnight, without heat, before placing them on a hotplate. This is important because organic rich samples overflow when they are heated too soon.
4. When the organic material that binds soil mineral particles together has been removed, the treatment should be stopped because it affects the mineral fraction as well. Several criteria are used to decide when to stop the oxidation:
   (a) When a light-brown foam no longer appears around the surface of the soil solution after the addition of H_2O_2 and, instead, rapid "self-oxidation" of the peroxide occurs (a vigorous reaction that usually exhausts itself within 5 minutes of H_2O_2 addition);
   (b) The appearance of bleached fragments of roots floating on the surface; and
   (c) Time.

   Do not try to completely oxidize the undecomposed organic particles. Benefits realized are not worth the time required nor the possibility of damage to minerals. Those large particles are not involved in binding minerals.

Filter Candling

1. Clean the watchglass and sides of each beaker with a rubber spatula (or finger), rinsing the residue into the beaker.

2. Place the beakers in a filtering rack, add a filter candle to each (do this before adding any water to prevent overflow), add some distilled water, stir to suspend the silt and clay, and then fill to the top with distilled water.
3. Turn on the vacuum after emptying the vacuum bottle.
4. When the last beaker is drained (less than 25 mL remaining), close off the vacuum with stopcocks, stop the suction, open the rinse water reservoir stopcock, and turn off the vacuum. Re-open the stopcocks to the beakers so that rinse water can flow through them. Rinse the filter candles with a wash bottle; use a finger to remove any residue from the candles, then rinse the finger!
5. Resuspend the silt and clay; refill with distilled water, repeating parts 3 and 4 until five beaker volumes (1,000-1,250 mL) have been filtered.
6. After the final filtering, carefully clean the sides and bottom of each filter candle, washing all mineral particles back into the beakers. Cover the beakers with watch-glasses and place in an oven for 24 hours at 105 °C.

Measuring the Oven-dry Weight

1. After oven drying, place the beakers in a desiccator to cool.
2. When cool (about 2 hours) weigh each one to 0.01-g accuracy, minimizing their exposure to ambient air before weighing. This is the weight used in all calculations, it must be accurate.

Dispersal

1. Add 10 mL of hexametaphosphate solution and 10-20 mL of distilled water to each sample and to a blank. (Note: We dispense hexametaphosphate from a repipette container. To assure solution uniformity, gently agitate the solution with a slow motion of the container. Calibrate the pipette and dispense one aliquot into a waste container to eliminate air bubbles in the neck of the dispenser.)
2. Label wide-mouthed shaker bottles, including one for the hexametaphosphate blank.
3. Carefully clean the beakers with a teflon policeman, being certain to remove the baked-on residue from the sides. Transfer the suspended soil to the appropriate shaker bottle and fill each bottle two-thirds full with distilled water. Seal the bottles with size 6½ rubber stoppers.
4. Save the tared beakers for the sand analysis.
5. Shake the solutions overnight (14-16 hours) on a reciprocating shaker, checking to be certain that they do not rattle—they will break. Avoid leaving the bottles on the shaker more than 16 hours; abrasion of mineral particles can cause small segments to break off, giving a measured particle-size distribution different from the natural distribution.
6. That same evening, fill the required number of labeled sedimentation cylinders with distilled water so that the water will equilibrate to room temperature.

Sand Separation

1. Construct a modified Whittig wash bottle (optional) (fig. 7) and fill it with distilled water from the first of the sedimentation cylinders. Save the remainder of the room-temperature water from the cylinder; it will be used to refill the wash bottle.
2. Place a glass funnel and a 300-mesh sieve on top of the first empty, labeled sedimentation cylinder.
3. Carefully remove the stopper from the first bottle and rinse the soil solution clinging to it back into the bottle.
4. Pour the soil suspension from the bottle through the sieve and into the cylinder. Be careful not to upset the sieve—it is precariously balanced.
5. Rinse the sides of the shaker bottle with distilled water, using the water jet to resuspend the silt and clay particles. Allow the sand to settle for 10-20 seconds, then pour the suspension through the sieve. Repeat the process five or six times. Careful decanting of silt and clay before the sand reduces sieve clogging and increases sieving speed.
6. Transfer the soil remaining in the shaker bottle to the appropriate beaker saved from the filter candling, using several rinses because fine particles resist transfer. Hold the shaker bottle in the light to be certain that all the soil has been transferred. (Note: An effective method for rinsing is to first aim a jet of water down the sides of the shaker bottle so that all soil particles move to the bottom. Then tilt the bottle to one side and wash the particles to the lower sides of the bottom. Pour the soil solution into the beaker and finally, while the opening of the bottle is still tilted downward toward the beaker, rinse the lower

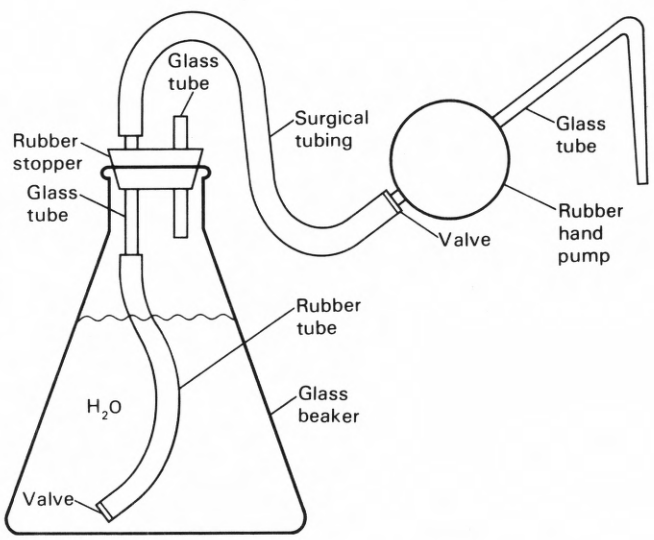

Figure 7. Construction of a Whittig-type wash bottle.

sides of the bottle where the remaining soil particles have collected, allowing the backwash to fall into the beaker.)

7. After each rinse, gently suspend the soil in the beaker and decant the suspension as was done in step 5 above. When no silt or clay remains in the beaker, any rinses of the shaker bottle that are still necessary should go directly through the sieve rather than into the beaker.
8. Use a wash bottle to gently rinse the inside of the sieve (especially the screen) so that the silt and clay particles that may have been trapped pass into the sedimentation cylinder. Next, rinse the outside of the screen so that silt and clay particles that have clung to it will fall into the cylinder. Rinse the funnel and fill the cylinder exactly to the 1-L mark. Cover with a large rubber stopper.
9. Use a jet of water to wash the sand on the inside of the sieve back into the beaker. This is done by aiming the wash bottle at the outside of the sieve and through the screen so that the wash will fall into the beaker. Rotate the sieve so that all sides are cleaned. Hold the sieve in the light to check for sand particles that still cling to the inside; rinse again if necessary.
10. Cover the beaker with a watchglass and dry at 105 °C for 24 hours.
11. Repeat for each sample including the hexametaphosphate blank.

Taring of Weighing Jars

1. Tare the weighing jars, recording jar number, sample number, and tare weight. The jars must be spotlessly clean and equilibrated to the temperature of the weighing room (2 hours to be safe). The lid, sides, and bottom of the jars should be wiped clean just prior to weighing; at the 0.1-mg accuracy required, fingerprints can cause significant errors.

Mixing of Samples in Sedimentation Cylinders

1. Use the plunger to suspend the silt and clay in the sedimentation cylinders at intervals of 2½ minutes or more (2½ minutes is the approximate time needed to take a pipette sample). Mix the blank as well. Record the exact time each sample is mixed. (Note: The sample is most safely mixed by rapid upward strokes and slow downward strokes of the plunger. Frequent short strokes at the cylinder bottom plus occasional long strokes are best. Slow the velocity of the plunger whenever it approaches the solution's surface.)
2. When removing the plunger from the cylinder, gently tap it against the lip of the cylinder so that little soil solution is removed on its stem and head. Rinse the plunger with distilled water over the sink and move to the next cylinder.

Pipette Sampling

1. If the cylinders are not in a constant temperature environment, record the temperature of the blank solution every 2-4 hours. Draw a plot of time (horizontal axis) vs. temperature. The average temperature for the settling period is at the point on the vertical axis crossed by a horizontal line that bisects the area defined by the temperature-time curve (see fig. 8). If available, the sedimentation should be done in a constant-temperature room.
2. Use the average temperature to determine the proper sedimentation time (table 3).
3. Prepare a 25-mL pipette with a rubber hand pump attached. The pipette must be cleaned with dichromate and rinsed with distilled H_2O. Become familiar with the use of the pipette before sampling; errors at this stage are simple to make and costly.
4. At the appropriate time, carefully sample at the 10-cm depth using the 25-mL pipette. Try to sample over a 10-12-s period. Empty the pipette into a labeled weighing jar. Rinse the pipette into the jar with distilled water. Continue this procedure on the remaining samples.
5. Evaporate the samples to dryness in a forced-draft oven at 105 °C (usually 24 hours). Place the jars, with lids open, in a desiccator to cool to room temperature. Before removing the jars from the desiccator, seal the jars with the lids. Measure and record the weights after wiping away fingerprints. Minimize the time the sample is exposed to ambient air by keeping all but the one sample being weighed in the covered desiccator. Reweigh the first sample to see if it adsorbed moisture; a weight change greater than 0.0005 g means that the samples must be redried and reweighed.
6. If <1-μm clay content is to be determined, do not remix the solutions. Instead, allow them to continue settling, taking temperature readings every 4 hours. Determine the average temperature from a graph as before; 28 hours from mixing is a typical sampling time. The sampling procedure is identical to that for <2-μm particles. Solution should be extracted at 10 cm below the original surface

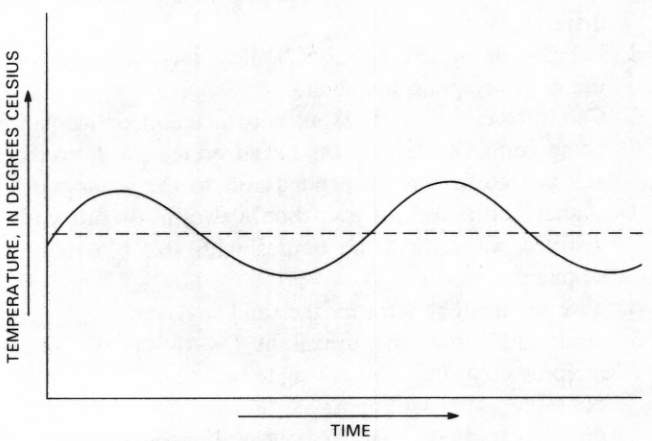

Figure 8. Example of temperature-time diagram used in particle-size analysis. Solid line indicates actual temperature; dashed line indicates average temperature.

Table 3. Settling times[1] for 2-, 5-, and 20-m particles to pass through 10 cm of water

[See Jackson (1969) for details on other temperatures and size fractions]

Temperature (°C)	2 μm (hour:min)	5 μm (hour:min)	20 μm (min:seconds)
20	8:00	1:17	4:48
21	7:49	1:15	4:41
22	7:38	1:13	4:35
23	7:27	1:11	4:38
24	7:17	1:10	4:22
25	7:70	1:08	4:16
26	6:57	1:07	4:10
27	6:48	1:05	4:04
28	6:39	1:04	4:00
29	6:31	1:03	3:55
30	6:22	1:01	3:49

[1]Assumes a particle density of 2.60.

because settling has been from that point. Drying and weighing are the same as in step 5.

7. Save the suspension until after the clay fraction calculations are completed in order to repeat analyses if necessary. A serious error has been made if the <1-μm fraction is larger than the <2-μm fraction.
8. If clay mineralogy is to be determined, resuspend the samples and take a sample which will supply a minimum of 50 mg of <2-μm material.

Sand Sieving

1. After cooling in a desiccator, weigh the sand fraction of each sample in the appropriate tared beaker.
2. Use a spatula to loosen them and transfer the sands to the top sieve in the sieve nest.
3. Shake the sands for 3 minutes on the mechanical shaker. Weigh and record the weights, save any fractions that are desired.

CALCULATIONS

1. Clay:

[weight jar + oven-dry sample] − [weight jar] − [average weight hexametaphosphate] = weight of particle fraction.

$$\frac{\text{weight of clay particle fraction}}{\text{weight of mineral fraction}} \times \frac{\text{1,000-mL solution}}{\text{25-mL sample}} \times 100$$

= percent clay-particle fraction in sample.

2. Sand:

$$\frac{\text{weight sand}}{\text{total weight of mineral fraction}} \times 100 = \text{percent sand in sample.}$$

3. Silt:

silt percent = 100 − (clay percent + sand percent)

ADDITIONAL REMARKS

We tested the efficacy of hand subsampling compared to using a sample splitter (table 4) and citrate-bicarbonate-dithionite (CBD) pretreatment (table 5). We found no significant differences in particle-size distribution between samples split or hand subsampled, and subsampling by hand was faster than sample splitting. There were some differences in particle-size distribution between pretreated and non pretreated samples. For example, percent sand was higher for sample 102, which received no CBD pretreatment, compared to pretreated samples. The same was not true for sample 132 (table 5; fig. 9). Because of the non-uniform effects caused by CBD pretreatment and because it is an additional and apparently unnecessary step in the procedure, we elected not to include it in our standard procedure.

Additional triplicate analyses further illustrate the level of precision which can be obtained by careful laboratory practice (table 6).

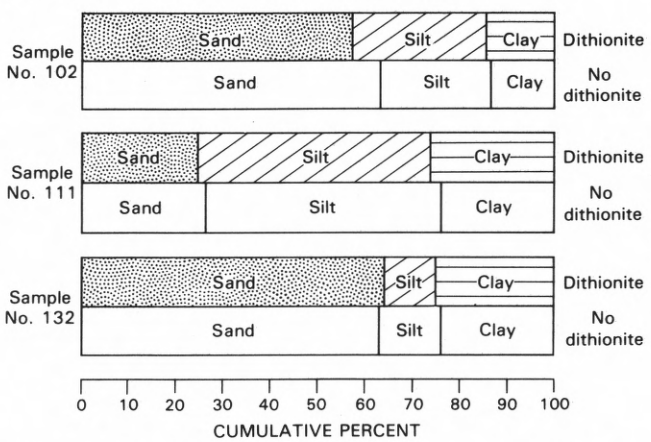

Figure 9. Effects of dithionite pretreatment on particle-size distribution. All samples were pretreated with Na hexametaphosphate; dithionite-treated samples were also extracted by citrate-bicarbonate-dithionite (CBD) reagent (Jackson, 1969). Replicates are indicated by a, b, c.

Table 4. Repeat determinations, in weight percent, of particle size for sample splitter vs. hand sampling

[111-1, 111-2, 111-3 sampled by spoon from carton of prepared soil after stirring contents of carton. 111-4, 111-5, 111-6 sampled using a sample splitter to obtain samples of desired size. Sample 111 is a BCt horizon (94-122 cm) from an R28 profile, Dry Creek chronosequence. $\bar{X}$, mean value for replicates; SD, standard deviation; CV, coefficient of variability (SD divided by $\bar{X}$)]

Sample	Oven-dry weight (g)	Oven-dry sand (g)	Sand	Silt	Clay		Sand				
					<2 μm	<1 μm	Very coarse	Coarse	Medium	Fine	Very fine
111-1	14.585	3.940	27.0	49.9	23.1	19.2	0.8	1.3	1.6	12.0	11.3
111-2	15.165	4.170	27.5	49.8	22.7	19.1	.6	1.5	1.7	12.1	11.6
111-3	14.745	4.060	27.5	49.5	23.0	19.1	.7	1.4	1.7	11.7	12.1
		$\bar{X}$	27.3	49.7	22.9	19.1	.7	1.4	1.6	11.9	11.6
		SD	.29	.21	.21	.06	.1	.1	.06	.04	.4
		CV	.01	.004	.009	.003	.1	.07	.03	.02	.03
111-4	14.355	3.900	27.2	49.6	23.2	19.2	.8	1.5	1.8	11.7	11.4
111-5	14.280	3.875	27.1	49.8	23.1	19.1	.7	1.5	1.8	11.9	11.3
111-6	14.500	3.905	26.9	50.1	23.0	19.1	.9	1.3	1.8	11.9	11.9
		$\bar{X}$	27.1	49.8	23.1	19.1	.8	1.4	1.8	11.8	11.5
		SD	.15	.25	.09	.06	.1	.1	.0	.11	.3
		CV	.005	.005	.004	.003	.1	.08	.0	.009	.03

Table 5. Effects of citrate-bicarbonate-dithionite pretreatment on particle-size distribution, in weight percent

[For each of the three samples: -1, -2, -3 received dithionite pretreatment; -4, -5, -6 did not. Sample 102 is a Bt2 (33-70 cm) from the M42 profile, 111 is a BCt (94-122 cm) from R28, and 132 is a Bt1 (33-80 cm) from the T11 profile, all from the Dry Creek chronosequence]

Sample	Oven-dry weight (g)	Oven-dry sand (g)	Sand	Silt	Clay		Sand				
					<2 μm	<1 μm	Very coarse	Coarse	Medium	Fine	Very fine
102-1	9.520	5.51	57.8	28.8	13.4	10.2	7.2	12.1	12.7	18.0	7.8
102-2	10.050	5.84	58.1	28.2	13.7	10.3	7.8	12.1	12.3	17.8	8.1
102-3	9.900	5.81	58.7	27.9	13.4	10.3	7.8	12.4	12.6	17.8	8.1
102-4	10.215	6.51	63.7	24.4	11.9	9.3	9.9	15.0	13.9	17.8	7.1
102-5	10.970	6.98	63.6	23.9	12.5	9.5	10.5	15.6	12.6	17.8	7.1
102-6	10.260	6.50	63.4	24.4	12.2	9.0	11.0	15.9	12.3	17.8	7.2
111-1	9.685	2.53	26.1	48.7	25.2	20.7	0.6	0.9	1.2	11.6	11.8
111-2	9.755	2.53	25.9	49.0	25.1	21.7	.6	1.1	1.5	11.5	11.2
111-3	10.210	2.63	25.7	48.9	25.4	21.4	.5	1.1	1.4	11.6	11.1
111-4	14.585	3.94	27.0	49.9	23.1	19.2	.8	1.3	1.6	12.0	11.3
111-5	15.165	4.17	27.5	50.2	22.7	19.1	.6	1.5	1.7	12.1	11.6
111-6	14.745	4.06	27.5	49.5	23.0	19.1	.7	1.4	1.7	11.7	12.1
132-1	11.025	7.11	64.5	10.4	25.1	24.3	8.2	22.0	13.2	14.7	6.4
132-2	10.710	7.00	65.4	10.6	24.0	22.6	9.6	22.4	13.0	14.7	5.7
132-3	10.780	7.04	65.2	10.7	24.1	22.5	9.7	21.7	13.0	14.9	5.9
132-4	10.450	6.88	65.9	10.5	23.6	23.1	9.5	22.7	13.4	14.6	5.7
132-5	10.690	7.00	65.5	10.7	23.8	22.3	9.8	22.6	13.0	14.2	5.8
132-6	10.835	6.56	60.5	18.6	20.9	20.6	10.9	21.4	11.4	11.9	5.0

