SAMPLING PROCEDURES AND CHEMICAL METHODS IN USE AT THE U. S. SALINITY LABORATORY FOR CHARACTERIZING SALT-AFFECTED SOILS AND WATERS[1/]

J. D. Rhoades and M. Clark[2/]

1/ Contribution from the U.S. Salinity Laboratory, USDA, Riverside, CA 92501.

2/ Supervisory Soil Scientist and Physical Science Technician, respectively.

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I. Introduction

The analytical methods described in this paper are those currently in use at the United States Salinity Laboratory for characterizing soil and water salinity and sodicity. Methods previously used are described elsewhere (U.S. Salinity Staff, 1954; Bower and Hatcher, 1962; Bower and Wilcox, 1965). Substitute methods were needed to increase output per man hour. The substitutions were not made because of inadequacies in previously used methods, and no comparisons of methodology are included in this report. Many suitable methods could be used, but our choices are based mainly on their compatability with available instrumentation and ranges of solute concentrations in samples to be analyzed.

Because of the wide range in sample concentrations and the many different types of analyses required by our various research programs, semi-automated instruments, with their greater flexibility, were chosen over fully-automated ones.

Characterizing salt-affected soils and waters requires standard procedures for sample collection, preparation, storage, and, especially, extraction. Such need arises because of: 1) the way in which crop tolerance to salts is evaluated, 2) the effects of such variables as temperature, partial pressure of CO_2, soil particle size, and time of contact on the solubilities of some salts, 3) the interaction between exchangeable cation and soluble salt composition as affected by the solid/solution ratio, and 4) the need to reference cation exchange capacity and exchangeable cation proportions to specific conditions (such as pH and soil/water ratio).

II. Sample Collection, Preparation and Reporting

We use field data description sheets for soil and water samples (sheet 1 and 2, respectively) so that laboratory data can be meaningfully interpreted.

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2/ Supervisory Soil Scientist and Physical Science Technician, respectively.

A. Soil Samples

1. Collection

Site selection and collection of samples for analyses must be undertaken with recognition that the reliability of analytical data for appraising soil salinity is largely controlled by the accuracy of sampling and degree to which it represents the field conditions. In cultivated areas, soil management history may be the most important factor in determining the salinity status. Thus, fields become the basic unit for sampling. Care must be taken so that only representative areas of the field are selected; locations close to fence rows, ditch banks, roads, field corners, etc., must be avoided. Factors which cause migration of salt, such as seasonal precipitation, irrigation, or phase in the crop cycle, should be accounted for relative to the sampling time.

Saline and sodic soils are quite variable. Soil properties often vary greatly with horizontal and vertical distance within the field and time of season. Hence, it is advisable to use paired sampling sites and to collect samples from both unaffected and affected areas. Such a practice will provide information on the range of problems involved.

Special features of micro-relief, i.e. a ridge, furrow, mound, or local low spot, influence the salinity and should be described in the sampling record as should the sample location so that another might be sampled if necessary.

The following recommendations are offered on when and how to sample. Sample when the soil is reasonably dry, and after all loose plant material and debris are removed from its surface. Sample separately any visible or suspected salt crusts on the soil surface. Using a soil tube or auger, sample the plow layer, usually a depth of about 15 centimeters, and also sample each important and distinctly different soil stratum to the depth of one to two meters. In the absence of profile development, intervals of 0 to 15, 15 to 30, 30 to 45, 45 to 60, 60 to 90 centimeters, etc., may be used. If a soil auger is used, be careful to prevent dislodgement of the successive upper strata while collecting the deeper stratum.

Take a sufficient number of samples to obtain a composite sample that will be representative of the area of concern. A minimum of three samples for each depth, and preferably six to eight, should be sufficient. To avoid contamination and to facilitate mixing of the samples, it is advisable to place each depth sample in a separate plastic bucket. After the samples are collected, transfer them separately to plastic, air-tight bags. The size of the sample depends on the salinity and water holding capacity of the soil. For routine work a minimum of 200 (clay soils) to 400 (sandy soils) grams is needed.

Samples should be taken before land is put into crop production and, in cropped land, at frequencies dictated by the expected or associated salinity hazard. For example, if the irrigation water

is quite saline or the water table shallow, soils should be sampled for salinity at least yearly. Depending on past management and cropping sequence, additional samples might be needed before seeding, so that the need for pre-irrigation could be ascertained, and before critical stages in the growth of sensitive crops, if potential excessive salinity is suspected.

2. Preparation

Soils should be air-dried before they are shipped or stored for any length of time (if water separates from the soil, the sample should be remixed before it is air-dried.

Upon arrival at the laboratory, the samples should be further air-dried. Then, reduce the clods and large aggregates to < 2 mm using a wooden or rubber roller, mallet, etc., or any effective method that will not pulverize the soil particles. Grind the samples until only coarse fragments that will not slake in water remain in the sieve (avoid fine grinding). Weigh and discard the > 2-mm material. Place the sieved soil on a plastic sheet; mix by rolling the soil and pulling opposite corners of the sheet; and then subsample to obtain the composite sample. Determine moisture content on part of the sample, and store the rest in a sealed plastic container in a cool, well-ventilated place. If gypsum and calcium carbonate are to be determined, grind subsamples of the < 2-mm material to pass an 80-mesh sieve.

