

## Chapter 14

**Salinity: Electrical Conductivity  
and Total Dissolved Solids**

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**INTRODUCTION**

The term salinity refers to the presence of the major dissolved inorganic solutes, essentially  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , in aqueous samples. As applied to soils, it refers to the soluble plus readily dissolvable salts in the soil or, more usually, in an aqueous extract of a soil sample. Salinity is quantified in terms of the total concentration (or, occasionally, the content) of such soluble salts. The diagnosis, assessment, management and need for reclamation of saline soils and the suitability of waters for various purposes, including irrigation, are evaluated using information of soil and water salinity.

For certain soil salinity considerations, it would be desirable to know the individual concentrations of the major solutes in the soil water over the range of water contents that occur in the field and to obtain this information in the field, without the taking of soil samples and the carrying out of laboratory analyses. No practical methods are available at present to permit such detailed determinations, but total salinity can be measured in situ using electrical signals from various types of sensors (Rhoades, 1978, 1990; Rhoades & Oster, 1986). The latter determinations are often sufficient for purposes of diagnosing, surveying, and monitoring soil salinity, and for assessing the adequacy of leaching and drainage, even though they only give information of total soluble salt concentration, and hence supplant the need for carrying out conventional laboratory analytical procedures; in other cases they greatly minimize the number of samples requiring compositional analyses because correlations frequently exist between salinity and the concentrations of individual solutes and their ratios within the same general area of the landscape (Skarie et al., 1987).

The total soluble salt concentration (or content) of a water can be determined from either measurement of its electrical conductivity (EC) or of its residue-weight upon evaporation to dryness after filtration. Likewise, soil salinity can be determined from either measurement made: (i) on an aqueous extract of the soil sample, (ii) or on a sample of displaced soil solution. Alternatively, soil

salinity can be measured in situ using buried porous electrical conductivity sensors that imbibe soil water or it can be estimated from EC measurements made on water saturated soil pastes. It also can be estimated from measurement of bulk soil EC made: (i) in situ using electrical probes, or (ii) remotely using electromagnetic (EM) systems. The appropriate method of measuring salinity should be selected based on the specific conditions, needs and equipment and manpower availability.

Water salinity is measured more accurately, quickly and simply from EC; however, for some purposes, total dissolved solids may be a more appropriate method of appraisal. If only a practical measure of soil salinity is needed, measurement of bulk soil EC made using either EM induction or four-electrode devices is recommended. To monitor soil water salinity as the soil dries between irrigations, either the imbibition—or the time domain reflectometric (TDR)—type of salinity sensor is recommended. When determination of the concentration of a particular solute is needed, then either extraction of soil samples or acquisition of soil solution samples is required, along with appropriate laboratory analysis. Collection of water samples from soils using suction-cup extractors is useful for field monitoring needs, but this procedure is usually limited to relatively wet soil conditions (Rhoades, 1978; Rhoades & Oster, 1986). Displacement of soil solution from soil samples collected and kept at field moisture content provides for a meaningful soil-water sample, but the laboratory procedures for acquiring the latter samples are more demanding. Soil sample extracts give “relative salinities” only, since the soils are adjusted to unnaturally high water contents during extraction.

A combination of the various salinity sampling/measurement methods minimizes the need for the more difficult and time-consuming collection, extraction and chemical analysis procedures. This combination approach is recommended when monitoring salinity changes, or when characterizing the salinity of large fields and projects. For the latter, extensive use of portable (better yet of mobile) EM and four-electrode equipment and techniques for measuring bulk soil EC and for assessing soil salinity in the field are recommended, with the supplemental use of the other methods only as needed for calibration purposes or for characterizing solute composition. Field methods for measuring bulk soil EC are described in *Methods of Soil Analysis*, Part I (Physical and Mineralogical Methods) of the SSSA Book Series (see Rhoades & Oster, 1986) and elsewhere (Rhoades, 1990), mobile versions of these systems are described by Rhoades (1992).

This chapter describes prevalent laboratory methods for determining salinity (soil and water) based on measurements of EC or total dissolved solids after evaporation at 180°C. It also describes laboratory methods for making and for obtaining aqueous extracts of soil samples<sup>1</sup>. Various methods for determining the

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<sup>1</sup> Methods for collecting samples of soil water per se are not provided in this chapter, but the following provides some useful references in this regard. Samples of soil solutions may be obtained from soils by means of displacement, compaction, centrifugation, molecular adsorption and vacuum or pressure extraction methods (Richards, 1941). Displacement methods are described by Adams (1974); combination displacement/centrifugation methods by Gillman (1976); Mubarak and Olsen (1976, 1977) and Elkhatab et al. (1986); a combination vacuum/displacement method by Wolt and

concentrations of individual inorganic solutes (i.e.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_3\text{BO}_3$ , etc.) in waters and soil extracts in common use in laboratories having modern instrumentation are described elsewhere in this publication. Analogous methodology suited to laboratories without such conveniences are given in an earlier publication (see Bower & Wilcox, 1965).

