

# Determining Soil and Water Sodicity from Electrode Measurements

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## ABSTRACT

A method is presented for estimating the sodium adsorption ratio (SAR) of the saturated soil-paste extract from three electrode measurements made directly in the saturated soil-paste. An analogous method is presented for the determination of the SAR of extracts and solutions solely from electrode measurements made in the extract or solution. Both methods are carried out without the use of pH and ionic strength buffers. The methods were tested on a widespread range of salt-affected soils and their extracts; they are deemed suitable for field applications in the diagnosis, screening, and classification of sodic soils and waters.

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## INTRODUCTION

The reclamation and management of salt-affected soils requires appropriate, practical methods for diagnosing salinity and sodicity and for determining amendment requirements. Such methods are also needed for monitoring effects of treatments and management practices (Rhoades, 1990).

Soil salinity refers to the presence of excessive levels of total dissolved inorganic solutes that affect soil chemical, physical and biological properties. Traditionally, saline soils have been defined and diagnosed from laboratory measurements of the electrical conductivity of extracts of saturated soil-pastes ( $EC_e$ , in units of dS/m at 25°C). The electrical conductivity (EC) of an aqueous solution is a practical index of its total ionic solute concentration, whereas  $EC_e$  is a practical index of the salinity of a soil. The saturated soil-paste (hereafter referred to as saturated-paste) provides the lowest water/soil proportion that will dissolve all of the immediately soluble salts present in the soil and that will permit enough extract to be readily separated from the paste with low pressure or vacuum systems for salinity/sodicity analysis purposes (U.S. Salinity Laboratory Staff, 1954). The water content of a saturated-paste, expressed as a percentage, is designated the saturation percentage (SP); SP is related to soil properties and is often approximated as twice field capacity.

Soil sodicity refers to the presence of excessive levels of sodium (Na) in the soil, given the accompanying levels of salinity and pH. It is generally the relative amount of Na adsorbed on the cation exchange sites of the soil that is most directly associated with the deleterious properties and problems of so-called sodic soils. Hence, such soils are diagnosed and defined from laboratory measurements of either exchangeable Na percentage (ESP) or the Na-adsorption-ratio of the extract [ $(SAR_e = Na/(Ca+Mg)/2)^{0.5}$ , where the cation concentrations are expressed as mmol/L<sup>-1</sup>], taking into account the accompanying pH of the extract ( $pH_e$ ) and level of salinity (i.e.,  $EC_e$ ; U.S. Salinity Laboratory Staff, 1954; Bower and Hatcher, 1962; Rhoades, 1982). The  $SAR_e$  has been used as a proxy for ESP in this diagnosis, because the two are so closely related and the former is more easily measured.

The various classes of salt-affected soils are traditionally defined in terms of the combinations of their  $EC_e$ ,  $SAR_e$ , and  $pH_e$  values and various management-related soil properties and classes are inferred from these values and from SP. These classes, properties, and management are discussed elsewhere (U.S. Salinity Laboratory Staff, 1954; Rhoades and Miyamoto, 1990).

Rhoades et al. (1989) showed that the speed in the determination of the  $EC_e$  of soil samples could be appreciably increased compared to conventional laboratory methods using simple electrode- and weight-measurements made directly on the saturated-paste. This procedure involves the measurement of the electrical conductivity of the saturated soil-paste ( $EC_p$ ) and the its volume-weight ( $W_p$ ). It saves the time required to collect the extract, which is often the most time consuming step involved in the traditional method of salinity appraisal. It also

makes field measurements more practical, since vacuum-extraction equipment is no longer required.

An analogous, simple, field-practical method for determining soil sodicity should prove even more useful than that for salinity, since  $SAR_e$  measurements are substantially more time consuming than  $EC_e$  measurements and are even more difficult to perform in the field. For this reason, we undertook to develop such a procedure; one that, like the earlier method, would involve solely measurements made directly in the saturated-paste, avoiding the collection of extracts. Additionally, in the case of sodicity, one which would eliminate the need for multiple cation analyses.

The following general approach formed the conceptual basis of the procedure. The value of  $EC_e$  would be estimated from  $EC_p$  and  $W_p$  using the previously developed method of Rhoades et al. (1989). In turn, the total cation concentration on a charge (C) basis ( $S_c$ , in  $mmol_c L^{-1}$ ) and ionic strength (I) of the extract would be estimated using conventional empirical relations between  $S_c$  and  $EC_e$  (such as that available in U.S. Salinity Laboratory Staff, 1954) and between I and  $EC_e$  (such as that available in Jurinak and Suarez, 1990). The vast majority of cations in most salt-affected soils are Na, calcium (Ca), and magnesium (Mg); potassium (K) is the next most abundant cation, but it is typically less than 10% of the total cations, on a  $mmol_c L^{-1}$  basis. Thus, the Ca plus Mg concentration of an extract can be estimated as the difference ( $S_c - Na_e$ ), where  $Na_e$  refers to the concentration of Na in the extract. In turn,  $SAR_e$  can be estimated from its defining relationship between  $Na_e$  and Ca plus Mg concentrations.

The attempts of Robbins and Meyer (1990) and of Munk (1992) to develop relations between SAR, pH and EC for both extracts and water samples demonstrate the interest in such relations and in the potential utility of using them for estimating SAR and screening soils for sodicity. However, neither of these approaches would be suitable for our purpose because the methods they developed still required the time consuming analytical steps involved in the collection and cation analysis of the saturated-paste extracts. Additionally, they employed statistical relations to estimate SAR from pH and EC which varied from one class of soil or water to another and which were neither robust nor generally very accurate. The methods given herein reduce these limitations.

## HYPOTHESIS AND OBJECTIVES

Measurements made with specific-ion electrodes are conventionally made in aqueous media with the addition of buffer-solutions to "normalize" for the effects of variable ionic-strength and pH on electrode response. Temperature is kept the same in both the calibration- and "unknown-" solutions in order to normalize any temperature effect on the electrode response. However, addition of buffers to the saturated-pastes is not appropriate, because such additions would affect the solubilities of the salt-minerals present in the soil, and hence, would alter the

value of  $SAR_e$ . Such additions would also interfere with the complementary determinations of soil salinity and pH, which are also needed in order to appraise soil sodicity by our proposed method. Thus, prerequisites of our proposed "paste-method" of sodicity appraisal are twofold. The first is the ability to account/compensate for the effects of variations in ionic-strength, temperature and pH that will exist among different soils on the Na-electrode measurements made in the saturated-pastes. The second is the ability to "correct" for any substantial additional interference caused by the presence of the solid phase of the paste, *per se*, on the Na-electrode response.

Based on the findings of Bower (1961), it was thought possible to correct EMF-measurements made directly in the saturated soil-paste with a Na-specific electrode for "suspension" effects and then to estimate Na concentration in the extract solution. The potential for such an approach was confirmed in preliminary studies where measurements made directly in saturated-pastes with a prototype "Hach<sup>2</sup> Na-specific electrode" were found to not be substantially affected by the presence of soil particles nor by exchangeable Na.

It would be senseless to attempt to develop the proposed sodicity method if: 1)  $SAR_e$  could not be suitably predicted given accurate knowledge of  $EC_e$ ,  $Na_e$ , and  $pH_e$  values, since the method is based on the use of estimates of these parameters, 2)  $Na_e$  could not be suitably estimated from Na-electrode measurements made without benefit of the use of pH and ionic-strength buffers, and 3) interferences caused by the presence of the solid phase of the saturated-paste can not be compensated for when Na-electrode measurements are made in it. Thus, this project was undertaken in three phases. The first-phase studies were undertaken to evaluate the potential accuracy for determining the SAR of extracts solely from knowledge of their  $EC_e$ ,  $Na_e$ , and  $pH_e$  values, as determined by standard analytical procedures. The second-phase studies were undertaken to evaluate the potential for determining  $SAR_e$  when  $Na_e$  was estimated from Na-electrode measurements made upon the extracts without benefit of the use of pH and ionic-strength buffers. The third-phase studies were undertaken to evaluate the potential for determining  $SAR_e$  when the values of  $EC_e$ ,  $Na_e$ , and  $pH_e$  are each estimated from electrode measurements made directly upon the saturated soil-paste. These evaluations were undertaken using three sets of saturated-paste extracts obtained from representative salt-affected soils. The division of the study into these three phases allowed the separate effects of the various potential errors involved in the proposed  $SAR_e$  estimation procedure to be better identified and quantified.