Preparation of Soil Samples for X-Ray Diffraction Analysis

By Peter Janitzky,
University of California, Davis

REFERENCE

L. D. Whittig, written commun., 1983.

PRINCIPLE

A 10-20-mg clay sample is smeared upon the surface of

Table 6. Reproducibility, in weight percent, of particle-size analysis by the pipette method

[Replicates are indicted by a, b c. Samples are from Merced River chronosequence (Harden,1985). $\overline{X}$, mean value of replicates; SD, standard deviation; CV, coefficient of variability in percent=SD divided by $\overline{X}$. Percent standard error estimated by average CV for samples from any chronosequence that had replicate determinations]

Sample description		Sand	Silt	Clay		Sand			
				<2 μm	<1 μm	Very coarse	Coarse	Medium	Fine and very fine
Post-Modesto No.14 VI C5 (n)	a	96.9	2.4	0.7	0.4	3.9	57.2	25.6	10.2
	b	96.5	2.6	.9	.9	4.5	60.1	23.4	8.5
	c	96.1	3.3	.6	.4	5.0	58.6	23.9	8.6
	$\overline{X}$	96.5	2.7	.7	.6	4.5	58.6	24.3	9.1
	SD	.40	.47	.15	.29	.55	1.45	1.15	.95
	CV	.41	17.8	20.8	50.9	12.3	2.4	4.7	10.5
Post-Modesto No. 17 II C3 (ox)	a	64.0	29.4	6.6	4.9	0.0	.1	1.7	62.2
	b	63.2	29.7	7.1	4.5	.0	.1	1.1	62.0
	c	65.4	27.7	6.9	5.0	.1	.2	1.8	63.3
	$\overline{X}$	64.2	28.9	6.9	4.8	.03	.1	1.5	62.5
	SD	1.11	1.08	.25	.26	0.06	.06	.38	.70
	CV	1.7	3.7	3.7	5.5	173.2	43.3	24.7	1.12
Post-Modesto No.14-2 A12	a	56.0	35.0	9.0	5.8	.1	3.2	5.8	46.8
	b	55.3	37.2	7.5	5.5	.1	2.5	6.0	46.6
	c	48.7	42.9	8.4	6.3	.1	3.3	4.4	40.9
	$\overline{X}$	53.3	38.4	8.3	5.8	.1	3.0	5.4	44.8
	SD	4.02	4.07	.75	.40	.0	.43	.87	3.35
	CV	7.5	10.6	9.1	6.9	.0	14.5	16.1	7.5
Post-Modesto No. 14 A12	a	37.3	51.6	11.1	7.6	.1	1.4	2.6	38.2
	b	43.3	45.5	11.2	7.9	.1	1.0	2.3	39.9
	c	36.6	52.0	11.4	8.0	.1	1.4	1.9	33.2
	$\overline{X}$	40.7	49.7	11.2	7.8	.1	1.3	2.3	37.1
	SD	3.68	3.64	.15	.21	.0	.23	.35	3.48
	CV	16.1	7.3	1.3	2.6	.0	18.2	15.5	9.4
Percent standard error for n samples	$\overline{X}$	6	10	11	17	46	12	6	7
	n	4	4	35	4	4	35	35	4

a porous ceramic plate. By means of a suction device, the clay material is successively saturated with the cations required in the various steps of X-ray analysis. The plate is reusable after cleaning.

EQUIPMENT

diamond saw and grinder for preparation of the ceramic plate

beaker, medium size

suction apparatus. This consists of a metal plate (45-cm long, 10-cm wide, 1-cm thick) supported by four short legs (5-cm long). The plate has lengthwise a row of 12 holes (15-mm diameter) at distances of 35 mm. A copper tube (2-cm diameter) with respective holes, soldered airtight to the bottom side of the plate, is connected to a suction flask and serves as a drain for the holes. Glued to the top side of the plate is a rubber gasket in which rectangles (25 by 18 mm) are cut for each hole. Rubber stoppers (No. 0) close all holes not occupied by the ceramic plates during the saturation procedure.

centrifuge

centrifuge tubes, 100 mL (2)

muffle furnace

spatula

REAGENTS AND MATERIALS

sodium chloride, saturated solution.

magnesium acetate, 1 *N* solution. Disolve 122 g of $Mg(CH_3COO)_2 \cdot 4H_2O$ in H_2O and dilute to 1,000 mL. Transfer some amount into a wash bottle for use. (Note: all solutions are made with distilled water.)

hydrochloric acid, pH 3.5. Set approx. 500 mL H_2O in a beaker on the magnetic stirrer, insert electrode of the pH meter, and add a few drops of 1 *N* HCl until a pH of 3.5 is reached. Store in wash bottle.

potassium chloride, 1 *N* solution. Dissolve 75 g KCl in H_2O and dilute to 1,000 mL. Transfer some part of it into a wash bottle.

1:1 glycerol–water solution. Store in dropper bottle

hydrochloric acid, approx. 6 *N* solution, 500 mL.

unglazed tile squares (usually 10-cm squares).

carborundum abrasive

PROCEDURE

Preparation of the Mounting Plates

Cut a square of unglazed tile with a diamond or carborundum saw into approximately 55- by 25-mm pieces (the tile may also be scored with a diamond pencil and broken to appropriate dimensions). Smooth the surface of the plates by wet-grinding with fine-grade carborundum abrasive on a glass plate (or use a grinder disc if available). Optimum thickness of the mounting tile is approximately 3 mm.

Place the pieces into a beaker with 6 *N* HCl, warm, and let stand until all blackness of the abrasive has disappeared from the tile pieces. Rinse them well in tap water followed by distilled H_2O.

Mounting the Clay Material

Concentrate a clay suspension from the pipette analysis by flocculating with saturated NaCl solution and centrifuging. Samples with a low clay content may require 200-300 mL of suspension to yield approximately 20 mg of clay.

Remove a small portion of the clay from the centrifuge tube with a spatula and apply it to a spot on the center of the tile. Use a glass slide to evenly smear the clay over the tile surface.

Treatments of the Sample for X-Ray Analysis

Place the tile carrying the clay smear over an open hole of the suction apparatus and apply suction. Wash five times with HCl pH 3.5, each time covering the surface of the tile completely with liquid.

Wash four times with 1 *N* Mg acetate
Wash five times with distilled H_2O
Allow sample to dry overnight
X-ray

If 1.4-nm spacing is obtained, continue as follows:

Return sample to the suction apparatus
Add 1:1 glycerol-H_2O solution
Apply suction until excess glycerol has passed through sample
X-ray

If 1.4-nm spacing persists, continue as follows:

Return sample to suction apparatus
Wash five times with H_2O
Wash five times with 1 *N* KCl
Wash five times with H_2O
Allow sample to dry overnight
X-ray

The final treatments consist of successive heatings of the sample (150 °C, 300 °C, 550 °C) in the muffle furnace for 2 hours. X-ray each cooled sample in order to observe the collapse of various clay species.

Bulk Density—Paraffin Clod Method

By Michael J. Singer,
University of California, Davis

REFERENCE

Blake, 1965.

PRINCIPLE

Methods of measuring bulk density include (1) coring, in which a core of known volume is driven into the soil to obtain a sample, (2) excavation, in which loose soil is removed and the volume of the excavation is determined by filling with sand or liquid, and (3) a clod procedure, in which an intact clod is removed from the soil for volume and weight measurement. The third procedure is described here.

Soils with coarse fragments present a special problem. Sample size must be increased proportionately as gravel size and soil volume occupied by gravel increases. For some soils very high in gravel content, a visual estimate of volumetric gravel content may be used. For nongravelly soils, a 200-250-g sample is convenient. The paraffin becomes a significant part of the total weight of smaller samples. For those soils with small-size coarse fragments, the clod procedure can be used and is described here.

An undisturbed soil sample is weighed and its volume calculated by determining the volume of water it displaces after the sample is coated with a waterproof material. Bulk density is calculated as the weight per unit volume, normally on an oven-dry basis.

EQUIPMENT

beam balance, modified to accept a container basket for the sample or to allow the sample to be attached directly to the balance lever arm

coarse basket to hold sample (optional)

string and paper clips

thin hair nets (optional)

paraffin or powdered Saran

warming container for the paraffin

oven

balance (two place)

PROCEDURE

Each clod is placed in the container basket, nylon hair net, or is firmly tied by fine thread or twine, depending on the clod strength. A fine thread or twine works well for all but the weakest clods. A nylon hair net is most rapid. Weigh the clod in air before coating. Briefly immerse the clod in 60 °C paraffin. Penetration into soils with coarse pores (sandy soils) is reduced if the paraffin is slightly cooler than 60 °C. Clay soil may be coated with slightly warmer paraffin. A brief immersion at the temperature slightly above the paraffin melting point helps to retard paraffin penetration into soil pores. One coating should be sufficient to waterproof the clod.

After the paraffin is solid, weigh the coated clod in air and in water. If the basket is used, also weigh it in air and water.

After weighing, the clod may be broken open and a sample of soil from the interior of the clod can be weighed, oven dried at 105 °C, and reweighed to determine the moisture content of the clod. Density can then be reported on an oven-dry basis.

If gravel-free bulk density is desired, a broken clod can be soaked in water overnight and washed through a 2-mm sieve. The gravel-free weight of the clod can be calculated using the weight and volume of the gravel as a correction factor.

Clod density at other water contents can be measured by first equilibrating the clods on a tension plate. After the clod is weighed in air and water, some paraffin is removed from one side, and the clod is placed, open side down, on a sand saturated with water. (A piece of filter paper or fine cloth is placed between the sand and clod to prevent sand grains from contaminating the clod.) The clod is saturated on the sand bed and is then equilibrated on a tension plate to the desired tension. The bottom of the clod is then recoated with paraffin, and the weights in air and water are taken.

Saran resin is recommended by the Soil Conservation Service as a coating material. It is difficult to obtain in small quantities, but otherwise it does work well. Saran is liquid at ambient temperatures and can be used in the field. It also is permeable to water vapor so none must be removed from the clod to get an oven-dry weight. Saran works best when clods are moist. Dry clods can be sprayed with water before coating to reduce Saran penetration. Several coatings of Saran are required for waterproofing.

The Saran resin dissolves readily (but slowly) in acetone or methyl ethyl ketone. Ratios of Saran to solvent of 1:4-1:8 are used. The solvent is placed in a disposable can or other (nonplastic) container on an electric stirrer and the resin is added slowly until all is in solution. Clods may be immersed directly in the mixture.

CALCULATIONS

$$\text{percent } H_2O = \frac{\text{wet sample weight} - \text{dry sample weight}}{\text{dry sample weight}}$$

$$Db_1 = \rho_w WC_d \div (WC_p - WC_{pw} + W_p - (W_p\, \rho_w/\rho_p))$$

$$Db_2 = (WC_d - W_g) \div (WC_d - WC_{pw} - W_p) - \frac{W_g}{2.65}$$

Db_1 = oven-dry bulk density
Db_2 = oven-dry gravel-free bulk density
ρ_w = density of water
WC_d = weight of oven-dry clod in air
WC_p = weight of coated clod in air
WC_{pw} = weight of coated clod in water
W_p = weight of paraffin in air
ρ_p = density of paraffin
W_g = gravel weight

$w_\rho = WC_p - WC_w$

WC_w = weight of moist clod in air

If the weight and density corrections for paraffin and water are ignored, the calculations become:

$$Db_1 = \frac{\text{weight in air}}{\text{weight in air} - \text{weight in water}}$$

$$Db_2 = \frac{\text{weight in air} - \text{weight >2 mm}}{(\text{weight in air} - \text{weight in water})} - \frac{\text{weight >2 mm}}{2.65}$$

Over the range of soil densities (1.34-1.97 g/cm^3), reproducibility of the method was quite good for soils from the San Joaquin Valley (table 7).

Determination of Soil pH

By Peter Janitzky,
University of California, Davis

REFERENCES

Jackson, 1958.
Peech, 1965b.

PRINCIPLE

The hydrogen-ion acitvity of the soil is measured on 1:1 soil-water or soil-KCl suspensions which have been equilibrated for a certain time. A repeated measurement after approximately 1 hour on the same sample serves as a duplicate. Other soil:solution ratios are used. This one was selected because it is convenient.

EQUIPMENT

pH-meter
combination electrode or electrode pair (optional)
beaker, 50 mL
watchglass to fit beaker
stirring rod

Table 7. Example of reproducibility of bulk-density measurements of triplicate samples by the paraffin clod procedure

[Replicates are indicated by a, b, c. $\bar{X}$, mean value for replicates; SD, standard deviation; CV, coefficient of variability in percent = SD divided by $\bar{X}$. Percent standard error estimated by average CV for samples from any chronosequence that had replicate determinations]

Sample description		Gravel weight as percent of clod weight	Density (g/cm^3)
Dry Creek Area:	a	0.4	1.74
Riverbank No. 28	b	.3	1.77
BCT	c	.2	1.61
	$\bar{X}$	.3	1.71
	SD	.1	.08
	CV	.33	.05
Riverbank No. 29	a	3.4	1.79
Bl	b	2.5	1.74
	c	3.2	1.79
	$\bar{X}$	3.03	1.77
	SD	.47	.29
	CV	.15	.02
B + C	a	21.8	1.72
	b	38.1	1.53
	c	8.1	1.79
	$\bar{X}$	22.6	1.68
	SD	15.0	.13
	CV	.66	.08
C	a	1.5	1.35
	b	1.7	1.39
	c	4.2	1.34
	$\bar{X}$	2.46	1.36
	SD	1.50	.03
	CV	.62	.02
Merced River Area:			
Turlock Lake No. 11	a	1.5	1.96
Btl	b	1.0	1.97
	c	1.6	1.93
	$\bar{X}$	1.37	1.95
	SD	.32	.02
	CV	.23	.01
Percent standard error	$\bar{X}$	-	3
for n samples	n	-	171

REAGENTS

potassium chloride, 1 *N* solution. Dissolve 74.56 g of KCl in H_2O and dilute to 1,000 mL

standard buffer solutions (pH 4 and 6.8)

PROCEDURE

Weigh 20 g of air-dried <2-mm soil into a 50-mL beaker. Add 20 ml of H_2O or KCl-solution, stir well, cover with watchglass, let stand overnight (14-16 hours). When ready to measure, set pH meter at a rate of 1 measurement/second. Stir sample with stirring rod, insert the electrode and let equilibrate. Register the value when no change occurs in the second decimal (x.xx) after 15 seconds. Remeasure after approximately 1 hour and note value as duplicate. If the meter does not have a setting for measurement rate, measure pH in the continuous mode to the same end point.

Several samples have been run in duplicate or triplicate to illustrate the reproducibility of this technique (table 8).

ADDITIONAL REMARKS

The 1:1 H_2O procedure is simpler than the saturation paste procedure because there is no uncertainty in measuring the appropriate amount of water. Preparing a saturated paste requires either some experience in evaluating soil moisture content by eye or the premeasurement of saturated conditions. The KCl pH provides a measure of exchangeable hydrogen because the K^+ replaces H^+ on the exchange complex. It is always lower than a pH measured in water. The close correlation between the results from these methods is shown in figures 10 and 11.

Table 8. Reproducibility of soil pH measurements by three methods

[Replicates are indicated by a, b, c. Samples are from Dry Creek chronosequence. $\overline{X}$, mean value for replicates; SD, standard deviation CV, coefficient of variability in percent = SD divided by $\overline{X}$. Percent standard error estimated by average CV for samples from any chronosequence that had replicate determinations]

Sample description		1:1 H_2O		1:1 1 N KCl		Saturation paste	
Riverbank	a	6.6	6.6	4.9	4.9	6.5	6.7
No.28	b	6.8	6.7	4.9	4.9	6.6	6.7
Bt2	c	6.7	6.7	4.9	4.9	6.5	6.8
	$\overline{X}$	6.7	6.7	4.9	4.9	6.5	6.7
	SD	.1	.05	0	0	.05	.06
	CV	.01	.01	---	---	.01	.01
Lab Std. No.1	a	8.0	7.1	7.0	6.9	7.7	7.7
	b	8.1	7.8	7.0	6.9	7.7	7.9
	c	8.1	7.8	7.1	7.0	---	---
	$\overline{X}$	8.1	7.6	7.0	6.9	7.7	7.8
	SD	.06	.40	.06	.06	0	.14
	CV	.01	.05	.01	.01	---	.02

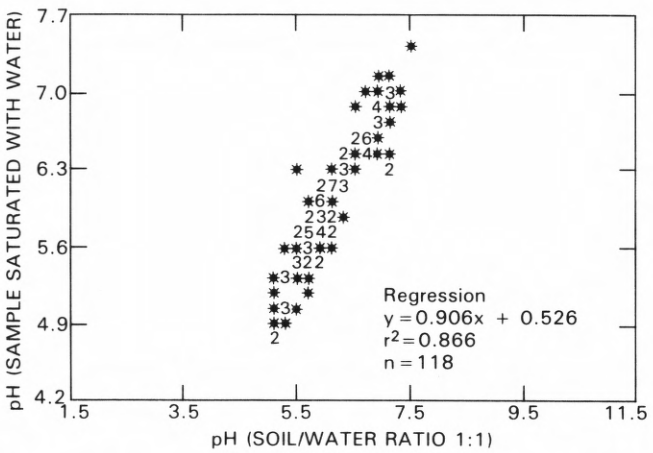

Figure 10. Regression and correlation of saturation pH with 1:1 water pH. Numbers indicate samples at that position. Regression statistics are given for least-squares line. Samples are from all chronosequences of this study.