## SATURATION AND OTHER AQUEOUS EXTRACTS

### Principles

Because present methods of obtaining soil water samples at typical field water contents are not very practical, aqueous extracts of the soil samples are usually made at higher than normal water contents for routine soil salinity diagnosis and characterization purposes. Because the absolute and relative amounts of the various solutes are influenced by the soil/water ratio at which the extract is made (Reitemeier, 1946), the soil/water ratio used to obtain the extract should be standardized to obtain results that can be applied and reasonably interpreted generally. Soil salinity is most generally defined and measured on aqueous extracts of so-called, saturated soil-pastes (U.S. Salinity Laboratory Staff, 1954). This water content (and water/soil ratio) varies with soil texture but is used because it is the lowest one for most soils for which sufficient extract can be practically removed from a soil sample for the compositional analysis of major constituents and because it is better related to soil-water contents under field conditions. For these same reasons, crop tolerance to salinity also is expressed in terms of the EC of the saturation extract ( $\text{EC}_e$ , Mass & Hoffman, 1977; Maas, 1986, 1990).

### Apparatus

1. Plastic containers with snaptight lids of 250-mL capacity or greater.
2. Vacuum line, suction apparatus (Richards filter funnel<sup>2</sup>, Buchner funnel, or commercial vacuum manifold) filter paper (medium grade, such as Whatman no. 50) and sample bottles [28.4 g (1 oz.) or larger, to collect and store extracts] with sealable caps.
3. Balance or scale accurate to at least 1 g.
4. Extraction bottles for soil suspensions.
5. Mechanical shaker.

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Graveel (1986); a simple field-pressure filtration method by Ross and Bartlett (1990); adsorption techniques by Shimshi (1966) and by Tadros and McGarity (1976) and centrifugation techniques by Davies and Davies (1963), Yamasuki and Kishita (1972), Gilman (1976), Dao and Lavy (1978), Kinniburgh and Miles (1983) and Elkhatib et al. (1987). Comparisons of the various methods have been made by Adams et al. (1980); Kittrick (1983); Wolt and Graveel (1986); Menzies and Bell (1988) and Ross and Bartlett (1990). The different suction-type samplers and other methods for sampling soil solution and various errors associated with them have been critically reviewed by Rhoades (1978), Rhoades and Oster (1986), Litaor (1988) and Grossman and Udluft (1991).

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<sup>2</sup> Richards, L.A. (1949).

### Reagent

1. Sodium hexametaphosphate  $[(\text{NaPO}_3)_6]$  solution, 0.1%. Dissolve 0.1 g of  $(\text{NaPO}_3)_6$  in water, and dilute the solution to 100 mL.

### Procedure

#### Saturation Extract

Weigh 200 to 400 g of air-dry soil of known water content into a tared plastic container having a snaptight lid. Weigh the container plus contents. Add distilled water to the soil with stirring until it is nearly saturated. Allow the mixture to stand covered for several hours to permit the soil to imbibe the water and the readily soluble salts to dissolve, and then add more water with stirring to achieve a uniformly saturated soil-water paste. At this point, which is generally reproducible to within  $\pm 5\%$ , the soil paste glistens as it reflects light, flows slightly when the container is tipped, slides freely and cleanly off a smooth spatula, and consolidates easily by tapping or jarring the container after a trench is formed in the paste with the side of the spatula. After mixing, allow the sample to stand (preferably for another 2 h), and then recheck the criteria for saturation. Free water should not collect on the soil surface, nor should the paste stiffen markedly or lose its glisten. If the paste is too wet, add additional dry soil of known amount (weight) to the paste mixture. Upon attainment of saturation, weigh the container plus contents. Record the increase in weight due to the amount of water added. Transfer the saturated soil paste to a filter funnel fitted with highly retentive filter paper. Apply vacuum, and collect the filtrate in a test tube or bottle. If the initial filtrate is turbid, refilter or discard it. Terminate the filtration when air begins to pass through the filter. Add 1 drop of 0.1%  $(\text{NaPO}_3)_6$  solution for each 25 mL of extract.

#### Extracts of Soil/Water Ratios of One:One and One:Five

Weigh a sample of air-dry soil of appropriate size, and transfer it to a flask or bottle. Add the required amount of distilled water (an equal weight for a 1:1 extract, 5 times the weight for a 1:5 extract), stopper the container, and shake it in a mechanical shaker for 1 h. If a mechanical shaker is not available, shake the container vigorously by hand for 1 min at least four times at 30-min intervals. Filter the suspension using highly retentive filter paper. (Discard or refilter the initial filtrate if it is turbid.) Add 0.1%  $(\text{NaPO}_3)_6$  solution at the rate of 1 drop/25 mL of extract.

