STATION VOOR DE GROENTEN- EN FRUITTEELT ONDER GLAS TE NAALDWIJK

De ionenbalans van het 1:2-volume-extract

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Inleiding

Op het routine laboratorium voor grondonderzoek worden alle monsters in duplo onderzocht ter controle op fouten. De vraag die zich voordoet is of het mogelijk zou zijn in enkelvoud te onderzoeken en controle uit te oefenen door onderlinge vergelijking van bepalingen of ionensommen.

Momenteel worden bij het routine grondonderzoek de volgende bepalingen verricht:

K^+, Mg^{++}, NO_3^-, Cl^-.

Voor een complete ionenbalans zouden ook de volgende bepalingen nodig zijn:

Na^+, Ca^{++}, NH_4^{++}, HCO_3^- en SO_4^{--}.

Bij een complete ionenbalans biedt vergelijking van de anionensom met de kationensom mogelijkheden tot vergelijking. Hetzelfde geldt voor de EC met de ionensommen.

Teneinde deze mogelijkheden nader te bestuderen zijn van 20 monsters uit het routine grondonderzoek 1:2 volume-extracten bereid en werden in deze extracten alle anionen en kationen bepaald. De resultaten worden in dit verslag behandeld.

Resultaten

De monsters die in het onderzoek werden betrokken werden enigszins geselecteerd. De selectie vond zodanig plaats, dat een redelijke verdeling over de grondsoorten werd verkregen en dat voldoende lage en hoge waarden aanwezig waren.

Het onderzoek heeft plaats gevonden op het research laboratorium en is in duplo uitgevoerd. De gemiddelde uitkomsten van de duplowaarden zijn opgenomen in de bijlagen 1 en 2.

Gemiddeld werden de in tabel 1 vermelde waarden gevonden. Tevens zijn in deze tabel de laagste en de hoogste waarden die werden gevonden opgenomen.

Bepaling	Gem.	Laagste	Hoogste	Gem. in % van totaal als me	 als mol
Na	4.67	1.65	10.22	12.0	16.7
K	2.44	0.34	5.38	6.2	8.7
Ca	9.12	1.30	27.71	23.4	16.3
Mg	2.99	0.49	7.41	7.7	5.4
NH_4	0.19	0.01	2.67	0.5	0.7
som Kat	19.41				
Cl	4.18	1.20	10.35	10.7	15.0
NO_3	4.90	0.64	14.14	12.6	17.6
SO_4	9.89	1.71	23.83	25.4	17.7
HCO_3	0.53	0.21	1.08	1.4	1.9
som An	19.50				

Tabel 1. Gemiddelde, laagste en hoogste waarden van de kationen en anionen in de 1:2 volume-extracten. Gehalten in me/l.

Zoals blijkt, zijn Na, Ca, Cl, NO_3 en SO_4 sterk vertegenwoordigd in de extracten. NH_4 en HCO_3 spelen een ondergeschikte rol.
Tussen enkele soorten ionen bestaat een nauwe correlatie. De volgende regressievergelijkingen werden gevonden:

$\mathrm{Na} = 0.893\ \mathrm{Cl} + 0.94$ $r = 0.946$

$\mathrm{Ca} = 0.949\ \mathrm{SO_4} - 0.27$ $r = 0.954$

Andere nauwe correlaties werden niet gevonden tussen de verschillende ione
Hoog gecorreleerd waren som kationen (SK) som anionen (SA) en EC.

$SK = 1.007\ SA - 0.22$ $r = 0.998$

$SK = 12.50\ EC - 3.28$ $r = 0.992$

$SA = 12.36\ EC - 2.94$ $r = 0.989$

Teneinde controle mogelijkheden na te gaan aan de hand van berekening van de EC door middel van de ionensamenstelling is de methode van McNeal, et al. (1970) op het materiaal toegepast. Hiermede wordt de EC berekend aan de hand van de ionensamenstelling en vergeleken met de gemeten EC. De afwijkingen tussen beide waarden moeten binnen nauwe grenzen blijven. McNeal et al. paste voor hun berekening verschillende methoden toe en wel:

1 Exponential relationship

$$EC = K_0C^b$$

2 Third-order polynomial

$$EC = K_1 + K_2C + K_3C^2 + K_4C^3$$

3 Linear-segment method.

$$EC = K_5 + K_6C$$

C is de concentratie aan idividuele ionen in de oplossing en de verschillende k-waarden zijn voor elk ion getabelleerd. De uitkomsten voor de verschillende ionen worden gesommeerd. De publicatie met de tabellen en een uitgewerkt rekenschema voor methode 3 - de hand rekenmethode - zijn opgenomen in aanhangsel 1.
De EC-waarden berekend volgens de drie methoden volgens McNeal et al. zijn opgenomen in bijlage 3. In tabel 2 zijn de gemiddelden, de gemiddelde afwijking ten opzichte van de gemeten EC en de spreiding van de afwijkingen berekend. De monsters zijn daartoe in twee groepen ingedeeld en wel in de tien hoogste en de tien laagste waarden.

Methode	Laagste waarden			Hoogste waarden		
	M	$\overline{d}$	S_d	M	$\overline{d}$	S_d
meten	1.05			2.58		
1	1.05	0.005	0.076	2.69	0.110	0.098
2	1.04	-0.008	0.083	2.80	0.215	0.161
3	1.00	-0.044	0.073	2.60	0.018	0.105

Tabel 2. Gemiddelde EC-waarden (M), gemiddelde afwijking van de berekende EC-waarden van de gemeten waarden ($\overline{d}$) en de spreiding van deze afwijkingen (S_d).

Zoals blijkt, wordt met de berekende EC-waarden de gemeten waarde goed benaderd. Gemiddeld geeft methode 3 de kleinste afwijking. De spreidingen van de afwijkingen lopen weinig uiteen. De variatie coëfficient is bij het laagste niveau ongeveer 7% en bij het hoogste niveau ongeveer 4%.
Met een overschrijdingskans van 5% worden dus afwijkingen gesignaleerd in de berekende EC van 14% bij een EC-waarde rond 1,00 en van 8% bij een EC-waarde rond 2,50.
Voorts is nagegaan welke afwijkingen worden verkregen tussen de som anionen en som kationen, evenals tussen de kationensom, berekend uit de EC en de gevonden kationensom. Hetzelfde is gedaan voor de anionensom. De berekende som kationen (SK_b) en anionen (SA_b) zijn verkregen uit de reeds eerder gevonden vergelijkingen. De monsters zijn weer ingedeeld in twee groepen.

Methode	Laagste waarden			Hoogste waarden		
	M	$\bar{d}$	S_d	M	$\bar{d}$	S_d
SK - SA	$\overline{SA}=10.24$	-0.23	0.491	$\overline{SA}=28.75$	0.06	0.953
SK_b - SK	$\overline{SK}=10.01$	-0.17	1.084	$\overline{SK}=28.81$	0.17	1.858
SA_b - SA	$\overline{SA}=10.24$	-0.21	1.081	$\overline{SA}=28.75$	0.21	2.222

Tabel 3. Gemiddelde ionensommen (M), gemiddelde afwijkingen tussen ionensommem ($\bar{d}$) en de spreiding van de afwijkingen (S_d).