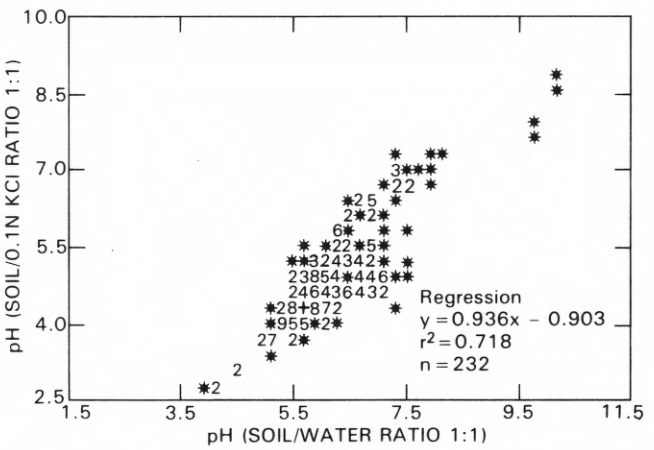

Figure 11. Regression and correlation of 1:1 KCl pH with 1:1 water pH. Numbers indicate samples at that position. Regression statistics are given for least-squares line. Samples are from all chronosequences of this study.

Cation-Exchange Capacity

By Peter Janitzky,
University of California, Davis

REFERENCE

Rible and Quick, 1960.

PRINCIPLE

The soil is leached by suction with a solution of $BaCl_2$ buffered with Triethanolamine at pH 8.1. The leachate is saved for the determination of extractable cations. Excess electrolyte in the Ba-saturated sample is removed by further leaching with water and alcohol. The air-dried sample is transferred to a shaker bottle and equilibrated with a saturated solution of $CaSO_4$ of known concentration (determined by titration with EDTA). On a filtered and titrated aliquot of the suspension, the amount of Ca^{++} exchanged for Ba^{++} is determined by subtracting the titration value from that of the blank.

EQUIPMENT

balance (Mettler, 0-120 g)
hotplate

mechanical shaker
magnetic stirrer (optional)
suction manifold
filter rack
automatic buret, 10-mL
suction flask, 250-mL
Buchner funnel, COORS No. 1, porcelain, 63-mm diameter
volumetric flask, 200 mL
volumetric pipettes, 100 mL, 5 mL
micro-pipette (Eppendorf), 1 mL, with disposable tips (optional)
Erlenmeyer flasks, 125 mL (2), 50 mL
beakers, 150 mL, 100 mL
shaking bottle, 8 oz
glass funnels, 75-mm diameter, 75-mm stem (2)
window glass, 1 piece about 20 by 15 cm
Whatman filter paper, No. 42, 5.5 cm
Whatman filter paper, No. 50, 11.0 cm
Whatman filter paper, 2V (folded), 15.0 cm
magnetic stirring bar, 4 cm long
pipette filler
weighing scoop, camel's hair brush, sampler spoon
rubber stoppers No. 2, 5, 6-l/2

REAGENTS

1. 0.5 *N* $BaCl_2$-0.2 *N* Triethanolamine extracting solution. Preparation of 8 L: Place 200 mL Triethanolamine (2,2,2-Nitrilotriethanol OR, Mallinckrodt No. 1908) into a 4000-mL beaker. Dilute to 2,000 mL with distilled H_2O, add approximately 95 mL 6 *N* HCl, make to a volume of 4,000 mL, and adjust pH to 8.1 on a magnetic stirrer. Transfer into a 9-L Pyrex storage bottle. Mix with 4,000 mL 1 *N* $BaCl_2$ solution (489 g of $BaCl_2 \cdot 2\ H_2O$/4 L). Protect the extracting solution from CO_2 by attaching a glass tube filled with sodium calcium hydrate (soda lime) to the air inlet.
2. Ethyl alcohol, 95 percent.
3. Saturated $CaSO_4$ solution. Add approx. 5 g of $CaSO_4 \cdot 2\ H_2O$ to 1 L distilled H_2O, shake on mechanical shaker for l0 minutes, filter suspension by suction, using a Buchner funnel with fritted glass bottom or filter paper No. 42.
4. Na-Versenate (EDTA) solution, 0.01 *N*. Dissolve 2.00 g of EDTA (disodium dihydrogen ethylene-diaminetetraacetate) in water and make to 1,000 mL in volumetric flask. Transfer solution into a plastic bottle. Dissolve in a volumetric flask, 0.500 g of oven-dried $CaCO_3$ (reagent grade) in 10 mL 3 *N* HCl and dilute to exactly 1,000 mL. To standardize the EDTA against the standard 0.0100 *N* Ca-solution, pipette 3 aliquots of 10 mL each of the Ca-solution into 125-mL Erlenmeyer flasks and dilute to about 50 mL. Add 5 mL of potassium hydroxide solution (25 percent aqueous solution) and 5 drops of Calcon indicator (0.4 percent solution in methanol). Proceed with titration as described just below under "Determination of Ca." Calculate the normality of the EDTA solution.

$$N_{EDTA} = \frac{N \text{ of } CaCl_2 \times \text{mL } CaCl_2}{\text{ml EDTA}}$$

PROCEDURE

Place 4.00 g of <2-mm air-dried soil into a 100-mL beaker. Fill a 150-mL beaker with 150 mL $BaCl_2$-TEA extracting solution. Add approximately 25 mL from this to the soil sample. Swirl the suspension lightly, digest for 30 minutes on hotplate at 40–50 °C to break up aggregates. Swirl intermittently. Cool to room temperature. Connect a 250-mL suction flask, fitted with a Buchner funnel and filter paper No. 42 (5.5 cm), to the vacuum line.

Transfer the suspension quantitatively to the Buchner funnel by rinsing the beaker with several small portions of the remaining extracting solution. Before pouring the suspension into the funnel, moisten the filter disc with a few drops of H_2O and wait a few seconds until vacuum is established in the suction flask. Leach the sample with small increments, using only slight suction, until all 150 mL of the Ba solution have passed through. Leach once with not more than approximately 20 mL H_2O from a wash bottle, uniformly rinsing the walls of the funnel.

Remove the funnel containing the sample and set it carefully aside (do not turn off the vacuum). If extractable cations are to be determined, transfer the leachate quantitatively into a 200-mL volumetric flask, make to volume, store 50-100 mL of the solution in a 125-mL Erlenmeyer flask. Save the extract in a refrigerator until ready for analysis (see next chapter). Dispose of the remainder.

Return funnel and suction flask to vacuum. Leach the sample additionally with two portions of 20 mL of H_2O, and two portions of 10 mL ETOH 95 percent, rinsing any soil carefully down to the bottom of the funnel.

Open vacuum completely; let soil pad and filter paper dry in the air stream for about one hour. Turn off vacuum.

Wipe off all moisture from the outer surfaces of the funnel, especially around the rubber stopper. Center a filter paper disc No. 50 (11.0-cm diameter) over the funnel and fold it evenly down over the outside of the rim. Pressing the circle tightly over the funnel with one hand, remove the funnel from the flask, invert it quickly and set it on a clean piece of window glass (approximately 170 cm^2). Tap the sides of the funnel with the wooden handle of a small spatula so that the soil pad and filter paper adhering to it will fall into the larger filter disk. Quantitatively remove all soil from the funnel with spatula and brush, taking care not to lose any material. Fold the larger disc and any material spilled on the glass plate and transfer both to an 8-oz shaker bottle.

Add exactly 100 mL of saturated $CaSO_4$ solution from a 100-mL volumetric pipette[1] (use pipette filler), stopper (rubber stopper No. 6½), and shake on mechanical shaker for 10 minutes. Filter approximately 20-30 mL of the suspension through a glass funnel fitted with a folded filter paper (2V) into a 50-mL Erlenmeyer flask, after discarding the first few milliliters of the filtrate (they usually show some cloudiness). Discard the remaining contents of the bottle.

Determination of Ca

Place a 3-mL aliquot (volumetric pipette or Repipete) of the filtrate into a 125-mL Erlenmeyer flask, and make to approximately 50 mL. Add 5 mL of potassium hydroxide (25 percent aqueous solution), and 5 drops Calcon indicator (0.4 percent solution in methanol). Titrate the solution with EDTA to a pure blue end point (no tinge of purple should remain), using a 10-mL automatic buret, and a magnetic stirrer. In order to better distinguish the end point, cover surface of stirrer with a filter paper disc, set a slightly overtitrated blank side by side with the sample and place a bright light behind the sample. When approaching the end point, the time intervals between the drops should be about 5 seconds.

With each batch of samples, run duplicates of blank $CaSO_4$ solution.

CALCULATION

meq Ca/100 g soil, or CEC =

$$(\text{mL EDTA}_{\text{blank}} - \text{mL EDTA}_{\text{sample}}) \times 0.01\,N\ \text{EDTA} \times 833.325$$

ADDITIONAL REMARKS

Method 2, the one described, was compared with several other methods using four soils (table 9).

In method 1, the soil is saturated with $CaCl_2$, excess salts are washed off with 80 percent acetone, Ca is displaced with Na using NaCl, and Ca is titrated with EDTA. This is the standard method of Jackson (1958, p. 64).

In method 3, the soil is equilibrated with 0.5 *N* $BaCl_2$ (pH 5.8) in a centrifuge tube. Supernatants are collected for analysis of extractable cations. Barium is leached with *N* NaOAC (pH 7.0). Excess Na^+ is washed away with ETOH, and Na on the exchange complex is displaced with *N* NH_4OAC.

Methods 4 and 5 are like method 2 except that 0.2 *N* $BaCl_2$ is used at pH 5.8 (method 4) and pH 8.1 (method 5).

The use of a barium salt buffered at pH 8.1 might raise doubts as to its usefulness for acid soils. It is well known that CEC values depend significantly on the kind of extracting agent. In view of the large variety of soil types occurring in the chronosequences studied, a consistent handling of the samples, with as little variation in the choice of analytical conditions as possible, appeared essential. Realizing, furthermore, the obvious disadvantages in the use of ammonium salts in the case of calcareous or vermiculitic soils, a procedure involving buffered barium chloride solution as the sole reagent for the determination of CEC, extractable cations and extractable acidity was chosen. The results of analyses of some soils with widely differing pH, organic matter content, and base saturation are shown in table 10. The overall balance of total cations (Ca + Mg + Na + K + "H") and CEC in each case attests convincingly to the usefulness of the method. Because no soluble salts were determined in the present study, no balances could be achieved in samples having appreciable concentrations of soluble cations (see last example in table 10). In such cases the amounts of soluble cations should be measured separately in a saturation extract.

[1]To ensure identical deliveries of the solution in case of larger numbers of samples, it is not advisable to use an automatic pipette because of adhesion of $CaSO_4$ to the glass walls after a certain time, hence the relatively longer cleaning procedure of automatic pipettes versus the simple pipette.

Extractable Cations

By Peter Janitzky,
University of California, Davis

REFERENCES

Rible and Quick, 1960.
Jackson, 1958.

PRINCIPLE

The concentration of extractable Ca, Mg, Na, and K is measured by means of an atomic absorption spectrophotometer in a soil extract which is obtained by leaching the soil with a solution of 0.5 *N* $BaCl_2$-0.2 *N* Triethanolamine buffered at pH 8.1. Preferably the extract obtained for the determination of the cation exchange capacity should be used (see Janitzky, "Cation-Exchange Capacity," this volume).

EQUIPMENT

atomic absorption spectrophotometer
volumetric flasks: 1,000 mL (2), 500 mL (1), 250 mL (1), 100 mL (6), 50 mL (1)
Nalgene bottles: 1,000 mL (3), 250 mL (1), 125 mL (6)
volumetric pipettes: 100 mL, 5 mL, 3 mL

Table 9. Example of reproducibility and comparison of methods for cation exchange capacity (meq/100 g soil)

[Percent standard error (of estimate) = standard deviation of replicate determinations divided by means of replicates (multiplied by 100), averaged for all samples with replicates. For example, 11 percent error of meq/100 g 10 ± 1.1 meq/100 g]

Sample	Method				
	1 Saturated $CaCl_2$	2 0.5 N $BaCl_2$ pH 8.1	3 0.5 N $BaCl_2$ pH 5.8	4 0.2 N $BaCl_2$ pH 5.8	5 0.2 N $BaCl_2$ pH 8.1
R13 Ap	8.8	10.9	9.4	8.4	9.7
	8.9	10.8	9.2	8.0	9.9
R14 Bt1	7.2	9.0	8.0	7.4	8.0
	--	8.8	8.4	7.5	7.5
Hillgate	--	14.9	--	13.4	14.0
	--	15.1	--	--	--
Contra Costa	--	33.6	--	32.3	31.1
	--	33.6	--	--	--
Percent standard error for n samples	$\bar{X}$	-	-	-	13
	n	-	-	-	16

Table 10. Effect of $BaCl_2$-Triethanolamine in the measurement of cation exchange capacity (CEC), extractable cations, and extractable acidity of various soils

Chronosequence	Horizon	UCD No.	pH	Percent C	Extractable		Total	CEC (meq/100 g)	Balance
					Cations	Acidity			
Colorado ----------	A	154	6.0	10.98	25.73	18.70	44.43	43.04	+1.39
Do ----------	A	148	5.5	6.60	16.40	3.27	29.67	29.05	+.62
Ventura ----------	A2	610	6.1	1.67	11.76	4.22	15.98	15.55	+.43
Do ----------	2AB	655	6.7	.86	25.84	5.63	31.47	31.51	-.04
Merced ----------	A	420	5.8	2.01	7.24	4.83	12.07	12.02	+.05
Do ----------6BC2		428	4.1	.02	8.20	12.63	20.83	20.00	+.83
Ventura ----------	4Btk2	647	8.1	.14	28.53	.56	29.09	29.64	-.55
Do ----------	9Coxk1	652	8.1	.06	19.77	0	19.77	15.45	+4.32

REAGENTS

1. Standard solutions, 1,000 ppm each (Jackson, 1958, p. 459). Store in 1,000-mL Nalgene bottles.
   Calcium: Dissolve 2.500 g of dried $CaCO_3$ in 60 mL 1 *N* HCl. Boil solution to expel CO_2, dilute to 1,000 mL.
   Magnesium: Dissolve 1.000 g metallic ribbon in 100 mL 1 *N* HCl, dilute solution to 1,000 mL.
   Sodium and potassium: Dissolve 2.542 g NaCl (dried at 110 °C) and 1.907 g KCl (dried at 110 °C) in H_2O, dilute solution to 1,000 mL.
2. Lanthanum-cesium solution for the reduction of interferences. Stock solution contains 2 percent La, 5,000 ppm Cs, 10 percent HNO_3. Weigh 23.455 g La_2O_3 and transfer to a dry 1,000 mL volumetric flask. Pour 100 mL concentrated HNO_3 into a graduated cylinder. Very slowly, milliliter by milliliter at first, add 36 mL of acid to the La, swirling constantly until most La is dissolved. Add H_2O to about half of the flask. Swirl until all salt is dissolved. Add remaining acid (64 mL). Add 6.335 g CsCl. After dissolution, let the solution cool to room temperature. Make to volume and store in a plastic bottle with tubing connector near bottom and connect to a 25-mL automatic buret (if available).
3. Ba-matrix for standards, 370 meq/L. Dissolve 45.2 g $BaCl_2$ x 2 H_2O in H_2O, dilute to 1,000 mL, and store in a plastic bottle.

PROCEDURE

Use the soil extract from the CEC determination. If CEC was not determined previously, obtain an extract using the method on pages 00 of this volume.

Following the recommendations for initial sample dilution given in table 11, pipette an aliquot of the soil extract into a 50-mL volumetric flask. Add 5 mL of La-Cs solution and make to volume. Analyze the diluted sample for Ca, Mg, Na, and K cations. Use standards recommended in table 12 and prepared as outlined in table 13.

1. Test for Mg by atomic absorption with the burner set at about a 45° angle to the light beam path. The standard curve should be linear to at least 10 ppm.
2. Test for Ca by atomic absorption with the burner set parallel to the light beam path. The standard curve should be linear for at least 10 ppm.
3. Test for Na and K by flame emission. The standard curve for these elements is nonlinear above about 0.5 ppm, but the combination of reproducibility and precision is best between about 0.5 and 5 ppm (particularly for Na).

Determine the approximate concentration of each element in the samples with the recommended standards, then change sample or standard concentrations as needed to obtain required accuracy.

CALCULATIONS

Based on 5 mL soil extract aliquot:

meq Ca/100 g soil = ppm Ca in sample × 2.50
meq Mg/100 g soil = ppm Mg in sample × 4.11
meq Na/100 g soil = ppm Na in sample × 2.18
meq K/100 g soil = ppm K in sample × 1.28

Table 11. Initial dilution recommendations for soil solution analyses by atomic absorption spectrophotometry

[CEC, cation exchange capacity]

CEC range (meq/100 g)	Dilution
<65	1 in 10 (5 mL in 50 mL)
65-100	3 in 50 (3 mL in 50 mL)[1]
>100	1 in 25 (2 mL in 50 mL)[1]

[1]Requires adjustment of $BaCl_2$ concentration of standards to 22 meq Ba/L (for 3-in-50 dilution) and 15 meq Ba/L (for 1-in-25 dilution), respectively.

Table 12. Initial concentration recommendations for atomic absorption spectrophotometry standard solutions

[CEC, cation exchange capacity]

CEC range----		<30 meq/100 g			30 to 65 meq/100 g		
Element	Blank (ppm)	Standards (ppm)					
		S1	S2	S3	S1	S2	S3
Ca	0	1	3	5	3	5	10
Mg	0	.5	1	3	1	3	5
Na	0	.5	1	3	1	3	5
K	0	1	3	5	3	5	10

Table 13. Preparation of standard solutions for atomic absorption spectrophotometry

1. Dilute stock solutions (prepare as needed):

Stock 1 (ppm)	Aliquot (mL)	Make to (mL)	Stock 2 (ppm)	Aliquot (mL)	Volumetric (mL)	Std. (ppm)
1,000	10	1,000	10	2	200	0.1
				10	200	.5
				20	200	1.0
		500	20	3	200	.3
				20	200	2.0
				30	200	3.0
				50	200	5.0
				100	200	10.0

Pipettes needed: 2-, 3-, 10-, 20-, and 50-mL
2. Add 20 mL La-Cs solution.
3. Add 20 mL of $BaCl_2$ (370 meq/L) solution (for 1-in-10 soil extract dilution only).
4. Bring to volume.
5. Make a blank solution. Add 25 mL La-Cs solution and 25 mL (for 1-in-10 soil extract dilution) $BaCl_2$ (370 meq/L) solution to a 250-mL volumetric flask and bring to volume.

