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Influence of Cations and Anions on the Electrical Conductivity Measurements of Ground Waters *

by

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Synopsis: Studies to find out the contribution of various ions to the electrical conductivity were conducted, using pure salt solutions and correlation studies to find out the relationship between electrical conductivity, total solids and various ions, using results of water analysis were taken up. It was found that electrical conductivity value was highly correlated with $\overline{Cl}$, $\overline{\overline{SO_4}}$ and $\overline{HCO_3}$. The contribution of $\overline{HCO_3}$ and $\overline{\overline{CO_3}}$ to electricl conductivity was very low. A method using a regression equation was proposed to avoid the gravimetric estimation of $\overline{\overline{SO_4}}$ and a method of calculating various ions using the above method in analysis of water samples and in alkalinity studies of soils has been indicated.

Introduction: The utility of various irrigation projects intended to increase the food production, depends largely on the quality of irrigation waters stored and supplied and also on the quality of ground waters in the ayacut area. But the absence of rapid methods of chemical analysis and also the inevitable use of some of the gravimetric methods of analysis which are not only tedious but also time consuming, are to-day the bottlenecks in the periodical intensive study of the ground waters in any area. So, with a view to overcome the above difficulties, Asghar and Dhawan (1947) undertook certain investigations and reported a significant correlation between the electrical conductivity values and total solids content of ground waters. United States Department of Agriculture (1954) had also reported a similar relationship between total solids and electrical conductivity values. Black (1957) had also proposed a relationship between the total solids and electrical conductivity in water soluble salts of soils.

But the electrical conductivity value, the determination of which is easy and quick, varies according to the amount of each cation and anion present and is also dependent upon the electrical conductivity values of each ion. So, this study was taken up to find out through the calculation and determination of multiple regression, the relationship of various ions to the electrical conductivity values and also to calculate the ions, now estimated by the gravimetric methods.

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Materials and Methods: Forty water samples collected from Pollachi Taluk of the Madras State were analysed for pH, electrical conductivity value, total solids and various cations and anions present, by the methods of analysis proposed by the United States Department of Agriculture (*loc. cit.*) Statistical analysis of the analytical results was done and the partial and multiple regression coefficients were worked out by the Doolittle method as given by Goulden (1956) with a view to study the interrelationship between the various ions and electrical conductivity of the irrigation waters.

In addition, preliminary work was done to study the influence of various ions on the electrical conductivity, using pure (ANALAR) solutions of sulphates, chlorides, bicarbonates and carbonates of Sodium, Potassium, Magnesium and Calcium of concentrations of 0, 2.5, 5, 10, 15, 20, 25, 50 and 100 meq/litre. The electrical conductivity was measured with the Solu-bridge apparatus.

Results: The electrical conductivity of solutions with pure salts at various concentrations are presented in Table I. When the relative influence of the anions on the electrical conductivity was studied, keeping the cation common, it was found that the contribution to conductivity value decreases in the order $Cl^{-} > SO_4^{--} > HCO_3^{-}$, CO_3^{--} (Plate I). Keeping the anion common, the order of contribution of the cations to the electrical conductivity was $K^{+} > Na^{+} > Mg^{++} > Ca^{++}$ (Plate II). The difference in the contribution of the monovalent ions K^{+} and Na^{+} is very little. Since most of the ground water samples contain very low concentrations of K^{+}, [Agarwal *et al* (1956), Govinda Iyer and Subramaniam (1960)], not much error will be introduced in assuming that both contribute to the same extent to the electrical conductivity values at low concentrations.

The results of chemical analysis of the forty water samples are presented in Table II and the results of statistical analysis of the analytical data are presented in Table III.