Zoals blijkt, zijn tussen de gemiddelde afwijkingen geen duidelijke verschillen bij de methoden. De spreiding is bij de methode SK - SA het kleinst. De variatie coefficient van de afwijkingen is bij het laagste niveau voor methode SK - SA ongeveer 5% en bij het hoogste niveau ongeveer 3%. Voor de beide andere methoden is de variatie coëfficient voor de laagste en de hoogste waarden respectievelijk ongeveer 11% en 7%.
Met een overschrijdingskans van 5% worden dus afwijkingen gesignaleerd in de ionensommen bij een waarde van ongeveer 10 van 10% en 22% voor respectievelijk de methode SK - SA en de beide andere methoden uit tabel 3. Bij een waarde van ongeveer 30 worden respectievelijk afwijkingen gesignaleerd van 6% en 14%.

Conclusies

Voor het verkrijgen van een redelijk kloppende ionenbalans is het noodzakelijk de volgende kationen te bepalen:

Na^+, K^+, Ca^{++}, Mg^{++} en NH_4^+.

Hoewel ammonium meestal slechts in zeer kleine hoeveelheden voorkomt moet dit ion toch worden bepaald omdat in een beperkt aantal gevallen enkele milliequivalenten in het 1:2 volume-extract aanwezig kunnen zijn. De volgende anionen dienen te worden bepaald:

Cl^-, NO_3^-, SO_4^{--} en HCO_3^-.

Hoewel bicarbonaat absoluut en ook relatief de geringste schommelingen vertoonde is de bepaling voor de ionenbalans noodzakelijk, daar de hoeveelheden toch nog vrij sterk kunnen variëren. In ons onderzoek tussen 0.2 en 1.1 milliequivalent per liter.
Controle van de bepalingen door middel van vergelijking van EC, kationensom en anionensom biedt slechts beperkte mogelijkheden. Bij een overschrijdingskans van 5%, dus als 1 op elke 20 analyses ten onrechte als fout zou worden aangemerkt, worden de volgende afwijkingen gesignaleerd.

Methode	Laag niveau EC ± 1.0	Hoog niveau EC ± 2.6
EC en EC-berekend	14%	8%
SK en SA	10%	6%
EC en (SK - SA)	22%	14%

De controle door middel van vergelijking van de gevonden ionensommen blijkt het meest gevoelig te zijn. Met behulp van deze methoden worden fouten ter grootte van 1 milli-equivalent gesignaleerd bij een laag niveau en van ongeveer 1.5 bij een hoog niveau. Voor de uitkomsten van bepalingen als calcium en sulfaat - die in grote hoeveelheden in het extract voorkomen biedt dit een redelijke bescherming tegen blunders. Voor de andere bepalingen is dit niet het geval. Een niet gesignaleerde afwijking van 1 à 1.5 milli-equivalent beloopt dan als spoedig 25% van de bepalingsuitkomst, hetgeen te hoog is.
Tenslotte moet nadrukkelijk op de beperkingen van dit onderzoek worden gewezen. Het is uitgevoerd met een beperkt aantal monsters. De analyses zijn uitgevoerd op het research laboratorium. Het moet niet uitgesloten worden dat op een routine laboratorium niet dezelfde nauwkeurigheid wordt gehaald. Anderzijds moet het niet uitgesloten worden geacht dat - vooral bij sterke automatisering - op een routine laboratorium een grotere nauwkeurigheid wordt gehaald dan op een research afdeling.
Al met al genoeg redenen om dit rapport voorlopig meer te beschouwen als een indicatie dan als een gegeven.

Bijlage 1

Resultaten anionen en kationen

me/l

Nr.	K	Na	Ca	Mg	NH_4	kat-ionen	NO_3	HCO_3	Cl	SO_4	an-ionen
1	1.96	3.99	8.41	4.14	0.15	18.65	6.91	0.29	3.16	7.77	18.13
2	0.34	2.76	2.12	0.74	0.10	6.06	0.64	0.62	1.96	2.94	6.16
3	1.10	3.12	6.07	2.18	0.09	12.56	2.12	0.64	2.50	7.89	13.15
4	4.57	8.76	17.00	7.36	0.08	37.77	10.14	0.86	6.64	20.62	38.26
5	2.64	2.41	5.45	1.62	0.06	12.18	5.27	0.60	1.46	5.46	12.79
6	3.00	6.51	16.98	3.91	0.02	30.42	5.20	0.28	4.98	20.81	31.27
7	1.94	1.74	6.39	2.04	0.09	12.20	3.46	0.46	1.57	5.93	11.42
8	0.76	1.65	1.30	0.49	0.03	4.23	0.87	0.65	1.20	1.71	4.43
9	3.11	6.84	6.13	2.48	2.67	21.23	1.17	1.08	8.86	11.08	22.19
10	3.26	4.80	11.66	3.34	0.09	23.15	5.14	0.41	4.62	10.75	20.92
11	1.10	3.56	2.45	0.80	0.01	7.92	1.09	0.87	2.91	3.42	8.29
12	1.17	4.72	4.31	1.01	0.06	11.27	3.21	0.58	3.87	4.40	12.06
13	4.98	10.22	16.47	5.63	0.02	37.32	10.34	0.60	10.35	15.99	37.28
14	5.38	4.19	7.78	3.42	0.02	20.79	8.13	0.25	3.87	9.18	21.43
15	3.14	6.08	7.33	3.12	0.01	19.68	5.24	0.21	5.58	8.36	19.39
16	0.73	2.37	4.44	1.38	0.04	8.96	1.59	0.32	1.74	5.82	9.47
17	1.70	4.88	8.29	2.43	0.04	17.34	6.86	0.37	4.04	5.64	16.91
18	4.61	4.92	27.71	7.41	0.04	44.69	14.14	0.80	5.20	23.83	43.97
19	0.50	2.72	2.92	1.18	0.06	7.38	0.76	0.38	2.64	3.94	7.72
20	2.80	7.20	19.26	5.10	0.04	34.40	5.68	0.24	6.42	22.32	34.66

Bijlage 2

Overige bepalingen

merk	mg/l P205	me/l N	me/l Ca+Mg	pH	mS/25°C E.C.
1	25	6.14	11.95	6.51	1.74
2	14	0.96	3.07	7.40	0.62
3	11	2.16	8.32	7.36	1.22
4	14	10.14	24.58	7.40	3.24
5	10	5.18	7.24	7.46	1.28
6	13	5.48	20.92	6.90	2.51
7	13	3.43	8.61	7.26	1.24
8	15	1.14	2.04	7.27	0.44
9	10	4.57	9.10	7.30	2.13
10	16	4.97	16.46	7.05	2.24
11	6.1	1.00	3.54	7.53	0.88
12	13	3.33	5.85	7.36	1.26
13	24	9.93	21.42	7.14	3.36
14	49	7.82	10.60	6.39	2.12
15	17	5.21	10.79	6.66	1.95
16	12	1.80	5.98	6.98	0.93
17	17	6.71	10.21	7.04	1.66
18	8.1	12.84	35.47	7.39	3.70
19	19	1.05	4.24	7.17	0.96
20	11	5.76	22.81	6.78	2.82

Bijlage 3

Berekende EC-waarden volgens McNeal et al.