3. Reporting

All soil samples brought to the laboratory should be numbered, and the numbers recorded in a soil accession book. The field information should be recorded in a soil data file for use in research and statistical surveys, for extrapolation to new situations, etc. Since salinity is seldom a unique property of soil, per se, the circumstances of the soil situation should be described in as much detail as possible.

B. Water Samples

The sample should be truly representative of the water to be analyzed. Samples from wells should be collected after the pump had been run for some time; and samples from streams and canals should be taken from running water.

The properties of samples collected from a river or stream, lake, or large canal, may vary with depth, flow rate of the water, and distance from bank, and time. It is best to take an integrated sample from top to bottom in the middle of the stream. If only a single grab sample can be collected, take it at mid-depth and mid-stream of the channel. Samples of waters must be taken at sufficient frequency to ascertain the time trends in quality.

For routine sampling of irrigation water, only 50 to 100 ml is needed. Plastic bottles should be rinsed two or three times with the water to be collected, filled to the top, and tightly capped. Samples should be refrigerated and analyzed as quickly as possible so

that chemical changes during storage will be minimized. Changes can result from biological activity, loss of dissolved CO_2, and chemical reactions, such as precipitation and oxidation. To prevent precipitation of $CaCO_3$, dilute the sample (two-fold) and add sodium hexametaphosphate (1 drop of 1000 ppm solution per 25 ml of sample).

If the concentrations of carbonate and bicarbonate must be determined accurately, pH and temperature should be determined at collection time using appropriate field techniques and equipment (Back and Barnes, 1961; and Rainwater and Thatcher, 1960). For most purposes this extra effort is unwarranted if sample bottles are filled to the top, refrigerated (∿4C°), and the contents analyzed within a few days after collection.

Before analysis, any excessive turbidity should be removed by centrifugation or an appropriate filtration procedure.

III. Soil Water Extracts

The major soluble cations and anions in the soil solution are Na, K, Ca, Mg, Cl, SO_4, and HCO_3. Minor amounts of NO_3 and CO_3 are usually present. The concentrations and relative proportions of these solutes must be known if the response of saline and sodic soils to various treatments is to be assessed. Ideally it would be desirable to know the solute concentrations in the soil solution at field water contents. However, the methods available to isolate soil solutions at such water contents are not suitable for routine purposes. Consequently, soil solutions are extracted from soils at some "higher-than-normal" water content. And that content must be standardized, because it governs the absolute and relative amounts of the various solutes in the extracts (Reitemeier, 1946). The amounts determined can then be applied and interpreted universally.

Criteria for assessing salinity and sodicity hazards were developed by the staff of the U. S. Salinity Laboratory and are based on the compositions of saturation extracts. This composition is used for relating crop yields, evaluating management problems, assessing need for reclamation, etc. Almost all crop tolerance data are expressed in terms of saturation extract salinities. For the preceding reasons, the saturation-paste extract is still recommended and is the extract in routine use at the U. S. Salinity Laboratory. However, the analytical methods to be described below can be used for any aqueous extract (soil/water ratios of 1:1, 1:5, etc.).

The Saturation Extract

To prepare a saturated soil paste, add distilled water to a sample of air-dry soil (200 to 400 g) and stir the mixture either manually or mechanically. Oven-dried soils should not be used because heating to 105C° partially converts gypsum, $CaSO_4 \cdot 2H_2O$, to $CaSO_4 \cdot 1/2\ H_2O$. The latter hydrate is more soluble in water than gypsum. Immediately, add sufficient water to nearly saturate the sample. Then, allow the mixture to stand for several hours to permit the soil to imbibe the water. After this imbibition period, add more water to achieve a

uniformly saturated soil-water paste (free of partially wetted clumps). At this point, the soil paste glistens as it reflects light, flows slightly when the container is tipped, slides freely and cleanly off the spatula, and consolidates easily when the container is jarred or tapped after a trench has been formed in the paste with the flat side of the spatula. After mixing, the sample should be allowed to stand -- preferably overnight, but at least for four hours; and then the criteria for saturation should be rechecked. Free water should not collect on the soil surface nor should the paste stiffen markedly or lose its glisten. If the paste is too dry, remix with more water. If the paste is too wet, additional dry soil should be added and the paste remixed.

To eliminate some of the subjectivity of the saturation extract method, Longenecker and Lyerly (1964) proposed wetting the sample on a capillary saturation table. Beatty and Loveday (1974) and Loveday (1972) suggested that the amount of water at saturation to be predetermined on a separate soil sample by use of a capillary wetting technique, and that the same amount be subsequently added to another soil sample. Allison (1973) recommended the slow addition of soil to water (oversaturation method) in order to speed paste preparation.

The soil paste is then filtered with suction on a Richards (1949) filter funnel, a Buchner funnel, or comparable vacuum funnel and Whatman No. 50 filter paper to obtain the saturation extract. If the initial filtrate is turbid, filter it back through the paste. Terminate the filtration when air begins to pass through the filter-cake. To the extent possible, suction and extraction time should be standarized as shown by Jacober and Sandoval (1971). Thymol added to the paste will minimize the effect of microbial activity on saturation extract composition during equilibration (Carlson et al., 1971).