Extractable Acidity

By Peter Janitzky,
University of California, Davis

REFERENCES

Peech, 1965a.
Soil Conservation Service, 1972.

PRINCIPLES

The soil is leached by suction with $BaCl_2$-Triethanolamine pH 8.1. The leachate and a blank containing the same amount of barium buffer are titrated with standard acid. Subtracting the titration value of the sample leachate from that of the blank determines the amount of Al^{3+} and H^+ ions replaced from exchange sites and released from dissociated acidic groups on the clay surface.

EQUIPMENT

balance
magnetic stirrer
suction manifold (optional, unless multiple samples are extracted simultaneously)
automatic buret, 50 mL (optional)
volumetric flasks, without stopper, 100 mL (2), 50 mL (2)
suction flasks, 500 mL (2)
Gooch crucible (COORS, size No. 4) with crucible holder (Walter)
beaker, 100 mL
magnetic stirring bar, 4 cm long
filter paper, Whatman No. 540, 2.4 cm diameter
weighing scoop, camel's hair brush, sampler spoon

REAGENTS

Buffer solution: 0.5 *N* $BaCl_2$-0.2 *N* Triethanolamine, pH 8.1. Prepare as shown in section on "Cation Exchange Capacity."

Replacement solution: 0.5 *N* $BaCl_2$ solution + 5 mL buffer solution per liter. To prepare 9 L: Dissolve 550 g $BaCl_2 \cdot 2\ H_2O$ in 8 L water, add 45 mL buffer solution, make to 9 L. Protect from CO_2 of the air with soda lime filter at the top.

Hydrochloric acid. 0.2 *N*. To prepare 18 L: Dilute 300 mL concentrated HCl to 18 L. Standardize the acid against 0.2 *N* standard NaOH solution and connect the storage vessel to a 50-mL automatic buret.

Brom Cresol green indicator, 0.1 percent aqueous solution.

Mixed indicator. Dissolve 1.250 g methyl red indicator and 0.825 g methylene blue indicator in 950 mL ethanol, make to 1,000 mL with H_2O.

PROCEDURE

Place 5.0 g of <2 mm air-dried soil into a 100-mL beaker. Fill a 50-mL volumetric flask with $BaCl_2$ buffer solution, and a 100-mL volumetric flask with replacement solution. Add approximately 15 mL of the buffer solution to the sample and let equilibrate for ½ hour, swirling it intermittently. Set up the Gooch crucible with filter paper and suction flask. Keep vacuum at a low level, moisten the filter paper with a few drops of H_2O and check for an accurate fit of the filter disc over the perforated bottom of the crucible. Transfer the sample quantitatively to the crucible with the remaining buffer solution, using several portions of it. Rinse the volumetric flask with a minute amount of H_2O[1], continue to leach the soil with small increments of replacement solution until all 100 mL have passed through. Rinse solution adhering to crucible and stem of the holder into the suction flask; also rinse the upper walls of the flask. Place a stirring bar into the flask. Add 2 drops Brom Cresol green and 10 drops mixed indicator. Using a magnetic stirrer (covered with a filter paper disc), titrate the solution with standardized HCl to a chosen end point in the range from green to purple. Titrate a blank, consisting of the same amounts of buffer and replacement solution, to precisely the same color.

CALCULATION

$$\text{extractable acidity (meq/100g)} = \frac{\text{mL HCl blank} - \text{mL HCl sample}}{\text{g sample}} \times N_{HCl} \times 100$$

NOTE: Decrease the amount of sample when leaching clay-rich soils, as these may have an inconveniently low leaching rate (as much as two days!).

ADDITIONAL REMARKS

The average standard error (of estimate) is 9 percent (of given value), as determined by replicate analysis of 12 samples.

[1]Addition of H_2O to the leachate will not affect the titration result. However, leaching time may considerably increase by adding unnecessary amounts of water. Always work with clean glassware (dichromate-cleaning-solution washed) in order to minimize errors resulting from incomplete transfers of suspensions and solutions.

Gypsum Determination by Electrical Conductivity

By Marith Reheis,
U.S. Geological Survey

REFERENCES

Bower and Huss, 1948.
Jackson, 1958.
Metson, 1961.
Soil Conservation Service, 1972.

PRINCIPLE

Pure water is a poor conductor of electricity; water containing dissolved salts conducts a current in proportion to the amount of salts present. A soil-water extract, dilute enough to dissolve all the gypsum present in the soil sample, is prepared by shaking an aliquot of soil in a measured amount of distilled water for 30 minutes on a mechanical shaker, then filtering and saving the extract. At this point, readings made on a conductivity bridge will reflect the total amount of soluble salts in the soil, and percent salt can be estimated by a multiplication factor. An aliquot of the extract added to acetone will precipitate gypsum, which is insoluble in acetone. Saving this precipitate and redissolving it in distilled water permits conductivity readings to be made on a solution containing only gypsum. This method is applicable to soils containing less than 4 percent gypsum in the <2-mm fraction.

EQUIPMENT

analytical balance
250-mL extraction flasks and stoppers (or plastic bottles)
oven
50-mL, 10-mL, and two 20-mL pipettes
rubber bulb for pipette
filter paper, medium porosity to fit Buchner funnel
Buchner funnel
vacuum flask
centrifuge and centrifuge tubes
Wheatstone bridge and conductivity cell (conductivity meter)
Celsius thermometer
200-mesh sieve (optional)
mechanical shaker (optional)

REAGENTS

distilled water
acetone, technical or reagent grade
0.01 *N* KCl (0.7456 g KCl dissolved in distilled water and brought to 1 L)

PROCEDURE

1. Estimate the amount of gypsum. Use 1:5 soil:water dilution if you think gypsum content is less than 1.3 percent. The following rules of thumb for dilutions may help:

No visible salts	= 1:5
Visible crystals	= 1:10
Soft nodular masses of crystals	= 1:50
Continuous masses of crystals	= 1:100

   If you have too much gypsum and not enough water, two problems will arise: (a) You will not dissolve all the gypsum and (or) (b) the conductivity meter will not measure it correctly. If gypsum content approaches 1.3 percent when you measure it, repeat experiment with a more dilute solution.
2. If gypsum is present in visible crystals, the sample should be finely ground (approximately to pass a 200-mesh sieve) to facilitate dissolution.
3. Weigh the appropriate amount of <2-mm air-dried soil (ovendrying converts gypsum to anhydrite). Place it in a plastic bottle with lid or an extraction flask with stopper. Add 50 mL distilled water with a pipette. About 50 mL of solution is ample for most conductivity meters. Use more suspension if the available conductivity meter requires large amounts of solution. Record soil weight and amount of water.
4. Stopper the bottle and shake, either (a) for 30 minutes in a mechanical shaker, or (b) by hand six times at 15-minute intervals.
5. Filter the solution in a Buchner funnel over the vacuum flask. Attempt to get a clear extract, but a slightly turbid liquid does not affect results significantly. Save the extract in another plastic bottle and discard the filter paper and soil. Rinse flask and funnel in distilled water and dry them before filtering successive samples, to avoid contamination and (or) dilution.

   At this point, if a measurement of total soluble salt content is desired rather than gypsum, go to step 9.
6. Pipette 20 mL of filtered extract into a centrifuge tube. Add 20 mL of acetone (use the rubber bulb to avoid acetone fumes) to the extract and swirl gently, then let sit. If gypsum is present in sigificant amounts, a white precipitate will form in about 5-10 minutes.
7. Centrifuge at 2,000 rpm for 3 minutes. Decant liquid and invert tubes so they drain for 5 minutes. Add another 10 mL of acetone, delivered so as to wash down the sides of the centrifuge tube, and stir the sample. Repeat centrifuging, decanting, and draining.
8. Pipette 40 mL distilled water to the tube with the precipitate, stopper it, and shake by hand until the precipitate is dissolved. At this point you can store the extract in a

tightly capped bottle until it is convenient to proceed.

9. Determine the conductivity cell constant by measuring conductivity of the 0.01 *N* KCl solution. Rinse the conductivity cell with KCl solution. Add fresh KCl solution and record the conductivity in decisiemens per meter (actual procedure varies depending on type of equipment used). Finally, rinse the cell with distilled water. Record temperature of the KCl solution. If many samples are to be measured, redetermine the KCl conductivity readings and check solution temperature after every 5-6 measurements.
10. Determine and record conductivity of the sample solution in decisiemens per meter using the same rinsing techniques described in step 9. If the KCl solution and sample solution have been standing together, the same temperature readings may be used for both. If not, measure the temperature of the sample solution.

CALCULATIONS

1. Obtain cell constant C.

$$C = \frac{\text{KCl conductivity (table 14) at measured temperature}}{\text{measured KCl conductivity}}$$

2. Determine temperature factor *F* for the sample solution from table 15 in order to standardize conductivity readings to 25 °C.

Table 14. Theoretical conductivity of 0.01 *N* KCl solution at varying temperatures (Metson, 1961)

Temperature °C	Conductivity (dS/m)
10	1.020
15	1.147
16	1.173
17	1.199
18	1.225
19	1.251
20	1.278
21	1.305
22	1.332
23	1.359
24	1.386
25	1.412
30	1.552

Table 15. Factors for converting sample solution conductivity measured at varying temperatures to the standard 25°C (Metson, 1961)

Temperature (°C)	Factor	Temperature (°C)	Factor
8	1.499	21	1.092
10	1.421	22	1.067
12	1.350	23	1.044
14	1.284	24	1.021
15	1.254	25	1.000
16	1.224	26	.979
17	1.196	28	.941
18	1.168	30	.906
19	1.142	32	.873
20	1.118	34	.843

3. Calculate conductivity *K* in decisiemens per meter at 25 °C for sample solution:

$$K = \text{measured conductivity } (C)(F)$$

4. Calculate meq $CaSO_4$ contained in final solution (step 3) of procedure (*X* mL H_2O):

$$\text{meq } CaSO_4 \text{ in } X \text{ mL } H_2O = K(12.5)(X \text{ mL } H_2O/1{,}000 \text{ mL})$$

5. Calculate meq $CaSO_4$ in 100 g soil using amount of soil measured in step 3 of procedure (*Y* g soil):

$$\text{meq } CaSO_4 \text{ in 100 g soil} = \text{meq } CaSO_4 \text{ in } X \text{ mL } H_2O\ (100 \text{ g soil}/Y \text{ g soil})$$

6. Calculate percent gypsum:

$$\text{percent gypsum} = \text{meq } CaSO_4 \text{ in 100 g soil } (0.0861)$$

Calculations for total soluble salts are the same as for gypsum with the exception of the equation. Calculate percent total soluble salts as:

$$\text{percent salts} = K(320)(10/Y \text{ g soil})$$

The quantity in parentheses accounts for dilutions different from the usual 1:5 if amount of soil added to 50 mL H_2O is not equal to 10 g.

ADDITIONAL REMARKS

Gypsum ($CaSO_4 \cdot 2H_2O$) occurs in a wide variety of soils with ustic, xeric, and aridic moisture regimes but is most common in aridic soils. Other forms of $CaSO_4$, namely anhydrite and hemihydrate, may be found in soils developed on deposits of saline lakes or marine evaporites, but unless the climate is extremely arid, these salts will hydrate to gypsum on exposure to the atmosphere. Determination of the presence and amount of gypsum in a soil is important for agricultural purposes and for accurate representation of the components of a soil. The apparent moisture factor used to convert air-dry soil weights to oven-dry (105 °C) soil weights will be too large for a gypsiferous soil because gypsum loses two water molecules from the crystal structure at 105 °C. An accurate measure of gypsum content is necessary in order to calculate the true oven-dry weight of soil (Nelson and others, 1978).

The conductivity method is a simple way of determining gypsum and total soluble salt content of soils. Two problems exist: (1) In soils which contain nongypsum $SO_4^=$ and $CaCO_3$, this method may measure the $CaSO_4$ formed in solution as original gypsum, and (2) conductance measured on calcareous soils will probably give values for total soluble salts greater than the true values because of the $CaCO_3$ in solution.

The major difficulty with the conductance method lies in dissolving the soil gypsum. The rate of solution is very slow for sand-sized gypsum crystals. Shaking longer than 30 minutes will help dissolution but carries the risk of dissolving more calcite or dolomite if they are present. Grinding the soil to a fine powder before adding water speeds dissolution, especially if gypsum is present in large, easily visible crystals. In such a case, however, the method of choice should probably be the crystal-water-loss method outlined next.

According to Bower and Huss (1948), other ions present in the soil will not seriously affect determination of gypsum by the conductivity method. Only potassium has any noticeable effect on measurements, and then only when its concentration in solution exceeds 10 meq/L—a rare occurrence in soil-water extracts. Comparison of the conductivity method to the standard SO_4 method shows good agreement. Conductivity measurements are reproducible to three significant figures.

Gypsum Determination by Crystal-Water Loss

By Marith Reheis,
U.S. Geological Survey

REFERENCE

Nelson and others, 1978.

PRINCIPLE

Determination of gypsum content in soil samples by crystal-water loss is an elegant method involving the principle that the crystal-water content of gypsum ($CaSO_4 \cdot 2H_2O$) is not lost when a sample is placed in a desiccator but is lost when the sample is heated to 105 °C. Heating at 105 °C converts gypsum to anhydrite ($CaSO_4$). The crystal-water content of gypsum is 20.91 percent in theory, but this number may not be attained in actual tests and should be determined for each laboratory location by tests on pure gypsum. This method is best for samples containing >4 percent gypsum.

EQUIPMENT

desiccator
oven
tared beakers, weighing jars, or similar equipment
analytical balance

REAGENTS

gypsum ($CaSO_4 \cdot 2H_2O$), reagent grade
dry silica gel

PROCEDURE

1. Place about 8 g of gypsiferous soil into a tared beaker (W_1) or other tared container and weigh to nearest milligram (W_2). Repeat with other samples and with about 4 g of reagent-grade gypsum.
2. Place beakers in a desiccator over silica gel and seal desiccator lid tightly. Dry over silica gel for at least 48 hours. Reweigh (W_3) the containers quickly, keeping only the one being weighed outside the desiccator.
3. Dry samples in a 105 °C oven for 24 hours. Transfer to the desiccator to cool to room temperature and weigh (W_4) a third time, being careful not to allow re-absorption of moisture.

CALCULATIONS

1. Determine crystal-water content of pure gypsum (Wc) and report to four decimal places:
$$Wc = (W_3 - W_4)/(W_3 - W_1)$$
2. Calculate air-dry (AD) to oven-dry (OD) ratio of soil sample and report to three decimal places:
$$\text{AD/OD} = (W_2 - W_1)/(W_4 - W_1)$$
3. Calculate percent gypsum on an oven-dry weight basis and report to one-tenth of a percent:
$$\text{gypsum percent} = (W_3 - W_4)(100)/(W_4 - W_1)(Wc)$$
4. Calculate percent gypsum on an oven-dry weight basis adjusted to equal a determination made by the standard SO_4 method and report to one-tenth of a percent:

$$\text{estimated gypsum percent, corrected to standard } SO_4 \text{ method} = \frac{(W_3 - W_4)(96.1) - 0.19}{(W_4 - W_1)(Wc)}$$

5. Adjust estimated percent gypsum for gypsum crystal water driven off during oven drying:

$$\text{estimated gypsum percent on oven dry + gypsum crystal water weight basis} = \frac{\text{estimated gypsum percent from step 4}}{1 + (\text{gypsum percent from step 3})(Wc/100)}$$

ADDITIONAL REMARKS

The crystal-water loss method is very economical in terms of laboratory equipment, chemicals, and human effort. Although the process takes several days to complete, actual work time is short. The method eliminates the problems of measuring nongypsum Ca^{++} and $SO_4^{=}$ and of getting gypsum into solution. The only major requirement is that all $CaSO_4$ be present as gypsum, not anhydrite or hemihydrate. This can be determined by obtaining X-ray diffraction patterns on whole soil samples ground to silt size. Nelson and others (1978) have calculated a standard error of estimate between the crystal-water-loss method and the standard SO_4 method of 1.8 percent.

Calcium and Magnesium Carbonates

By Michael Machette,
U.S. Geological Survey

REFERENCES

Dreimanis, 1962.
Association of Official Analytical Chemists, 1950.

PRINCIPLE

Soil samples containing calcium and (or) magnesium carbonates are oven dried and crushed to pass an 80-mesh sieve (0.18 mm), although crushing to pass a 200-mesh sieve (0.075 mm) will improve the precision of the analysis. The sample is placed in a flask, attached to the Chittick apparatus, and digested with 6 *N* hydrochloric acid. The evolved gas is collected under monitored conditions of temperature and pressure. Carbonate content is calculated from the volume of evolved gas (corrected to conditions of standard temperature and pressure), dry sample weight, and the molecular weight of the carbonate mineral being analyzed. Calcium and magnesium carbonates are differentiated by the rate at which they dissolve and generate gas. This analysis is modified from Dreimanis (1962) to accept variable sample weight and incorporates minor changes to improve the quality of the analyses.

EQUIPMENT

Chittick apparatus (see fig. 12):
- decomposition flask (A) with 2- or 3-hole stopper
- pipette, 25-mL size (B)
- stopcock (C)
- gas measuring tube, 200-mL capacity(D)
- leveling bulb (E)
- glass and tygon tubing
- mounting rack
- magnetic stirring apparatus (F)
- ring stand for magnetic stirrer (G)
- mortar and pestle
- mechanical sample splitter
- wash bottle for acid
- sieves (2 mm, 0.18 mm, 0.075 mm)
- desiccator
- vented oven, 110 °C
- analytical balance
- 11-19 extra flasks
- six magnetic stirring bars
- thermometer, Celsius
- barometer, millimeter type
- timer

REAGENTS

hydrochloric acid, 50 percent (approximately 6 *N* HCl)
methyl orange indicator. Dissolve 0.5 g indicator in 1L distilled water
displacement solution. Dissolve 100 g of sodium chloride or sodium sulfate decahydrate in 350 mL distilled water. Add about 1 g of sodium bicarbonate and 2 mL of methyl orange indicator. After the bicarbonate is dissolved, add sufficient dilute sulfuric acid to make the solution acid (definite pink color). The solution, used in the gas measuring tube and leveling bulb, seldom needs replacement. Occasional addition of distilled water to replace that which is lost by evaporation will prevent crystallization of salt.