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<sup>2</sup>The citation of particular products is for the convenience of the reader and does not imply any particular endorsement of the USDA or its agents. A Cooperative Research and Development Agreement (CRADA) was developed between Hach Co. and ARS to commercialize the salinity measurement method of Rhoades et al. (1989) and the sodicity measurement method described in this paper.

## MATERIALS AND METHODS

Samples of 86 soils representative of typical salt-affected soils, including sodic soils, were freshly collected for this project. The soil samples came from Arizona, California, Colorado, Egypt, Idaho, India, North Dakota, and Texas. The extracts of the saturated soil-pastes of all 86 soils were obtained using standard methods (U.S. Salinity Laboratory Staff, 1954). The extracts were analyzed by standard methods (Rhoades, 1982) for the following properties:  $EC_e$  using a YSI model 32 conductance meter<sup>3</sup> and a Beckman<sup>3</sup> small volume flow-through, conductivity-cell; Na, K, Ca, Mg, and  $SO_4$  concentrations using an AES, ICP analyzer<sup>3</sup>; Cl concentration using an Amino, automatic chloride titrator<sup>3</sup>;  $HCO_3$  concentration using a Brinkman Metrohm potentiometric titrator<sup>3</sup>, and Beckman<sup>3</sup> glass pH-electrode;  $NO_3$  concentration using a Hitachi<sup>3</sup> spectrophotometer, and pH and temperature using a Hach One pH meter<sup>3</sup> and new-version, Hach One combination dispensing pH electrode<sup>3</sup> ("jelly electrode") and temperature sensor. The saturation percentage (SP) values of the pastes were determined by oven drying. Additionally,  $EC_e$  and SP were estimated from measurements made directly on the saturated soil-pastes using the " $EC_p/W_p$ " method of Rhoades et al. (1989).

### Determining SAR from Sum of Cations and Sodium (Phase I)

As discussed previously, since the sum of cations ( $S_c$ , in  $mmol_c L^{-1}$ ) in extracts is related to  $EC_e$  (in dS/m), and since these cations in salt-affected soils are predominantly composed of Na, Ca, and Mg, SAR could be predicted as

$$\text{prd SAR} = Na / ([S_c - Na] / 2)^{1/2} \quad [1]$$

where prd SAR represents predicted SAR. Two commonly referenced relations between  $EC$  and  $S_c$  exist that can be used to estimate  $S_c$  from  $EC$  for purposes of Equation [1]. One is derivable from data given in Handbook 60 ( $\log S_c = 1.000 + 1.008 \log EC$ ; Figure 4, U.S. Salinity Laboratory Staff, 1954). The other is the one published by Marion and Babcock (1976:  $\log S_c = 0.990 + 1.055 \log EC$ ). The former relation is based solely on extracts of salt-affected soils; the latter is based on a very small set of samples, of which only six were saturated-paste extracts. A deficiency in both of these relations is that the effect of cation and anion composition on the  $EC/S_c$  relation is missing. As evident in Figure 2 of Handbook 60, the  $EC/S_c$  relation varies with salt-type. While the relationship in Figure 4 of Handbook 60 is reasonably good for the general makeup of salts that occur in the extracts of most salt-affected soils, a better relation should be obtainable if the "chemistry" of the extract could somehow be included. We undertook to incorporate some of this effect into the  $EC/S_c$  relation by the introduction of a pH term as:

$$\log(S_c) = b_0 + b_1 \log(EC_e) + b_2 (pH - 8.4) \quad [2]$$

The pH term was conceived as a means to adjust for differences in the EC/ $S_c$  relation for chloride-(pH~6), sulphate-(pH~7.7), and carbonate-(pH>~8.4) dominant salt-types. Since the "Handbook 60" and "Marion and Babcock" relations did not include pH, we used our eighty six sample data-set to estimate the parameters in Equation [2] and then we tested all three relations for their suitability in predicting SAR from Equation [1] using the analytical data for the 86 samples. This test was carried out as follows: concentrations of Na, Ca and Mg in these extracts were determined by ICP analysis. The SAR<sub>c</sub> values of these extracts were calculated from these concentrations. Corresponding values of SAR<sub>c</sub> for these same solutions were predicted from Equation [1] using the Na<sub>c</sub> values and each of the three values of  $S_c$  obtained from the three different methods described above for estimating  $S_c$  from  $E_c$ . The observed correspondences between the measured and predicted values of SAR<sub>c</sub> were used to determine: 1) how well SAR values of salt-affected soil extracts can be estimated solely from reasonably accurate measurements of Na concentration and EC with and 2) which EC/ $S_c$  model is the more appropriate to use in this regard.

### Determining Sodium in Solutions from Unbuffered Electrode Measurements (Phase II)

An initial Phase II study was carried out using a preliminary version of Hachs' new-generation Na-electrode and 45 soil samples which came mostly from California and Colorado. This set of samples is referred to as the 1st-set. A subsequent Phase II study was carried out using the current version of Hachs' Na-electrode and 39 soil samples. This set included soils from multiple sites throughout the Western United States and a few soils from Egypt and India; it is referred to as the 2nd-set. A final Phase II study was carried out using 13 samples (11 of which were a subset of the 2nd-set of soil samples), hereafter referred to as the 3rd-set. The current version of Hachs' Na-electrode was also used in this final study.

Saturated-pastes were prepared of all three soil-sets. Their extracts were collected and analyzed for EC, cations (Na, Ca, Mg, and K), anions (Cl, SO<sub>4</sub>, HCO<sub>3</sub>, CO<sub>3</sub>, and NO<sub>3</sub>) and pH. The SAR<sub>c</sub> values calculated from these analyses were used as a standard of comparison with those determined with the Hach Na-electrode measurements made without the conventional use of pH and ionic strength buffers.

Sodium activities in the extract solutions were determined from the readings obtained with the Na- and pH-electrodes immersed in the extracts using the following equation:

$$\log A_{Na} = \alpha_0 + \alpha_1 mV + \alpha_2 pH \quad [3]$$

where,  $A_{Na}$  is the Na activity, mV is the "steady" Na-electrode reading, pH is the "steady" pH-electrode reading and  $\alpha_0$ ,  $\alpha_1$ , and  $\alpha_2$  are empirically determined regression coefficients established for the Na-electrode using the calibration standard-solutions described in Table 1. Since no buffers were added to these

extracts or solutions, a pH term was included in this equation to compensate for pH effects on the Na-electrode response. Justification for this approach is given later. Steady Na-electrode and pH readings were normally obtained after about 1-3 minutes.

The solutions used to calibrate the Na-electrode were synthesized from magnesium chloride, sodium chloride and sodium bicarbonate salts to produce solutions with SAR values ranging between about 1-100, EC values between about 1-20 dS/m and pH values between about 5.5 to 10.5. These ranges were selected to cover those of relevance for essentially all sodic soil appraisal needs. Calcium salts were avoided to prevent problems associated with  $\text{CaCO}_3$  precipitation. The Na activities of these solutions were determined using their analytically determined solute compositions and the CARBCHEM program of Suarez (1977). These activities were then regressed against the corresponding Na-electrode millivolt and pH values (obtained with the electrodes equilibrated in these solutions) to produce a calibration equation for the Na-electrode adjusted for pH interference-effects (Equation [3]). The observed  $R^2$  value of 0.997 and the t-test values associated with the mV and pH parameters show that Na activity was significantly (0.0001) correlated with both of these two factors and that an excellent Na-electrode calibration was obtained without the use of pH and ionic strength buffers. An analysis of the calibration regression-residuals revealed that the relative percent error (RPE<sup>3</sup>) was only 6.1%. These results indicated that accurate Na concentrations of aqueous media can be obtained using Na-electrodes without use of ionic strength and pH buffers. The practical utility of this latter method to determine Na concentrations of unbuffered solutions with a Na-electrode differs from the conventional approach only in that the calibration of the electrode is accomplished using standard solutions varying in EC and pH, as well as in Na activity (not concentration).

Based on the above-described finding, Equation [3] was adopted and used to calibrate the Na-electrodes used in the Phase II and III studies. Calibrations of the Na-electrode were obtained using the five standard-solutions shown in Table 1 immediately before the Na-electrode was used to measure a batch of extracts (or, in the Phase III study, a batch of saturated-pastes). In this way, day to day variations in electrode performance, if any, were compensated for in the determinations of the Na activities. A test was made to see if the Hach Na-electrode needed to be calibrated for pH effects each time the electrode was used. This was done by

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<sup>3</sup>The RPE is defined as  $RPE=100(10^e-1)$ , where  $e=\log(pNa)-\log(Na)$ , and (pNa) represents the predicted Na activity. The RPE is a useful measure of prediction accuracy, since it effectively "back-transforms" the error distribution to the original scale. For example, if the standard deviation of the RPE is 5%, then approximately 68% of the predictions will fall within 1 standard deviation (e.g.;  $\pm 5\%$ ) of the true levels (assuming the residual errors are approximately normally distributed). Likewise, approximately 95% of the predictions should fall within 2 standard deviations (e.g.;  $\pm 10\%$ ).