Monster no.	Rekenmethode *			Gemeten (bijlage 2)
	1	2	3	
1	1.84	1.88	1.74	1.74
2	0.65	0.63	0.64	0.62
3	1.23	1.24	1.18	1.22
4	3.42	3.60	3.34	3.24
5	1.31	1.31	1.24	1.28
6	2.65	2.78	2.60	2.51
7	1.21	1.20	1.13	1.24
8	0.49	0.48	0.50	0.44
9	2.26	2.28	2.16	2.13
10	2.14	2.19	2.02	2.24
11	0.87	0.85	0.84	0.88
12	1.23	1.23	1.18	1.26
13	3.56	3.74	3.46	3.36
14	2.16	2.21	2.07	2.12
15	1.98	2.01	1.89	1.95
16	0.91	0.90	0.88	0.93
17	1.79	1.80	1.69	1.66
18	3.93	4.15	3.81	3.70
19	0.79	0.77	0.77	0.96
20	2.97	3.12	2.90	2.82

* 1 - Exponential
2 - Thira-order
3 - Linear-segment

Rekenschema voor EC-waarden volgens McNeal et al., 1970

Lineaire segmenten model

Gevonden ionenbalans

Ca	51.9	me/l	
Mg	52.5		
Na	147		
K	0.6		som kationen 252
SO_4	24.6		
CO_3	0		
HCO_3	1.4		
Cl	226		som anionen 252

Zoveel als aanwezig Ca uitdrukken als (Ca, Mg) SO_4.
Indien meer SO_4 aanwezig zo veel als aanwezig Mg uitdrukken als (Ca, Mg) SO_4.
Voorts ionen uitdrukken als procenten van de som anionen of kationen.
Zo ontstaat:

Ca	27.3	me/l	10.8% van som K of A
Mg	52.5		20.8
Na	147		58.3
K	0.6		0.2
SO_4	0.0		0.0
CO_3	0		0.0
HCO_3	1.4		0.6
CL	226		89.7
$(CaMg)SO_4$	24.6		9.8

Aanhangsel 2

Daarna indeling per ion in klassen volgens McNeal.

dus Ca = 27.3 → klasse < 50
Mg = 52.2 klasse 50 - 100
Na = 147 klasse 100 - 200
enz.

Vervolgens de vergelijking opzoeken in tabel 3. De regressiecoëfficient vermenigvuldigen met de concentratie in me/l. Het intercept vermenigvuldigen met het percentage gedeeld door 100. Zo wordt verkregen:

			Bijdrage tot EC	
			Regressie	Intercept
Ca	0.0414C + 0.055		1.130	0.006
Mg	0.0269C + 0.44		1.412	0.092
Na	0.0373C + 0.54		5.483	0.315
K	0.0660C + 0.030		0.040	0.000
HCO_3	0.0348C + 0.029		0.049	0.000
Cl	0.0563C + 1.14		12.724	1.023
$(Ca,Mg)SO_4$	0.0629C + 0.183		1.547	0.018
		som	22.385	1.454

tesamen 23.839
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CALCULATION OF ELECTRICAL CONDUCTIVITY FROM SOLUTION COMPOSITION DATA AS AN AID TO IN-SITU ESTIMATION OF SOIL SALINITY

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An important aspect of models for plant growth on salt-affected soils is a knowledge of the vertical and lateral distribution of salt content and matric potential in the soil. The distribution of salt content depends upon the initial salinity of the soil solution, the exchange properties of the soil, the pattern of water extraction by plants, the rate of movement of soil solution, the salinity and salt composition of the irrigation water, the extent of leaching, and the composition of the gas phase of the soil. The development of accurate plant growth models depends upon experimental verification of predictions made by each of the different models. One such test which can be made at low matric potentials is the *in-situ* measurement of electrical conductivity (EC) of the soil solution with salinity sensors (2, 5, 8). This requires the conversion of predicted solution-composition data to EC values. Consequently, a method of computation is required whereby the EC of mixed-salt solutions can be calculated. Once such a method has been developed and tested on solutions of known composition and EC, it can serve as the basis for testing models of salt movement and plant-water extraction, using salinity sensors.

A second use for calculated EC values is in the periodic checking of the accuracy of the salinity sensors themselves. Such checks may be required occasionally if the sensors have been installed for periods in excess of several months. In this case it is necessary to take a soil sample near the sensor and determine the salinity of the sample. Such a determination can be made on a sample of soil solution extracted with a pressure-plate or pressure-membrane apparatus, but may be in error due to "salt sieving" at field-water contents (1). An alternative approach is to determine the ionic composition of the saturation extract of this sample, extrapolate the data to field-water content, and convert the final data to an EC value in order to verify the stability of the sensor. Ion concentrations rarely vary in a simple inverse manner with soil-water content, because of changes caused by salt precipitation, ion-exchange, mineral weathering, and repulsion of anions from the vicinity of charged soil surfaces. Extrapolation of solution composition data from one relatively high water content to another by the use of models taking some or all of these phenomena into account has already been demonstrated to be feasible (6, 11). The current work aids in the extrapolation of data to the much lower water contents found in the field as well.

The present paper evaluates several methods for calculating EC of mixed-salt solutions from ion-concentration data, and compares measured and calculated electrical conductivities for 193 soil-saturation extracts for which adequate data on ion composition were available. Methods have been selected which combine a reasonable mixture of accuracy and simplicity. Comparisons of calculated values for EC with values from *in-situ* EC sensors are included in a forthcoming publication which describes the models being used for the extrapolation process.

ELECTRICAL CONDUCTIVITY METHODS

Background Material

The methods for calculating EC were developed for mixed-salt solutions containing those ions most commonly found in significant concentrations in natural waters and soils. These are the cations Ca^{2+}, Mg^{2+}, Na^+, and K^+, and the anions SO_4^{2-}, Cl^-, HCO_3^-, and CO_3^{2-}. The NO_3^- anion was also treated, but results are not presented because of the limited importance of this species in salt-affected soils. Calculations were

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[1] Contribution from the U. S. Salinity Laboratory, Soil and Water Conservation Research Division, Agricultural Research Service, USDA, Riverside, California.