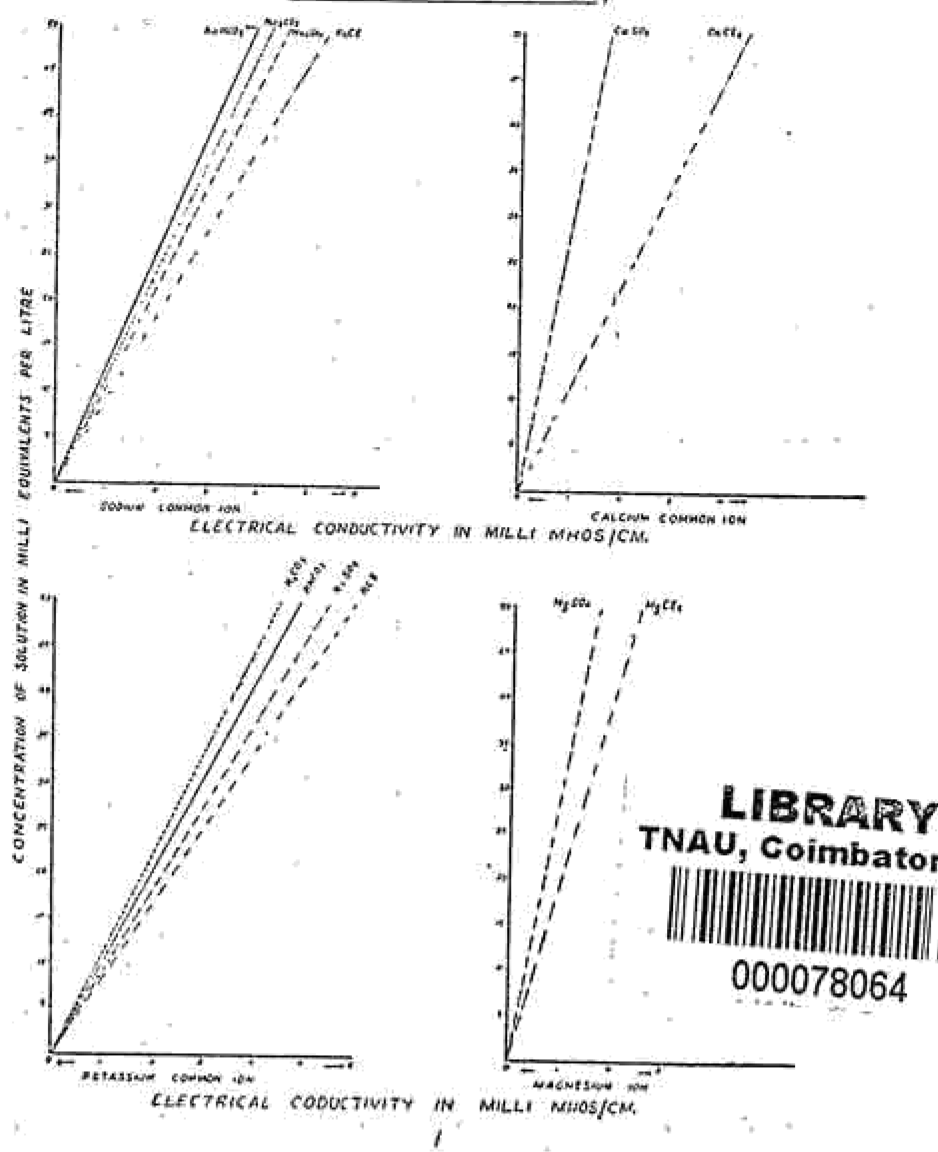
The statistical analysis has revealed that the correlation in all cases except between bicarbonates and electrical conductivity, between sum of bicarbonates and carbonates and electrical conductivity, and bicarbonates and sulphates put together and electrical conductivity, is highly significant. The correlation between electrical conductivity and bicarbonates (or sum of bicarbonates and carbonates) and also bicarbonates and sulphates put together and electrical conductivity was not significant.

Discussion: From the results presented above with pure solutions, it is clearly seen that chlorides contribute more than any other anion to the electrical conductivity, while the contribution of bicarbonates and carbonates is very low. Similar results are also obtained with the analysis of water samples. The magnitude of contribution of each ion to electrical conductivity as revealed by the pure solutions agrees with the results obtained in the statistical analysis of the data also.

PLATE I.