TABLE 1. Compositions of solutions used for calibrating the Na-electrode.

Lab ID No.	pH	EC	Na	Mg	HCO <sub>3</sub>	Cl	SAR
		dS/m	mmol/l				(mmol/l) <sup>1/2</sup>
1	5.5	1.2	5.7	4.2	0.0	9.8	3.9
2	10.4	1.2	7.2	5.5	7.2	5.7	4.3
3	8.5	4.2	34.0	7.8	14.1	27.3	17.2
4	5.5	18.2	166.6	10.1	0.0	179.5	74.0
5	9.9	15.1	199.4	9.7	186.9	10.26	90.5

carrying out an F-test of the equivalence of the pH parameter values obtained in each calibration batch used in the 1st, 2nd and 3rd data sets. The resultant non-significant F-test results (F-value < 1) showed that the pH parameter did not vary significantly among the many different calibration-batches used in these data sets. The average pH parameter value obtained was 0.0212. Hence, this value was used as the pH parameter value in Equation [3] in all of the Na-electrode calibrations and for all estimations made of Na activities in the extracts or saturated-pastes in this project.

Sodium concentrations were calculated from Na activities, as inferred from the Na-electrode readings and EC and pH measurements as follows. First, the ionic strengths (I) of the extracts were estimated from their EC<sub>e</sub> values using the following formula, which was a modification of that of Jurinak and Suarez (1990),

$$I = 0.0127(\delta EC_e) \quad [4]$$

where  $\delta$  represents a correction factor used to compensate for the seepage of reference solution from the Na- and pH-electrodes into the extracts during measurements. This correction was only performed upon the 1st data-set, since only the earlier version of the Hach Na-electrode was observed to introduce enough reference solution into the extract during the analysis period to alter EC<sub>e</sub> significantly.<sup>4</sup> No increase in EC<sub>e</sub> was observed when the current-version, Hach Na-electrode was used in the measurements made upon the 2nd and 3rd sets of soil extracts. Hence, for these cases  $\delta$  was set equal to 1.0.

<sup>4</sup>The value of  $\delta$  was estimated as  $\gamma = 1.159 \ln EC_e - 0.726 \ln V + 0.080 (\ln EC_e * \ln V)$ ,  $\delta = \exp \gamma + 1$ , where V represents the volume (in mL) of the extract solution. This relation was developed empirically using experimental data (data not given).



Next, the activity coefficient for Na was calculated from ionic strength (I), after Truesdell and Jones (1974), using Equation [5a]

$$\log \gamma = \tau_1 I^{1/2} / (1 + 4\tau_2 I^{1/2}) + 0.0751 \quad [5a]$$

where

$$\log \tau_1 = -1.15083 + 93.642/\kappa + 0.001830\kappa \quad [5b]$$

$$\log \tau_2 = 0.76645 + 30.770/\kappa + 0.000606\kappa \quad [5c]$$

and I is ionic strength and  $\kappa$  is temperature in degrees kelvin.

Finally, the Na concentration of each extract was calculated by dividing its Na activity, as determined from the electrode measurements and Equation [3], by its appropriate activity coefficient (obtained from Equation [5a]).

### Determining SAR<sub>e</sub> from Electrode Measurements Made in Saturated-Pastes (Phase III)

Prediction of the Na concentrations in the aqueous phase of the saturated-pastes (thus predictions of Na<sub>e</sub>, i.e., prd Na<sub>e</sub>) from electrode measurements made directly in the saturated-pastes were carried out in the same manner as in Phase II, with the following additions: 1) the electrode measurements were, of course, made in the saturated-pastes rather than in the extracts; 2) the pH readings made directly in the saturated-paste (pH<sub>p</sub>) were adjusted to estimate their equivalent extract values (est pH<sub>e</sub>); 3) EC<sub>e</sub> was estimated from EC<sub>p</sub> and W<sub>p</sub> using the method of Rhoades et al. (1989); and 4) the Na concentrations estimated from the Na-electrode mV readings made in the pastes were adjusted for the "suspension" interference effects, as explained below.

An empirical correction was made to the pH values measured in the pastes (pH<sub>p</sub>) in order to estimate their corresponding pH<sub>e</sub> values because it was observed that pH<sub>e</sub> exceeded pH<sub>p</sub> below a pH<sub>p</sub> value of about 8.0 (Figure 1). The linear spline model shown in Equation [6] was used to estimate this correction:

$$\text{pH}_e - \text{pH}_p = b_0 + b_1(\text{pH}_p), \text{ for } \text{pH}_p \leq 8.05 \quad [6a]$$

$$\text{pH}_e - \text{pH}_p = 6.265 - 0.778(\text{pH}_p) \quad [6b]$$

with the restriction that the regression coefficients,  $b_0$  and  $b_1$ , are such that  $b_0 + b_1(\text{pH}_p) = 0$  at 8.05. The spline knot value of 8.05 and the values of the  $b_0$  and  $b_1$  coefficients were obtained using an iterative, optimization process and a standard nonlinear least-squares algorithm (Freund and Littell, 1991: SAS procedure NLIN, method DUD) designed to minimize the overall mean square error (MSE) of the regression model fit to the pooled pH data-sets (1st, 2nd, and 3rd). The resultant values for the  $b_0$  and  $b_1$  coefficients (and standard errors) were determined to be 6.265(0.68) and 0.778(0.09), respectively (see Equation [6b]), and the cut-off point of pH<sub>p</sub> past which the equation would not be employed was determined to

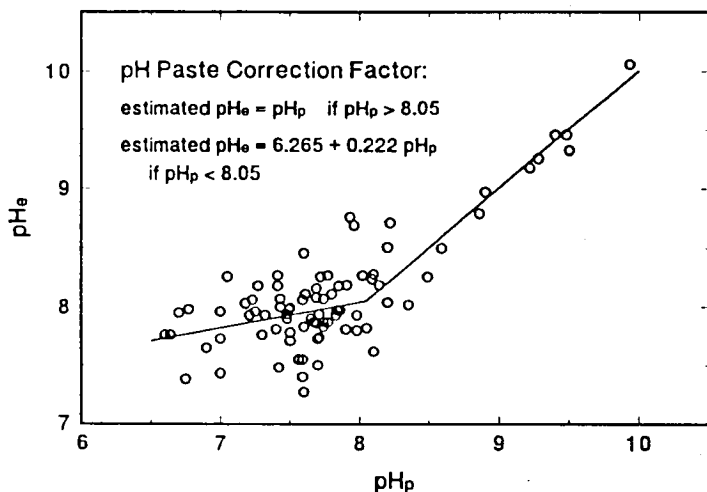


FIGURE 1. Relation between the  $\text{pH}_e$  and  $\text{pH}_p$  values observed in the 86 sample data-set, along with the curve fit to this relation.

be 8.05(6.265/0.778). Substitution of these values into Equation [6b] results in Equation [6b]. Based on these results the  $\text{pH}_p$  values were adjusted using the following equations (Equations [7a] and [7b]) to estimate the equivalent  $\text{pH}_e$  value (est  $\text{pH}_e$ ); a graphical display of this "correction" relation is shown in Figure 1:

$$\text{est } \text{pH}_e = \text{pH}_p, \text{ if } \text{pH}_p > 8.05 \quad [7a]$$

$$\text{est } \text{pH}_e = 6.265 + 0.222(\text{pH}_p), \text{ if } \text{pH}_p \leq 8.05 \quad [7b]$$

Initially, an attempt was made to correct the mV-readings of the Na-electrodes immersed in the saturated-pastes ( $mV_p$ ) by subtracting from them an EMF-factor ascribed to the suspension effect ( $\Delta_{EMF}$ ) as,

$$\text{est } mV_e = mV_p - \Delta_{EMF} \quad [8a]$$

$$\Delta_{EMF} = 0.19843 \log \Theta \quad [8b]$$

$$\Theta = EC_p / EC_e (0.0237SP^{0.6657}) \quad [8c]$$

where  $\kappa$ ,  $EC_p$ ,  $EC_e$ , and  $SP$  are as previously defined, est  $mV_e$  is the estimated mV reading of the Na-electrode of the extract,  $mV_p$  is the mV reading of the Na-electrode in the saturated-paste and  $\Theta$  is an empirical relation derived from a combination of information contained in Bower (1961) and Rhoades et al. (1989). In our approach, the value of  $EC_e$  used in Equation [8c] is the value predicted

from  $EC_p/W_p$  by the method of Rhoades et al. (1989). Since  $\Theta$  is always greater than 1, the adjustment for the "suspension" effect serves to lower the measured millivolt readings ( $mV_p$ ). Based on the limited finding of Bower (1961), it was anticipated that  $\Theta$  would capture both the salinity and textural effects involved in the "suspension" effect ( $\Delta_{EMF}$ ). However, in preliminary studies, it was found to "over-correct" in the lower ranges of Na concentration ( $mV_p$  readings).