### Calculations

Calculate the saturation water percentage (SP) of the saturated paste from the weight of oven-dry soil ( $W_s$ ) and the weight of water ( $W_w$ ) added ( $W_w$ ), including that initially present in the soil sample as,

$$SP = 100 \cdot W_w / W_s. \quad [1]$$

### Comments

The extraction ratios (1:1, 1:5, etc.) are easier to make than that of saturation, but they are less well related to field soil water composition and content. More importantly, salinity and compositional errors from dispersion, hydrolysis, cation exchange, and mineral dissolution increase as the water/soil ratio increases (Reitemeier, 1946). As a compromise, Sonneveld and van den Ende (1971) recommended a 1:2 (1 part soil = 2 parts water) *volume* extract, since it is closer to the saturation extract ratio but quicker to make. When relative changes rather than absolute solute concentrations are needed, these wider extraction ratios have the advantages of speed and greater volume.

The EC of extracts of gypsiferous soils decreases less, as the water/soil ratio increases, due to the dissolution of gypsum. This gypsum dissolution exaggerates the concentration of soluble salts present in the soil at lower water contents, especially those existing under field conditions.

Soil samples should not be oven-dried before extracting for determination of soluble salts, because heating to 105°C converts at least a part of the gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ) to plaster of paris ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ). The latter hydrate has a higher solubility in water than does the former. The solubilities of other salts and minerals also may be affected.

The weight of soil required will depend on the number and kind of determinations to be made on the extract, the analytical methods employed, and the salt content of the soil. In general, from one-fourth to one-third of the water in saturated soil pastes can be practically removed by vacuum filtration.

In determinations of extract water contents, especially when a high ratio of soil to water is used, it is desirable to correct for the water content of the soil sample. For example, an air-dry sample containing 2% water on an oven-dry basis can be adjusted to a soil/water ratio of 1:1 by adding 98 mL of water to 102 g of air-dry soil. At soil/water ratios of 1:5 or greater, no correction is ordinarily made for water in the air-dry sample.

Special precautions should be taken in preparing a saturated soil paste with peat and muck soils or very fine or very coarse-textured soils (Prichard et al., 1983). If possible, peat and muck soils should not be allowed to dry appreciably following collection because their saturation water content changes with dehydration. Peat and muck, especially if coarse or woody, require an overnight imbibition period to obtain a definite endpoint for the saturation point. After the first wetting, pastes of these soils usually stiffen upon standing. Adding water and remixing then yields a mixture that usually retains the characteristics of a saturated paste. With fine-textured soils, enough water should be added immediately, with a minimum of mixing, to bring the sample nearly to saturation. This minimizes the formation of clumps of soil during stirring, speeds the mixing process, and helps attain a more definite endpoint. Care also should be taken not to unduly overwet coarse-textured soils. The presence of free water on the surface of the paste after standing is an indication of oversaturation in the case of coarse-textured soils. Even small amounts of free water can lead to appreciable errors in saturation paste water contents for these materials. However, the effect on the value

of the EC of the extract ( $EC_e$ ) is small and usually does not significantly affect salinity diagnoses.

Sodium hexametaphosphate is added to the extract to prevent the precipitation of  $CaCO_3$  from the extract upon standing. The quantity of  $(NaPO_3)_6$  solution added increases the Na concentration about 0.5 ppm, or 0.02 mmol/L, which is inconsequential compared with the possible loss of  $CaCO_3$ . Alternatively, a subsample of the extract should be analyzed immediately or immediately diluted twofold and used for the Ca and alkalinity determinations.

Alternative methods of preparing the saturated soil paste have been described by Longenecker and Lyerly (1964), who proposed wetting the soil sample on a capillary saturation table, by Beatty and Loveday (1974) and Loveday (1972), who recommended predetermining the amount of water at saturation on a separate soil sample using a capillary wetting technique, and by Allison (1973), who recommended slowly adding soil to water (oversaturation method). Similar results are obtained with these methods. The choice of method is primarily one of personal preference.

Thymol can be added to the paste to minimize the effect of microbial activity on saturation extract composition during equilibration (Carlson et al., 1971).

The extracts should be stored at about 4°C until analyzed.

## ELECTRICAL CONDUCTIVITY OF WATERS AND AQUEOUS EXTRACTS

### Principles

Electrical conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. It is generally related to the total solute concentration and can be used as a quantitative expression of dissolved salt concentration, even though it is also affected by the mobilities, valences and relative concentrations of the individual ions present in the solution.

The determination of EC generally involves the physical measurement of resistance (R) in ohms. The R of a conducting material (such as a saline solution) is inversely proportional to its cross-sectional area (A) and directly proportional to its length (L). The magnitude of the R measured therefore depends on the characteristics (dimensions and spacings) of the conductivity cell and electrodes. Specific resistance ( $R_s$ ) is the R of a cube of the sample 1 cm on edge. Practical conductivity electrodes are not of this dimension and measure only a given fraction of the specific R; this fraction ( $R/R_s$ ) is commonly referred to as the cell constant (K).

The reciprocal of R is conductance (C). It is expressed in reciprocal ohms, or mhos. When the cell constant is applied, the measured conductance at a specified temperature is converted to specific C, the reciprocal of the specific R (herein called EC)

$$EC = \frac{1}{R_s} = K/R. \quad [2]$$

Electrical conductivity has been customarily reported in micromhos per centimeter ( $\mu\text{mho/cm}$ ) or in millimhos per centimeter ( $\text{mmho/cm}$ ). In the International System of Units (SI), the reciprocal of the ohm is the siemen (S) and, in this system, EC is reported as S/m or as dS/m. Therefore,  $1\text{S} = 1\text{ mho}$  or  $1\text{ dS/M} = 1\text{ millimho/cm}$ .