INFLUENCE OF VARIOUS IONS ON THE ELECTRICAL CONDUCTIVITY OF WATER

(KEEPING CATION AS COMMON ION)

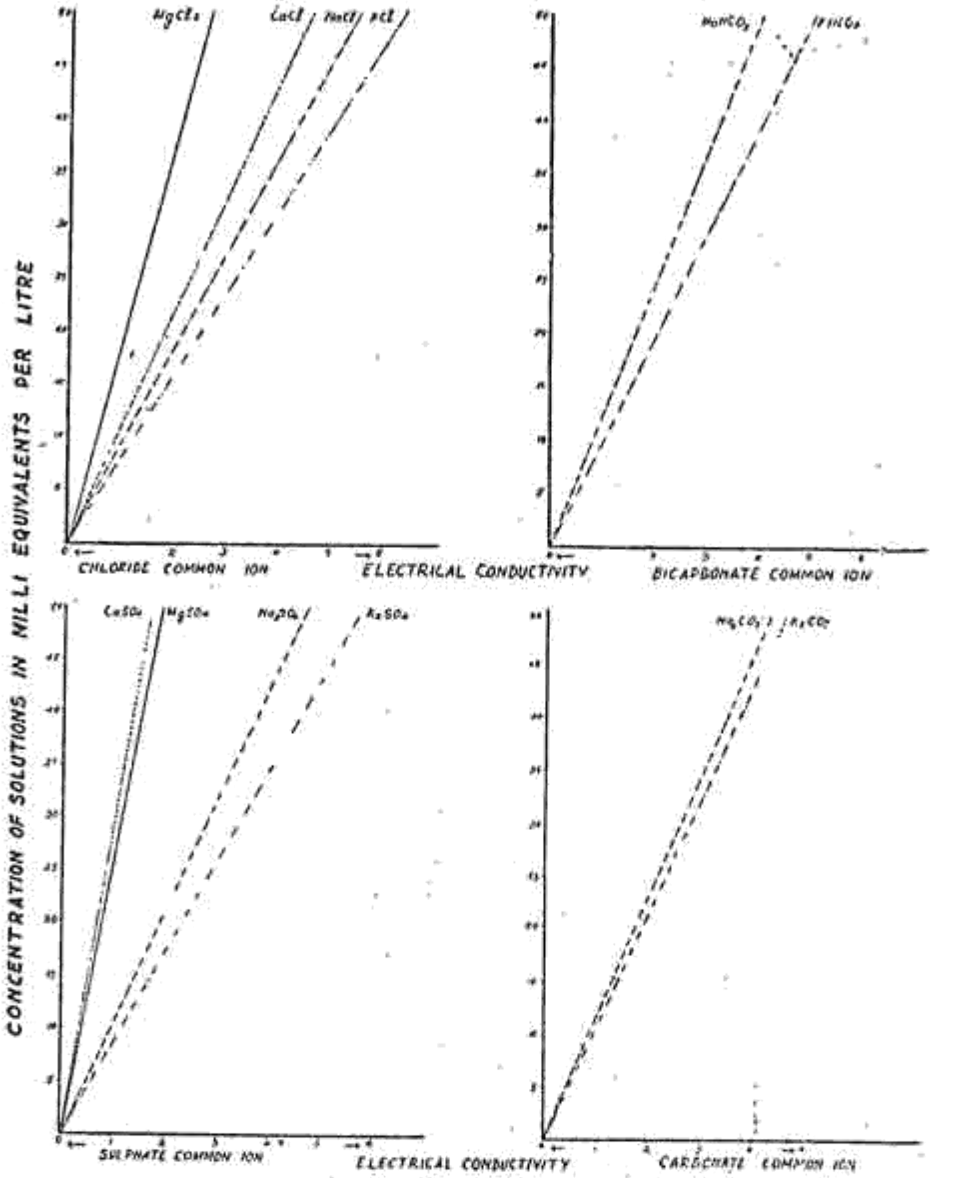


In the statistical analysis of the ground waters, it is seen that the total solids value is highly correlated with the electrical conductivity value and as such the electrical conductivity can be taken as a measure of total solids. It is also seen that except in cases where bicarbonates (and/or carbonates) are involved, there is a very high correlation and as such there exists a close relationship between the various ions and electrical conductivity values. A very highly significant correlation of 0·98 was obtained when the electrical conductivity values were correlated with the three anions, chlorides,

PLATE II.