A 1000 ppm solution of sodium hexametaphosphate (0.1 g/100 ml) should be added to the extract (one drop per 25 ml of extract) to inhibit the precipitation of calcium carbonate during storage. Alternatively, a subsample should be diluted two-fold and used for the calcium and alkalinity determination. The extracts and subsamples should be stored at ∿4C° until analyzed.

IV. Soluble Cations and Anions

A. Sequence of Analyses

Alkalinity and pH should be determined immediately on fresh extracts or the solutions treated with hexametaphosphate. Next determine electrical conductivity; it is a useful means of estimating total salt concentration (meq/l ≃ 10.EC, in mmho/cm). The cations can be determined in any sequence. After any three of the four cations are determined, the remaining one can be estimated, for purposes of obtaining an appropriate aliquot, by deducting the sum of the three concentrations, in meq/l, from 10.EC, in mmho/cm. Nitrate and chloride are determined next since they are simpler to analyze than SO_4. Next determine SO_4; estimate the appropriate aliquot from the difference of (Ca + Mg + Na + K) and (alkalinity + NO_3 + Cl). Finally, determine boron. Methods used for the above analyses are described below.

B. Pipetting, Diluting, and Dispensing

Batches of samples are run through semi-automated sample handling instruments, after solutions (within the required concentration ranges) are prepared. Pipetting, diluting, and dispensing operations are performed using a semi-automated instrument and for this purpose we use a Micromedic Model 25000[3/]. With this device a desired volume (adjustable) is drawn into a flexible, plastic combination pickup/delivery tube and then discharged into a vial along with a second liquid, which may be either a diluent or reagent. The tip is rinsed automatically, since the diluent is delivered after the discharge of the aliquot. The device can also be used as a reagent dispenser, delivering one or two liquids through a delivery tip.

Common aliquot sizes employed in our analyses range from 0.050 to 1.00 ml. Final volume for all atomic absorption analyses is 7.00 ml, therefore dilution factors commonly range from 7 to 140. To insure accuracy, we run standards and samples exactly the same.

C. Weighing

We expedite the weighing and taring operations by batch processing samples as much as possible, by using a semi-automatic direct readout-digital electronic balance (Ainsworth Digimetric Balance Model 30-DT) which automatically zeros itself, tares the sample container, integrates the reading, and transmits the actual sample weight to a recorder and calculator system (described under Calculations).

D. Calculations

In many of our analyses we obtain printouts of instrument readings made sequentially and automatically. To facilitate calculations of sample concentrations and data reduction, we use a programmable calculator (Hewlett-Packard 9830 A). The calculator is programmed by a magnetic tape having the proper instructions for each solute. Calibration parameters and raw data are computed, and the results are printed on a summary sheet. For weighing operations, the calculator also serves as a data storage file; it stores the wet weights until dry weights are determined and then concurrently calculates per cent water, air-dry/oven-dry ratios, saturation percentage, etc.

E. pH and Alkalinity

Apparatus:

a. Automatic potentiometric titrator (Metrohm E436 potentiograph and E4360 titrator; Switzerland).

[3/] Mention of a trademark or proprietary product throughout the manuscript does not constitute a guaranteee or warranty of the product by the U. S. Department of Agriculture, and does not imply its approval to the exclusion of other products that may also be suitable. This information is provided for the benefit of the reader.

b. Single probe combination pH electrode (Metrohm CH-9100).

Reagents:

a. pH 4.00 and 7.00 standard buffer solutions.

b. Standard HCl (0.0200 N).

Procedure:

Calibrate the pH meter with the two standard buffer solutions. Rinse electrode, immerse in sample solution (1 to 20 ml) -- contained in 50 ml plastic beaker along with a micro-size, Teflon-coated magnetic stirring bar -- and initiate the automatic titration operation, using the full-titration-curve display mode. The initial potential recorded on the strip chart is the sample pH. The volumes of titrant delivered to produce inflection points for CO_3 and HCO_3 are obtained from the titration curve (pH vs. volume of standard acid delivered from automatic burette).

Calculations:

CO_3, in meq/l = 2P $\underline{N}$ 1000/aliq.,

where P is ml of standard HCl of normality $\underline{N}$ to reach the CO_3 inflection point (pH = 8.3) and aliq. is the sample volume in ml.

HCO_3, in meq/l = (T-2P) $\underline{N}$ 1000/aliq.,

where T is total ml of standard HCl of normality $\underline{N}$ to reach the HCO_3 inflection point (pH = 4.5), P is the ml of standard HCl required to reach the CO_3 inflection point, and aliq. is the sample volume in ml. The blank is determined with CO_2-free distilled water.

F. Electrical Conductivity

Electrical conductivity, EC, of an extract is a useful indicator of the total concentration of solutes in the extract. Since most soil extracts and waters have conductivities much less than one mho/cm, EC x 10^3, called millimho per centimeter (mmho/cm), is the most convenient and practical unit of conductivity for most salinity work. The new SI standard for expressing EC is sieman per meter (S/m). One S/m equals 10 mmho/cm.

The electrical conductivity of aqueous salt solutions increases with increase in temperature (about 2% per degree C); hence, EC should be referenced to a standard temperature of 25C° by adjustment factors (Table 15, U.S. Salinity Laboratory Staff, 1954), or by internal circuitry within the conductance meter.

For conductivity determination we use a direct-readout, temperature-compensating conductivity meter originally designed for us and now commercially available.