Electrolytic conductivity (unlike metallic conductivity) increases with temperature at a rate of approximately 1.9% per degree Centigrade. Since each ion has a different temperature coefficient, for precise work, conductivity ideally should be determined at 25°C. However, EC can be measured at other known temperatures and corrected to the 25°C reference using appropriate temperature coefficients (usually based on NaCl). Sodium chloride solutions have a temperature coefficient that closely approximates that of most surface- and groundwaters. Potassium chloride solutions have a lower temperature coefficient of conductivity than typical water aqueous solutions.

## Apparatus

### Conductance Meter

Any instrument capable of measuring conductance with an error not exceeding 1%, or 1  $\mu\text{S}$ , whichever is greater, is suitable. The instrument may be an automatic or manually operated wheatstone bridge, a deflection meter or a self-recording recorder or indicator. The preferred instrument is one which measures the ratio of the alternating current (1000 Hz) through the cell to the voltage across it, since it gives a more linear reading of conductance, and one which also includes automatic temperature sensing and compensation.

### Thermometer

For high-precision measurements, sample temperature is critical, and special electrical thermometers are desired in the instrument along with circuitry to compensate for temperature. When the instrument is not provided with automatic temperature compensation, sample temperature ( $t$ ) should be manually determined using a thermometer and the EC values measured at temperature  $t$  then adjusted to the reference value of 25°C using temperature-correction relations (or tables). For high-precision determinations, use a thermometer accurate to the nearest 0.1°C and covering the range of 20 to 30°C. For routine or field determinations, a thermometer accuracy of 0.5°C is adequate. If the measuring instrument is provided with a manual temperature compensator, adjust this to the measured sample temperature. If it has automatic compensation, allow sufficient time to permit equalization of sample and conductivity cell temperatures. If it has neither, measure and record the temperature of the samples at which the conductance is measured and adjust the value using an appropriate temperature-correction relation (see text below).

### Conductivity-Cell/Electrodes

Select a conductivity-cell having a cell constant appropriate to the EC of the sample (see Table 14-1). Flow-through cells should be used for measuring

Table 14-1. Recommended cell constants for various conductivity ranges.

| Range of conductivity | Cell constant   |
|-----------------------|-----------------|
| dS/m                  | m <sup>-1</sup> |
| 0.00005-0.020         | 0.0001          |
| 0.001-0.2             | 0.001           |
| 0.01-2                | 0.01            |
| 0.1-20                | 0.10            |
| 1-200                 | 0.50            |

solutions of EC values lower than 0.01 dS/m, in order to avoid contamination from the atmosphere. Recommended rate of flow through the cell is 0.3 m/s. In all other cases, pipet type- or dip-type cells can be used. The cell system should assure the retention of calibration under expected conditions of flow, pressure and temperature changes and should be resistant to corrosion. Ideally, it should be equipped with a means for the accurate measurement of sample temperature as discussed above. Either platinum—or nonplatinum type electrodes—can be used, depending upon accuracy requirements. Platinum type electrodes are more accurate. Electrodes made of durable common metals can be used for continuous monitoring or field use.

### Reagents

1. Platinizing solution. One gram chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) plus 12 mg lead acetate in 100 mL of pure water (EC < 0.001 dS/m).
2. Cleaning solution. Mixture of one part by volume of isopropyl alcohol, one part of ethyl ether, and one part of HCl (1 + 1).
3. Standard potassium chloride (KCl) solution, 0.010 M. Dissolve 0.7456 g of reagent grade anhydrous KCl in pure water (EC < 0.001 dS/m) and add more water to make to 1 L at 25°C. Store in a glass-stoppered borosilicate glass bottle. This reference solution has an EC of 1.413 dS/m at 25°C and is suitable for most solutions when the cell has a constant between one and two. For other cell constants use stronger or weaker KCl solutions, as listed in Table 14-2.

### Procedure

#### Preparation of Platinum Electrodes

Clean, new platinum-electrodes with chromic-sulfate acid solution and platinize the electrodes before use. Immerse the electrodes in the platinizing solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect the positive side of the battery to a piece of platinum wire and dip the wire into the solution. Continue the resulting electrolysis reaction until both cell electrodes are coated with platinum black. Use a current such that only a small quantity of gas is evolved. Subsequently, clean and replatinize the electrodes whenever the readings become erratic or a sharp endpoint can not be obtained or when visual examination shows some platinum black has flaked off. Rinse electrodes thoroughly after use and keep immersed in distilled water when not in use.