Due to this over-correction, an alternative empirical correction approach was developed. This approach was based on the observation that without any correction the errors in the predictions of log Na concentration [ $(\log(Na_c) - \log(\text{prd } Na_c))$ ] were negatively correlated with the  $\log(SAR_c)$  values. This systematic bias was utilized as a means to correct the estimates of Na concentrations in the extracts. Because  $\log(SAR_c)$  values would not be known, a reasonable "proxy" variable for it was defined as the difference  $\alpha = \log(EC_c) - \log(\text{prd } Na_c)$ . The merit of this approach is illustrated in Figure 2. This figure shows the differences between the actual values of Na concentration in the extracts and those predicted from the  $mV_p$  readings using no correction for suspension effects other than the correction for pH described above (i.e., using the methods described in phase II and estimates of  $EC_c$  and  $pH_c$  obtained from  $EC_p$  and  $pH_p$ , respectively). In this figure, the residuals between measured and predicted Na concentrations in these extracts are seen to be related to the "proxy" factor,  $\alpha = \log(\text{prd } EC_c) - \log(\text{prd } Na_c)$ . The fitted curve (quadratic spline model) in Figure 2a represents the estimated prediction bias. This curve was defined by the following quadratic spline equation:

$$\log(Na_c) - \log(\text{prd } Na_c) = b_0 + b_1\alpha + b_2\alpha^2 \quad [9]$$

where  $b_0$  and  $b_1$  are regression coefficients,  $\alpha = \text{minimum}(\gamma, -0.85)$ ,  $\gamma = \log(\text{prd } EC_c) - \log(\text{prd } Na_c)$  and the restriction is imposed that  $b_1 = 2 * b_2 * 0.85$  (to ensure a strictly continuous model). The determined values of the coefficients (and standard errors) were  $b_0 = -1.7842$  (0.1076),  $b_1 = -2.7231$  (0.2637) and  $b_2 = -1.6018$  (0.1551). The optimal "knot" value of -0.85 was obtained by an iterative optimization process analogous to that previously described for pH (i.e., Equation [7]). These results showed that this model described the error-bias in the data well, explaining about 71% of the residual error.

An attempted use of  $\Delta_{EMF}$  in Equation [8b], estimated from  $\Theta$ , tended to overcorrect the  $mV$  readings (as mentioned earlier). However, this biased correction consistently reduced the magnitude of the average "suspension-effect" error. Therefore, it was hypothesized that the residuals obtained from the quadratic spline model of Figure 2a might still be related to  $\Theta$ . In fact, the residuals were found to be related to  $\Theta$ , as is shown in Figure 2b. Hence, a  $\log(\Theta)$  term was incorporated into the quadratic spline model (Equation [9]) in order to obtain an improved bias correction relation as:

$$\log(Na_c) - \log(\text{prd } Na_c) = b_0 + b_1\alpha + b_2\alpha^2 + b_3\log(\Theta) \quad [10a]$$

$$\log(Na_c) - \log(\text{prd } Na_c) = -0.999 - 2.446\alpha - 1.4439\alpha^2 - 0.381[\log(\Theta)] \quad [10b]$$

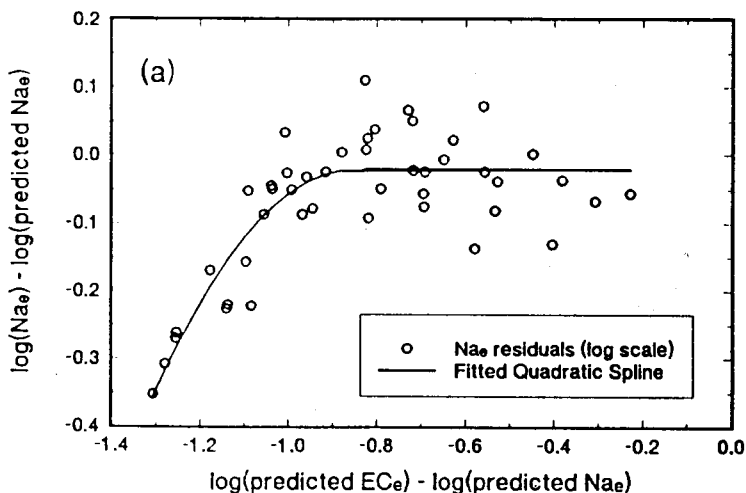


FIGURE 2a. Relation between the differences between  $\log(\text{Na}_e)$  and  $\log(\text{prdNa}_e)$  values and the differences between  $\log(\text{prdEC}_e)$  and  $\log(\text{prdNa}_e)$  observed in data-set 1, along with the quadratic spline model fit to this relation.

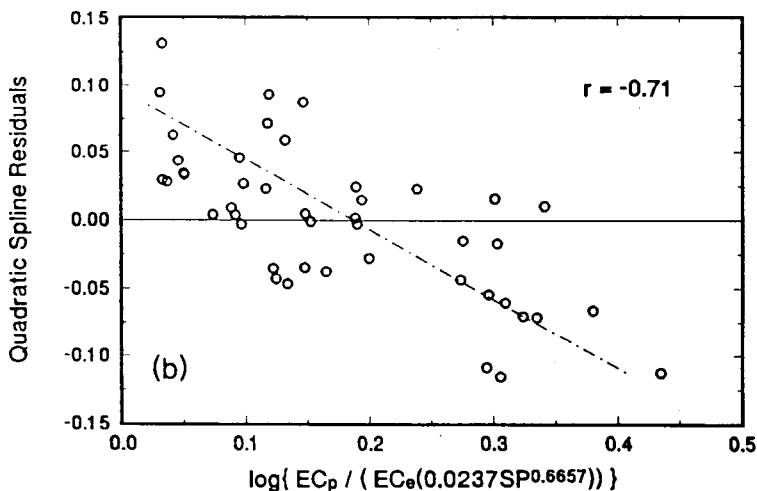


FIGURE 2b. Relation between the quadratic spline residuals (computed as the differences between the observed and estimated paste-prediction bias; see Figure [2a]) and the  $\log(\Theta)$  values used to compensate for the "suspension" effect on the sodium-electrode measurements observed in data-set 1, along with the curve fit to this relation.

where the coefficients were established using data from the 1st data-set. The standard errors of the parameters  $b_0$ ,  $b_1$ ,  $b_3$ , and  $b_4$  were determined to be 0.079, 0.187, 0.110, and 0.055, respectively. The resulting model had a  $R^2$  value of 0.865 and a MSE of 0.00152.

Based on the preliminary findings, the following two-step approach was selected as an appropriate means to estimate  $Na_e$  from electrode measurements made directly in saturated-pastes. First, the  $Na_e$  values are approximated from the  $mV_p$  readings exactly as described previously in Phase II (i.e., as though the electrode readings were made in the extract), with the exceptions that  $pH_e$  is estimated from  $pH_p$  using Equation [7]. Then, this initial prediction of  $Na_e$  is adjusted using Equation [11] (a rearrangement of Equation [10b]) to obtain the final estimate of  $\log(Na_e)$ , i.e.,

$$\log(\text{biasadj } Na_e) = \log(\text{prd } Na_e) - 0.999 - 2.446\alpha - 1.439\alpha^2 - 0.381[\log(\Theta)] \quad [11]$$

where  $\alpha$  is the difference  $[\log(\text{prd } EC_e) - \log(\text{prd } Na_e)]$  and  $\Theta$  is the value  $[(EC_p/EC_e) * 0.0237 * SP^{0.6657}]$ .