Apparatus:

a. Conductivity meter (Aquatronics Model 390, Digital Conductivity Monitor).

b. 1.5 ml conductivity flow cell with automatic temperature compensation (Aquatronics Model XPC-010T-pp).

c. Vacuum line and suction flask.

Reagents:

Standard KCl solutions (0.010 and 0.100 N); for 0.010 N solution (1.412 mmho/cm at 25C°) dissolve 0.7456 grams of KCl in distilled water, and add water to make 1 liter at 25C°. For 0.100 N solution (12.900 mmho/cm at 25C°) use 7.456 grams of KCl.

Procedure:

Rinse and fill the conductivity cell with the standard KCl solution. Adjust the conductivity meter to read the standard conductivity. Rinse and fill the cell with the soil extract or water sample and read the EC, corrected to 25C°, directly from the digital display.

Comments:

Because of marked differences in the equivalent weights and equivalent conductivities and the variable proportions of the major solutes in soil extracts and water samples, the relations between EC and salt concentration and EC and osmotic pressure are only approximate; but they are useful. These relations are:

a. total cation (or anion) concentration, meq/liter ≃ 10 x EC in mmho/cm, or 100 x EC in S/m.

b. salt concentration, mg/liter ≃ 640 x EC in mmho/cm or 6400 x EC in S/m.

c. osmotic pressure, atm ≃ 0.36 x EC in mmho/cm or 0.036 x EC in S/m.

G. Soluble Cations

Calcium, magnesium, sodium, and potassium are all determined using an automatic absorption spectrophotometer with an automatic system for sample transport, sequencing, siphoning, reading, and recording.

Apparatus:

a. Atomic absorption spectrophotometer (Perkin Elmer Model 503).

b. Sampling and sequencing system (Perkin Elmer Auto-200 Automatic sampling system modified with delay-relay after Harang, 1976).

c. Acetylene gas (commercial grade).

Reagents:

a. Suppressant solution for Ca and Mg: Lanthanum chloride made up of 29.0 grams La_2O_2 + 250 ml concentrated HCl + water to make up to 500 ml. Add to aliquot and diluent (distilled water) to give 10% by volume of $LaCl_3$ in final solution.

b. Suppressant solution for Na and K: dissolve 6.358 grams $LiCl_2$ in distilled water to 1 liter (0.15 N). Add to aliquot and diluent (distilled water) to give 10% by volume of $LiCl_2$ in final solution.

c. Standard cation solutions, in meq/l: Ca (0-0.4), Mg (0-0.1), Na (0-1), and K (0-0.1).

Procedure:

Adjust A.A. unit controls and settings for the cation to be run (see Table 1). Set A.A. readout to read the upper and lower standard solutions. Then, initiate transport/readout system which automatically positions a sequence of samples, siphons and aspirates the samples in the air/acetylene flame, reads, and records (on a printout) the concentration of the cation in the aspirated solution. Standard solutions are inserted into the sampling rack every 20 samples to insure stability of instrument calibration during the automated run. Two hundred samples can be processed per hour, without attendance, after the delay/relay-modified automatic sample processing system has been initiated.

Calculations:

Concentration of cation in original sample, meq/liter = (A.A. readout, meq/l in aspirated sample) x (dilution factor). With calcium the dilution factor must include the 1:1 pre-dilution made at sampling time to prevent precipitation of $CaCO_3$ during storage.

H. Chloride

The concentration of chloride in solution is quantitatively determined by electrometric titration with silver. Silver ions are

automatically generated coulometrically, and the end point is indicated amperometrically (elapsed time is indicated to the nearest 0.1 second). Since the rate of Ag^+ generation is constant, the amount of chloride precipitated is proportional to time. The proportionality between duration of titration and concentration is established using standard chloride solutions and a blank.

Apparatus:

Automatic coulometric/amperometric chloride titrator (Aminco chloride titrator).

Reagents:

a. Nitric-Acetic Acid/PVA: Slowly add 1.8 grams of powdered PVA (Polyvinyl alcohol) to ∿ 100 ml of heated (∿ 90C°) demineralized water, stir until dissolved and cool to room temperature. Add 6.4 ml of concentrated nitric acid and 100 ml of glacial acetic acid to a liter volumetric flask containing 600 ml of demineralized water and mix thoroughly. Add the cooled PVA solution to the nitric-acetic acid solution, mix, cool, and make to volume with demineralized water. Store this nitric-acetic acid/PVA reagent in a tightly stoppered container at room temperature. This reagent is usable for at least 12 months.

b. Chloride standard solutions: 1, 4, 16, 160 meq/l.

Procedure:

Add 4 ml of nitric-acetic acid/PVA reagent together with a sample aliquot (< 3 ml) to a titration vial. Position vial in titrator, immersing electrode assembly into the solution; zero the timer and initiate automatic titration at low, medium, or high current setting. Note the titration times of blank, standards, and samples.

Calculation:

Cl in meq/l = (K)(titration time of sample minus that of blank)/aliq.,

where K is a standardization factor and aliq. is sample size in ml.

K = (volume of Cl standard in ml)(concentration of Cl standard in meq/l)/(titration time of standard minus blank).