Table 17-2. Conductivity of KCl solutions at 25°C.

| Concentration | Conductivity |
|---------------|--------------|
| <i>M</i>      | dS/m         |
| 0.001         | 0.147        |
| 0.01          | 1.413        |
| 0.02          | 2.767        |
| 0.05          | 6.668        |
| 0.1           | 12.900       |
| 0.2           | 24.820       |
| 0.5           | 58.640       |
| 1             | 111.900      |

### Calibration of Cell

Rinse conductivity cell with at least three portions of 0.01 *M* KCL solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. Measure *R* (or *C*) of this portion and note the temperature. Repeat the measurement on additional portions of the reference KCL solution until the *R* value obtained remains constant within the required limits of precision.

Compute cell constant

$$K = (0.001413) (R_{KCL})/[1 + 0.019(25 - t)], \quad [3]$$

where  $R_{KCL}$  is the measured *R* (ohms) and *t* is measured temperature (°C).

### Measurement of Sample Conductivity

Rinse cell with one or more portions of sample. Ideally, adjust *t* of the final portion of sample to 25 ± 0.1°C and measure *R* or *C*; if not practical or necessary to adjust the *t* of the sample to 25°C, measure *t* and *R*, or *C*, at the same *t*. The technique used should be the same as that employed to calibrate the cell. Record these values.

### Calculation

When sample *R* is measured, conductivity (dS/m) at 25°C is

$$EC_{25} = 1,000 K[1 + 0.019(25 - t)]/R_x, \quad [4]$$

where  $R_x$  is measured *R* of the sample (ohms), *t* is the measured *t* and *K* is the cell constant ( $m^{-1}$ ).

When sample conductance is measured, conductivity (dS/m) at 25°C is

$$EC_{25} = C_x (1,000) K[1 + 0.0191(25 - t)], \quad [5]$$

where  $C_x$  is measured *C* of the sample (mhos).

Report the conductivity at 25°C in terms of dS/m to the nearest 1% of determined conductivity.

## Comments

Laboratory measurements of EC are relatively accurate. Errors are usually related to electrode fouling and inadequate sample circulation.

Besides being used to define and measure soil and water salinity and crop tolerances to salinity, EC is used to estimate aliquot size for chemical analysis, to check reliability of chemical analyses, to estimate total dissolved solids in a sample (by multiplying conductivity, in dS/m, by an empirical factor varying between 5.50 to 9.00 depending on the soluble components and temperature), to evaluate and express corrosion likelihood, and to assess the purity of demineralized water (freshly distilled water has a conductivity of 0.0005 to 0.002 dS/m, increasing after a few weeks of storage to 0.002 to 0.004 dS/m due to absorption of atmospheric  $\text{CO}_2$  and  $\text{NH}_3$ ).

Exposure of a sample to the atmosphere may cause changes in conductivity, due to the loss or gain of dissolved gases or water. This is quite important in the case of waters with low concentrations of dissolved electrolytes. Carbon dioxide, normally present in the air, can drastically change the EC of "pure" waters, as can atmosphere containing ammonia or acid gases. Contact with air should be avoided by using flow-through type conductivity-cells.

Because of marked differences in the equivalent weights, equivalent conductivities, and proportions of major solutes in soil extracts and water samples, the relationships between EC and salt concentration or between EC and osmotic pressure are only approximate. They are still quite useful, however. These relationships are:

1. Total cation (or anion concentration), mmoles charge/liter  $\cong 10 \times \text{EC}$ , in dS/m,
2. Total dissolved solids, mg/liter  $\cong 640 \times \text{EC}$ , in dS/m,
3. Osmotic pressure, kPa at  $25^\circ\text{C}$   $\cong 0.36 \times \text{EC}$ , in dS/m.

Pure water of low and known conductivity should be used in the preparation of the standard KCl solutions. The EC of this water should be added to that given in Table 14-2 and used in Eq. [3] to determine the cell constant, since the conductivity of the reference solution is that of the water plus that of the added KCl.

The temperature coefficient varies with concentration and upon the nature and composition of the dissolved electrolytes. The lower the concentration, the higher the coefficient, due to the effect of temperature upon the dissociation of water. The best way to correct for the temperature effect on conductivity is to hold the temperature of the sample and cell constant at  $25 \pm 0.5^\circ\text{C}$ . If this cannot be done, the next best way is to make determinations of sample EC at several temperatures, to plot the paired readings and to interpolate the EC at  $25^\circ\text{C}$  from the smoothed curve. For less-accurate needs, the EC at  $25^\circ\text{C}$  (in dS/m) can be calculated by multiplying the EC measured at the measured temperature by an appropriate coefficient  $f_t$ . The value of  $f_t$  can be estimated as  $[1 + 0.0019 (25 - t)]$ .

For routine field or laboratory testing, the cell constant of the conductivity cell should be determined and periodically checked by comparing instrument

readings taken with reference conductivity solutions at a known temperature, preferably 25°C.

For other discussions of EC see American Society for Testing and Materials (1986) and Helrich (1990).

## ELECTRICAL CONDUCTIVITY OF SATURATED SOIL PASTES AND DETERMINATION OF SOIL SALINITY

### Principles

Soil salinity, in terms of  $EC_e$ , may be estimated from measurement of the EC of the saturated soil-paste ( $EC_p$ ) and estimates of saturation percentage (SP). The measurement of  $EC_p$  and the estimate of SP can be made using an EC-cup of known geometry and volume. The method is suitable for both laboratory and field applications, especially the latter, because the apparatus is inexpensive, simple and rugged and because the determination of  $EC_p$  can be made much more quickly than of  $EC_e$ .

