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.THE ELECTRIC CONDUCTIVITY AND
THE IONIC BALANCE OF SOIL SOLUTIONS.

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THE ELECTRIC CONDUCTIVITY AND
THE IONIC BALANCE OF SOIL SOLUTIONS.

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Introduction:

- Electric conductivity (E_c) is a parameter of a soil solution which is easily measured. It is accurate and it can be used as index to check the validity of analytical results of water samples or soils solutions. A convenient way to locate a potential error in an analysis is to compare the sum of cations (S^+) and the sum of anions (S^-) which should be equal because of the electroneutrality of the solution. A significant deficit will show either the possibility of existing ions not determined (mostly NO_3^- , but possibly HPO_4^- or NH_4^+ in agricultural soils) or an error in analytical result. In this second case one cannot ascertain which of S^+ or S^- is the nearest of the true value except if a relation exists between E_c and the total concentration C_T . This last parameter being equal to S^+ and S^- when the result of analysis are correct.

- Many authors have proposed relations (table 1) between the experimental value of total concentration called C_o , and E_c as measured by a Wheatstone conductivity bridge. All this relations are useful, but the chemical nature of the solution is generally not considered and the field of application of these equations is limited. A more sophisticated approach as been made by relating the ionic strength (I) of the solution to E_c (Ponamperuna and al. 1973, Griffin and Jurinak 1973). That implies the laborious calculation of activities for each ionic species (Adams 1971) and the estimation of ion-pair concentration if the ionic strength is greater than 20mmol^- (Rieu 1980).

- Table 1: Experimental relation $C_o = kc^a + k'$ according to different authors: (units: C_o in meq/l^{-1} , E_c in mScm^{-1})

Author	: year	: a	: k	: k'	: range of E_c	: ref.
Campbell	: 1948	: 1,065	: 10,37	: 0	: 0-70	: (3)
Richards	: 1954	: 1,00	: 10,1	: 0	: 0-4	: (12)
-	: -	: 1,091	: 9,92	: -	: 0-50	: (12)
Mac Neal	: 1970	: 1,00	: 12,88	: -3,61	: 0-10	: (7)

- The purpose of this paper is to present a single relation between the total experimental concentration C_o , and the measured electric conductivity E_c which takes into consideration the ionic composition of the solution. In this work, we assume that the ratio of the concentrations of monovalents ions over bivalent ones (d) is representative of the behaviour of the solution as far as its conductance is concerned:

$$d = (\text{Na} + \text{K} + \text{Cl} + \text{HCO}_3 + \text{NO}_3) / (\text{Ca} + \text{Mg} + \text{SO}_4 + \text{CO}_3)$$

$$C_o = (S^+ + S^-) / 2 \quad (\text{experimental})$$

$$C_T = (S_t^+ = S_t^-) \quad (\text{theoretical})$$

This assumption is supported by the values of activity coefficients of differently charged ions as shown in table 2.

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- Table 2: Activity coefficients of ions in aqueous solution (Kielland, 1937).

Ion	:	K ⁺	Cl ⁻	Na ⁺	HCO ₃ ⁻	Mg ⁺⁺	Ca ⁺⁺	CO ₃ ⁼	SO ₄ ⁼
γ ₁ (I=1 mmol ⁻¹)	:	0,96	0,96	0,93	0,93	0,87	0,87	0,87	0,87
γ ₂ (I=100 mmol ⁻¹)	:	0,76	0,76	0,77	0,77	0,45	0,40	0,38	0,36
100(γ ₁ - γ ₂ / γ ₁)	:	21	21	17	17	48	54	56	58

From an ionic strength of 1mmol⁻¹ to 100mmol⁻¹ the coefficient of activity of monovalent and bivalent ions commonly found in water and soil extracts diminishes respectively by an average of 21% and 54%. It means that at equivalent ionic strength, a solution containing more divalent ions will produce more ion-pairs, the resulting conductance being smaller than in a solution containing a majority of monovalent ions: This evidence is shown in fig 1. where the value of Co/Ec is plotted against C_t. For a given concentration C_t ratio C_t/E_c is high for CaSO₄ and MgSO₄ solutions known to form ion-pairs, intermediate for CaCl₂ and low for NaCl which does not form ion-pairs.