I. Nitrate

Nitrate activity is determined using a specific-ion electrode; its value provides a check on cation/anion balance, although occasionally it is an appreciable fraction of the anions in saline waters.

Apparatus:

a. Electrometer (Fisher Model 520 digital pH/ion meter).

b. Specific nitrate ion electrode (Orion Model 93-07).

c. Calomel Reference Electrode (Beckman Model 39170).

Reagents:

Standard nitrate solutions: 0.01, 0.10, 1.00, 10.0, and 100 meq/liter.

Procedure:

Prepare electrode according to manufacturer's directions. Place electrodes in 5 to 10 ml of sample or standard solutions and record millivolt readings. Determine concentration of nitrate in sample by comparison with standard curve.

J. Sulfate

Concentration of sulfate in samples is determined by one of two methods, depending on amount of sample available and its estimated SO_4 concentration (SO_4 is estimated, as already mentioned, by difference). A turbidimetric method is used whenever a sample is expected to contain at least 5 meq/l SO_4. When the concentration is less, a potentiometric titration is made using a specific lead electrode.

1. Turbidimetric Method

Sulfate ion is converted to a $BaSO_4$ suspension under controlled conditions. The resulting turbidity is determined spectrophotometrically, and the sulfate concentration determined from a standard curve.

Apparatus:

a. Absorption Spectrophotometer (Bausch and Lomb Spectronic 400-3; an automatic sample handling, evaluation, and data printing system).

b. Magnetic stirrer.

Reagents:

a. Barium chloride crystals (20-30 mesh $BaCl_2.2H_20$).

b. Conditioning Reagent: Add 75 grams NaCl and 275 ml water to a 500-ml volumetric flask, along with a magnetic stirring bar; add, with stirring, 30 ml conc. HCl, 100 ml absolute ethanol, and 50 ml glycerol; rinse glycerol flask and pour rinses into the volumetric

flask; continue stirring until NaCl dissolves; remove stirring bar and make to volume with distilled water.

c. Standard sulfate solutions: 0 to 1 meq/liter.

Procedure:

Remove suspended material from sample, if present, by filtration or ultra centrifugation. Run a blank to correct for color interference and unremovable suspended material. Dilute sample until sulfate concentration is less than 1 meq/l. Transfer 100-ml aliquots of standards, blank, and diluted samples into 250-ml Erlenmeyer flasks. Add 5.00 ml of conditioning reagent to each flask with a 5-ml automatic pipetter. Introduce a clean magnetic stirring bar into the flask of the sample to be analyzed (read blank first, then standards, then samples in that order). Place flask on magnetic stirrer preset at constant speed (fastest speed possible without splashing, and do not change speed once runs are begun). While stirring, add, all at once, 0.2 g of barium chloride crystals with a measuring spoon. Stir for exactly 60 seconds then remove flask from stirrer. Read maximum absorbance with spectrophotometer set at 340 nm after 1 to 3 minutes. Construct standard curve and determine concentration of SO_4 in final solution by comparison.

Calculation:

Concentration of sulfate in sample, meq/liter = (dilution factor) x (concentration of sulfate from standard curve).

Reference:

American Public Health Association, American Water Works Association, Water Pollution Control Federation (1976). Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp 496-498.

2. Potentiometric Method:

When present at concentrations less than 5 meq/liter, sulfate is determined by titration with lead perchlorate; and the endpoint (presence of excess Pb^{++}) is detected potentiometrically using a specific, lead-ion sensitive electrode.

Apparatus:

a. Same automated potentiometric titrator described for pH and alkalinity determination.

b. Specific Pb electrode, Orion Model 94-82.

c. Reference electrode, Orion Model 90-02; fill outer chamber with 1 M $NaNO_3$; fill inner chamber with Orion Solution No. 90-00-02.

Reagents:

a. Methanol, ASC grade.

b. $Pb(ClO_4)_2$, 0.002 and 0.005 N.

c. $NaClO_4$, 0.100 N.

d. NaOH, 6 N.

e. $HClO_4$, 0.014 N.

f. Standard SO_4 solution, 3.00 meq/liter.

Procedure:

Transfer an aliquot containing about 0.004 meq of sulfate into a 50 ml beaker and, using the automatic pipetter/diluter, add 0.6 ml $NaClO_4$ solution. Dilute the mixture to 5 ml with distilled water; then add 11 ml methanol. Adjust pH to 4.3 - 4.4 with dropwise additions of either $HClO_4$ or NaOH, as needed, using pH meter. Place magnetic stirring bar in beaker, insert electrodes (the mv reading should be in the range -240 to -280), and titrate with standard $Pb(ClO_4)_2$ solution using the automatic titration apparatus. Determine the equivalence point from the inflection point of the titration curve.

Calculation:

SO_4, in meq/l = (V) (N)/Aliq.,

where V and N are volume, in ml, and normality of standard $Pb(ClO_4)_2$ used in titration to endpoint, respectively, and aliq. is the sample volume, in ml.

Comment:

The lead electrode is subject to poisoning. If the potential reading is greater than -240 to -280 mv, the electrode should be polished and cleaned.

Reference:

Goertzen, J. O., and J. D. Oster. 1972. Potentiometric titration of sulfate in water and soil samples using a lead electrode. Soil Sci. Soc. Am. Proc. 36: 691-693.