INFLUENCE OF VARIOUS IONS ON THE ELECTRICAL CONDUCTIVITY OF WATER

(KEEPING THE ANION AS THE COMMON ION)



sulphates and bicarbonates taken together. When chloride alone was correlated with electrical conductivity, the correlation coefficient was 0·90, while chloride and sulphate taken together when correlated with electrical conductivity gave a correlation coefficient of 0·98. But when chloride and bicarbonate taken together were correlated with electrical conductivity, the correlation coefficient was only 0·93, which is not appreciably higher than the correlation coefficient of 0·91 obtained for chloride alone with electrical conductivity. Similarly the correlation coefficient obtained by correlating sulphate alone with electrical conductivity (0·46) is not improved appreciably by correlating sulphates and bicarbonates together with electrical conductivity. Further the correlation coefficient of 0·98 obtained when chlorides and sulphates taken together are correlated with electrical conductivity, is not at all improved by taking together all the three anions, chlorides, sulphates and bicarbonates together and correlating with the electrical conductivity. So, it is evident from all these that the bicarbonates and/or carbonates do not contribute much to the electrical conductivity values.

As already stated a very highly significant correlation was obtained when the electrical conductivity values were correlated with the three anions, chlorides, sulphates, and bicarbonates taken together or with the two anions chlorides and sulphates taken together and also when chlorides alone were correlated with electrical conductivity values. Determination of electrical conductivity, chloride, carbonates and bicarbonates can be done in the field itself through simple measurements or titrations. So, using the multiple regression equations involving the four factors, electrical conductivity values, chlorides, sulphates and bicarbonates, or the first three factors alone, the approximate amounts of sulphates could be calculated, thus overcoming the actual estimation of sulphate by the gravimetric method of estimation.

In ordinary normal irrigation waters, the sum of all the anions present will be equal to the total amount of cations present in solution. Among the cations normally present in irrigation waters, as calcium and magnesium can be estimated by the versenate method and as potassium can be determined by simple titration methods, the only other cation sodium, can be easily determined by subtracting the sum of the cations determined from the total anions present and this will enable any field worker to quickly assess the approximate amount of sodium salts present in the irrigation waters. This procedure, if adopted, is likely to prove a very useful tool for the field workers when they want to study the quality of irrigation waters over a large area and that too in a short time. The above method can also be adopted in the alkalinity studies of soils, since water extracts of soils alone are taken and also since the same cations and anions are estimated as in ground waters.

Summary: Using pure salt solutions, the contribution of various ions to the electrical conductivity value was studied. The results of a number of water samples collected from a wide area were statistically analysed to find out the relationship between the electrical conductivity values, total solids and various cations and anions. Electrical conductivity value was

highly correlated with the three anions, chlorides, sulphates and bicarbonates or with the first two anions, chlorides and sulphates taken together. The contribution of the bicarbonates to the electrical conductivity was very low and the addition of the bicarbonates did not improve the correlations to any significant extent. So, a method using the multiple regression equation was proposed to avoid the gravimetric estimations which are time consuming and tedious. A possible method of calculating the various cations from the above procedure in the analysis of water samples and also in the alkalinity studies of soils has also been indicated.

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TABLE I.

Influence of Various Ions on the Electrical Conductivity of water.

I (KEEPING ANION COMMON)

Common ion	Chloride				Sulphate				Bicarbonate		Carbonate			
Concentration in meq/litre	NaCl	KCl	$MgCl_2$	$CaCl_2$	Na_2SO_4	K_2SO_4	$MgSO_4$	$CaSO_4$	$NaHCO_3$	$KHCO_3$	Na_2CO_3	K_2CO_3	$MgCO_3$	$CaCO_3$
2·5	0·35	0·40	0·10	0·30	0·35	0·40	0·10	0·10	0·25	0·325	0·25	0·30	...	...
5·0	0·60	0·70	0·25	0·55	0·60	0·65	0·25	0·20	0·45	0·55	0·50	0·50	...	...
10·0	1·20	1·40	0·50	1·00	1·10	1·30	0·45	0·40	0·90	1·10	1·00	1·00	...	...
15·0	1·70	2·00	0·80	1·40	1·60	1·95	0·65	0·60	1·30	1·60	1·40	1·50	...	...
20·0	2·20	2·60	1·00	1·90	2·15	2·40	0·80	0·75	1·70	2·00	1·90	1·90	...	...
25·0	2·80	3·20	1·30	2·30	2·60	3·00	1·00	0·90	2·00	2·60	2·20	2·40	...	...
50·0	5·40	6·00	2·45	4·50	4·50	5·50	1·75	1·70	4·00	4·90	4·25	4·50	0·05	...
100·0	9·50	11·00	4·50	8·50	9·00	10·50	3·10	3·00	7·50	9·00	8·00	8·50	0·20	0·05

TABLE I(a)

Influence of Various Ions on the Electrical Conductivity of water.