Experimental:

In order to find the proposed relationship, 375 results of analysis of natural waters or soils solutions were reviewed from ORSTOM & ACSAD files. In a first step, they have been set according to the value of d and Ec. In a second step unwanted samples were eliminated in order to keep only two or three results for each interval of d and each interval of Ec. That lead finally to keep only 114 samples. This selection was made to obtain unbiased samples, with respect to Ec and d. A low value for d represents samples rich in bivalent ions, mainly Ca and SO₄, while a high value of d is characteristic of samples containing mostly NaCl. Very few values of d greater than 6 and lower than 0,4 were found in the files. The original distribution of the 375 samples is shown in fig 2a and 2b and the characteristics of the 114 samples used in the calculation of relationship are tabulated in table 3.

- Table 3: Distribution of Ec and d for 114 waters samples.

	: Ec/mScm ⁻¹ < 0,3	: < 1,0	: < 2,0	: < 4,0	: < 8,0	: < 8	: n
d : 0,4-0,07	: 2	3	3	2	2	2	14
d : 0,7-0,90	: 1	3	2	3	2	2	13
d : 0,91-1,10	: 2	2	1	1	2	2	10
d : 1,31-150	: 3	2	2	1	2	5	15
d : 1,1-13	: 2	2	2	3	3	2	14
d : 1,51-1,80	: 1	2	1	2	4	3	13
d : 1,81-2,20	: 3	2	-	1	4	1	11
d : 2,21-2,60	: -	3	2	4	3	2	14
d : 2,61-4,20	: -	1	3	-	3	3	10
total	: 14	20	16	17	25	22	114

The calculations on these 114 samples were made as follows: for each interval of d, the relationship: LnCo=aLnEc + b was calculated by linear regression. The results are given in table 4. The values of the slope a are different for each interval of d, while the coefficient b seems reasonably constant over the range d=0,7 to d=4,2. There are two possible equations:

(c) $\text{LnCo} = 1,049 \text{ LnEc} + 2,387$

Which takes the average value of a and b over the whole range of d values, and:

(d) $\text{LnCo} = (1,092 - 0,027 d) \text{ LnEc} + 2,287$

which accounts for the variation of a, in the same interval of d values:

$a = 1,092 - 0,027 d \quad r = 0,84$

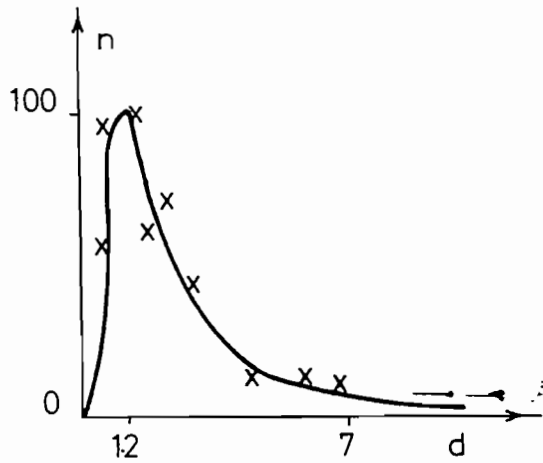


Fig.2_a: Distribution of d for 375 water samples.

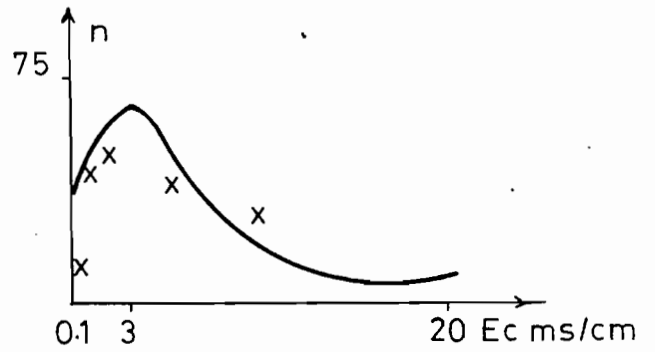


Fig.2_b: Distribution of Ec for 375 water samples.

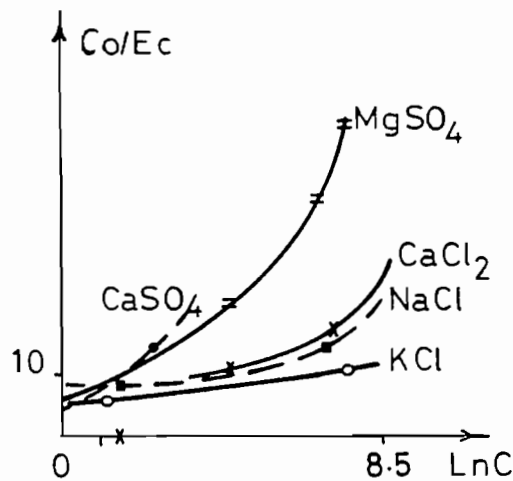


Fig.1: Values of co/Ec for single salt solution.