K. Boron

Concentration of boron in samples is determined by formation of the colored boric acid-azomethine complex and spectrophotometry.

Apparatus:

Same automated spectrophotometric system as described for turbidimetric sulfate determination.

Reagents:

a. Prepare the buffer masking solution by dissolving 250 g of ammonium acetate and 15 g of ethylenedinitrilotetraacetate acid disodium salt (i.e., disodium ethylenediamine tetraacetate, EDTA disodium salt) in 400 ml of deionized distilled water and slowly adding 125 ml of glacial acetic acid.

b. Prepare azomethine-H reagent by dissolving 0.45 g of azomethine-H in 100 ml of 1% L-ascorbic acid solution. Fresh reagent should be prepared each week and stored in a refrigerator.

c. Prepare a stock solution containing 20 ppm boron by dissolving 0.1143 grams of boric acid in one liter of water. Prepare standards containing 0.5 to 8 ppm boron by diluting the stock solution with water.

Procedure:

Pipette 1 ml of blank, standard solution, or sample into a 15-ml polypropylene tube, and then add 2 ml of buffer. Mix contents of tube using an electrical stirrer. Next add 2 ml of azomethine-H reagent. Stir thoroughly and then allow to stand at room temperature for 30 minutes. Measure concentration at 420 nm. Determine concentration of boron in sample by comparison with standard curve (0 to 8 ppm).

Calculation:

H_3BO_3 in mg/l = (conc. read from standard curve)(dilution factor).

Reference:

John, Matt K., Hong H. Chuah, and John H. Neufeld. 1975. Application of Improved Azomethine-H method to the determination of boron in soils and plants. Anal. Letts. 8(8): 559-568.

L. Accuracy of Analyses

Some errors are practically unavoidable in analytical work. The analyst's skill and judgment largely control the extent of such errors. The validity of the results must be evaluated after chemical analyses are completed. The analytical methods described yield results of moderate accuracy, probably with less error than the variation due to sampling.

We examine the analytical results to detect gross errors by looking for expected interrelationships among the constituent cations and anions. We first check analyses for chemical balance (the sum of the equivalents of cations in solution must equal the sum of the anions). We are satisfied if the sum of cations and anions differ by no more than 3 to 4 percent. Larger deviations indicate either a large error in one or more of the determinations or the presence of some undetermined constituent, but a good balance is not conclusive evidence that each of the determinations is accurate nor that all constituents have been determined. Therefore, we look for additional expected relations in the analyses. For solutions having EC values less than 10 mmho/cm, we check to see whether the EC in mmho/cm multiplied by 10 is approximately equal to the total cation or anion concentration in meq/l. If CO_3 is present in titratable amounts, the pH of the extract must be > 8.3. The HCO_3 concentration seldom exceeds 10 meq/liter in the absence of CO_3. Sample results from a sequence of soil depths are compared for presence of a sample deviating from the others in profile trend. More extensive tests are described by the American Public Health Association and American Water Works Association (1976).

V. Cation Exchange Capacity

The method used for determining cation exchange capacity (CEC) is applicable to arid lands, and to calcareous and gypsiferous soils. The two-step procedure involves 1) saturation of cation exchange sites with sodium by "equilibrations" of the soil with a 60% ethanol solution (pH 8.2) of 0.4 N NaOAc - 0.1 N NaCl, and 2) extraction with 1.0 N, magnesium nitrate. Total sodium and chloride in the extract are subsequently determined. The former consists of some soluble sodium carried over from the saturation step plus the exchangeable sodium. Soluble sodium can be determined from total chloride; thus exchangeable sodium can be obtained by subtraction and is the calculated CEC.

Apparatus:

a. Atomic absorption spectrophotometer (same as described in soluble cations section).

b. Centrifuge (International No. 2).

c. 50-ml, round-bottom, narrow-neck centrifuge tubes.

d. Ultrasonic disperser (Branson Sonifier Model No. 185 and micro tip focusing horn).

e. Reciprocating shaker.

Reagents:

a. Saturating solution: 0.4 N NaOAc - 0.1 N NaCl, 60% ethanol solution adjusted to pH 8.2. Determine Na to Cl ratio, (Na/Cl) sat. sol.

b. Extracting solution: 1.0 N $Mg(NO_3)_2$.

Procedure:

Weigh out 4 to 5 grams of air-dry soil (correct for air-dry moisture content) and place in centrifuge tube. Add 33 ml of saturating solution, stopper the tube, and shake for 5 minutes. Unstopper and centrifuge at RCF = 1000 until the supernatant is clear (about 5 minutes). Decant the supernatant and discard. Add fresh saturating solution, insert sonifier tip and sonify for 10 to 30 seconds to disperse sediment, then continue as above. Make four successive "equilibrations," discarding the supernatant each time. (If the soil is initially high in salts, EC > 2 mmho/cm, wash the soil once with 33-ml of water before the saturation step, because excessive washing may cause the loss of particles during decantation). Then add 33 ml of extracting solution, shake for 5 minutes, centrifuge until the supernatant is clear, and decant the liquid into a 100-ml volumetric flask. Repeat the extraction steps two more times, and make to volume. Determine Na (Na_t) and Cl (Cl_t) in dilutions of this extracted solution, using the same analytical methods described for these ions in the soluble salt section; however, use standards made up in the extracting solution. Chloride is determined so that the soluble sodium (Na_{sol}) carried over from the saturation step to the extraction step can be deducted from the total sodium. This difference is exchangeable sodium (CEC).

$$CEC = (Na_t - Na_{sol}) = Na_t - (Cl_t)\ (Na/Cl)_{sat.sol.}$$

Calculation:

CEC in meq/100 g = (10/wt soil sample in g) [(Na conc in meq/l) (DF_{Na}) - (Cl conc in meq/l) (DF_{Cl}) $(Na/Cl)_{sat.sol.}$],

where DF represents the dilution factor, i.e., (final analytical volume in ml)/(sample volume in ml).