The utility of this approach was evaluated using the 2nd and 3rd data sets, since these data were not used in the development of the relations contained in Equations [7] and [11].

## RESULTS AND DISCUSSION

### Phase I: Determining SAR from Sum of Cations and Sodium

A central assumption of any statistical modeling approach is that the calibration data is representative of the samples for which the predictive model will be applied (in our case of the salt-affected soils of the Southwestern United States). The data of Table 2 show that the soils included in this project contain a wide range of  $Na$ , SAR, EC, and pH levels and proportions and hence should include the various major types of salt-affected soils found in Southwestern United States and elsewhere.

The fit of Equation [2] to the 86 extracts used in this study resulted in Equation [12],

$$\log(S_e) = 1.0202 + 1.0445 \log(Ec_e) - 0.0373(pH_e - 8.4) \quad [12]$$

The corresponding standard errors for the  $b_0$ ,  $b_1$  and  $b_2$  coefficients were 0.0087, 0.0113 and 0.0103, respectively. The pH term was found to be highly significant (the t-test value of -3.613 was significant at the  $p=0.0005$  level). The model (Equation [12]) produced significant results, since the  $R^2$  value was 0.991 with a MSE estimate of 0.0024. A visual indication of this correlation is given in Figure 3a.

The statistical findings of the evaluation of the suitability of the three methods for estimating  $S_e$  in the extracts from  $EC_e$  and from combined  $EC_e$  and  $pH_e$  values are given in Table 3a, distinguishing data-set 1 from the combined data of sets 2

TABLE 2. Descriptive statistics for the SAR<sub>c</sub>, Na<sub>c</sub>, EC<sub>c</sub>, and pH<sub>c</sub> properties of the data-sets.

Data-set	Parameter	SAR <sub>c</sub> (mmol <sub>c</sub> /l)	EC <sub>c</sub> (dS/m)	pH <sub>c</sub>	Na <sub>c</sub> (mmol <sub>c</sub> /l)
1	N	45	45	45	45
	mean	13.77	6.19	7.99	51.01
	std. dev.	14.50	7.01	0.42	70.97
	min.	0.93	0.69	7.27	2.11
	25%	3.30	1.33	7.80	6.81
	median	8.64	3.57	7.96	16.76
	75%	19.45	7.07	8.18	54.87
	max.	>60	27.3	10.06	263.22
2/3	number	41	41	41	41
	mean.	22.25	6.41	8.20	53.56
	std. dev.	19.62	7.47	0.60	69.20
	min.	0.15	0.20	6.87	0.30
	25%	7.27	1.73	7.90	10.70
	median	13.79	4.00	8.07	32.51
	75%	32.67	8.04	8.41	66.21
	max	>60	30.0	9.45	356.20

and 3. These results show that Equation [12], which included pH, gave more accurate predictions of S<sub>c</sub> (prd S<sub>c</sub>) than did the relations of Handbook 60 or Marion and Babcock (1976), since it had the smallest prediction-variance in this statistical analysis, judging from the Press residuals (Myers, 1986). These Press residuals were computed by sequentially deleting each observation one at a time, estimating each deleted response, and then calculating the difference between the estimated and observed values, to permit the computed prediction variances to be directly comparable. Additionally, the data of Table 3a show that only Equation [12] produced unbiased predictions of log(S<sub>c</sub>) across both data-sets. The pH values of data-set 2/3 tended to be significantly higher than that of data-set 1. Nearly one fourth of data-set 2/3 had pH values in excess of 8.4, while one sample of the 45 in

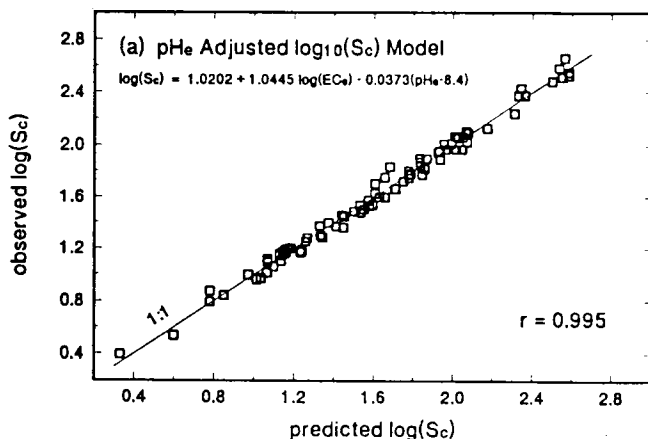


FIGURE 3a. Correlation plots relating the values of  $\log(S_c)$  measured in the 86 sample data-set with those predicted by Equation [12].

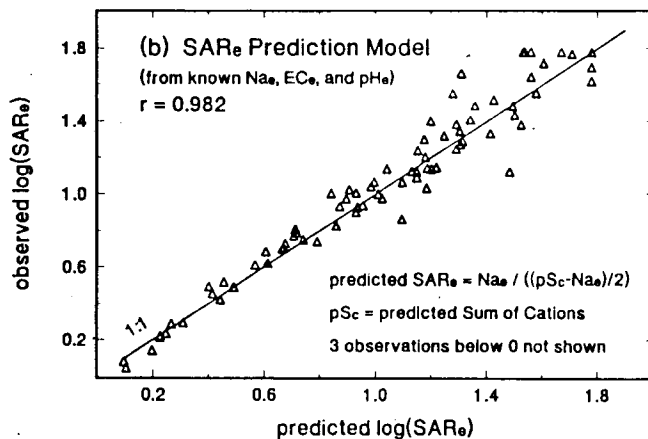


FIGURE 3b. Correlation plots relating the values of  $\log(SAR_c)$  measured in the extracts of the 86 sample data-set with those predicted using Equations [1] and [12].

TABLE 3a. Analysis of residuals for the three  $S_c$  prediction models.

Data-set (sample count)	Statistical Parameter	Prediction Model		
		Eq.[12]	M & B	Handbook 60
1 (N=45)	mean	0.0116	0.0505	0.0218
	std. dev.	0.0478	0.0471	0.0479
	t-score	1.63	7.20	3.06
	prob(>t)	0.1112	0.0001	0.0038
	mspe	0.00237	0.00472	0.00272
	median	0.0171	0.0544	0.0217
	$Q_3-Q_1$	0.0465	0.0550	0.0627
2/3 (N=41)	mean	-0.0123	0.0196	-0.0086
	std. dev.	0.0504	0.0534	0.0597
	t-score	-1.56	2.36	-0.93
	prob(>t)	0.1253	0.0234	0.3601
	mspe	0.00263	0.00317	0.00355
	median	-0.0322	0.0044	-0.0227
	$Q_3-Q_1$	0.0757	0.0831	0.0734

Press residuals were used for the Equation [12] model; the mean square prediction error (mspe) is defined as the uncorrected sum of squares divided by the sample size.

data-set 1 had a pH above 8.4. The conclusion is that the prediction-bias obtained using the  $S_c/EC$  relations of Handbook 60 and Marion and Babcock (1976) were due to this variation in pH and their lack of ability to adjust for this variation.

The correspondence obtained between the measured  $SAR_c$  values and those predicted using Equations [1] and [12] and the analytically determined values of  $EC_c$ ,  $Na_c$ , and  $pH_c$  for the 86 samples is shown in Figure 3b. A non-parametric median sign-test was used to test for bias in our predictions of  $SAR_c$ . This test was preferable to a t-test, since the  $SAR_c$  prediction involved an upper cut-off limit of 60 (discussed later) which can affect both the mean and standard deviation residual estimates. Additionally, prediction accuracy was measured by computing how many of the predicted  $SAR_c$  values fell within 10, 20, and 50% of the measured values. These statistical results are given in Table 3b. The median log residual



TABLE 3b. Analysis of residuals for  $SAR_e$  predicted using Equations [1] and [12] and true data.

Statistical Parameter	Residual Statistics
Number	86
Num>0	47
median	0.0225
Sign Score	5.0
Prob(>S)	0.3261
Prediction Limits	Prediction Accuracy
Z< 10%	32.6%
Z< 20%	66.3%
Z< 50%	90.7%

Z represents the percentage of predicted  $SAR_e$  values within 10, 20, and 50% of the known values; true data refers to use of analytically determined values of  $Na_e$ ,  $EC_e$ , and  $pH_e$ . The sign test is used to test whether the median residual value is significantly different from zero.

error was 0.0225, which was not significantly different from zero according to the nonparametric sign test. For this case, 33, 66, and 91% of the predicted values of  $SAR_e$  were within 10, 20, and 50% of the measured values, respectively. This correspondence represents the best that can be reasonably expected from the use of Equations [1] and [12]. Such accuracy is deemed adequate for our purposes. The questions remaining are whether similar results can be obtained when the  $EC_e$ ,  $Na_e$ , and  $pH_e$  values are estimated by our Na-electrode and saturated-paste measurement methods. Findings in these regards are given in the following Phase II and Phase III sections, respectively.