Table 4: Values of the coefficients a and b in the relation $\text{LnCo} = a\text{LnEc} + b$ for different intervals of $d = S^2/S^1$.

d	r	a	b	\bar{d}	d	r	a	b	\bar{d}
0 - 0,7	0,9992	1,089	2,412	0,6	1,51-1,8	0,9995	1,027	2,400	1,7
0,71-0,9	0,9993	1,038	2,421	0,8	1,81-2,2	0,9994	1,035	2,402	1,9
0,91-0,9	0,9990	1,072	2,337	1,0	2,21-2,6	0,998	1,031	2,348	2,4
1,11-1,3	0,9991	1,090	2,369	1,2	2,61-4,2	0,997	0,988	2,393	3,8
1,31-1,5	0,9995	1,050	2,400	1,4	average		1,049	2,387	-

In order to test the relations (c) and (d), two experiments have been made: In the first one, seventeen water samples, not used for the statistics leading to relations (c) and (d) have been selected. For all this samples the difference between S^+ and S^- was less than 5%. The value C_0 was calculated according to the relations given in table 1, and by the relations (c) and (d). The relative deviation around the true value C_T was calculated and given in columns a, b, c, d. of table 5.

The relation (d) proposed in this paper gives the best estimation of C_T as shown by the value of $100(C_T - C_0)/C_T$ which is the lowest, the values obtained by the Richard's set of two equations underestimate slightly C_0 the difference $C_T - C_0$ being positive for most of the samples. The values obtained from the equation $\text{LnCo} = 1,065 \text{LnEc} + 2,339$ (Campbell) and $\text{LnCo} = 1,049 \text{LnEc} + 2,387$ (this work) are identical. The first giving a narrower and the second a more homogeneous distribution around C_T .

Table 5: Precision of estimated C_t by different relations:

Datas (waters and soil solutions):				$\Delta C = 100 (C_t - C_0)/C_t$				average
N°	C_t	E_c	S^2/S^1	(a)	(b)	(c)	(d)	
	meq/l	mS/cm	d	%	%	%	%	
AOSAT :	1,85	0,20	0,70	- 1,0	- 9,1	- 8,7	- 4,5	- 7,5
A 140 :	3,12	0,33	0,65	- 2,1	- 6,7	- 9,0	- 6,0	7,5
H2SAT :	6,48	0,66	0,75	- 2,8	- 2,8	- 8,6	- 7,5	6,5
109-12:	7,05	0,73	0,25	- 5,2	- 4,5	- 10,9	- 9,7	7,5
ASAT :	19,5	1,70	0,80	+ 6,3	+ 11,9	+ 2,5	+ 1,4	8,0
B 25 :	24,5	1,90	1,30	- 16,1	+ 21,7	+ 12,9	+ 12,4	- 17,5
403-4 :	30,0	2,50	1,20	+ 8,3	+ 15,9	+ 5,2	+ 4,2	- 9,5
B-60 :	46,2	3,63	2,00	+ 11,4	+ 20,7	+ 8,9	+ 10,2	- 12,7
L-35 :	42,4	4,02	1,40	- 7,6	- 6,7	+ 10,4	- 11,3	6,0
14-4 :	77,0	6,50	2,25	+ 1,1	+ 0,7	- 0,7	+ 2,7	- 3,0
D :	71,5	7,02	2,40	- 15,6	- 16,0	- 17,5	- 12,6	14,0
M20-40:	91,0	7,30	0,90	- 5,3	+ 4,6	+ 3,8	0,0	- 6,5
111-12:	112	9,30	1,25	+ 0,4	- 0,8	- 0,8	- 2,9	2,0
159-4 :	135	9,75	0,95	+ 13,1	+ 12,0	+ 12,1	+ 8,6	- 14,0
29-4 :	123	11,20	3,60	- 10,4	- 12,0	- 11,5	+ 2,2	- 9,0
574-1 :	171	13,90	1,15	0,0	- 2,4	- 0,6	- 3,8	1,5
D 118 :	210	15,70	1,70	+ 7,3	+ 4,7	+ 6,9	+ 7,5	- 8,5
n = 17:	arithmetic average			10,7	9,0	7,8	6,2	-
	algebraic average			- 2,0	+ 3,2	- 0,8	- 0,5	-