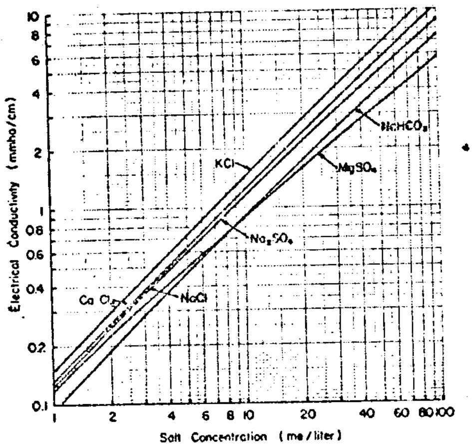

FIG. 1. Electrical conductivity as a function of salt concentration for single-salt solutions of several common salts.

restricted to total salt concentrations of 0–200 meq./liter for all ions but Na^+ and Cl^-. Calculations involving the latter ions were extended to 500 meq./liter. These ranges cover most common agricultural situations. Only values for EC at 25°C were considered, but the same approach could be taken at other temperatures as well.

Despite the good correlation between EC and total salinity which is observed for many natural waters (12), single salt solutions can vary by 25 to 50 per cent in their EC at a given concentration (fig. 1). As a result, estimating the EC of one salt solution from that of another can easily produce errors of the same magnitude.

Several attempts have been made to predict the EC of mixed-salt solutions from ion-concentration data (3, 9, 10). Such attempts become excessively complex whenever more than 3 or 4 ionic species are considered, and wherever attempts are made to cover wide concentration ranges. At low concentrations, ion mobility can be assumed independent of concentration, so that the ratio of conductivity to ion concentration (the equivalent ionic conductance) remains a constant. The conductivity of dilute salt solutions can be estimated by assuming the conductivity values of the constituent ions to be additive. Assuming that such values are additive can lead to errors of 15 to 103 per cent when EC data for common salts are linearly extrapolated from a salt concentration of 1 meq./liter to a concentration of 100 meq./liter. Most workers have found that adding the conductivity values of individual ions provides only a rough approximation to the conductivity of mixed-salt solutions at high salt concentrations.

Several useful equations which attempt to take into account electrical and ionic interactions have been developed for calculating the EC of single-salt solutions at salt concentration (C) values up to 50 or 100 meq./liter or higher (3, 10). They are commonly in the form of a power series, reducing to the equivalent ionic conductance values for dilute solutions, and involving expansion in terms of C^n at higher concentrations, where ^{n} is chosen as either ½ or 1 for the different models. Equations involving a single C term raised to a variable power have also been tested for simple salt solutions over limited concentration ranges. None of the equations is applicable for complex mixed-salt solutions over wide salt-concentration ranges, as is commonly found in soils. Hence the following approach was adopted for the current study.

Ion Conductivity Allocation

The basic data used in developing all but one of the methods for calculating EC of mixed-salt solutions were individual-ion electrical conductivities at 0.5, 1, 2, 5, 10, 20, 50, 70, 100, 200, and 500 meq./liter. To obtain such values, EC data from the literature were tabulated for single-salt solutions containing combinations of the nine common ions listed above (including NO_3^-). Because of similarities in ionic size and mobility, the EC of KCl at each concentration was assumed to arise from equal contributions of K^+ and Cl^-. Other salts containing K^+ were assumed to have an EC equal to the sum of the EC of K^+ at the appropriate salt concentration, and the EC of the anion accompanying K^+ in the respective salt. A similar approach was taken to obtain the EC at each concentration for cations accompanying Cl^- in the common chloride salts. The resultant EC for Na, Ca^{2+}, or Mg^{2+} was used to obtain the EC for SO_4^{2-}, HCO_3^-, CO_3^{2-}, or NO_3^- from the EC of the respective sulfate, bicarbonate, carbonate, or nitrate salt at each concentration. The EC values for SO_4^{2-}, HCO_3^-, CO_3^{2-}, and NO_3^- which were obtained from the respective potassium salts were also used to obtain an EC for Na^+, Ca^{2+}, or Mg^{2+} at each concentration. The table thus formed contained a single EC for

K^+ and for Cl^- at each salt concentration, and 2 to 5 values for the EC of each of the other ions at each concentration, depending upon the number of data available for each of the single-salt solutions. The general suitability of this approach was evident when values for the EC of individual ions at each concentration were averaged and then summed to produce estimates of the EC of single-salts containing these ions at the same concentration. Such values were in error by less than 1 to 2 per cent throughout the salt-concentration range studied.

The only exceptions were solutions of $CaSO_4$ and $MgSO_4$, where calculated EC at any given salt concentration was consistently too low by 25 to 50 per cent. This probably resulted from ion-pair formation, which is known to occur for these two salts. This problem was handled by mathematically partitioning the Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions into both salt and ionic fractions. As much Ca^{2+} and SO_4^{2-} as possible were first allocated to the $CaSO_4$ species and then as much of the remaining SO_4^{2-} as possible was mathematically paired with Mg^{2+} to form the $MgSO_4$ species. As both salts are similar in their EC-salt concentration relationships, all $CaSO_4$ and $MgSO_4$ [hereafter designated as $(Ca, Mg)SO_4$] was assigned the EC of $MgSO_4$ at a concentration equal to the sum of the $CaSO_4$ and $MgSO_4$ concentration in the solution. The contribution to the total EC from the remainder of the Ca^{2+}, Mg^{2+}, or SO_4^{2-} was calculated from values for single-ion EC in the normal manner.

Single-Salt Solutions

Three different methods were tested for calculating values for individual-ion EC over the concentration range from 1 to 200 or 500 meq./liter, using concentrations listed above. Appropriate individual ion EC values from each model were paired and summed for comparison with single-salt values of EC from the literature. The first method was an exponential relation of the form $EC = k_oC^b$, where C equals the concentration of the ion in meq./liter and k_o and C^b are arbitrary constants. The fitting process used for individual-ion values of EC was a linear regression of log EC on log C, and thus was weighted toward the highest and lowest ion concentrations (table 1). This caused single-salt values of EC at intermediate concentrations to be underestimated by several tenths of a mmho./cm. after summing values for the EC of individual ions as calculated by this method.

Considerably better fit over the entire ion-concentration range was provided by a second method, using third-order polynomials of the form $EC = k_1 + k_2C + k_3C^2 + k_4C^3$. Single-salt values for EC calculated by summing individual-ion EC values obtained with this method were in error by less than a tenth of a mmho./cm. throughout most of the salt-concentration range (table 1). This is better than had been hoped for, despite the larger number of constants used for the fitting process with this method. Furthermore, nearly equal quantities of positive and negative errors provided a better opportunity for cancellation of errors in mixed-salt solutions. All errors did not arise from imperfect fit between the polynomials and actual EC-concentration relationships for the respective ions. Analytical errors were also included, as were errors arising from the use of averaged values for individual-ion EC at each concentration instead of specific individual-ion data for the salt in question. The polynomial method proved to be the most accurate of the methods tested for estimating the EC of single-salt solutions from individual-ion EC data.