## Phase II: Determining Sodium in Solutions from Unbuffered Electrode Measurements

This section describes the findings of the studies undertaken to determine if  $SAR_e$  can be suitably determined when the concentrations of Na in the extracts are estimated from  $EC_e$ ,  $pH_e$ , and  $Na_e$  when the latter is estimated from Na-electrode measurements made in the extracts without the conventional use of ionic strength and pH buffers.

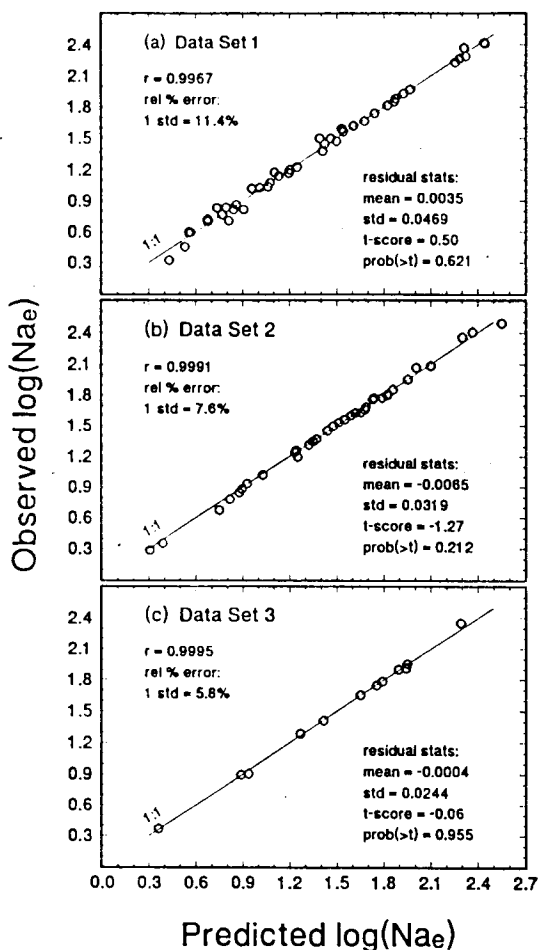


FIGURE 4. Correlation plots relating the values of  $\log(\text{Na}_e)$  measured in the extracts of data-sets 1, 2, and 3 with those predicted from electrode-measurements of Na, EC, and pH made in the extracts.

The correspondence between the  $\text{Na}_e$  concentrations determined by ICP analysis and those estimated by our unbuffered Na-electrode technique is presented in Figure 4. As this figure shows, the estimated  $\text{Na}_e$  concentrations were in good agreement with those obtained by ICP analysis. The standard deviation of the Relative Percent Error (RPE) associated with the 2nd set of extracts was 7.6%; the analogous value for the 3rd set was 5.8%. The RPE for the 1st set was higher (12.5%) in this earlier data-set in which the preliminary Na-electrode was

employed. The t-tests performed on these data showed that the predictions were unbiased in each data-set. According to unpublished Hach tests, the expected prediction error in Na concentration using buffers and standard Na-electrode methods is about 5%.

These results imply that the accuracy of  $\text{Na}_e$  concentration estimates that can be obtained using the Hach Na-electrode and our unbuffered-techniques should be adequate for our purposes (achieving a reasonable estimate of  $\text{SAR}_e$ ), since the prediction errors are small and unbiased. Direct evidence to support this conclusion are given in the Phase III section that follows. This "non-buffered" technique could also be advantageous for use in monitoring situations, where in-situ measurements of Na concentration, or activity, are required, and in other such situations where buffers can not be added to the solution to be analyzed.

### Phase III: Determining $\text{SAR}_e$ from Electrode Measurements Made in Saturated-Pastes

The data presented so far imply that: 1)  $\text{SAR}_e$  can be estimated sufficiently well for purposes of soil-sodicity appraisal given sufficiently accurate estimates of  $\text{Na}_e$ ,  $\text{EC}_e$ , and  $\text{pH}_e$  and 2) the concentration of Na in extracts (i.e.,  $\text{Na}_e$ ) can be estimated accurately enough for this purpose from Na-electrode measurements made in the extracts without the conventional use of buffers, given reasonably accurate estimates of the  $\text{EC}_e$  and  $\text{pH}_e$  values of the extracts. Thus, what remains to be determined for our purposes is whether  $\text{Na}_e$ ,  $\text{EC}_e$ , and  $\text{pH}_e$  values of extracts can be estimated with sufficient accuracy when the electrode-measurements are made directly in saturated-pastes. The rest of this section presents results of the studies undertaken to make this remaining determination.

It has already been shown that  $\text{EC}_e$  can be determined accurately in soils of the central San Joaquin Valley of California from the measurement of the EC and volumetric-water content of the saturated-paste (Rhoades et al., 1989). A test of the general appropriateness of these relations was made using the more widespread soil data-sets of this study. The results are given in Figure 5. These data show good correspondence between the observed and predicted values of  $\text{EC}_e$ . The poorer fit obtained for data-set 2 was caused by insufficient time being given to some of the saturated-pastes of this set to equilibrate before they were extracted. The time requirement was lengthened considerably for these relatively low-salinity/high-sodicity soils which slowly imbibed water<sup>5</sup>. Evidence supporting this

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<sup>5</sup>These highly sodic soils swelled and absorbed waters to a very great extent and required up to 24 hours to reach a stable saturation percentage; solution extracts removed from their saturated paste before equilibrium were significantly lower in  $\text{EC}_e$  than those obtained after equilibrium. Due to time constraints, 80% of the paste and extract readings obtained in the 2nd data-set were made after only a 4 hour "equilibration" period. Upon further analysis, this time interval was found to be insufficient for these very highly sodic soils. This time was extended to 24 hours for the 3rd soil data-set.

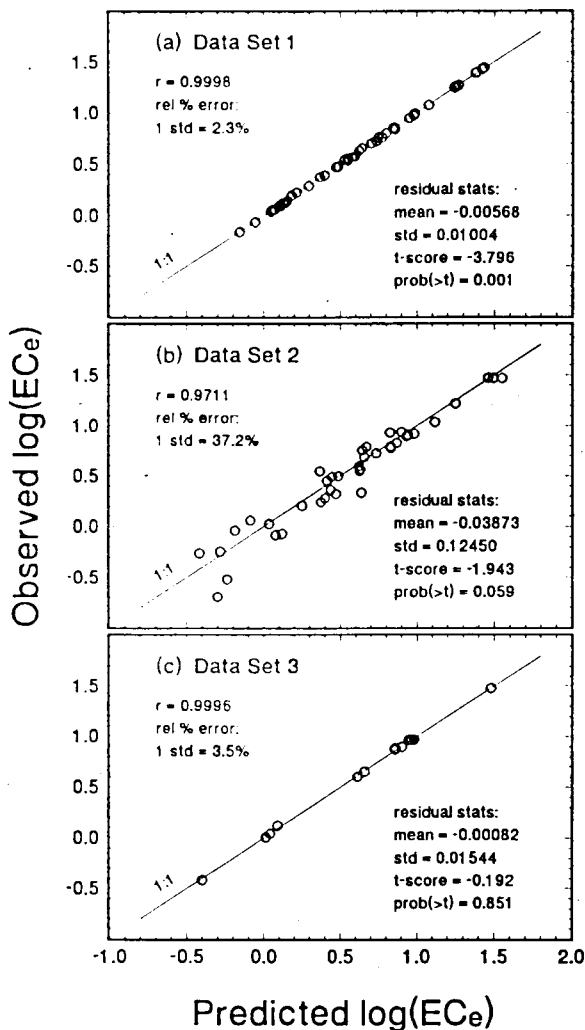


FIGURE 5. Correlation plots relating the values of  $\log(\text{EC}_e)$  measured in the extracts of data-sets 1, 2, and 3 with those predicted from measurements of the EC of the saturated soil-paste by the method of Rhoades et al. (1989).