Rhoades et al. (1989a) have shown that the following relation describes the EC of saturated soil pastes,

$$EC_p = \left[ \frac{(\theta + \theta_{ws})^2 EC_e EC_s}{(\theta_s) EC_e + (\theta_{ws}) EC_s} \right] + (\theta_w - \theta_{ws}) EC_e, \quad [6]$$

where  $EC_p$  and  $EC_e$  are as defined previously,  $\theta_w$  and  $\theta_s$  are the volume fractions of total water and solids in the paste, respectively,  $\theta_{ws}$  is the volume fraction of water in the paste that is coupled with the solid phase to provide a series-coupled electrical pathway through the paste,  $EC_s$  is the average specific EC of the solid particles, and the difference  $(\theta_w - \theta_{ws})$  is  $\theta_{wc}$ , which is the volume fraction of water in the paste that provides a continuous pathway for electrical current flow through the paste (a parallel pathway to  $\theta_{ws}$ ). Assuming the average particle density ( $\rho_s$ ) of mineral soils to be 2.65 g/cm<sup>3</sup> and the density of saturation soil-paste extracts ( $\rho_w$ ) to be 1.00,  $\theta_s$  and  $\theta_w$  are directly related to SP as follows

$$\theta_w = SP \div \left[ \frac{\rho_w 100}{\rho_s} + SP \right], \quad [7]$$

$$\theta_s = 1 - \theta_w. \quad [8]$$

As shown by Rhoades et al. (1989a,b), the SP of many mineral soils can be adequately estimated in the field for purposes of salinity appraisal from the weight of the paste-filled cup. Figure 14-1 may be used for this purpose, for details of the relations inherent in this figure see Wilcox (1951).

Electrical conductivity of the saturation extract can be determined from measurement of  $EC_p$  and SP (using Eqs. 6-8), if values of  $\rho_s$ ,  $\theta_{ws}$  and  $EC_s$  are known. These parameters can be adequately estimated, as demonstrated by

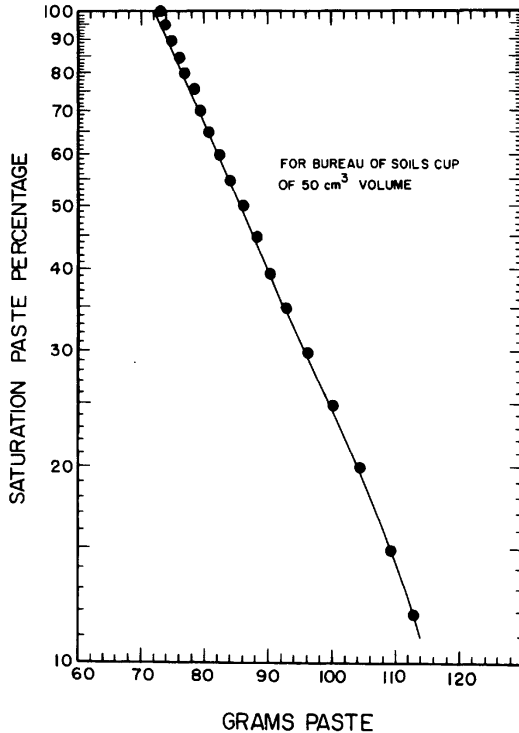


Fig. 14-1. Theoretical relation between saturation percentage (SP) and weight (g) of 50 cm<sup>3</sup> of saturated paste, assuming a particle density of 2.65 g/cm<sup>3</sup>.

Rhoades et al. (1989a). For typical arid land soils of the southwestern USA,  $\rho_s$  may be assumed to be 2.65 g/cm<sup>3</sup>;  $EC_s$  may be estimated from SP as  $EC_s = 0.019 (SP) - 0.434$ , and the difference ( $\theta_w - \theta_{ws}$ ) may be estimated from SP as  $(\theta_w - \theta_{ws}) = 0.237 (SP)^{0.6657}$ .

### Apparatus

1. Conductance meter. Almost any laboratory C meter can be used, preferably a temperature compensating type as described in "Apparatus." An example is shown in Fig. 14-3.
2. Large cup-type conductivity cell. The 50-cm<sup>3</sup> volume "Bureau of Soils" cup is suitable (U.S. Salinity Laboratory Staff, 1954). An example is shown in Fig. 14-2.
3. Portable balance. Capable of weighing accurately to the nearest 0.5 g. An example is shown in Fig. 14-2.

### Reagents

1. Standard potassium chloride solutions, 0.010 and 0.100 M solution. Same as described in "Reagents."



Fig. 14-2. Picture of portable balance used in the field to determine the weight of the saturated soil-paste filling the "Bureau of Soils" cup.