TABLE 1

Absolute error in calculating electrical conductivity of single-salt solutions from individual ion conductivities

Salt	Third-Order Polynomial						Exponential Relationship						Source*
	Salt Concentration (meq/liter)						Salt Concentration (meq/liter)						
	1	5	10	50	100	200	1	5	10	50	100	200	
	(mmho/cm.)						(mmho/cm.)						
$CaSO_4$	+.031	−.041	−.070	—	—	—	−.008	−.058	−.105	—	—	—	1
$MgSO_4$	+.035	−.035	−.059	+.038	−.036	+.002	−.004	−.052	−.094	−.220	−.201	+.078	1
Na_2SO_4	+.025	−.014	−.032	+.013	−.040	−.487	−.008	−.072	−.147	−.555	−.760	−.639	1, 2
Na_2CO_3	—	+.006	−.033	−.007	+.110	+.063	—	−.033	−.102	−.433	−.526	−.200	1
$Ca(HCO_3)_2$	+.013	−.007	+.001	—	—	—	−.001	−.019	−.031	—	—	—	1
$Mg(HCO_3)_2$	—	−.016	−.008	+.198	+.094	—	—	−.036	−.076	−.051	+.315	—	1
$NaHCO_3$	+.013	−.008	−.018	+.031	−.056	—	−.005	−.038	−.079	−.300	−.377	—	1
$CaCl_2$	+.021	−.011	−.025	+.039	+.110	—	−.002	−.032	−.067	−.192	−.150	—	2
$MgCl_2$	−.002	−.011	−.006	+.114	−.043	.000	−.004	−.039	−.083	−.187	−.534	−.352	1, 2
NaCl	+.021	−.001	−.015	+.027	+.117	+.053	−.005	−.040	−.086	−.356	−.527	−.528	1
KCl	+.017	−.008	−.021	−.006	+.023	+.010	−.003	−.031	−.065	−.250	−.323	−.240	1, 3

* 1 = International Critical Tables (4). 2 = Harned and Owen (3). 3 = Robinson and Stokes (9).

As both the exponential and polynomial methods are cumbersome for hand calculations of EC for mixed-salt solutions, a third method was tested in which individual-ion EC and concentration data were also approximated by a series of linear segments. Slopes and appropriate intercepts for EC as a function of salt concentration were obtained over the following concentration ranges: 5 to 50, 50 to 100, 100 to 200, and 200 to 500 meq./liter.

Mixed-Salt Solutions

All three of the above methods can be applied directly to single-salt solutions. For mixed-salt solutions, however, both the polynomial and linear segment methods overestimate the values for EC when the full intercept for each ion is used in calculations. This is reasonable, because all intercepts for a given method are of comparable magnitude, and only a single average intercept should be used for a mixed-salt solution. Hence the intercept value for each cation was multiplied by the fraction of the total cation population represented by the cation. Cations in the $(Ca, Mg)SO_4$ species were included among the cation population for this calculation. A similar procedure was used for each anion. For hand calculations, approximate estimates by visual inspection usually suffice for these average intercept values.

A fourth method of estimating the EC of mixed-salt solutions having approximately constant composition but variable total salinity is the use of a regression equation between EC and total salt concentration. Such an approach was applied to the soil-saturation extracts of the current study, and will be discussed below. Attempts were also made to allocate the ions of mixed-salt solutions to a series of single salts, and to calculate the EC of mixed-salt solutions from EC values of the appropriate single salts. Such an approach is more artificial than an individual-ion approach, and in no cases led to significant improvement in the EC values that were calculated. In general, the use of single-salt EC values tended to produce poorer estimates of EC for mixed-salt solutions than did corresponding individual-ion approaches. Thus such approaches will not be considered in this paper.

METHODS AND MATERIALS

Data for the EC of single-salt solutions as a function of concentration were taken primarily from the International Critical Tables (4), with supplementary values from Harned and Owen (3) and Robinson and Stokes (9). All values were for 25°C., and in the salt-concentration range of 0.5 to either 200 or 500 meq./liter. These data were fit with the three methods listed in the previous section, after forming appropriate individual-ion EC data.

Solution composition and EC data for 193 soil-saturation extracts were taken from the files of the U. S. Salinity Laboratory from the period 1960–1969. The samples came from California, North Dakota, Texas, and 13 foreign countries.

Electrical conductivity was measured at 1000 cps. with an Industrial Instruments[3] bridge, using a conductivity cell having a cell constant of approximately 20. All values of EC were converted to equivalent values at 25°C. through the use of conversion factors derived from standard tables (12). The conductivity cell was calibrated with KCl solutions of known concentrations. Solution concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, HCO_3^-, CO_3^{2-}, and NO_3^- were determined with standard analytical techniques (12). Concentrations of SO_4^{2-} were determined by difference.

Calculations of EC for the soil-saturation extracts were performed on an IBM 360-90 computer. Computations for all 193 solutions required approximately 6 to 8 seconds of central

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[3] Trade names are included for the convenience of the reader, and do not imply preferential endorsement of the product by the U. S. Department of Agriculture.

processing time for allocation of (Ca,Mg)SO$_4$, calculation of individual ion and total EC, ordering of results, linear regression analysis on the data grouped into each of 6 EC ranges, and tabulation of residuals between calculated values of EC and EC calculated from the regression equation for the range in EC in question.

RESULTS AND DISCUSSION

The complete set of coefficients developed for calculation of EC values for individual ions from ion-concentration data is given in table 2. When third-order polynomials from the table are used for mixed-salt solutions, k$_1$ values must be multiplied by the fraction of cations or anions in solution represented by the given ionic species. No such corrections are required when using the exponential method. In both cases, the necessary calculations are performed most efficiently with a digital computer. The set of linear equations recommended for hand calculation of EC for mixed-salt solutions over various ion-concentration ranges is given in table 3. As with the third-order polynomial method, weighted intercepts should be used with the linear equations for mixed-salt solutions. In practice, the average intercept can usually be estimated visually to within 0.1 mmho./cm. A fourth method was developed from the regression of EC on total salt concentration. Only the 141 soil-saturation extracts having an EC of 10 mmho./cm. or less were used for this regression. The regression equation could then be used to estimate EC from total salt concentration. The regression equation for the 141 saturation extracts was EC = 0.280 + 0.0776 C, where C is total salt concentration in meq./liter. The correlation coefficient for this model in the EC range 0 to 10 mmho./cm. was 0.985. This method is the simplest of those used, but it suffers from the need for a rather large set of EC and total salinity data from which to derive the initial regression equation for a given set of waters. Obtaining such data for soil solutions would require considerable effort in many cases. Furthermore, as the required regression equation changes with salt composition (e.g., fig. 1), the accuracy which is obtained by a general conversion of total concentration to EC is often poorer than that from other approaches. This will be further treated below. This method could be improved by grouping waters according to salt composition, and by using different regression equations for waters of each group. As the number of groups increases, however, the method becomes increasingly similar to the linear segment method based on individual-ion data. Thus no grouping of solutions according to salt composition was undertaken for the current appraisal of the regression method.