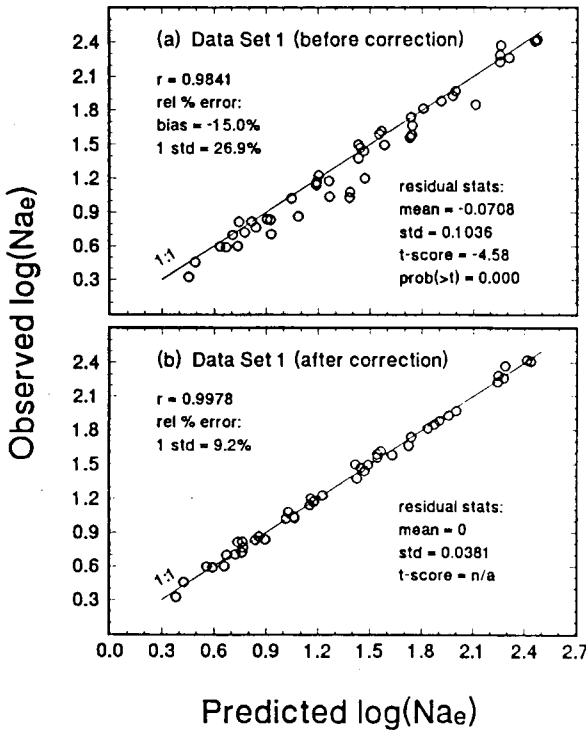


FIGURE 6. Correlation plots relating the values of  $\log(\text{Na}_e)$  measured in the extracts of data-set 1 with those predicted from electrode-measurements of Na, EC, and pH made in the saturated-pastes with and without correction for the "suspension" effect by means Equation [11].

conclusion is seen in Figure 5. The data set 3 soils are the 13 soils of data set 2 with poor correspondence which were repeated using longer equilibration times. These results demonstrate the general applicability of the  $\text{EC}_p/W_p$  method of Rhoades et al. (1989) for determining  $\text{EC}_e$  and the relations inherent in it, even though they were established solely with the California soils.

The observed values of the  $\text{Na}_e$  values for the extracts of the 1st data set and those estimated, with and without the use of Equation [11], are compared in Figure 6. These results show that the predictions of  $\text{Na}_e$  based on Na-electrode measurements made directly in the saturated-paste were biased (t-score value of -4.58, significant below the  $p=0.001$  level) and were quite variable. On the average the predicted values of  $\text{Na}_e$  (prd  $\text{Na}_e$ ) without adjustment (i.e., without use of Equation [11]) were higher than the measured values of  $\text{Na}_e$  by about 15% and the standard deviation of the relative percent error was about 27%. As shown in

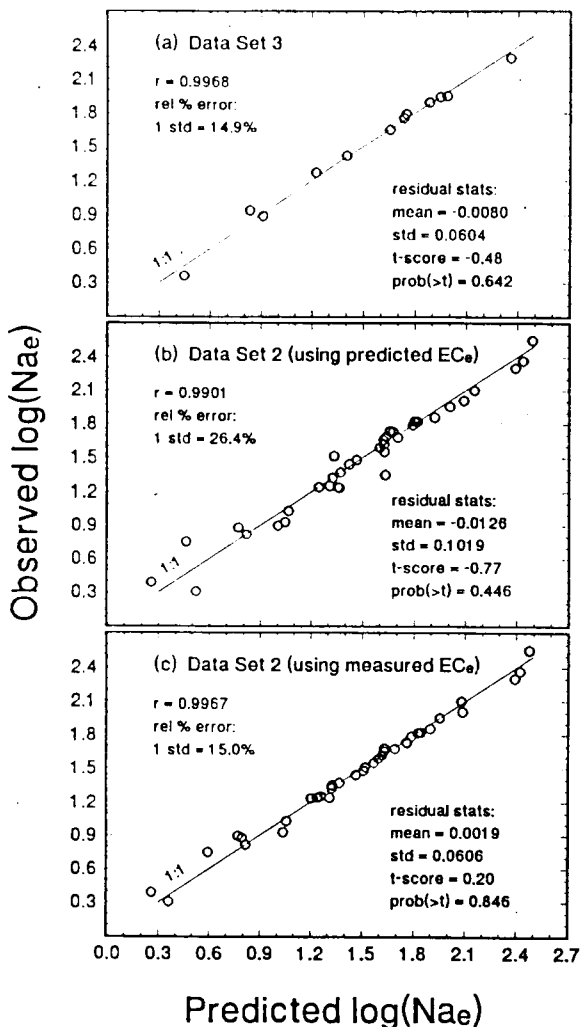


FIGURE 7. Correlation plots relating the values of  $\log(\text{Na}_e)$  measured in the extracts of data-sets 2 and 3 with those predicted by Equation [11] using electrode-measurements of Na, EC, and pH made in the saturated-pastes and, in the case of data-set 2, using measured and predicted values of  $\text{EC}_e$ .

Figure 6, much better results were obtained using Equation [11]. The bias was removed, the standard deviation was reduced to 9.2%, the standard deviation of the log residuals was 0.0381 and the standard deviation of the log Press residuals was 0.0408. Both of these were slightly less than 0.0469, which was the standard deviation obtained in the Phase II study where the electrode-measurements were made in the extracts.

Since Equation [11] was established using data-set 1 results, its more general applicability was evaluated using data-sets 2 and 3. These results are given in Figure 7. The upper section of this figure shows the excellent results obtained using Equation [11] with the data-set 3 samples; the log residual mean was not significantly different from zero, as judged by the t-test results. The middle section shows that poorer correspondence between measured and predicted values of  $\log(\text{Na}_e)$  was obtained for data-set 2 (which contained more than typical error in the estimate of  $\text{EC}_e$  for the reasons given earlier). The importance of accurate  $\text{EC}_e$  estimates in the determination of  $\text{Na}_e$  by our method is confirmed by the improved results, shown in the lower section of Figure 7, that were obtained when measured values of  $\text{EC}_e$  were substituted for those estimated from the  $\text{EC}_p/W_p$  measurements. However, in all three cases, the  $\text{Na}_e$  concentrations predicted from the direct paste measurements were unbiased, as judged by t-test results.

While these results show that accurate estimates of  $\text{EC}_e$  are needed to obtain accurate predictions of Na concentrations in extracts based on saturated-paste measurements, as we will show later, even such errors in  $\text{EC}_e$  estimates as those made in data-set 2 will not seriously compromise our ability to estimate  $\text{SAR}_e$  values using our proposed "paste method".

The  $\text{SAR}_e$  values predicted from the electrode-measurements made directly in the saturated-pastes were determined using Equations [1], [7], [11], and [12]. A predicted  $\text{SAR}_e$  value of 60 was defined when predicted values of  $S_e$  were less than estimated values of  $\text{Na}_e$  and/or values of predicted  $\text{SAR}_e$  were greater than 60. The limit of 60 was selected as a practical upper meaningful level of  $\text{SAR}_e$  for our purposes, since the deleterious effects of exchangeable Na on soil properties are essentially fully manifested by this level (Shainberg and Singer, 1990). Graphical representations of the measured and predicted values of  $\text{SAR}_e$  obtained in this manner are given in Figure 8, along with analogous results obtained in the Phase II study (i.e., when the electrode-measurements were made in the extracts). Note that all predictions applicable to the saturated-paste measurements were based on estimates of  $\text{EC}_e$  and  $\text{pH}_e$ , as well as  $\text{Na}_e$ . These figures show that satisfactory estimates of  $\text{SAR}_e$  were obtained, regardless of whether the electrode-measurements were made in the extracts or in the saturated-pastes, provided the appropriate adjustments were applied in the latter case.