- (a) $\Delta C = 100(C_t - C_0)/C_t$ for $\text{LnCo} = 1,065 \text{LnEc} + 2,339$ (Campbell 1948)
 (b) ΔC for $\text{LnCo} = 1,091 \text{LnEc} + 2,294$ (Richard's 1954) ($E_c < 4 \text{ mS/cm}$)
 (c) ΔC for $\text{LnCo} = 1,049 \text{LnEc} + 2,387$
 (d) ΔC for $\text{LnCo} = (1,092 - 0,027d) \text{LnEc} + 2,387$
 (b') " " $\text{LnCo} = \text{LnEc} + 2,312$

- Use of the equations (a), (b), (c), and (d):

In a second experiment the ability of the different relations to detect a possible error in an analysis was tested for seventeen samples found in the literature. The value $\Delta C = 100 (C_t - C_o) / C_t$ was calculated and correlated with the relative deviation around the ionic balance: $\Delta S = 100 (S^+ - S^-) / S^+$ as given by the analysis. The calculation was made for the same equations (a), (b), (c), (d). The correlations have been calculated starting from $\Delta S = 8,5\%$ because this is the average precision of application of relations (a), (b), (c), and (d). The coefficients of correlation found were:

$$\begin{array}{ll} \text{(a)} & r = 0,489 \\ \text{(b)} & r = 0,876 \\ \text{(c)} & r = 0,883 \\ \text{(d)} & r = 0,915 \end{array}$$

Despite an exact ionic balance for samples 1 and 2, 4, 5, 6, calculated ΔC indicates that either C_t or E_c is erroneous. This will be discussed later on; $r(d)$ indicates a better ability to detect a possible error in an analysis by using equation (d).

Table 6: Correlation between $|\Delta C| = 100 (|C_t - C_o|) / C_t$ and $\Delta S = 100 (|S^+ - S^-|) / S^+$

N°	$ \Delta S $ %	$d = S^2 / S^1$ -	E_c mS/cm	CT meq/l	$\Delta C(a)$ %	$\Delta C(b)$ %	$\Delta C(c)$ %	$\Delta C(d)$ %	
1	0,00	1,9	3,33	51,0	20	-34	-22	-21	
2	0,80	1,2	8,83	205	49	48	48	47	
3	5,40	0,7	7,22	87,0	2,0	1,5	0,5	4,5	
4	7,00	1,9	4,91	50,0	-13	-12	-15	-14	
5	8,00	4,1	6,50	82,0	7,0	6,8	5,5	16,5	
6	8,40	1,6	1,50	12,5	-28	-21	-33	-33	
7	9,80	0,7	0,80	8,2	0,0	1,5	-5,0	-5,0	
8	10,0	2,3	13,1	150	-7,0	-9,4	-8,0	-2,5	
9	10,2	1,3	0,58	5,80	-0,5	0,9	-6,5	-6,0	
10	11,0	1,4	1,32	13,6	-2,0	2,0	-7,0	7,0	
11	13,6	1,2	9,75	129	9,0	7,8	8,0	5,5	
12	17,6	2,3	5,02	50,0	-15	-15	-18	-15	
13	17,8	1,2	19,3	284	15	12	15	12	
14	19,4	4,1	1,72	15,2	-21	-18	-26	-22	
15	21,0	1,9	41,4	629	13	8,4	13	16	
16	27,8	6,5	0,78	6,10	-31	-23	-37	-42	
17	28,0	1,8	14,9	247	25	23	25	26	
Coefficient of correlation $\Delta S = \alpha \Delta C + \beta$					0,489	0,876	0,883	0,915	n=10

- Range of application of equations (a), (b), (c), and (d):

A last experiment was made to evaluate for which kind of water the proposed equations best apply: Fifty results of water analysis were selected at random in the literature, only soil extracts and natural waters of arid zones were considered. The fitness of the ionic balance expressed as the average of $100(S^+ - S^-) / S^+$ was equal to 4,7% value which is equivalent to expected unavoidable analytical errors. The results were divided into six groups defined by

the following indexes:

- 1) Sodium adsorption ratio : $SAR = Na / ((Ca+Mg)/2)^{1/2}$ (US sal. lab. 1954).
- 2) Chloride-alkali index : $CAI = 1 - (Na+K)/Cl$ (Schoeller 1958).
- 3) Chloride-bicarbonate index : $CBI = Cl / (HCO_3 + CO_3)$ (in Polemio 1980).