PROCEDURE

Sample Preparation

1. To optimize the precision of the analysis, use an 80- or 200-mesh dry sample which will produce the maximum volume of the measuring burette (200 mL). Individual Chittick analyses require a maximum of 0.75 g for samples containing 100 percent carbonate and 7.5 g for samples containing 10 percent carbonate.
2. Label clean, dry decomposition flask (A) and weigh using an analytical balance with 0.001-g accuracy. Record this measurement as the tare weight.
3. Place sample into tared flask and dehydrate at 105 °C. Place flask in desiccator until it cools to room temperature. Record the new flask weight. The difference between this new weight and the tare weight is the sample weight (W).

Determination

Modified slightly from Chittick apparatus instructions and description by Dreimanis (1962).

1. Place a magnetic stirring bar in the flask with the sample and attach the flask to the Chittick apparatus (fig. 12). Make sure that seal is airtight by slightly wetting the rubber stopper.
2. Open stopcock (C) and, by means of the leveling bulb (E), bring the displacement solution in the gas measuring tube up to the −10-mL graduation mark, above the zero mark. (This 10 mL is equal in volume to that of the acid which is used to decompose the sample. If more acid is used (that is, with large samples), then the level of the displacement solution must be adjusted accordingly.)
3. Allow apparatus to stand 1–2 minutes so that the pressure within the apparatus equilibrates with that of the room. Measure room temperature and pressure at this time. Additional measurements are necessary only if conditions change during the course of the analyses.

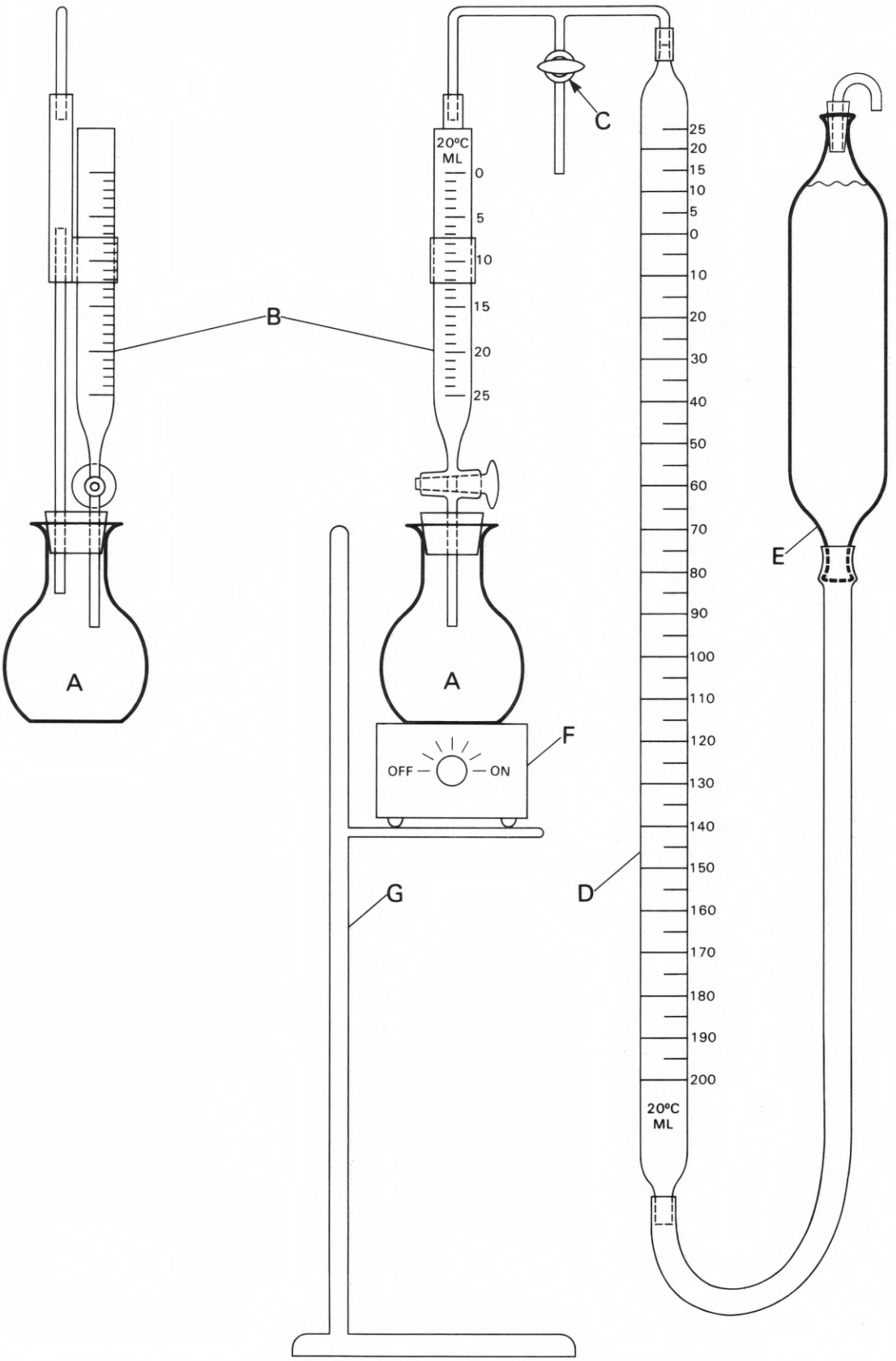

Figure 12. Chittick apparatus and accessory equipment used to analyze calcium and magnesium carbonates in soils (modified form Dreimanis, 1962). A, decomposition glass; B, pipette; C, stopcock; D, gas measuring tube; E, leveling bulb; F, magnetic stirring device; G, ring stand.

4. Turn on magnetic stirring device (F), thereby agitating the contents of the flask. Close stopcock (C) and lower the leveling bulb (E) several centimeters to reduce pressure in the apparatus. Fill the pipette (B) with acid and record its level. Open the pipette, slowly introducing acid into the decomposition flask (A). From this point on in the analysis, gas that is being liberated can escape up through the pipette or cause the displacement solution to overtop the leveling bulb. Thus, the gas measuring tube (D) must be kept at equal levels by progressively lowering the leveling bulb; some acid must be kept in the pipette. Close the pipette when 10 mL of acid have entered the flask. If you introduce too much acid, adjust the measure of final gas volume by subtracting the volume of excess acid.
5. Most of the calcite in soil samples will be dissolved within the first minute of the reaction, yet one should wait 5 minutes to read the final volume in the measuring tube, especially if the sample has not been ground to the 200-mesh size. During digestion of the $CaCO_3$ there may be a slight increase in the temperature within the flask. A good rule of thumb is to add 1 °C to the room temperature reading for each 50 mL of gas generated in excess of 50 mL. Such changes, usually 1-2 °C, can be measured with a thermometer inserted into the flask through a three-hole stopper. Dreimanis (1962, p. 521) recommends using the air temperature within the flask when calculating the gas volume at standard conditions of temperature and pressure.
6. If the sample volume of gas continues to increase during this interval, the sample may contain dolomite. In such cases, Dreimanis (1962, p. 521) recommends making both a first reading at 30 seconds to 1 minute, which is used to determine calcite content, and a second reading 15-45 minutes after beginning the analysis, which is used to determine dolomite content. Samples that contain dolomite should be crushed to pass a 200-mesh sieve.
7. When the reaction has stopped, open the stopcock, return the leveling bulb to the −10-mL level, and remove the flask with decomposed sample.

CALCULATIONS

The Chittick apparatus is designed primarily for determination of the volume of CO_2 evolved from carbonates reacting with acid. The operating procedures supplied by the manufacturer of the apparatus (Sargent-Welch Scientific Company) are written for the determinations from baking powder; nevertheless, the volume of CO_2 can easily be converted to calcite (A) or dolomite (B) content:

(A) Weight percent of $CaCO_3$ = weight percentage of CO_2 × 100.09/44.01, where 100.09 is the molecular weight of $CaCO_3$ and 44.01 is the molecular weight of CO_2.

(B) Weight percent of $CaMg(CO_3)_2$ = weight percentage of CO_2 × 144.40/88.02, where 144.40 is the molecular weight of $CaMg(CO_3)_2$ and 88.02 is the weight of two moles of CO_2.

1. For convenience, the records of the analyses are kept in tabular form from left to right: flask weight with sample, flask tare weight, sample weight (*W*, in grams), gas volume (*V*, in milliliters), temperature (in degree Celsius) and pressure (in millibars), correction factor (*Cf*) for standard temperature and pressure (see Association of Analytical Chemists, 1950, p. 821-875, for the correction factors), corrected volume (*Vc* in milliliters; $Vc = V \times Cf$), and percent calcium carbonate or magnesium carbonate.
2. The following calculations are for percent calcium carbonate; percent magnesium carbonate is calculated using the appropriate molecular weights. Percent $CaCO_3 = 1.7\ g/W \times (100.09/44.01) \times Cf \times (V/10)$; for example, $1.7\ g/4.0\ g \times (2.27) \times 0.90 \times (185/10) = 16.0$ percent
3. The correction factor (*Cf*) for the Chittick apparatus is based on a constant sample weight of 1.7 g; therefore, *W* (in grams) is used as a denominator to allow for variable sample weight. The constant value of 10, also an artifact of the Chittick apparatus, is used as a denominator of *Vc* to convert the resultant value into percent carbonate.
4. A simplified equation for percent $CaCO_3$ which incorporates the correction factor:

$$\text{percent } CaCO_3 = V/W \times \text{pressure (mm)}/(°C + 273) \times 0.16$$

ADDITIONAL REMARKS

Dreimanis (1962, p. 525) found that the probable errors (not exceeded in half the samples analyzed) for the results of the Chittick apparatus were ±30 percent of the calcite content and ±30 percent of the dolomite content. By modifying the procedure to accept variable sample weight and using sample weights which produce the maximum allowable volume of gas (200 mL), the probable errors can be reduced. Replicate analyses of seven splits from a variety of soil samples (low to high $CaCO_3$ content) and from reagent-grade calcite (100.0 percent $CaCO_3$), using the preparation and testing methods described above, are shown in figure 13.

The analyses of pure calcite have a standard deviation (*s*) of about 2 percent, which is attributable to the Chittick method itself. Analyses of soil samples have relatively higher standard deviations, which range from a low of 1.5 percent to a maximum of 3 percent of the reported mean value $\bar{X}$; (this is termed the coefficient of variability). The slightly higher error limits for soil samples are attributable to their natural inhomogeneity and to inadequacies of the splitting process. Still, on the basis of our tests, we would expect that two-thirds of analyses (the population within one standard deviation) of soil samples with 50 percent $CaCO_3$ would be accurate within ±1.0 percent $CaCO_3$

The method of analyzing calcium and magnesium carbonates using the Chittick analyses were found to have the following advantages (Dreimanis, 1962):

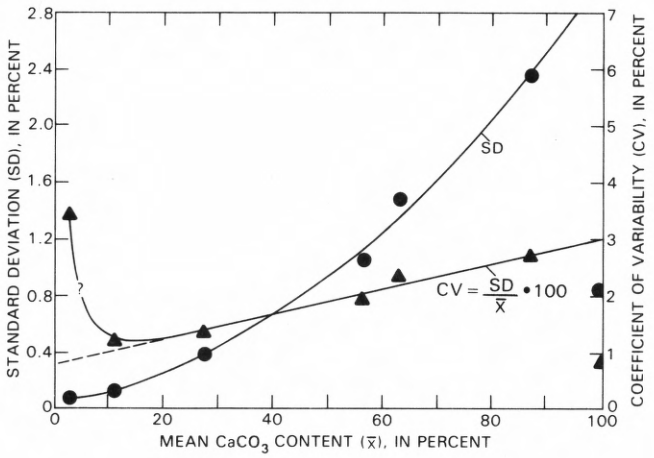

Figure 13. Replicate analyses of $CaCO_3$ content on calcareous soil samples and reagent-grade $CaCO_3$ (100.01 percent).

1. The procedure is simple, clean, and uses equipment that requires little space and is relatively inexpensive. The analyses can be done even in a field laboratory.
2. Preparation of the samples is similar to that of particle-size determinations and handling the apparatus requires only a few minutes per sample. When set up for production work, one analyst can perform as many as 30-40 analyses per day, thereby affording an inexpensive measure of soil carbonate content.
3. The precision and accuracy of the analyses are on a par with methods using atomic-absorption spectrometry, X-ray fluorescence, and colorimetric titration.

Carbonate coatings, which remain on gravel clasts after sieving, must be dissolved to determine their contribution to the total mass of soil $CaCO_3$. This process involves weighing oven-dry gravel, dissolving the coatings with 6*N* HCl, decanting the acidic solution, and washing the gravels free of any $CaCl_2$ (the residue from digestion of $CaCO_3$). The gravels are dried and reweighed; the net loss is the weight of $CaCO_3$ coatings on the gravel.

Total Carbon

By Michael J. Singer,
University of California, Davis

REFERENCE

Allison and others, 1965.

PRINCIPLE

Dry combustion of a ground soil sample in a high-temperature commercial furnace oxidizes all carbon containing compounds to CO_2. The CO_2 is swept from the sample in a stream of clean dry O_2. The CO_2 is absorbed, and the difference in weight prior to and after sample oxidation is used to calculate total C.

EQUIPMENT

commercial induction furnace and combustion train
sample crucible and lid
Nesbitt tower
stop watch
spatula
balance (analytical)
sample tray
aluminum foil

REAGENTS

oxygen in compressed gas cylinder
iron accelerator (commercial)
copper metal accelerator (commercial)
Ascarite
zinc metal (20 mesh)
MnO_2
catalyst tube
dehydrating agent

PROCEDURE

Place a 0.05-0.20-g <80-mesh soil sample (see chapter on "Sample Preparation") in the sample crucible. The amount of sample depends on the expected carbon content. Use a small amount for A horizons and larger amounts for B and C horizons. Weigh the soil to the nearest milligram.

Mix 0.5 g Cu metal accelerator with the soil. Place 4.0 g of iron accelerator on top of the soil and cover the crucible with a single-hole lid. Place the sample in a tray with numbered holes and cover the tray tightly with Al foil. As many as ten samples an hour can be run if everything works correctly, so prepare sufficient samples, blanks, and standards for the time available.

Turn on the induction furnace at least one-half hour before the first blank is to be run. Allow O_2 to sweep through the combustion train (fig. 14) for 10 minutes at 0.1 L/min. Remove and weigh the Nesbitt tower to ± 0.1 mg. Continue this until a constant weight is obtained. At this point, the apparatus is ready for samples and standards.

Routine operating conditions are a 1½-minute burn at 300-400 mA plate current and 30-60 mA grid current. After the burn, the system is purged with O_2 for 1½ minutes. Oxygen flow is increased for sample burns to 2 L/min. The Nesbitt tower valve must be closed when it is not connected to the combustion train. Plastic disposable gloves may be worn to reduce the problem of weighing fingerprints, or tongs may be used when weighing the Nesbitt tower.

CALCULATIONS

CO_2 weight = Nesbitt tower weight after burn − tower weight before burn

$$\text{percent C} = \frac{\text{weight } CO_2 \text{ sample} - \text{weight } CO_2 \text{ blank}}{\text{oven dry soil weight}} \times 0.2727 \times 100$$

Reproducibility of the analysis is fairly good with practice. Example data are shown in table 16.

Organic Carbon (Walkley-Black Method)

By Peter Janitzky,
University of California, Davis

REFERENCE

Allison, 1965.

PRINCIPLE

"Oxidizable matter in a soil sample is oxidized by $Cr_2O_7^{2-}$, and the reaction is facilitated by the heat generated when two volumes of H_2SO_4 are mixed with one volume of 1 *N* $K_2Cr_2O_7$-solution. The excess $Cr_2O_7^{2-}$ is determined by titration with standard $FeSO_4$ solution, and the quantity of substances oxidized is calculated from the amount of $Cr_2O_7^{2-}$ reduced." (Black and others, 1965, p. 1372).

EQUIPMENT

balance
magnetic stirrer with stirring bar (4 cm)
suction manifold (optional)
Repipete, 10 mL capacity, with dispenser (Labindustries) (optional)
automatic buret, 25 mL (optional)
suction flask, 500 mL
Buchner funnel, COORS No. 1
Erlenmeyer flasks, 500 mL (2)
Repipete (or repeating pipette "Tilt-A-Pet"), 20 mL (optional)
beaker, 100 mL
filter paper, Whatman No. 42, 5.5 cm
weighing scoop, brush, sampler spoon or spatula
volumetric pipettes may substitute for Repipetes, etc.

REAGENTS

Potassium dichromate, 1 *N* solution. Dissolve 49.04 g $K_2Cr_2O_7$ (dried at 105 °C) in H_2O, make to 1,000 mL. Store in Pyrex bottle, transfer some amount to a Repipete dispenser.

Ferrous sulfate, 0.5 *N* solution. Dissolve 140 g of $FeSO_4 \cdot 7H_2O$ in approximately 500 mL H_2O; add 15 mL concentrated H_2SO_4. Dilute to 1,000 mL, but leave solution in volumetric flask until room temperature is established (overnight), then make to exact volume. Store in Pyrex bottle with bottom outlet, connect to 25 mL-automatic buret.

Sulfuric acid, concentrated.

Ortho-phenanthroline-ferrous complex, 0.025 M solution. Dissolve 3.71 g of O-phenanthroline monohydrate and 1.74 g of $FeSO_4 \cdot 7H_2O$ in H_2O and dilute the solution to 250 mL. Store in plastic bottle.