TABLE 2

Coefficients used for computer calculation of electrical conductivity (EC) for mixed-salt solutions from individual ion concentrations

Species	Third-Order Polynomial (Method 2)*				Exponential (Method 1)†	
	$k_1 \times 10^2$	$k_2 \times 10^2$	$k_3 \times 10^4$	$k_4 \times 10^7$	k_0	b
Ca^{2+}	1.608	4.834	−1.323	3.762	.05641	.9202
Mg^{2+}	−1.208	5.065	−2.749	9.106	.05099	.9102
Na^+	1.155	4.718	−0.448	0.383	.04748	.9495
K^+	0.825	6.973	−0.722	1.664	.07263	.9706
SO_4^{2-}	3.090	5.984	−1.716	3.408	.06900	.8973
CO_3^{2-}	5.281	5.268	−1.202	2.026	.07330	.8719
HCO_3^-	1.071	3.755	−0.192	−3.401	.04143	.9501
Cl^-	1.919	6.760	−0.357	0.353	.07206	.9671
NO_3^-	0.193	6.617	−1.211	·2.510	.06538	.9586
(Ca, Mg) SO_4	7.459	7.84	−2.882	7.176	.1133	.8463

* EC (mmho/cm.) = $k_1 + k_2C + k_3C^2 + k_4C^3$

† EC (mmho/cm.) = k_0C^b C = Ion concentration (meq/liter)

TABLE 3

Recommended equations for hand calculation of electrical conductivity for mixed-salt solutions (Method 3)

Ion Concentration	<50 *meq./liter*	50–100 *meq./liter*	100–200 *meq./liter*	200–500 *meq./liter*
Species	*Electrical conductivity (mmho/cm.)*			
Ca^{2+}	.055 + .0414 C*	.26 + .0355 C	.40 + .0350 C	.94 + .0323 C
Mg^{2+}	.060 + .0356 C	.44 + .0269 C	−.17 + .0329 C	2.20 + .0210 C
Na^+	.023 + .0452 C	.27 + .0402 C	.54 + .0373 C	1.85 + .0306 C
K^+	.030 + .0660 C	.23 + .0620 C	.46 + .0597 C	1.14 + .0563 C
SO_4^{2-}	.077 + .0507 C	.59 + .0407 C	1.22 + .0332 C	2.50 + .0268 C
CO_3^{2-}	.070 + .0470 C	.51 + .0382 C	1.26 + .0307 C	2.70 + .0238 C
HCO_3^-	.029 + .0348 C	.32 + .0291 C	—	—
Cl^-	.030 + .0660 C	.23 + .0620 C	.46 + .0597 C	1.14 + .0563 C
NO_3^-	.034 + .0603 C	.40 + .0528 C	.92 + .0474 C	3.05 + .0367 C
(Ca, Mg) SO_4	.183 + .0629 C	.87 + .0492 C	1.62 + .0417 C	3.00 + .0348 C

* C = Ion concentration (meq./liter)

The 193 soil saturation-extract analyses used for comparing the various EC methods represented a wide range of salt concentrations and compositions. Some general properties of this group of solutions are presented in table 4. Nearly three-fourths of the solutions had electrical conductivities less than 10 mmho./cm., with approximately half falling between 1 and 10 mmho./cm. All but three of the high HCO$_3^-$ waters fell in the EC range of 0 to 1 mmho./cm. Seven of the nine waters having an EC greater than 50 mmho./cm. fell into the >¾ Cl$^-$ group, as did 12 of the 13 waters having an EC between 25 to 50 mmho./cm. Thus, although wide ranges of total salinity and solution composition were studied, the salinity and composition values were somewhat interdependent. Poor fit of the different methods in certain ranges may suggest ionic associations which are not adequately treated by the methods used.

TABLE 4

Properties of soil saturation extracts used for electrical conductivity calculations

Electrical Conductivity	No. of Samples	Percent	Predominant Anions	No. of Samples	Percent
(mmho/cm.)					
0-1	45	23.3	>½ HCO_3	30	15.5
1-3	44	22.8	SO_4-HCO_3	21	10.9
3-10	52	26.9	>¾ SO_4	44	22.8
10-25	30	15.5	SO_4-Cl	20	10.4
25-50	13	6.7	Cl-SO_4-HCO_3	28	14.5
50-100	9	4.7	Cl-SO_4	17	8.8
	—	—	>¾ Cl	33	17.1
	193	99.9		—	—
				193	100.0

Representative data used for calculation of EC of soil-saturation extracts from the various methods are given in table 5, along with measured and calculated EC values. The solutions were selected by arraying the 193 sets of experimental data in order of increasing EC, and then selecting every 8th set of data.

Despite the imperfect fit of the exponential method (method 1) to individual-ion and single-salt EC values, this method provided quite good values for the EC of mixed-salt solutions over much of the EC range. Calculated values for EC were generally within ±0.2 mmho./cm. of measured EC values up to 7 mmho./cm., and within ±1.0 mmho./cm. up to 20 mmho./cm. As the exponential method commonly under-predicted the EC of single-salt solutions, the fit of this model for mixed-salt solutions suggests that the values for individual-ion EC are not strictly additive throughout the entire salt-concentration range. Ion interactions in mixed-salt solutions apparently lower the values for individual-ion EC to the point that they agree reasonably well with values calculated from the exponential method.

Use of third-order polynomials for relating individual-ion concentrations to EC proved satisfactory for single-salt solutions. When applied to soil-saturation extracts, this same method (method 2) gave calculated values for EC which agreed well with measured values up to approximately 3 mmho./cm. Measured EC then was consistently over-estimated throughout the remainder of the EC range. Calculated and measured EC generally agreed within ±0.2 mmho./cm. up to 3.5 mmho./cm., and within ±1.0 mmho./cm. up to 7 mmho./cm. The method would thus work well for calculating the EC of most irrigation waters, but would fail for the more important task of calculating EC for soil solutions.

TABLE 5

Representative data used for the calculation of electrical conductivity of soil saturation extracts by several methods