Comment:

The solubilities of gypsum and $CaCO_3$ in the saturating solution are sufficiently low (5.8 and 4.0 meq/liter for gypsum and calcite, respectively) and the ratio of Na to Ca (100:1) is sufficiently high to assure essentially complete saturation of the CEC with Na. Washing is omitted; and, hence, all the errors associated with it are avoided. The errors associated with the extraction step are minimized by use of $MgNO_3$, rather than NH_4OAC, since Mg is not fixed in soils nor does it extract many nonexchangeable cations (Rhoades and Kreuger, 1968).

References:

a. Polemio, Mario, and J. D. Rhoades. 1977. Determining

cation exchange capacity: a new procedure for calcareous and gypsiferous soils. Soil Sci. Soc. Am. J. 41: 524-528.

b. Rhoades, J. D., and D. B. Kreuger. 1968. Extraction of cations from silicate minerals during the determination of exchangeable cations in soils. Soil Sci. Soc. Am. Proc. 32: 488-492.

VI. Exchangeable Cations

We only determine exchangeable sodium and potassium in our laboratory to characterize salt-affected soils. When the remainder of the cation exchange capacity needs to be partitioned between calcium and magnesium, we do so using their determined proportions in the saturation extract and relative cation absorption exchange affinities by the method of Reitemeier (1945).

Apparatus:

Same equipment described in cation exchange capacity section.

Reagents:

Extracting solution: 1.0 $\underline{N}$ $Mg(NO_3)_2$.

Procedure:

Place 4 to 5 grams (oven-dry weight basis) of samples in centrifuge tubes. Add 33 ml of extraction solution to each tube, stopper, and shake for 5 minutes. Remove stopper and centrifuge at RCF = 1000 until the supernatant is clear (about 5 minutes). Decant the supernatant into a 100-ml volumetric flask. Add fresh 33 ml extraction solution, and disperse the soil using the sonifier (about 10 to 30 seconds); then, continue as with the first extraction. Extract the sample again, combine all three extracts into the volumetric flask, and make to volume. Determine the concentration of sodium and potassium on suitable aliquots by atomic absorption spectrophotometry, using standards prepared with the same extracting solution.

Calculations:

a. Magnesium nitrate extractable cations, in meq/100 g = (cation concentration of extract, meq/liter) (dilution factor) (10)/soil weight in g.

b. Soluble cations, in meq/100 g = (cation concentrations of saturation extract, in meq/l) (saturation percentage)/1000.

c. Exchangeable monovalent cations, in meq/100 g =

(extractable cations, in meq/100 g) - (soluble cations, in meq/100 g).

d. Exchangeable divalent cations, DX, in meq/100 g = (cation exchange capacity, CEC, in meq/100 g) - (sum of exchangeable sodium and potassium, in meq/100 g).

e. Exchangeable magnesium, MgX, in meq/100 g =

$$DX \frac{(Mg)}{(Mg) + 1.6\ (Ca)}$$

where ( ) represents concentration in saturation extract in meq/liter.

f. Exchangeable calcium, CaX, in meq/100 g = DX - MgX.

Reference:

Reitemeier, R. F. 1945. Effect of moisture content on the dissolved and exchangeable ions of soils of arid regions. Soil Sci. 61: 195-214.

VII. Gypsum Requirement

Exchangeable sodium must be determined for calculation of the amounts of chemical amendments needed to reduce the exchangeable sodium percentages of sodic soils to desired levels. The following method is recommended for estimating both the amount of exchangeable sodium in a soil and the gypsum requirement when exact information on the exchangeable sodium content and cation exchange capacity are not otherwise available. In this method soil is reacted with an excess of gypsum and the amount of sodium released to solution is determined.

Apparatus:

Same as described in Section IV.

Reagents:

a. Gypsum powder: $CaSO_4.2H_2O$ (< 200 mesh).

b. Ethanol-glycol: Mix 100 ml of ethylene glycol with 900 ml of ethanol.

Procedure:

Weigh 5 grams of air-dried soil into a centrifuge tube; add 33 ml ethanol-glycol, stopper, and shake for 5 minutes. Remove stopper and centrifuge at RCF = 1000 until the supernatant is clear. Decant and discard supernatant. Transfer soil sediment into a 125-ml flask; add 1 gram powdered gypsum and 100 ml of distilled water,

stopper the bottle, and shake for 5 minutes in a mechanical shaker. Filter the suspension, and determine the sodium concentration of a suitable aliquot as described in Section IV. G.