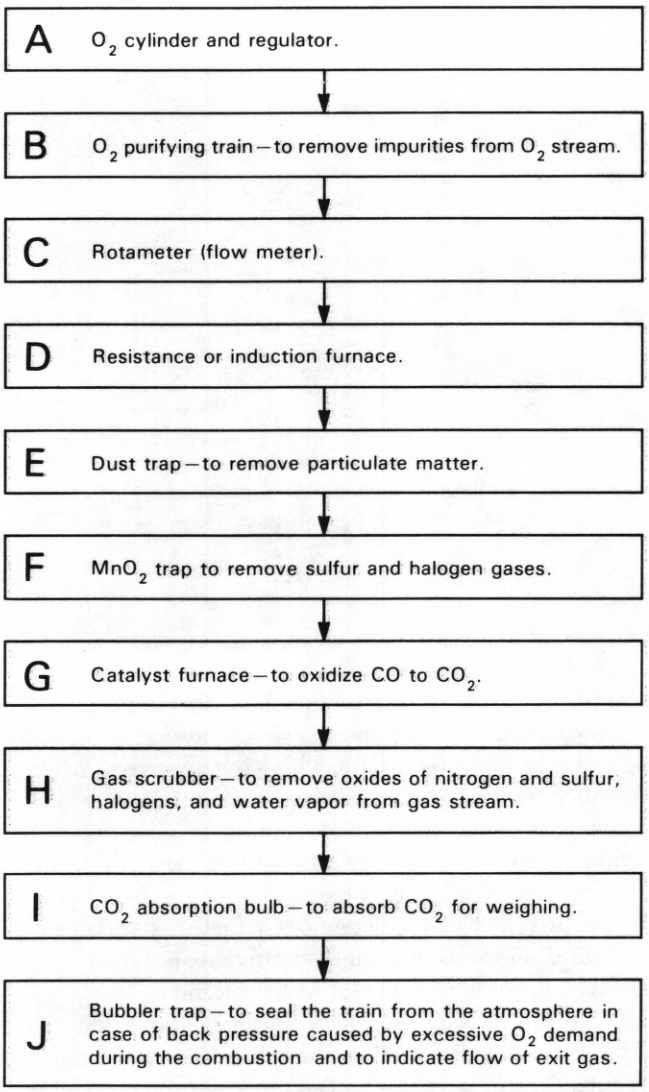

Figure 14. Flow chart of dry-combustion train (modified from Black and others, 1965, p. 1355).

PROCEDURE

Use soil ground to pass an 80-mesh sieve. For the sample, choose a weight depending upon the estimated organic matter content. For surface horizons of average mineral soils, 0.5-1.0 g may suffice. In the case of dark-colored surface material from forest soils use not more than 0.1-0.25 g. Samples of 1 g are usually sufficient for middle and lower

Table 16. Example of reproducibility of total carbon analyses by dry combustion

[Replicates are indicated by a and b. Samples are from Colorado chronosequences. $\bar{X}$, mean value for replicates; SD, standard deviation; CV, coefficient of variability in percent = SD divided by $\bar{X}$. Percent standard error estimated by average CV for samples from any chronosequence that had replicate determinations]

Sample description		Percent carbon
Profile-5, A horizon	a	12.08
	b	13.23
	$\bar{X}$	12.65
	SD	.81
	CV	6.43
Profile-6, A horizon	a	10.88
	b	11.09
	$\bar{X}$	10.98
	SD	1.08
	CV	9.80
Profile-3, A horizon	a	5.45
	b	6.05
	$\bar{X}$	5.75
	SD	.42
	CV	7.38
Percent standard error for n samples	$\bar{X}$	5
	n	9

parts of the profile. Transfer the weighed sample carefully to a 500-mL Erlenmeyer flask. Knock the walls of the flask gently to minimize adhesion of the material to the upper parts of the flask. At the same time, weigh out approximately 1.0 g of the material into a weighing bottle for moisture determination (dry overnight at 105 °C).

From a Repipette, add 10.0 mL potassium dichromate solution to the sample, swirl gently to disperse the soil in the solution. Add the same amount of solution to another 500-mL flask for the blank. Using a Repipette (or any other rapid dispensing device), rapidly add 20 mL of concentrated H_2SO_4, directing the stream into the suspension. Immediately swirl the flask for 1 minute, let cool on a heat-resistant surface for approximately 30 minutes, then add 200 mL H_2O. Treat the blank the same way.

Filter the suspension through a Buchner funnel, transferring it quantitatively to the 500-mL suction flask, taking care not to lose any of the liquid in the course of this operation.[1] Rinse walls of the funnel and soil pad 2-3 times with a few milliliters of H_2O to ensure complete recovery of dichromate ions from the suction flask.

Remove the funnel and discard the soil. Rinse the upper walls of the suction flask, add a stirring bar, and place the flask on a magnetic stirrer. (Place a filter paper disc under the flask for better observation of the end point.) Add 2-3 drops of O-phenanthroline-ferrous complex indicator, titrate the solution with 0.5 *N* ferrous sulfate from a 25-mL automatic buret (because of a gradual change of titer in the $FeSO_4$ solution by aging, flush the buret 2-3 times with solution from the dispensing bottle prior to titrating a set of samples). As the end point is approached, the solution takes on a greenish cast and then changes to dark blue green. At this point, add the ferrous sulfate drop by drop until the color changes sharply from blue to orange red (maroon color in reflected light).

Titrate the blank solution in the same manner.

[1]It is not essential to remove every sand grain from the Erlenmeyer flask, thereby unnecessarily diluting the leachate.

CALCULATIONS

$$N_{FeSO_4} = \frac{\text{mL } K_2Cr_2O_7 \times N\ K_2Cr_2O_7}{\text{mL } FeSO_4}$$

$$\text{meq } FeSO_4 = \text{mL } FeSO_4 \times N_{FeSO_4}$$

$$\text{organic C percent} = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4) \times 0.003 \times 100}{\text{grams oven-dry sample}} \times 1.33$$

$$= \frac{(10 - \text{meq } FeSO_4) \times 0.399}{\text{grams oven-dry sample}}$$

ADDITIONAL REMARKS

The commonly used correction factor 1.33 may be replaced by a more suitable value found experimentally. If more than 75 percent of the dichromate is reduced, repeat the procedure with a smaller sample. Filtration of the suspension prior to its titration greatly facilitates the discernment of the end point. However, this filtration may not be necessary in the case of small samples (as much as 0.25 g).

Reproducibility of the analysis is excellent, as is shown by data from a number of samples with a wide range of carbon contents (table 17). The analysis is rapid and is one of the best wet- chemical procedures available in the soils laboratory. Samples with large amounts of manganese or with carbonates may give erroneously high values. Consult the original reference for how to deal with these problems. We have found the method to be quicker and more reproducible than the dry-combustion method. In addition, no special equipment is necessary. Carbon content determined by the Walkley-Black method is compared with that determined by dry combustion in figure 15.

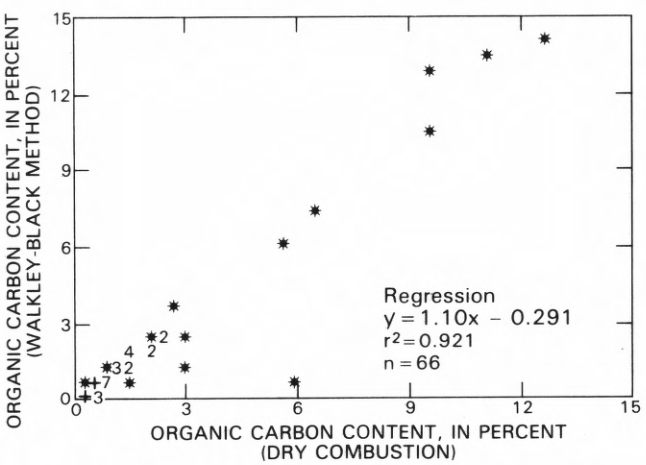

Figure 15. Correlation and regression for Walkley-Black and dry-combustion methods used to determine carbon content. Numbers indicate samples at that position. Regression statistics are for least-squares line. Samples are from all chronosequences of this study.

Table 17. Example of reproducibiliy of organic carbon analyses by the Walkley-Black procedure

[Replicates are indicated by a and b. $\bar{X}$, mean value for replicates; SD, standard deviation; CV, coefficient of variability in percent = SD divided by $\bar{X}$. Percent standard error estimated by average CV for samples from any chronosequence that had replicate determinations]

Sample description		Percent carbon
Colorado:		
Profile-5, A horizon	a	13.66
	b	14.03
	$\bar{X}$	13.84
	SD	.37
	CV	2.6
Profile-4, A horizon	a	7.24
	b	7.26
	$\bar{X}$	7.25
	SD	.01
	CV	.14
Profile-3, A1 horizon	a	5.82
	b	5.88
	$\bar{X}$	5.85
	SD	.05
	CV	.85
Dry Creek:		
North Merced No. 2, BA1 horizon	a	2.59
	b	2.60
	$\bar{X}$	2.6
	SD	.005
	CV	.19
Merced area		
Holocene No. 8, A1 horizon	a	2.27
	b	2.24
	$\bar{X}$	2.25
	SD	.02
	CV	.88
Modesto No. 31, A1 horizon	a	1.23
	b	1.23
	$\bar{X}$	1.23
	SD	0
	CV	0
Riverbank No. 9, A2 horizon	a	.29
	b	.28
	$\bar{X}$	.28
	SD	.005
	CV	1.7
Riverbank No. 9, C horizon	a	.03
	b	.03
	$\bar{X}$	.03
	SD	0
	CV	0
Percent standard error for n samples	$\bar{X}$	4
	n	7

Total Nitrogen

By Peter Janitzky,
University of California, Davis

REFERENCES

Bremner, 1965.
Association of Official Analytical Chemists, 1950.

PRINCIPLE

The nitrogen in the soil sample is converted to ammonium (NH_4^+ by digestion with concentrated sulfuric acid. This conversion is promoted by (1) an addition of potassium sulfate which raises the temperature of digestion, and (2) mercuric oxide acting as a catalyst in the oxidation of organic matter.

The ammonium in the digested sample is liberated as NH_3 by distillation with sodium hydroxide-sodium thiosulfate solution and collected in boric acid. Back-titration of the ammonium borate, with standard sulfuric acid, gives the amount of nitrogen released from the sample.

EQUIPMENT

analytical balance
micro-Kjeldahl digestion rack
distillation apparatus, as designed by F. E. Broadbent, Dept. of Land, Air and Water Resources, University of California, Davis (see fig. 16), or other appropriate distillation apparatus
microburet (Eppendorf), 2 mL (optional)
magnetic stirrer
29/12 weighing bottle with lid
volumetric flask, 1,000 mL
per sample and blank: two 100-mL micro-Kjeldahl digestion flasks, two 125-mL Erlenmeyer flasks
wire basket for the Kjeldahl flasks
volumetric pipette, 15 mL (or Repipette)
serological pipette, 10 mL (or 5-mL Repipette)
graduate cylinder, 25 mL.
weighing scoop and brush
glass beads

REAGENTS

1. Boric acid-indicator solution. Dissolve 20 g of H_3BO_3 in approximately 900 mL H_2O. Prepare a 0.2-percent solution of Methyl Red indicator and a 0.2-percent solution of Brom Cresol green indicator in ethanol. Make a mixture of the indicator solutions, using one part Methyl Red and five parts Brom Cresol green. Add 10 mL of this Mixture to the H_3BO_3 solution and make to 1,000 mL. Store in darkness.
2. Sodium hydroxide-sodium thiosulfate solution. Dissolve 500 g NaOH pellets and 50 g $Na_2S_2O_3 \cdot 5H_2O$ in water and make to 1,000 mL.
3. Potassium sulfate-mercuric oxide mixture. Grind and mix together 100 g K_2SO_4 and 5 g HgO, store in vial.
4. Sulfuric acid, 0.1000 *N*. Transfer ampule of standard "DILUT-IT" 1 *N* H_2SO_4 quantitatively to 1,000-mL volumetric flask and make to volume. Store in ground-glass stoppered reagent bottle.

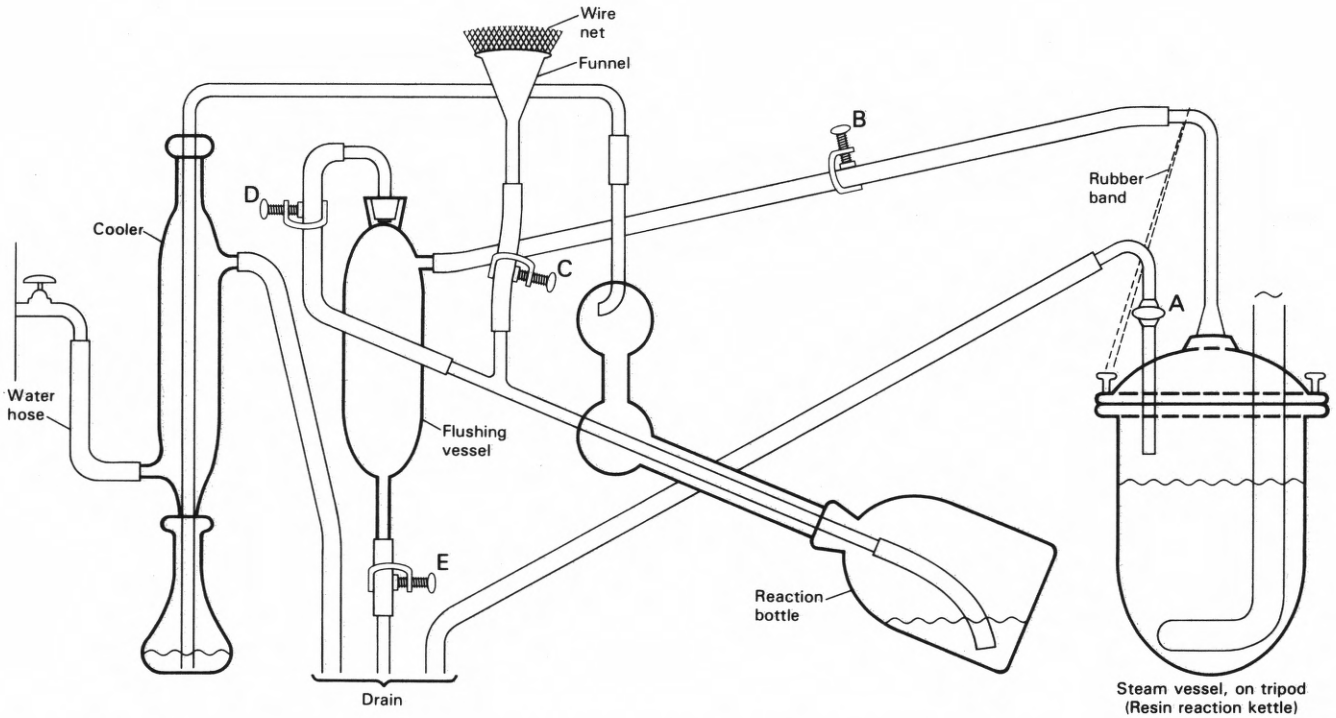

Figure 16. Nitrogen distillation apparatus designed by F. E. Broadbent. *A*, stopcock. *B-E*, clamps.

PROCEDURE

Place 3 g of <80 mesh soil in a weighing bottle and dry overnight at 105 °C. Cool in desiccator. Cover weighing bottle rapidly with a lid when opening the desiccator.

Mark two Kjeldahl flasks per sample with a permanent felt pen. Weigh 1 g dry soil on the analytical balance (to 0.1 mg) as fast as possible, transfer quantitatively to Kjeldahl flask. Add approximately 1.3 g K_2SO_4-HgO mixture (weighed on an ordinary balance). Add five glass beads, mix contents.

From a serological pipette or Repipette slowly add 5 mL concentrated H_2SO_4, washing soil and salt mixture down the walls of the flask.

Digestion

Set initial temperature on digesting rack at a low setting (about 1) as long as frothing of the sample occurs. Gradually raise to 3-4. Digest for approximately 1-2 hours, until color of contents becomes uniformly white or light-green.

Turn off power, let flasks cool on the rack. Then place them in the wire basket. Slowly add 15 mL H_2O rinsing the walls. Mix, let cool.

DISTILLATION (fig. 16)

Pipette 15 mL boric acid indicator solution with volumetric pipette or Repipette into 125-mL Erlenmeyer flasks.

Fill steam vessel of distillation apparatus to two-thirds with distilled H_2O. Open stopcock *A*, remove clamps *B* and *C*. Close clamps *D* and *E*. Turn on power (regulator setting approximately 100). Turn on water for cooler. Bring water in vessel to boil.

Carefully transfer contents of Kjeldahl flask with several small rinsings to funnel fitted with a piece of wire net to catch the glass beads (save these for further runs). Rinse wire net with a few milliliters H_2O from wash bottle. Remove the net, rinse funnel.

Add 20 mL NaOH-$Na_2S_2O_3$ solution from a graduated cylinder. Rinse funnel. Without delay set clamp *C*, remove clamp *D*, and close stopcock *A*. Immediately place the Erlenmeyer flask containing the H_3BO_3 solution under the cooler, so that the outlet of the cooler is slightly submerged below the level of the solution.

Collect approximately 40-45 mL distillate (solution turns blue after distillation of NH_3 has begun). Rinse outlet, remove the flask, stopper, and store in darkness until titration.

Flush out soil suspension from bottle by opening stopcock *A* and simultaneously closing clamp *B*. When most suspension has collected in the flushing vessel, open clamp *E*. Let drain, close clamp *E*, remove clamps *B* and *C*, set clamp *D*. Place wire net on funnel. Apparatus is ready for the next sample. After finishing the last sample, turn off power and water for cooler, remove all clamps and rubber band.

Titration

Pour approximately 20-30 mL of standard H_2SO_4 from storage bottle into a 50-mL Erlenmeyer flask. Keep it stoppered between sample titrations. Fill the micro-buret from this flask, adjust to full volume (bubble free).

Place the Erlenmeyer flask containing the distillate on a magnetic stirrer, set a light source (desk lamp) nearby. Add H_2SO_4 slowly, keeping tip of buret submerged.

Titrate to a straight pink end point.

Carry two blanks (1.3 g salt mixture, five glass beads, 5 mL concentrated H_2SO_4) through the digesting and distilling procedure.

CALCULATION

$$\text{percent } N = \frac{(\text{mL } H_2SO_4 \text{ sample} - \text{mL } H_2SO_4 \text{ blank}) \times N_{H_2SO_4} \times 1.4}{\text{sample weight in grams}}$$

Citrate-Bicarbonate-Dithionite (CBD) Extractable Iron and Aluminum

By Peter Janitzky,
University of California, Davis

REFERENCES

Jackson, 1958, 1969.

PRINCIPLE

Amorphous, organic, and various crystalline oxides of iron and aluminum are solubilized and chelated by digestion of the soil with a solution of sodium citrate buffered with sodium bicarbonate at pH 7.3. Sodium dithionite added to the hot suspension effects a reduction of the iron and aluminum in solution. After flocculating the soil with sodium chloride and centrifuging the suspension, a clear supernatant is obtained. A second digestion and two subsequent washings with citrate solution complete the extraction. All supernatants are collected in a volumetric flask and made to volume.

Although requiring some additional steps in the procedure, a separation of iron and aluminum from the bulk of salts present in the extracting solution appears advantageous for two reasons. First, in cases where large numbers of samples are involved, the extracts can be stored for a much longer period prior to analysis without the risk of changes in the solutions. Second, the high salt content of the solutions is not very suitable for aspiration in the atomic absorption spectrophotometer. Regular burners clog, which necessitates lengthy shutdown periods for cleaning.