### Procedure

Rinse and fill the conductivity cup with KCl solution. Adjust the conductivity meter to read the standard conductivity. Rinse and fill the cup with the saturated soil-paste, tap the cup to dislodge any air entrapped within the paste. Level off the paste with the surface of the cup. Weigh the cup plus paste, subtract the cup tare weight to determine the grams of paste ( $W_p$ ) occupying the cup. Connect the cup electrodes to the conductivity meter and determine the  $EC_p$ , corrected to 25°C, directly from the meter display.

### Calculation

Obtain the SP value from Fig. 14-1 corresponding to  $W_p$ . Obtain  $EC_e$  from Fig. 14-4 given  $EC_p$  and SP, using the curve corresponding to the SP value, or calculate  $EC_e$  using the following equation

$$EC_e = (-b \pm \sqrt{b^2 - 4ac})/2a, \quad [9]$$

where  $a = [\theta_s (\theta_w - \theta_{ws})]$ ,  $b = [(\theta_s + \theta_{ws})^2 (EC_s) + (\theta_w - \theta_{ws}) (\theta_{ws} EC_s) - (\theta_s) EC_p]$  and  $c = -(\theta_{ws})(EC_s)(EC_p)$ .

### Comments

Sensitivity analyses and tests have shown that the estimates used in this method are generally adequate for salinity appraisal purposes of typical mineral

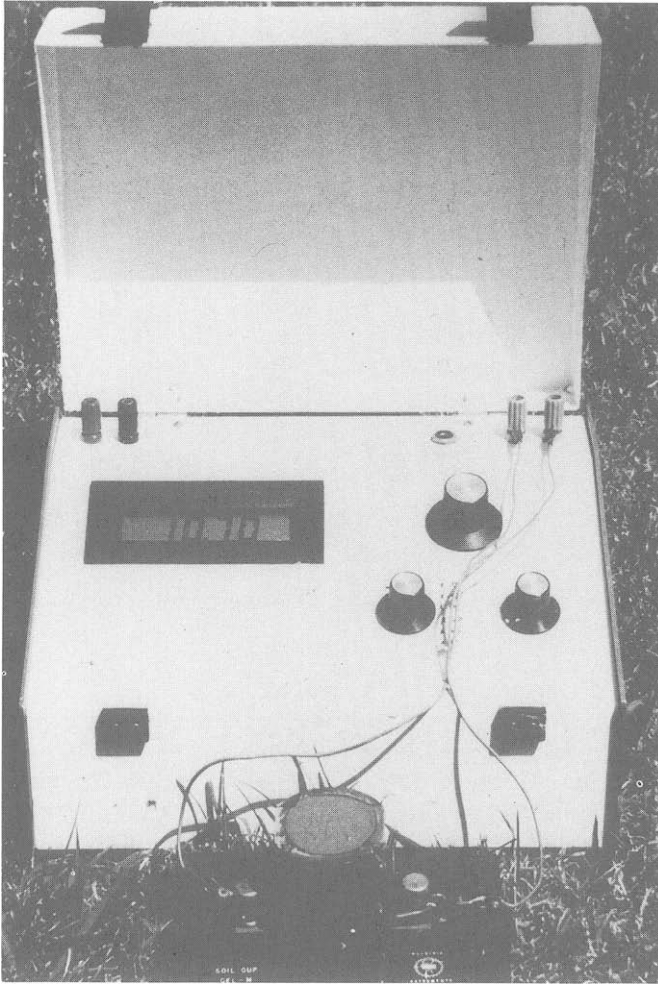


Fig. 14-3. Picture of "Bureau of Soils Cup" filled with saturated soil paste connected to conductance meter.

arid-land soils of the southwestern USA (Rhoades et al., 1989b). For organic soils or soils of very different mineralogy or magnetic properties, these estimates may be inappropriate. For such soils, appropriate values for  $\rho_s$ ,  $EC_s$  and  $\theta_{ws}$  will need to be determined using analogous techniques to those of Rhoades et al. (1989a).

It should be noted that  $(EC_e \theta_e)$  is not equivalent to  $(EC_w \theta_w)$  because different amounts of soil are involved in the two measurements. The relation between these two products is

$$(EC_w \theta_w)/\rho_b \approx EC_e SP/100. \quad [10]$$

Data to support this is given in Rhoades et al. (1989b, 1990).