Calculation:

a. Exchangeable sodium, meq/100 g ≃ (Na concentration in filtrate, meq/l) (10) (DF)/(weight of soil sample, gram oven dry-weight), where DF is the dilution factor in the sodium analysis.

b. Estimate fraction of exchangeable sodium that must be removed from the soil, taking into consideration soil type, crop tolerances, etc. Express the amount of the total to be removed, as Δ exchangeable sodium, in meq/100 gram.

c. Gypsum requirement, meq/100 gram ≃ (Δ exchangeable sodium, meq/100 grams) (1.3), where 1.3 is an approximate efficiency factor (U. S. Salinity Laboratory Staff, 1954).

VIII. Soil $CaCO_3$

The kind and amount of chemical amendment to be used for the reclamation of sodic soils depends upon the soil characteristics, the desired rate of reclamation, and economic considerations. One of the principal characteristics of a soil influencing amendment selection and rate of application is its alkaline-earth carbonate content. The following manometric method is satisfactory for routine soil carbonate analyses. In the method, the CO_2 pressure buildup caused by reaction of acid and soil carbonate is related to $CaCO_3$ content by comparison with standards.

Apparatus:

a. 20-ml bottles with rigid bakelite caps in which several 1-mm holes are drilled.

b. Self-sealing solid rubber gaskets cut to fit the caps and make air-tight sealable bottles.

c. Hypodermic needles (24- or 25-gauge).

d. A manometer filled with colored water (2-mm glass tubing).

e. Small plastic soil cups (about 3 ml in volume).

f. Mechanical shaker.

Reagents:

a. Homogeneous carbonate-free soil.

b. Calcium carbonate powder.

c. 2 N HCl saturated with $MgSO_4.7H_2O$.

Procedure:

Add 4 ml of acid solution to each bottle; then place plastic cup containing 1-gram sample of soil (or standard sample) carefully into the bottle so that no contact is made between acid and sample. Seal bottle with gasket and lid, insuring a gas-tight seal. Plunge a hypodermic needle through the rubber gasket by means of one of the small holes in the cap, allowing the external and internal pressures to equalize. Remove the needle and agitate (about 70 rpm) the bottle mechanically end-over-end for 10 minutes to insure decomposition of the carbonate by the acid. The increased pressure due to the release of carbon dioxide, is then read on the manometer. To do this, insert the hypodermic needle, which is connected to the manometer, through the rubber gasket via a second hole in the plastic cap. Read the pressure value once it equalizes. Determine the soil sample content of $CaCO_3$ equivalent by comparison with the standard curve covering a $CaCO_3$ range appropriate for the samples being analyzed.

Comments:

Some special precautions must be observed in this determination. The volumes of the bottles must be identical. The total volume of soil plus acid mixture must be kept constant. The temperature must be held constant throughout each set of determinations. Standards should be run with each set of determinations and in the same soil/acid proportions (small differences in particle densities between mineral soils may be neglected).

Reference:

Williams, D. E. 1949. A rapid manometric method for the determination of carbonate in soils. Soil Sci. Soc. Am. Proc. 13: 127-129.

IX. Gypsum Content

Some sodic soils contain gypsum and can be reclaimed simply by leaching. Often the gypsum is only present in the subsoil; deep plowing will mix it with the surface soil such that the gypsum can become reactive with exchangeable sodium. The potential for reclaiming soil by leaching can be estimated if the soil gypsum content is known. Such knowledge is also needed for soil salinity appraisal, since the electrical conductivity of extracts is affected by the solution of gypsum. In qualitative test for gypsum, a small amount of acetone is added to

an aliquot of saturation extract, or other suitable extract, and the relative amount of gypsum is estimated from the intensity of the precipitation or turbidity produced. The following method is suitable for routine quantitative analyses of soil gypsum content.

Apparatus:

a. Centrifuge or filtration system.

b. Other equipment as described in sulfate analysis section.

c. Mechanical shaker.

Reagents:

Same as described in sulfate analysis section.

Procedure:

Combine the sample with enough water to dissolve all the gypsum. (The proper water/soil ratio can be determined from the filtrates of a series of water and soil mixtures increasing in water/soil ratio. The proper one is the lowest one resulting in the greatest amount of sulfate released into the filtrate per unit weight of soil.) Agitate the soil/water mixture for 30 minutes in a mechanical shaker. Collect the aqueous extract by filtration or centrifugation; and determine sulfate in a suitable aliquot. Also determine sulfate in the saturation extract.

Calculations:

a. Soluble SO_4 at saturation percentage, meq/100 grams = (SO_4 concentration of extract, meq/l) (saturation percentage)/1000.

b. Soluble SO_4 at more dilute water content, meq/100 grams = (SO_4 concentration of dilute extract, meq/l) (moisture percentage of dilute extract)/1000.

c. Gypsum content of soil, meq/100 grams = (soluble SO_4 at more dilute water content, meq/100 grams) - (soluble SO_4 at saturation percentage, meq/100 grams).

d. Gypsum content of soil, percent = (gypsum content of soil, meq/100 grams) (0.0861).

X. General References

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XI. Appendix

The following are estimates of the number of samples that can be analyzed per day by the methods described in Section IV, assuming one person devoting full time to one method.

Constituent	Number of Samples
pH and Alkalinity	150
Electrical Conductivity	500 plus
Soluble Cations	400
Chloride	150
Nitrate	300 plus
Sulfate - Turbidimetric	100
Sulfate - Potentiometric	75
Boron	200