Sample No.	Ionic Concentration (meq./liter)									Electrical Conductivity (*mmho/cm.*)					
	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	CO_3^{2-}	HCO_3^-	Cl^-	Total	Measured	Method 1†	Method 2	Method 2a	Method 3	Method 4
13360	1.0	0.4	0.7	0.1	0.8	0	0.9	0.5	2.2	0.24	0.24	0.24	0.24	0.29	0.45
13368	2.0	1.3	0.2	0.3	1.5	0	2.6	0.3	4.4	0.41	0.44	0.42	0.42	0.44	0.62
12431	2.6	1.2	1.5	0.1	1.4	0	2.0	2.0	5.4	0.53	0.58	0.55	0.55	0.56	0.70
13383	1.2	0.4	4.3	0	2.2	0	3.2	0.5	5.9	0.61	0.63	0.56	0.56	0.56	0.74
12253	2.0	2.7	3.5	0.6	3.3	0	5.3	0.2	8.8	0.70	0.82	0.78	0.78	0.76	0.96
13559	0.9	0.0	7.0	0	1.0	0	3.3	3.6	7.9	0.83	0.79	0.80	0.80	0.80	0.89
13677	7.7	2.5	2.0	0.2	9.2	0	1.6	1.4	12.4	1.12	1.13	1.08	1.08	1.03	1.24
12245	1.0	2.2	12.9	0.1	9.1	0	6.8	0.3	16.2	1.36	1.50	1.52	1.52	1.44	1.54
13388	14.6	2.0	1.0	2.3	6.6	0	11.9	1.4	19.9	1.74	1.76	1.77	1.77	1.63	1.82
13377	2.4	0.6	19.6	0.3	5.5	0	13.9	3.5	22.9	2.20	2.04	2.10	2.10	2.01	2.06
12404	6.4	4.3	13.5	0.9	13.0	0	1.4	10.7	25.1	2.43	2.48	2.47	2.47	2.33	2.23
12868	0.8	0.9	32.1	0.1	18.3	1.0	12.0	2.6	33.9	2.99	3.04	3.27	3.27	3.13	2.91
12246*	4.9	7.4	30.4	0.2	35.0	0.2	7.3	0.3	42.9	3.46	3.73	3.98	3.81	3.71	3.61
12264	4.7	13.3	32.2	0.3	45.7	0.2	4.3	0.3	50.5	4.11	4.30	4.03	4.31	4.32	4.20
12415	16.3	12.8	21.8	0.4	6.1	0	1.7	43.5	51.3	5.33	5.27	5.56	5.07	5.29	4.26
12251	17.6	17.9	49.2	0.6	83.7	0	1.5	0.1	85.3	6.59	6.85	7.51	6.75	7.13	6.90
12247*	18.8	29.1	65.5	0.4	110.4	0	3.0	0.1	113.8	8.24	8.81	9.70	8.78	8.88	9.11
12329	21.2	10.5	85.1	0.5	104.2	0	2.2	10.9	117.3	9.42	9.63	10.5	9.57	9.81	9.38
12389	5.5	19.4	90.5	0.8	14.5	0	2.2	99.5	116.2	11.4	11.4	12.1	11.1	11.7	(9.30)
12401	17.8	16.6	105	1.5	50.5	0.1	2.3	88.0	140.9	13.1	13.0	13.9	12.9	13.1	(11.2)
12397	22.6	23.0	127	0.6	23.2	0.1	2.9	147	173.2	16.8	16.4	17.5	16.4	16.7	(13.7)
12406	51.9	52.5	147	0.6	24.6	0	1.4	226	252.0	22.9	23.9	25.1	23.0	23.8	(19.8)
12408	86.2	85.3	147	0.8	22.1	0	1.2	296	319.3	28.3	30.3	31.1	—	29.7	(25.1)
12373	130	115	329	21.4	58.0	0	2.4	535	595.4	50.2	54.8	55.2	—	53.0	(46.5)
13357	53.1	9.5	872	17.1	232.5	0	4.2	715	951.7	74.4	83.2	87.9	—	79.8	(74.1)

* 0.1 to 0.3 meq./liter NO_3^- also present, but ignored in the calculations.

† Method 1 = exponential relationship; Method 2 = third-order polynomial; Method 2a = corrected third-order polynomial; Method 3 = linear-segment method; Method 4 = linear regression on total salt concentration.

Although several approaches might have been used to bring measured and calculated EC into closer agreement, it was decided to maintain the simplicity of the polynomial method for single-salt solutions, and to lump the correction for more concentrated mixed-salt solutions into a single calculation. Calculated EC was fit to experimental EC in the EC range 3–25 mmho./cm. using the third-order polynomial

$$EC_{final} = 1.133 + 0.5633\ EC_{calc} + 0.03003\ EC_{calc}^2 - 0.0007079\ EC_{calc}^3.$$

These corrected values comprise column 2a in table 5. They were generally within ±0.2 mmho./cm. of the measured EC up to 7 mmho./cm., and within ±0.5 mmho./cm. of the measured EC up to 25 mmho./cm. No attempts were made to extend the range beyond 25 mmho./cm. Improvements at higher values of the EC would have been at the expense of agreement in the low and moderate EC ranges. Solutions having higher values of EC contain mainly NaCl, for which adjustments of calculated EC should not be necessary. The range of EC values up to 25 mmho./cm. covers most solutions encountered in irrigation agriculture. Whenever the composition of mixed-salt solutions approaches that of single-salt solutions, use of uncorrected EC may prove more acceptable. Corrected and uncorrected values of EC agreed within ±0.2 mmho./cm. up to 4 mmho./cm., and within ±1.0 mmho./cm. up to 15 mmho./cm. Thus the error in estimating EC of essentially single-salt solutions from corrected values of EC would usually still be acceptable.

Also included in table 5 are values calculated from the linear segment or hand calculator method (method 3). These values are similar to those calculated from the exponential method. The linear segment method tends to underestimate values for individual-ion EC, because of the concave shape of the EC-concentration relationships for most individual-ions and single-salt solutions. Thus, as with the exponential method, a fortunate cancellation of errors leads to much of the agreement between experimental values of EC and those calculated with this model. The model generally provides values within ±0.2 mmho./cm. of measured values up to 6 mmho./cm., and within ±1.0 mmho./cm. up to nearly 40 mmho./cm. Despite the fact that such excellent agreement is largely fortuitous, the lack of exact fit for single-salt solutions is more tolerable in this case. Use of a larger number of increments or of a more complicated expression for the EC-concentration relationship of each ion would have rapidly taxed the capacity of a hand calculator. The model can be improved at very high salt concentrations by using the slope for each ion which corresponds to the total concentration of the solution, rather than to the concentration of the particular ion. Such refinement is not required for most EC calculations below 30 mmho./cm., however.

The final column in table 5 contains values of EC calculated from the regression of EC on total concentration for the 141 solutions having experimental EC between 0 and 10 mmho./cm. This method (method 4) gave consistently high results at values of EC less than 1 mmho./cm., due to the greater weighting given higher values of EC during the regression calculation. With this exception, consistent errors between calculated and measured EC were largely eliminated by the fitting process. Despite this fitting, however, variations between calculated and measured EC were commonly greatest for this model. Such variations for values of EC less than 1 mmho./cm. could be eliminated by separating the data into high-salinity and low-salinity values, and fitting a regression equation to each set. No advantage would be gained by separating the data into more than two data sets, however, unless such separation were done on the basis of salt composition. As mentioned previously, such a separation was not considered for the present study. No consistent pattern of variations with EC was observed, and thus no attempt was made to adjust values as done for the third-order polynomial method. The linear segment, exponential, and corrected polynomial methods gave better estimates of measured EC in ⅔ to ¾ of the cases for both the 0–10 and 10–25 mmho./cm. EC ranges. The regression approach is a simple and useful one for groups of solutions having more uniform compositions than do the solutions of the current data set. However, a rather large number of samples should be run before a proper regression equation is developed for each group of solutions, and the regression would commonly shift as solution composition changes during water extraction by growing plants. Thus the approach is of limited value as a general model for EC calculations.