EQUIPMENT (for sample groups of eight)

centrifuge
hotplate (2, if possible)
20-mL Repipette ("Tilt-A-Pet") (optional)
5-mL Repipette ("Tilt-A-Pet") (optional)
600-mL beakers (3)
stopwatch
thermometer
spatula
100-mL beaker
100-mL centrifuge tubes (9) with rack
stirring rods with rubber policemen (8), 25 cm long
10-mL serological pipette
500-mL volumetric flasks (8)
washbottles (3)
stirring rod with plunger (rounded rubber stopper), 25 cm long
250-mL beakers with watchglasses (8)
25-mL volumetric pipette
25-mL graduated cylinder
rubber gloves
40-mL conical centrifuge tubes (8) with rack
dropper bottles (2)
air-jet (a 10-cm glass tube of 3-mm diameter, one end of which is drawn out to a narrow tip, the other end connected with polyethylene tubing to an air-pressure line)
25-mL volumetric flasks (8)
glass funnels, 8-cm diameter (8)
filter paper, folded, Whatman #2^V, 12.5 cm
filter rack
plastic bottles

REAGENTS

Sodium citrate ($Na_3C_6H_5O_7 \cdot 2\ H_2O$), 0.3 *M* solution (88 grams per liter). At least 1,300 mL are needed for the extraction of eight samples.

Sodium bicarbonate ($NaHCO_3$), 1 *M* (84 g/L).

Sodium dithionite ($Na_2S_2O_4$), powder. For convenient handling during the procedure, transfer some amount to a 100 mL beaker, crush any lumps with sampler spoon. Keep storage jar tightly closed.

Sodium chloride (NaCl), saturated solution. Prepare approximately 500 mL, transfer one half of it into a 250-mL wash bottle.

Nitric acid (HNO_3), concentrated

Ammonium hydroxide (NH_4OH), diluted solution (approximately 1:5) (dropper bottle).

Ammonium hydroxide (NH_4OH), concentrated (dropper bottle).

Brom Cresol Purple indicator (mix 0.1 g of the dry powder in a mortar with 18.5 mL 0.01 *N* NaOH, dilute to 250 mL with distilled H_2O.

Ammonium chloride (NH_4Cl), 1 percent solution. Fill a 500-mL wash bottle.
Hydrochloric acid (HCl), 6 *N*.
Hydrochloric acid (HCl), 1 *N*.

PROCEDURE

Extraction

Place 4.00-g soil samples, ground to pass an 80-mesh sieve, into eight 100-mL centrifuge tubes. Add to each 40 mL sodium citrate and 5 mL sodium bicarbonate from 20-mL and 5-mL Repipettes, respectively. Mix suspensions with glass rods + rubber policemen, leave rods in the tubes.

Place the eight tubes in two 600-mL beakers (four in each). Fill the beakers with distilled water slightly above the level of the suspensions in the tubes. A third beaker, containing a centrifuge tube with a thermometer and approximately 50 mL water, is filled with water in an analogous way.

Place all three beakers on a hotplate that has been calibrated for a maximum temperature of 75 °C.

When the temperature has reached 70-75 °C, add about 1 g sodium dithionite powder to the first sample with a spatula, stir for 1 minute (stopwatch), and continue with the next sample in a similar manner. Do not allow the temperature to exceed 80 °C. A second addition of dithionite is made as soon as the last (eighth) sample has been treated. With intermittent stirrings, remove the tubes from the beakers after a minimum of 15 minutes digestion time.

Add to each sample 5 mL of saturated NaCl solution (serological pipette), stir the suspension and remove the stirring rod, rinsing it with saturated NaCl solution from a washbottle.

Centrifuge samples at 1,600-1,800 rpm for 5 minutes, or until a clear supernatant is obtained. Collect solutions in 500-mL volumetric flasks. Repeat the digestion procedure in an identical manner.

After collection of the second extract, add to each tube 40 mL of sodium citrate and 5 mL saturated NaCl solution. Stir with a plunger. Rinse the plunger with NaCl solution from a washbottle. Centrifuge.

Centrifuging the samples at this stage may occasionally take longer to settle the suspension than was required in previous steps. The organic matter content appears to influence the suspension. Samples from lower horizons usually need the least centrifuging time. Collect supernatants in volumetric flasks and wash samples with citrate and NaCl a second time. Make solutions to volume with distilled water.

Jackson (1969) recommends one extraction with two washings for all samples with less than 5 percent iron and two extractions each with two washings for samples with more than 5 percent iron. We tested the method using one soil with moderate and one soil with high iron content (table 18). There was a small increase in iron recovered with two digestions compared to one for soil sample 703. The number of washings did not change the iron recovery appreciably. There was considerable increase in iron recovered with two digestions compared to one for soil sample 705. It appears that two digestions followed by two washings is an efficient and thorough procedure. Fewer extractions or washings may not fully recover iron, while more than two adds additional time to the procedure without significantly improving recovery.

Table 18. Citrate-bicarbonate-dithionite (CBD) iron and aluminum extraction tests using two soil samples from the Santa Cruz chronosequence

[All samples were 4 g. Sample 703 is a BA2 horizon and 707 is a 2BC2 horizon from profile 1]

Sample	Digestions (number)	Washings (number)	Fe (percent)	Al (percent)
703	1	1	1.58	0.32
	1	2	1.59	.32
	1	3	1.59	.32
	2	1	1.64	.34
	2	2	1.60	.35
	2	3	1.60	.34
	3	1	1.64	.36
	3	2	1.64	.36
705	1	1	4.29	.43
	1	2	4.33	.43
	1	3	4.40	.45
	2	1	4.44	.46
	2	2	4.51	.47
	2	3	4.40	.47
	3	1	4.48	.48
	3	2	4.40	.35

Aluminum concentration appeared to increase slightly with each additional extraction. Additional washings did not appreciably increase the Al recovery.

Place 25 mL aliquots (volumetric pipette) of the extracts into 250-mL beakers and evaporate to dryness. To avoid spattering, reduce heat of the hotplate to about 40 °C and cover the beakers with watchglasses during the evaporation of the last 5-10 mL of solution.

Increase the temperature of the hotplate to 80-100 °C For each sample fill a 25-mL graduated cylinder with 15-mL concentrated HNO_3 (use rubber gloves), lift the watchglass from the beaker, add the acid and rapidly return the watchglass to the beaker. This is a violent reaction, work should be done in a fume hood. Evaporate the liquid until there are about 5-10 mL of acid left. Decrease heat. After all frothing has subsided, uncover beakers halfway, and let solutions evaporate to dryness. Treat the samples on the hotplate two or three times with 5-mL portions of H_2O_2 in order to achieve a complete destruction of any citrate still present after the treatment with HNO_3. Minute amounts of citrate ions will prevent the precipitation of iron and aluminum in the subsequent step of NH_4OH separation described below.

After the final evaporation, rinse watchglasses and inner walls of the beakers with a few milliliters of 1 *N* HCl from washbottle, leave beakers uncovered on the hotplate for approximately 1 minute until the salt crust has dissolved, then remove from hotplate and let cool. Quantitatively transfer the solutions with water to 40-mL conical centrifuge tubes. Make to volume of about 35 mL. Add three drops of Brom Cresol Purple indicator, insert air-jet adjusted to moderate bubbling,

and add concentrated NH_4OH dropwise from a dropper bottle until the solution begins to become cloudy, indicating the precipitation of iron and aluminum. Now add diluted NH_4OH (1:5) dropwise, and stop addition of the base as soon as the yellowish color of the suspension sharply darkens to a brownish tone. The liquid turns purple upon standing, while the orange-brown and colorless precipitates of iron and aluminum slowly settle to the bottom of the tube.

Centrifuge the samples for 3 minutes at 1,500 rpm and discard the supernatants. Wash precipitates once with 1 percent NH_4Cl by directing a stream of the solution from a washbottle into the material at the bottom of the tubes. Also rinse the tube walls, bringing the volume to approximately 30-mL. Centrifuge and discard supernatant.

Dissolve precipitates by adding to each 3-mL 6 *N* HCl. After dissolution, which takes approximately 10-15 minutes, transfer solutions carefully (small funnel) to 25-mL volumetric flasks, and make to volume. In order to eliminate possible cloudiness due to presence of Si, filter solutions through fluted filter paper (Whatman #2^V, 12.5 cm) into 50-mL plastic storage bottles.

EQUIPMENT

atomic absorption spectrophotometer
micropipettes (Eppendorf): 1 mL and 0.5 mL, with disposable tips (optional)
analytical balance
volumetric flasks: 1,000 mL (1), 100 mL (1), and a sufficient supply of 50-mL and 25-mL sizes
volumetric pipettes: 50-mL (1), 15-mL (1), 10-mL (1), 5-mL (1)
plastic bottle, 1,000 mL

REAGENTS

analytical iron wire
analytical aluminum wire or sheet
hydrochloric acid (HCl), 6 *N*
lanthanum-cesium solution (preparation see under "Cation Exchange Capacity").

PREPARATION OF STANDARDS

Weigh out 1.000 g iron wire and 1.000 g aluminum wire, place in 1,000-mL volumetric flask, dissolve in 80-mL 6 *N* HCl. Make to volume with distilled H_2O, transfer to a 1,000-mL plastic bottle, and mark "1,000 ppm Fe + Al." Using volumetric and micropipettes, prepare standard solutions as follows:

For iron:

Stock 1 (ppm)	Aliquot (mL)	Make to (mL)	Stock 2 (ppm)	Aliquot (mL)	Volumetric (mL)	Standard (ppm)
1,000	10	100	100	1	100	1.0
			100	5	100	5.0

For aluminum:

Stock 2 (ppm)	Aliquot (mL)	Volumetric (mL)	Standard (ppm)
100	10	100	10.0
100	50	100	50.0

To each standard add 10-mL La-Cs solution and bring to volume.

Prepare a blank by adding 10-mL La-Cs solution to a 100-mL volumetric flask and bringing to volume.

SAMPLES

The general relationship between the concentration of Fe or Al in the extract (in parts per million) and the percentage of Fe or Al in the soil is expressed by the formula:

$$\text{percent Fe or Al in the soil} = \frac{\text{ppm} \times \text{dilution} \times 50}{\text{weight of soil} \times 1{,}000}$$

Because the standard curve for Fe is linear for as much as 5 ppm, dilutions of the extracts ranging from 1:25 to 1:100 are required in most cases. Using 4-g samples, this corresponds to the following amounts of iron in soil: A 1:25 dilution places samples of up to 1.5 percent Fe within the linear range of the standard curve, dilutions of 1:50 and 1:100 place those of up to 3.1 percent and 6.25 percent respectively, within the linear range.

Because concentrations of CBD extractable aluminum are generally small, rarely reaching 0.5 percent in the samples, aliquots of the extracts should be as large as feasible. 15-mL aliquots taken from the 25-mL extracts and made to volume in 25-mL volumetric flasks usually give results that are well within the analytical range.

Before bringing the aliquots of the samples to volume, add La-Cs solution at a ratio of 1:10 of the final volume.

ADDITIONAL REMARKS

Removal of organic matter from the soil samples by treating them with H_2O_2 prior to the CBD-extraction procedure does not seem to significantly change the results of the analysis as indicated in table 19. Pretreatment of A horizons with H_2O_2 before CBD reduces centrifuging time and is recommended.

Table 19. Effect of organic matter removal upon the amount of iron determined

Sample	Percent Fe in soil	
	H_2O_2 pretreated	Not pretreated
Lab standard (Reiff Series)	1.45	1.45
Merced PM 16, (0-2 cm)	1.42	1.43
Merced PM 16, 2C20x (25-35 cm)	1.63	1.63

Harden (fig. 17) tested the effect of grinding on the percent of iron extracted by CBD. She found there was no significant difference in Fe between the treatment groups at the 5 percent level.

The average percent standard error (of estimate) for dithionite iron is 2 percent, as determined by replicate analysis of seven samples.

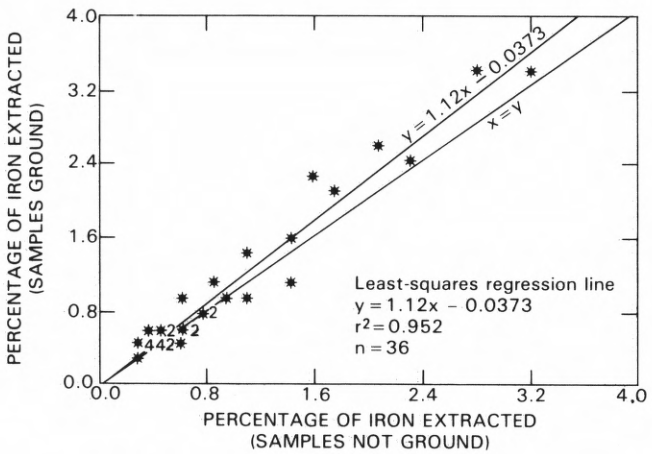

Figure 17. Percent Fe extracted by citrate-bicarbonate-dithionite (CBD) for 36 ground versus unground samples from the Merced chronosequence (Harden, 1982a). Numbers indicate samples at that position.

Oxalate-Extractable Iron and Aluminum

By Ann Walker,
U.S. Geological Survey

REFERENCE

McKeague and Day, 1966.

PRINCIPLE

Extraction of soils by acidified ammonium oxalate provides a measure of a more chemically active form of iron (Schwertmann, 1973), as compared to the dithionite extraction. More specifically, the oxalate reagent, which is acid (pH 3) and a strong chelating agent, extracts X-ray amorphous hydrous oxides of iron such as grain coatings and stains, as well as organically bound iron and microcrystalline ferrihydrite. In comparison, the dithionite reagent is believed to extract these forms of iron oxides plus the "less chemically active" forms such as hematite and goethite. Oxalate-extractable forms of aluminum include organically bound and X-ray amorphous Al (McKeague and others, 1971).

Two aspects of the oxalate extraction merit special attention. First, Arshad and others (1972) showed that the oxalate solution extracts iron from primary dioctahedral and trioctahedral minerals, especially magnetite. In accordance with Arshad and others (1972), Walker (1983) tested soils developed on the Merced Formation of this project and demonstrated that magnetite was dissolved by oxalate but not dithionite solutions. She concluded that in order to measure pedogenic forms of iron with the oxalate treatment, one must first remove magnetite from the samples, especially if the parent materials are rich in this mineral.

In contrast, Walker (1983) recommended not removing magnetite for dithionite treatment because pedogenic Fe such as hematite, goethite, and amorphous grain coatings readily form in and around the magnetite grains. Although the removal of magnetite may be necessary for the oxalate procedure, there are distinct disadvantages to this pretreatment. The ratio of oxalate- to dithionite-extractable iron (Alexander, 1974) and the difference between the extractable amounts of iron become much less useful as pedogenic indices because the two extraction methods are applied to samples of very different pretreatments.

The second aspect is that of grinding soil samples before sample extraction. This project generally grinds samples to 80-mesh for organic carbon and iron oxide analyses, although Walker (1983) ground samples to pass a 100-mesh sieve for the oxalate procedure. Sample grinding increases the efficiency of extraction and ensures that small samples are representative of the <2-mm sample. As Arshad and others (1972) demonstrated, however, grinding (especially to sizes finer than about 20 μm) also increases the possibilities of exposing trioctahedral minerals to the oxalate solution. For the oxalate pretreatment, it is important to grind only those grains coarser than 80- or 100-mesh and to grind only as long as is needed to pass the sample through the sieve. This can be accomplished by frequently sieving the sample during grinding.

EQUIPMENT

hotplate
sample shaker
V-shaped Nalgene centrifuge tubes
centrifuge
marker tape or pens
aluminum foil
volumetric pipettes
30-mL beaker
50-mL conical flasks
50-mL volumetric flasks
opaque storage (dark Nalgene) bottles
wash bottle
analytical balance

REAGENTS

0.2 *M* acidified NH_4-oxalate. Dissolve 7.10 g ammonium oxalate in distilled water and bring to volume in a 250-mL volumetric flask. Adjust the pH to 3.0 with a saturated solution of oxalic acid. This will take about 50-mL. Store in dark Nalgene bottle.

10,000 ppm K. Add 9.59 g KCl in distilled water and bring to volume in a 500-mL volumetric flask. Store in Nalgene bottle.

100 ppm Al standard. Dissolve 0.100 g granular Al (purified) in 15-mL 6 *N* HCl. Bring to volume in a 1-L volumetric flask with distilled water. Store in Nalgene bottle.

100 ppm Fe standard. Dissolve 0.100g Fe wire in 15-mL 6 *N* HCl. Bring to volume in a 1 L volumetric flask with distilled water. Store in Nalgene bottle.

concentrated HNO_3.

Standard Preparation

1. Pipette 0, 0.5, 1.0, 1.5, 2.0, 2.5 mL of 100-ppm Fe (0, 1, 2, 5, 8, 10-mL Al of 100-ppm Al) into 100-mL volumetric flasks.
2. Pipette 10 mL 0.2 *M* acidified NH_4-oxalate into each flask.
3. Add 8 drops concentrated H_2SO_4 and 1.0 mL concentrated HNO_3.
4. Pipette 10 mL 10,000 ppm K into each.
5. Bring to volume with distilled water and mix thoroughly.

Store in Nalgene bottles. Use the clear 125-mL bottles for the zero ppm standards and the standards to be used for calibration (Fe_o 1.5, Fe_d 1.5, Al_o 5.0, Al_d 1.0). The remaining standards can be stored in dark bottles. Mix standards thoroughly before pouring them from the flask into the bottle. Discard unneeded samples.