A non-parametric median sign-test was again used to test for bias in the predictions of  $\text{SAR}_e$  and new 10, 20, and 50% classification accuracy estimates were calculated. Some of these statistical results are given in Table 4. The median log residual error was 0.0146 when  $\text{SAR}_e$  was predicted from electrode-

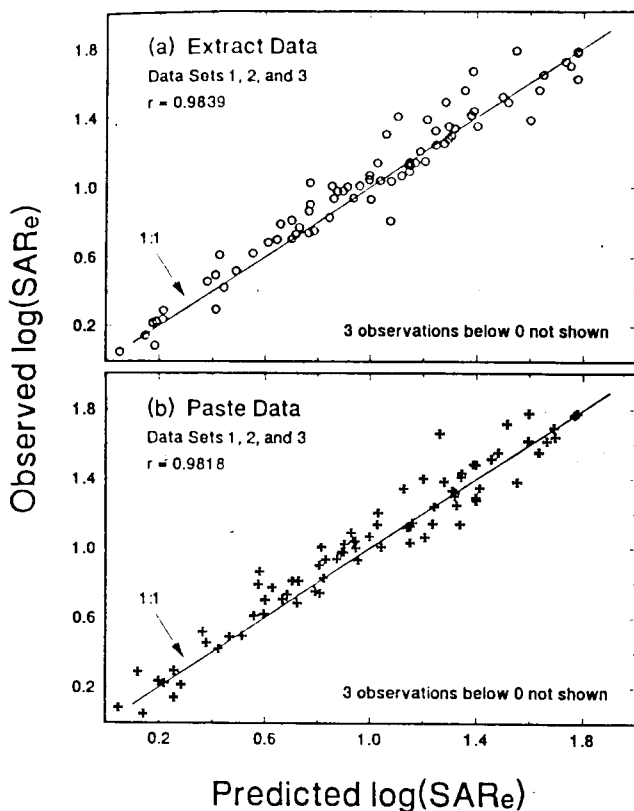


FIGURE 8. Correlation plots relating the values of  $\log(\text{SAR}_e)$  measured in the extracts of the 86 sample data-set with those predicted from electrode-measurements of Na, EC, and pH made in the extracts (extract data) and in the saturated-pastes (paste data).

measurements made in the extracts, which was not significantly different from zero according to the nonparametric sign test. For this case, 43, 66, and 88% of the predicted values of  $\text{SAR}_e$  were within 10, 20, and 50% of the measured values, respectively. In comparison, the median log residual error was 0.0261 when  $\text{SAR}_e$  was predicted from electrode-measurements made directly in the saturated-pastes. This latter error was only marginally different from zero, since the significance level of the sign-test was 0.0748. This small bias is concluded to have resulted from the inclusion of the biased predictions in data-set 2 which, as explained previously, were the result of the poorly estimated values of  $\text{EC}_e$ . For this case, 33, 55, and 88% of the predicted values of  $\text{SAR}_e$  were within 10, 20, and 50% of the measured values, respectively.



TABLE 4. Analysis of residuals for  $SAR_e$  predicted from electrode-measurements of extracts and pastes.

Statistical Parameter	Residual Statistics	
Number	86	86
Num>0	47	49
Median	0.0146	0.0261
Sign Score	6.5	8.5
Prob(>S)	0.1821	0.0748
Prediction Limits	Prediction Accuracy	
	Extracts	Pastes
Z < 10%	43.0%	32.6%
Z < 20%	66.3%	54.7%
Z < 50%	88.4%	88.4%

Z represents the percentage of predicted  $SAR_e$  values within 10, 20, and 50% of the known values. The sign test is used to test whether the mean residual value is significantly different from zero.

We stated earlier that large errors in the estimates of  $EC_e$  would not necessarily result in large errors in the prediction of  $SAR_e$  from measurements made in saturated-pastes. This can be demonstrated using the  $SAR_e$  predictions calculated from the  $EC_e$  measurements associated with data-set 2. When measured values of  $EC_e$  were used, the median log residual error was exactly zero and 26, 51, and 88% of the predicted values fell within 10, 20, and 50% of the measured values, respectively. When the estimated values of  $EC_e$  were used, the median log residual error was 0.0691, which was significantly different than zero. Hence, the average predicted  $\log(SAR_e)$  level was 0.0691 units less than the analytically determined  $\log(SAR_e)$  level, which translates to about a 17% under-prediction bias. However, 28, 44, and 88% of the predicted values of  $SAR_e$  were still within 10, 20, and 50% of the measured values. Thus, the primary effect of the error made in the estimate of  $EC_e$  was to simply cause a bias in the  $SAR_e$  prediction, but not a substantial error in the overall accuracy of the prediction. This is due to the fact that Equation [11] tends to produce positively correlated prediction errors in estimates of  $Na_e$  and  $EC_e$ . In other words, if a large error is inadvertently made in the estimate of

TABLE 5. Comparison of measured and predicted SAR<sub>c</sub> levels.

Measured SAR <sub>c</sub> Level	SAR <sub>c</sub> Levels Predicted from Electrode-Measurements of Extracts						Total
	0-5	5-10	10-20	20-40	40-60	>60	
0-5	20	0	0	0	0	0	20
5-10	2	14	2	0	0	0	18
10-20	0	5	15	1	0	0	21
20-40	0	0	5	8	1	0	14
40-60	0	0	0	1	3	3	7
>60	0	0	0	1	0	5	6
Total	22	19	22	11	4	8	86
Measured SAR <sub>c</sub> Level	SAR <sub>c</sub> Levels Predicted from Electrode-Measurements of Pastes						Total
	0-5	5-10	10-20	20-40	40-60	>60	
0-5	19	1	0	0	0	0	20
5-10	6	12	0	0	0	0	18
10-20	0	6	10	5	0	0	21
20-40	0	0	3	10	1	0	14
40-60	0	0	1	2	4	0	6
>60	0	0	0	1	0	5	6
Total	25	19	14	18	5	5	86

EC<sub>c</sub>, then a correspondingly large error will tend to be induced in the estimate of Na<sub>c</sub>. Hence, the estimate of SAR<sub>c</sub> will not be seriously degraded, since it is based on a ratio of predicted Na<sub>c</sub> to predicted EC<sub>c</sub>. In summary, errors of the magnitude expected in the estimates of either Na<sub>c</sub> or EC<sub>c</sub> will not translate to excessively large errors in the prediction of SAR<sub>c</sub> using these relations.

A further comparison of the observed and predicted SAR<sub>c</sub> values obtained for all the soils used in this study are shown in Table 5, in terms of class intervals. For the purposes of this test, both the observed and predicted SAR<sub>c</sub> values were classified into one of six intervals: 0-5, 5-10, 10-20, 20-40, 40-60, and >60. These classes are generally associated with little, minimal, moderate, strong, very strong,

and extreme sodicity problems, respectively. The predictions of  $SAR_e$  class based on electrode-measurements made in saturated-pastes are concluded to be essentially as good as those based on analogous measurements made in extracts. Both means of prediction are deemed to be sufficiently accurate over the entire meaningful range of interest ( $SAR_e$  0-60) for our intended field method (i.e., as a practical sodicity screening and diagnosis procedure).

It is further noted that the ability to determine  $SAR_e$  is not fundamentally limited by the accuracies of our developed methods to estimate  $Na_e$  and  $EC_e$  in extracts from measurements made directly upon the saturated-paste, but rather in the ability to estimate the sum of Ca plus Mg concentrations in the extracts from the difference  $S_c - Na_e$ . For the above reason, a potentially better approach might be to combine the use of a Na-electrode with a hardness-electrode in the saturated-paste measurements and to use the mV-ratio so obtained, along with  $EC_e$  to predict the (Na/Ca+Mg) concentration-ratio and, in turn, the  $SAR_e$  value. This approach would avoid the problems associated with both the "suspension-effect" errors associated with the electrode measurements made in the saturated-pastes, the errors involved in estimating sum of cations in the extract from  $EC_e$  and those involved in estimating the sum of Ca plus Mg as the difference of  $S_c - Na_e$ .

## CONCLUSIONS

The experimental results presented herein show that suitably accurate estimates of  $Na_e$  and  $SAR_e$  can be obtained for purposes of soil sodicity appraisal from electrode (Na, EC, and pH) measurements made on either unbuffered extracts or saturated-pastes of salt-affected soils. Appropriate procedures, calibration methods and prediction relations which account for the effects of temperature, ionic-strength, and pH and, in the case of saturated-pastes, for "suspension effects", on the electrode measurements and determinations of  $Na_e$  and  $SAR_e$ , are provided for both the extract and saturated-paste methods.

The developed methods were concluded to be inherently limited by the inability to estimate the sum of Ca plus Mg concentrations in extract solutions from  $EC_e$  and  $Na_e$ . We conclude that this limitation, plus the need for correcting for "suspension-effect" interferences on electrode measurements, might be overcome by the paired use of Na- and "hardness"-electrodes to measure the saturated-paste mV-value associated with the Na/Ca+Mg ratio and the development of a model relating  $SAR_e$  to this ratio.

We also conclude that the salinity appraisal technique of Rhoades et al. (1989) developed for San Joaquin Valley, CA soils is generally reliable for purposes of salinity measurement and appraisal of salt-affected soils. Test kits for salinity and sodicity appraisal purposes will be developed by the Hach Company using this latter method and the sodicity-determination method described herein, respectively.

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