The scatter diagram for EC calculated by the linear segment method (method 3) as a function of measured EC is given as fig. 2. Regression equations and correlation coefficients for the 0–100 and 0–25 mmho./cm. EC ranges are as follows:

0–100 mmho./cm.

$$EC_{calc} = -0.3608 + 1.064\ EC_{meas} \quad r = 0.982$$

0–25 mmho./cm.

$$EC_{calc} = -0.1859 + 1.049\ EC_{meas} \quad r = 0.993$$

The relation is thus adequate for reliable prediction of EC in the field solution-composition range for irrigated soils, as originally intended for the methods of this study.

In table 6 are summarized the pertinent statistical data for 6 EC ranges into which the soil saturation-extract data were grouped. Correlation coefficients are not given, but in most cases they ranged between 0.960 and 0.996. Regression coefficients for all but the regression method (method 4), were consistently greater than 1.0 at moderate and high salt concentrations, verifying the tendency of the methods to over-predict EC for concentrated mixed-salt solutions. The linear segment method (method 3) predicted EC more closely in this respect. Standard errors of estimate (not given) were commonly around 3 to 5 per cent of the median EC for each EC range. The greatest consistency over the widest EC range was given by the linear segment method. This method also produced relatively low average values for the difference between calculated and measured EC over the widest EC range of the methods tested. Standard deviation of the difference between calculated and measured EC once more showed the linear segment method to be the most consistent of the group. Although the polynomial method (method 2) performed poorly, this was mainly because of the consistent over-prediction of EC at moderate and high salt concentration. This is evident by comparing the magnitude of the average differences and standard deviations for this method

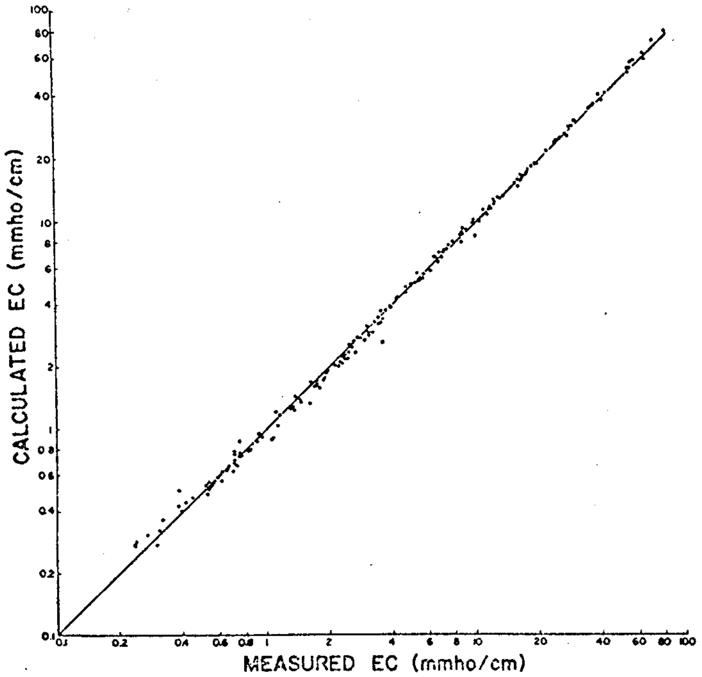

FIG. 2. Electrical conductivity calculated by summing linear equations in individual ion concentrations (Method 3) versus measured electrical conductivity.

within each given range. Use of the corrected polynomial method (method 2a) decreased the average differences in the 3 to 10 and 10 to 25 mmho./cm. EC ranges to +0.055 and −0.105 mmho./cm., respectively (not shown). In a similar manner, the respective standard deviations of the differences were decreased to 0.411 and 0.555 mmho./cm. Thus the corrected polynomial method performed best of all methods tested up to an EC of 25 mmho./cm. The regression method (method 4) gave the poorest agreement between calculated and measured EC up to 50 mmho./cm. This is particularly evident from the standard deviation values.

TABLE 6

Summarized statistical parameters describing various methods for calculating electrical conductivity (EC) of 193 soil saturation extracts

Group	EC >Range (*mmho/cm.*)	No. of Samples	Regression Coefficient				Avg. Difference* (*mmho/cm.*)				Standard Deviation of Differences (*mmho/cm.*)			
			Method 1†	Method 2	Method 3	Method 4	Method 1	Method 2	Method 3	Method 4	Method 1	Method 2	Method 3	Method 4
I	0-1	45	1.057	1.054	.947	.891	+.027	+.007	+.011	+.169	.0568	.0169	.0421	.1807
II	1-3	44	.964	1.041	.981	.809	−.002	+.029	−.072	−.080	.0918	.1092	.1286	.1848
III	3-10	52	1.073	1.186	1.065	1.132	+.098	+.586	+.130	−.098	.3835	.8469	.4085	.6390
IV	10-25	30	1.077	1.099	1.044	.867	+.215	+1.130	+.261	−1.037	.5982	1.370	.5084	1.810
V	25-50	13	1.064	1.065	1.019	.793	+1.727	+2.524	+.828	−3.561	2.088	2.840	1.399	5.037
VI	50-100	9	1.199	1.418	1.108	1.219	+5.374	+6.787	+2.665	−1.767	6.736	9.246	3.954	3.686

* Calculated EC—Measured EC.

† Method 1 = exponential relationship; Method 2 = third-order polynomial; Method 2 = corrected third-order polynomial; Method 3 = linear-segment model; Method 4 = linear regression on total salt concentration.

SUMMARY AND CONCLUSIONS

To test extrapolation of saturation-extract analyses to field-water contents, and to provide a means to test the performance of salinity sensors, several methods for calculating the electrical conductivity (EC) of mixed-salt solutions have been developed and tested on saturation-extract data from 193 soils. Most methods were based on the additivity of values for individual-ion EC in both single-salt and mixed-salt solutions. Calculated and measured EC commonly agreed to within ±0.2 mmho./cm. up to 4-6 mmho./cm., and to within ±1.0 mmho./cm. up to 15-40 mmho./cm., depending upon the method used.

A single third-order polynomial for each ion proved satisfactory for predicting the EC of most single-salt solutions containing the ion and a counter-ion. The main exceptions were solutions containing Ca^{2+} and SO_4^{2-}, Mg^{2+}, and SO_4^{2-}, or both. Such solutions consistently gave low EC values. The three species were subsequently allocated to $(Ca,Mg)SO_4$, and assigned a single EC-concentration relationship, for all mixed-salt solutions.

Despite the agreement between calculated and measured EC for single-salt solutions, calculated values for mixed-salt solutions were consistently high above an EC of 3 mmho./cm. Satisfactory agreement was obtained by applying a correction factor to the values of EC calculated from the polynomial method. Good agreement of calculated and measured EC was also obtained when exponential or linear-segment methods were used for the calculations. The two latter methods gave low values for the EC of single-salt solutions, and hence compensated somewhat for the trend toward high EC in mixed-salt solutions. The linear segment method for calculating EC is sufficiently simple for routine calculations with a hand calculator, but both the exponential and corrected polynomial methods are best handled with a digital computer. All three methods consistently gave more accurate results than did a regression of EC on total concentration.

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