The limit values selected for these indexes were:

- 1) $SAR < 3$ corresponding to waters having a low relative activity of sodium in exchange reactions with soils.
- 2) $3 < SAR < 53$ corresponding to waters having a high sodium hasard.
- 3) $CAI < 0,5$ corresponding to waters or soil extracts containing chloride as NaCl only.
- 4) $-10 < CAI < -1$ corresponding to solutions containing other salts of sodium and potassium in addition to chloride.
- 5) $0 < CBI < 1$ and 6) $CBI > 2$ defining waters having a deficit or an excess of chloride as compared to carbonates, respectively.

Interpretation of results:

ΔC was calculated again by (a), (b), (c), (d) for each water and soil solution. The averages calculated within each groups are reported table 7a-7b.

Table 7a: Values of the algebraic average of ΔC

1/n $\Sigma \Delta C$ for equations:					n	Group
(a)	(b)	(c)	(d)			
2,5	3,8 (2)	-2	-3	12	SAR < 3	
-2	-2 (1)	-4	-0,5	12	3 < SAR < 50	
-1,5	0,7 (1)	-4,5	-1	12	CAI < 0,5	
2,5	7,9 (2)	-2	-2	12	-10 < CAI < - 1	
2	3,2	-3	-2	11	0 < CBI < 1	
-1,5	0,6 (1)	-4	-1	11	CBI > 2	
2,0	3,0	-3,2	-1,6	56	Average	

The values of $1/n \Delta C$ and $1/n |\Delta C|$ are given within each groups and for the whole set of 56 samples. equations (a) and (b) give the smallest values for the arithmetic average and for the algebraic one as well. The set of two equations used in column (b) for $E_c < 4$ mS/cm and $E_c > 4$ mS/cm does not give better results, making the use of two different parameters a and b unnecessary in the range of conductivities investigated ($E_c < 20$ mS/cm) therefore we suggest to use either equation (a) when the calculator of d is to be avoided, and the use of equation (d) when a simple desk calculation allows the calculation of C_o by the mean of the equation $\ln C_o = (1,092 - 0,0027d) \ln E_c + 2,387$ which gives slightly better results in all the above mentioned cases. It should be noted however that the difference is small and that no statistical treatment has been done to test the significance of this difference. That will be the purpose of another study.

Table 7b: Average of the calculated from absolute values.

Values of $1/n \sum \Delta C $ (for $\Delta C = 100(C_T - C_o)/C_o$)						Group				
(a)	:	(b)	::	(c)	:	(d)	:	n	:	
5	:	7,9	(2)	5	:	4	:	12	:	SAR < 3
5,5	:	5,1	(1)	6	:	5,5	:	12	:	3 < SAR < 50
5,5	:	7,3	(1)	5,5	:	4	:	12	:	CAI < 0,5
5	:	8,8	(2)	5	:	5,5	:	12	:	-10 < CAI < -1
5	:	7,6	(1)	5,5	:	6	:	11	:	0 < CBI < I
5,5	:	5,3	(1)	6	:	4	:	11	:	CBI > 2
5,2	:	7		5,5	:	4,8	:	56	:	Average

- (1) $\text{LnCo} = 1,091 \text{ LnEc} + 2,294$ (0-50 mS/cm . Richards handbook 60 p. 12)
 (2) $\text{LnCo} = 1,00 \text{ LnEc} + 2,312$ (0-4 mS/cm. Richards handbook 60 p. 70)

Spotting an erroneous analysis:

The main object of using the equation discussed above is to use the value of E_c which is easily determined to detect an error in an analysis of natural aqueous solutions. Detecting a possible error spares the tedious task of making all the successive determination of Ca, Mg, Na, K, Cl, SO_4 , HCO_3 and possibly CO_3 and NO_3 again, to reach a reasonably low value of $(S^+ - S^-)/S^+$. The use of one equation gives a reasonable probability of detecting error only if the calculated ΔC is greater than 10%. The use of combined equations, for instance (a) and (b) and (d) multiplies the probability of finding an error by using $|\Delta C|$ or ΔC , the later values giving more information on were to search for an analytical inaccuracy. For instance in table 6: the sample N°2 gives a systematic positive deviation ΔC , indicating either an E_c underestimated or an C_T overestimated, the distinction being easy by a simple look on the results, but for sample N°4 which gives a systematic negative deviation, the detection of the error will be more difficult, because both values of E_c and C_T seem acceptable. This will need more work, particularly by the thorough consideration of other indexes, as PH, $(1 - \text{Na}/\text{Cl})$ for instance.

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