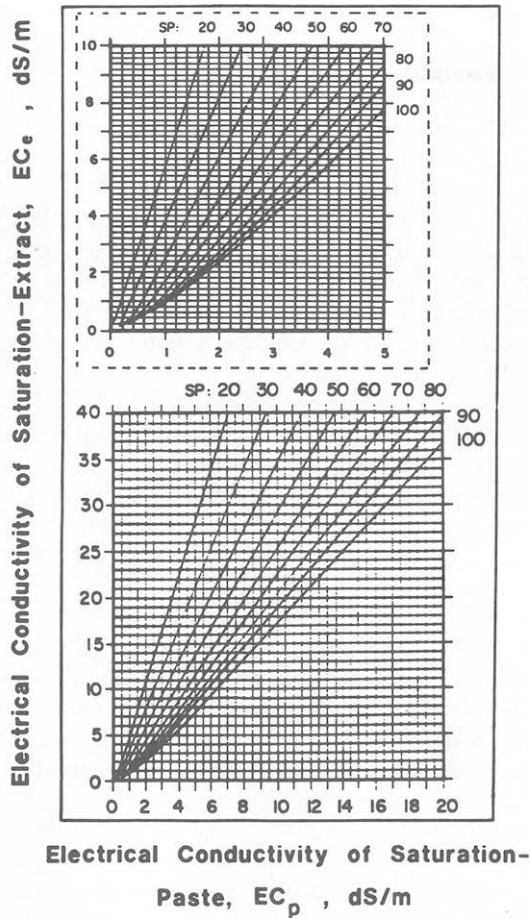


Fig. 14-4. Relations between electrical conductivity of saturated soil-paste ( $EC_p$ ), electrical conductivity of saturation extract ( $EC_e$ ) and saturation percentage (SP), for representative arid-land soils.

## TOTAL DISSOLVED SOLIDS IN WATERS AND AQUEOUS EXTRACTS

### Principles

The amount (concentration) of total dissolved solids in a sample is determined by weighing the residue obtained after evaporating a sample that has been filtered to remove particulate matter. A sample is filtered through a standard membrane (usually  $0.45 \mu\text{m}$  in pore size) filter and the filtrate is evaporated to dryness in a weighed dish and dried to a constant weight of  $180^\circ\text{C}$ . The increase in weight represents the total dissolved solids. The definition is operational since certain colloids may not be removed by filtration and the evaporation residue usually differs in composition from the dissolved matter initially present in the water.

### Apparatus

1. Sample reservoir. A chemically resistant container of 1- to 4-L capacity.
2. Glass Petri dish. 150-mm diam.
3. Evaporating dish. A straight-wall or round bottom dish of 80- to 100-mm diam. and approximately 200-mL capacity made of platinum, porcelain or high-silica glass.
4. Heater. A controlled electric hot plate, infrared lamp or steam bath which is capable of maintaining the t of the evaporating sample near the boiling point.
5. Muffle furnace. Capable of operation at  $550 \pm 50^\circ\text{C}$ .
6. Desiccator. Large sealable chamber provided with a desiccant containing a color indicator of moisture concentration.
7. Drying oven. Capable of operation at  $180 \pm 2^\circ\text{C}$ .
8. Analytical balance. Capable of weighing to an accuracy of 0.1 mg.
9. Filtration apparatus. Any suitable commercial membrane filtration system capable of removing particulates  $>0.45$  mm in size.

### Procedure

Heat clean evaporating dish to  $180 \pm 2^\circ\text{C}$  for 1 h in oven, store in desiccator until needed, weigh just before use. Choose sample volume to yield upon evaporation approximately 25 mg of residue, if only the amount of residue is to be determined, or 100 mg of residue if it is to be analyzed for composition. Pass the measured volume of sample through the filter membrane and then follow with three successive 10-mL volume increments of distilled water. Quantitatively transfer the filtered sample aliquot to a sample reservoir. Fill an evaporating dish (that previously has been ignited at  $600 \pm 25^\circ\text{C}$  for 1 h, cooled in a desiccator and weighed) to nearly full with a portion of the sample. Heat the dish to evaporate this portion, but do not allow it to boil or dry. Periodically add more of the sample from the reservoir to the dish until the reservoir is empty. Rinse the reservoir several times with pure water, adding the rinsings to the contents of the evaporating dish. Then evaporate the remainder of the material in the dish to near dryness. Transfer to a  $103^\circ\text{C}$  oven and complete the evaporation. Dry the dish + contents for 1 h at  $180 \pm 2^\circ\text{C}$ , cool in a desiccator, and then weigh. Repeat the cycle of drying (1 h periods), cooling, desiccating and weighing until a constant weight is obtained or until loss in weight is no more than 4% of the previous weight or 0.5 mg, whichever is less. Record the weight of residue as total dissolved matter.

### Calculation

Calculate the concentration of total dissolved solids in milligrams per liter (essentially parts per million), as follows

$$\text{total dissolved solids, mg L}^{-1} = (A - B)1000/\text{sample volume, mL}, \quad [11]$$

where A is weight of dried residue plus dish (mg) and B is weight of dish (mg).



## Comments

Highly mineralized waters with a considerable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and/or  $\text{SO}_4^{2-}$  content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

Samples high in  $\text{HCO}_3^-$  require careful drying at  $180^\circ\text{C}$  to insure complete conversion of  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$ . The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Residues dried at  $103$  to  $105^\circ\text{C}$  may retain not only water of crystallization but also some mechanically occluded water. Loss of  $\text{CO}_2$  will result in conversion of  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$ . Loss of organic matter by volatilization usually will be very slight. Residues dried at  $180^\circ\text{C}$  will lose almost all mechanically occluded water. Organic matter may be lost by volatilization, but not completely destroyed. Some carbonates may be converted partially to oxides.

The results may not agree with the theoretical value for solids calculated from the chemical analysis of the sample. In general, evaporating and drying water samples at  $180^\circ\text{C}$  yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values obtained through drying at the lower temperature.

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