PROCEDURE

1. Place 0.50 ± 0.0020 g air-dried soil (ground to pass a 100-mesh sieve) in a V-shaped 15-mL Nalgene centrifuge tube. Keep stoppers in order and never mix them. Number the tubes.
2. Add 10 mL 0.2 *M* acidified NH_4-oxalate to each tube, stopper tightly. Wrap the tubes (three at a time) in aluminum foil as soon as possible and secure them with a rubber band. Groups of three are used because this number conveniently fits the centrifuge carriers. Be sure and mark the tops of the tubes or you could centrifuge them upside down! Twist tops on for best fit. Note the time.
3. Place the tubes horizontally on the shaker for 4 hours at the low setting. Rubberband the tubes together and place between plastic bottles on shaker.
4. After shaking, the samples are centrifuged (still in the foil) at 2,500 rpm for 15 minutes and decanted into a 30-mL beaker. As you uncork the centrifuge tubes, there may be some soil stuck against the cork. Try to remove it by side pressure with the cork as you uncork the tube. If some soil still remains, remove it with your finger.
5. Place a 5-mL aliquot into a 50-mL conical flask. Put the extra from the beaker in the appropriate waste beaker.
6. Into each solution add 4 drops concentrated H_2SO_4 and 0.5 mL or 22 drops of concentrated HNO_3. Place the flasks on an approximately 275 °F hotplate to digest for 30-60 minutes. Ideally the solution will be clear or light yellow at this point. About half way through the digestion, add three more drops of HNO_3 to all samples. The color should disappear, but it may not, a longer digestion time will be necessary. Fe-rich samples will start out darkest.
7. Dissolve any precipitate with a few drops of hot distilled water. Take the samples off the hotplate and let cool.
8. Transfer the solution quantitatively to a 50-mL volumetric flask with a funnel and wash into flask with distilled water. Wash with distilled water about three times.
9. Add 5 mL of 10,000-ppm K via pipette to the solution.
10. Bring to volume with distilled water.
11. Transfer the solution to a 690-mL dark bottle and store in the refrigerator until ready to run on the atomic absorption spectrophotometer.

ADDITIONAL REMARKS

The average standard error (of estimate) is 24 percent, as determined from replicate analysis of 13 samples.

Removal of the Magnetic Fraction

By Peter Janitzky,
University of California, Davis

PRINCIPLE

A finely crushed sample is exposed to a magnet. Magnetic particles attach themselves to the magnet from which they are collected and weighed.

EQUIPMENT

analytical balance

magnetic stirrer with a light-colored top (otherwise attach a sheet of paper)

stirring bar (teflon), 5 cm long, 1 cm diameter, attached to an approximately 5-cm-long piece of soft rubber tubing

glass plate, approximately 30 x 20 cm.

tongs, stainless steel
crucible, porcelain or glass, 4 cm tall, 4.5 cm diameter
weigh boat, polystyrene, disposable, 43 mm
small artist's paint brush, camel's hair, round tip, size 3-5

PROCEDURE

Weigh 1.000-5.000 g of soil sample ground to pass an 80-mesh sieve into a weigh boat tared to the fourth place. Transfer the sample quantitatively into a crucible. Holding a magnetic stirring bar by the rubber tube attached to it as indicated under "Equipment," thoroughly stir the sample to insure close contact between the magnet and the soil. Magnetic particles will attach themselves to the bar around its tip. As they also carry along some soil particles, knock the bar against the inner walls of the crucible a few times to remove excess soil from the magnetic material. This need not be quantitative at this stage.

Position a clean glass plate over a magnetic stirrer such that its right half will be located over the stirrer center. Gently rub the stirring bar with the stainless steel tongs until it appears clean. Carefully tap the material adhering to the tongs on the glass plate near its right edge. Repeat the procedure until no more visible accumulation of particles (blackening) occurs on the stirring bar.

Turn on the magnetic stirrer. Slowly increase the stirrer power to a medium setting. The magnetic particles on the plate will separate from the soil and migrate toward a spot above the center of the stirrer. Gently stir the remaining soil with a camel's hair brush while slowly moving the glass plate to the right. Let particles collect to a whirl. Carefully stir it with the brush and move the plate farther while brushing together any visible "outsiders" circling on more distant courses. By now the material should be free of any adhering soil. When the whirl has come within approximately 5 cm of the left edge of the glass plate, turn off the stirrer and remove the plate (vertically away from the stirrer at first). Brush material carefully into the original weighing boat. Record the weight and calculate the percentage of magnetic material.

The sample left in the crucible can be saved for other analyses or discarded.

Quite small weights of magnetic materials can be removed quantitatively from soil samples as shown in table 20.

Table 20. Results of removing magnetic materials from several soils by exposing them to a magnet

Chronosequence	Sample No. and horizon	Soil (g)	Magnetic materials (g)	(percent)
Honcut Creek	HOS-5, Bt2	2.5530	0.0012	0.05
Honcut Creek	HOS-10, C1	2.3595	.0267	1.13
Honcut Creek	HOS-10, 2C2	2.4588	.0071	.29
Merced	PM 14, 4C3ox	3.9273	.0012	.03
Merced	PM 15, A	1.1948	.0086	.72
Merced	R 32, A2	3.8659	.0578	1.49

Total Phosphorus (Extraction)

By Richard Meixner,
University of California, Davis

REFERENCE

Lambert, 1976.

PRINCIPLE

The sample is thoroughly oxidized at high temperature, and the phosphorus is extracted with hydrochloric acid. The phosphorus is analyzed colorimetrically.

EQUIPMENT

muffle furnace capable of 550 °C temperature
analytical balance
spatula
50-mL beaker
watch glass
hotplate
100-mL Nalgene centrifuge tube and cap
centrifuge capable of 2,000 rpm
sample bottles and caps

REAGENTS

concentrated HCl (12 *N*)
distilled water

PROCEDURE

Carefully weigh 1.000 g of 80-mesh soil into a labeled beaker. Use a label which will not be destroyed at 550 °C. Place the beaker with sample into the muffle furnace at 550 °C for 4 hours. Remove the beaker and allow to cool. When it is cool to the touch, add 10 mL of concentrated HCl, cover with a watch glass, and heat to just below the boiling point on the hotplate for 4 hours. Do not allow the solution to lose more than one-half its original volume. After 4 hours cool and quantitatively transfer the entire contents of the beaker to a labeled 100-mL Nalgene centrifuge tube which has been previously calibrated for a 50-mL volume. Add distilled water to the 50-mL mark. Cap, shake, and centrifuge the sample at 1,800-2,000 rpm for 5 minutes. Decant the solution into a labeled bottle and save for analysis.

Phosphorus is analyzed using an ammonium molybdate colorimetric procedure which is described in the "Phosphorus Analysis" section.

CALCULATIONS

The final volume of the extracting solution is 50 mL minus the volume of the 1-g sample. Assuming a specific

gravity of 2.6-2.7, the sample volume is approximately 0.4 cm^3. The absorbance reading on the colorimeter or spectrophotometer is converted to concentration by use of a standard curve and corrected for volume of extracting solution and weight of soil.

$$\text{concentration in aliquot} \times \text{any dilution factor} \times \frac{\text{extraction volume}}{\text{weight of sample}} = \text{P in } \mu g/g$$

$$\mu g/mL \times \frac{mL}{mL} \times \frac{mL}{g} = \frac{\mu g}{g}$$

Phosphorus Fractionation (Extraction)

By Richard Meixner,
University of California, Davis

REFERENCES

Williams, and Walker, 1969.
Williams, and others, 1967.

PRINCIPLE

Inorganic phosphate is found in various forms in soils. The classification of these different forms has evolved over the years. This extraction procedure uses the nomenclature of Williams and Walker (1969). The first extraction removes "easily soluble" forms of P or non-occluded P. The following extractants sequentially remove the more tightly held forms of P including that which is held by Fe, Al, or Ca. Some P is trapped (occluded) within other minerals. This is also extracted with this method.

EQUIPMENT

muffle furnace
hotplate
reciprocating shaker
analytical balance
spatula
stirring rods
100-mL Nalgene centrifuge tube with cap
wash bottle
100-mL graduated cylinder
volumetric flasks
500- or 1,000-mL reagent storage bottles with caps
50-mL plastic sample storage bottle with cap
50-mL Pyrex beaker
watch glass
500-mL beaker

REAGENTS

0.5 *M* NH_4Cl
0.5 *M* NH_4F pH 8.2
0.1 *N* NaOH
1.0 *N* NaOH
citrate-bicarbonate (0.3 *M* sodium citrate, 1 *M* $NaHCO_3$)
$Na_2S_2O_4$ powder (dithionite)
0.5 *N* HCl
1.0 *N* HCl
12.0 *N* HCl
80-mesh soil
4.0 *N* NH_4OH
NaCl-saturated solution
36 *N* H_2SO_4

PROCEDURE

The step-by-step procedure is illustrated in table 21.

1. NH_4Cl extraction
   a. Weigh 1 g of air-dried <80-mesh soil and place in a labeled 100-mL Nalgene tube with a mark at 50 mL.
   b. Add 0.5 *M* NH_4Cl to the 50-mL mark. Cap, shake vigorously, and place the tube on a reciprocating shaker for one-half hour.
   c. After the extraction, centrifuge the sample (1,800-2,000 rpm for 5 minutes) and decant the solution into a labeled plastic (Nalgene) bottle to be kept for analysis.
2. NH_4F extraction
   a. After decanting the NH_4Cl solution, add 0.5 *M* NH_4F (adjusted to pH 8.2 with 4 *N* NH_4OH) to the 50-mL mark. Cap, shake, and place the tube on a reciprocating shaker for 24 hours.
   b. After the extraction, centrifuge the sample and decant the solution into a labeled bottle.
3. 1st NaOH extraction
   a. After decanting the NH_4F solution, add 0.1 *N* NaOH to the 50-mL mark. Cap, shake, and place the tube on a reciprocating shaker for 17 hours.

Table 21. Step-by-step procedure for phosphorus fractionation

[P fraction is grouped as in Williams and Walker (1969)]

	P fraction
1. 0.5 M NH_4Cl for 30 minutes	non-occluded P
2. 0.5 M NH_4F, pH 8.2, for 24 hours	non-occluded P
3. 0.1 N NaOH for 17 hours	non-occluded P
4. Dithionite-citrate-bicarbonate extraction	occluded P
5. 1 N NaOH for 17 hours	occluded P
6. 0.5 N HCl for 1 hour; if this fraction contains > 20 ppm P also do 1 N HCl for 4 hours	calcium P
7. Ash 1 hour (550 °C) 1 N HCl for 16 hours	residual organic P
8. Ash for 4 hours, digest in 12 N HCl for 4 hours	occluded P

b. After the extraction, add 1 mL of saturated NaCl solution. Cap, shake, and centrifuge the sample, decanting the solution into a labeled bottle.
c. If the decantate is colored by organic material, several drops of 36 *N* H_2SO_4 may be added to flocculate it.

Note: Some methods use 0.1 NaOH that is 1 molar in NaCl for flocculation.

4. Dithionite-citrate-bicarbonate extraction
   a. After decanting the NaOH solution, add 40 mL of 0.3 *M* sodium citrate and 5 mL of 1 *M* $NaHCO_3$ and heat the sample in a water-filled beaker on a hotplate to 70 °C under a fume hood. Do not let the temperature exceed 75 °C. At 80 °C there is the possibility of FeS precipitation.
   b. Add 1 g of $Na_2S_2O_4$ and stir the solution vigorously with a stirring rod, repeating the stirring at one-minute intervals for 5 minutes.
   c. Allow the solution to cool and then centrifuge the sample. If there is no problem with flocculation, add distilled water to the 50-mL mark. Cap, shake the contents thoroughly, and centrifuge. Decant the solution into a labeled bottle. If flocculation does not occur, add 1 mL of saturated NaCl solution, shake, and centrifuge the sample, repeating this until flocculation occurs.
5. 2d NaOH extraction
   a. After decanting the CBD solution, add 1 N NaOH to the 50-mL mark. Cap, shake, and place the tube on a reciprocating shaker for 17 hours.
   b. After the extraction, centrifuge the sample and decant the solution into a labeled bottle.
6. HCl extraction
   a. After decanting the second NaOH solution, add 0.5 *N* HCl to the 50-mL mark. Cap, shake, and place the tube on a reciprocating shaker for 4 hours.
   b. After the extraction, centrifuge the sample and decant the solution into a labeled bottle.
   c. If the HCl extract from b contains more than 20 ppm of phosphorus, do another extraction using 50 mL 1 *N* HCl. Cap, shake, and place the tube on a reciprocating shaker for an additional 4 hours. Centrifuge and decant the solution into a separate labeled bottle. The result from the analysis of this second extract is added to the result of the first to give a final figure for this fraction.
7. Residual organic P extraction
   a. Transfer the sample to a 50-mL beaker using distilled water. Cover with a watch glass and evaporate slowly to dryness.
   b. Ash the sample in a muffle furnace at 550 °C for 4 hours.
   c. After cooling, transfer the sample back to the Nalgene tube, using 1 *N* HCl and a rubber spatula. Add 1 *N* HCl to the 50-mL mark. Cap, shake, and place the tube on a reciprocating shaker for 16 hours.
   d. After the extraction, centrifuge the sample and decant the solution into a labeled bottle.
8. Residual inorganic P extraction
   a. Transfer the sample to a 50-mL beaker using distilled water. Cover with a watch glass and evaporate slowly to dryness.
   b. Ash the sample in a muffle furnace at 550 °C for 4 hours.
   c. After cooling sufficiently to handle, add 10 mL of concentrated HCl (12 *N*). Heat the sample on a hotplate, just below the boiling point for 4 hours. Do not allow the sample to lose more than one-half of its 10-mL liquid volume.
   d. After digestion, transfer the sample back to the Nalgene tube and add distilled water to the 50-mL mark. Cap, shake, and centrifuge the sample, and decant the solution into a labeled bottle.

ADDITIONAL REMARKS

This is a lengthy and time-consuming procedure which has been thoroughly evaluated in the scientific literature over the years. It has its supporters and detractors, but overall the data appear to have been accepted by the soil science community. Additional work is needed to determine if the fractionation data are useful in determining age relationships of soils.

Phosphorus Analysis

By Richard Meixner,
University of California, Davis

REFERENCES

Kurtz, 1942.
Murphy, and Riley, 1962.
Petersen, and Corey, 1966.

PRINCIPLE

An aliquot of each phosphorus fraction is mixed with ammonium molybdate. The color intensity of the blue phospho-molybdate complex, varies with the phosphorus concentration which is determined on a spectrophotometer at 660-nm wavelength.

EQUIPMENT

spectrophotometer
100-mL graduated cylinder

50-mL, 100-mL, 250-mL, 1-L, 2-L volumetric flasks
pipettes 0.5-5 mL
plastic film or parafilm
reagent storage bottles
test tube
test-tube rack
Bunsen burner, ring stand, asbestos pad
oven
desiccator with desiccant

REAGENTS

NH_4MoO_4 KSb-tartrate
36 *N* H_2SO_4
p-nitrophenol indicator
ascorbic acid
isobutyl alcohol
ethyl alcohol
1 *N* HCl
0.3 *M* H_3BO_3
KH_2PO_4
1 *N* NaOH

PROCEDURE

Two reagents (A and B) are used in the determination. They must be made correctly and must be fresh to work correctly.

Reagent A

Weigh 12.0 g NH_4MoO_4 and 0.2743 g KSb-tartrate. Add the NH_4MoO_4 to approximately 200 mL of distilled water in a 2-L volumetric flask and gently heat while occasionally swirling the contents in the flask. Add the KSb-tartrate, remove from the heat, and swirl vigorously. A small amount of solid crystals will remain at this point.

Add 800 mL of room-temperature (or cooler) distilled water to the flask and swirl to mix. Carefully add 139 mL of 36 *N* H_2SO_4. The heat generated from this strongly exothermic reaction will dissolve the remaining salt. Care should be taken at this step. Allow to cool to room temperature, make to volume, and store in a reagent bottle in the refrigerator.

Reagent B

Weigh out 1.32 g of ascorbic acid and add it to a 250-mL volumetric flask. Bring to volume with room-temperature reagent A. (Or add cold solution to the neck of the volumetric flask and allow it to equilibrate to room temperature and then dilute to volume.) This solution should be made each day that sample solutions are analyzed, generally just before use.

Additional solutions

1. Variation 1: 0.3 *M* H_3BO_3 solution.
2. Variation 2: Sulpho-molybdate solution Add 60 g of NH_4MoO_4 to approximately 500 mL of distilled water in a 1-L volumetric flask. Add 84 mL of 36 *N* H_2SO_4. Allow this solution to cool and dilute to volume.

Phosphorus standards

1. Stock solution: 100 ppm phosphorus
   a. Weigh 0.4394 g of oven-dry KH_2PO_4.
   b. To the KH_2PO_4 in a 1-L volumetric flask, add approximately 800 mL of distilled water.
   c. Add 5 mL of 36 *N* H_2SO_4 and dilute to volume. Store in a labeled plastic (Nalgene) bottle.
2. Working solution: 5 ppm phosphorus
   a. Pipette 5 mL of the standard solution into a 100-mL volumetric flask and dilute to volume. This solution should be freshly prepared each time standards are made.
3. Standards: 0.05-, 0.1-, 0.2-, and 0.5-ppm phosphorus solutions are prepared in 50-mL volumetric flasks and appropriate aliquots of the extraction reagent blank added.

Color development procedure

1. Normal method
   a. Add an aliquot (0-0.5 μg P) of the sample solution to a 50-mL volumetric flask.
   b. Add distilled water to give approximately 20 mL of solution.
   c. Add two drops of p-nitrophenol indicator and adjust the pH with NaOH (1 *N* suggested) until a bright yellow color appears. Then add HCl until the bright yellow just disappears. Due to Fe in some sample solutions, the end point may be obscured by reddish and (or) brownish-yellow colors. Some samples also may form a cloudy suspension with NaOH addition [$Fe(OH)_x$ gel] that sometimes persists after the end point is reached. Reagent B (2.5 *N* H_2SO_4) easily dissolves this suspension.
   d. Add 8 mL of reagent B and swirl the flask. Dilute to volume, cover with a piece of parafilm, and mix thoroughly.
   e. The blue color develops within 10 minutes and the solutions may be read in one-half hour at 660 nm on a spectrophotometer.
2. Variation 1: Borate addition to the NH_4F inorganic phosphorus fraction. Add 15 mL of 0.8 *M* H_3BO_3 to the NH_4F extracts after steps a through c and mix thoroughly before the addition of reagent B. A fluoro-borate complex prevents fluoride interference with the formation of the phospho-molybdate complex.
3. Variation 2: Alcohol extraction of the CBD inorganic phosphorus fraction.
   a. Pipette 2 mL of the CBD extract into a small test tube.
   b. Add 6 mL of the sulpho-molybdate solution.

c. Add 5 mL of isobutyl alcohol. Stopper (or cover with plastic) and shake vigorously once a minute, three times.
d. Allow the isobutyl phase to separate.
e. Pipette a 2 mL aliquot of the isobutyl phase into another test tube.
f. Add 6 mL of reagent B and 5 mL of ethyl alcohol.
g. Allow the alcohol phase to separate and use it for colorimetry in one-half hour at 660 nm.

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