II (KEEPING CATION COMMON)

Common ion	Sodium				Potassium				Magnesium		Calcium			
Concentration in meq/litre	NaCl	Na_2SO_4	Na_2CO_3	$NaHCO_3$	KCl	K_2SO_4	K_2CO_3	$KHCO_3$	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$	$CaCO_3$	$MgCO_3$
2·50	0·35	0·35	0·25	0·25	0·40	0·40	0·30	0·33	0·20	0·10	0·30	0·10	...	...
5·00	0·60	0·60	0·50	0·45	0·70	0·65	0·50	0·55	0·25	0·25	0·55	0·20	...	...
10·00	1·20	1·10	1·00	0·90	1·40	1·30	1·00	1·10	0·50	0·45	1·00	0·40	...	...
15·00	1·70	1·60	1·40	1·30	2·00	1·85	1·50	1·60	0·80	0·65	1·40	0·60	...	...
20·00	2·20	2·05	1·90	1·70	2·60	2·40	1·90	2·00	1·00	0·80	1·90	0·75	...	...
25·00	2·80	2·60	2·20	2·00	3·20	3·00	2·40	2·60	1·30	1·00	2·30	0·90	...	...
50·00	5·40	4·50	4·25	4·00	6·00	5·50	4·50	4·90	2·45	1·75	4·75	1·70	...	0·05
100·00	9·50	9·00	8·00	7·50	4·00	10·50	8·50	9·00	4·50	3·10	8·50	3·00	0·03	0·20

(Temperature - 27° C)

TABLE II

Chemical Analysis of Ground waters.

S. No.	E. C.	Total Solids ppm.	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	SO_4^{--}	HCO_3^{-}	CO_3^{--}	pH
1.	0·60	836	4·0	0·90	2·73	1·0	1.03	5·6	—	7·3
2.	2·10	1742	8·5	4·60	10·13	9·4	7·53	6·3	—	7·5
3.	0·80	502	3·2	0·90	4·10	1·0	0·10	7·1	—	7·6
4.	0·60	270	3·4	1·80	1·83	0·8	1·03	5·2	—	7·8
5.	0·45	850	2·3	0·92	3.26	0·8	0·28	5·4	—	9·5
6.	0·45	196	3·0	0·88	0·97	1·0	0·69	3.8	—	7·2
7.	0·80	1002	2·8	1·39	5·32	1·6	1·41	6.6	—	7·6
8.	0·70	626	3·8	0·72	3·42	1·4	1·54	5·0	—	7·7
9.	0·55	936	3·6	0·90	1·59	1·2	0·09	4·8	—	7·8
10.	0·55	834	2·8	1·42	1·22	0·8	0·14	4·5	—	7·7
11.	0·70	1014	2·4	0·81	3·81	1·0	0·12	6·0	—	7·7
12.	1·00	820	3·4	1·33	7·72	2·2	2·55	7·7	—	7·5
13.	0·90	900	3·4	0·18	6·11	2·0	0·09	7·7	—	7·1
14.	0·60	330	2·9	1·07	2·07	0·8	0·94	5·2	—	7·9
15.	0·40	970	2·8	0·09	0·38	0·4	0·07	2·8	—	7·2
16.	2·80	2156	8·2	9·43	10·84	13·0	1·27	5·2	—	7·7
17.	0·80	1000	3·6	1·12	5·03	1·6	3·90	4·3	—	7·4
18.	2·20	2126	10·0	1·26	16·51	4·2	19·07	4·5	—	7·7
19.	1·60	1936	7·0	0·27	4·88	5·6	1·85	4·7	—	7·2
20.	1·10	1274	2·0	0·52	8·12	2·3	0·84	7·5	—	8·2
21.	0·40	836	2·7	1·09	0·05	0·7	0·34	1·6	1·2	7·8
22.	1·60	1200	5·7	2·99	8·78	7·5	2·57	4·2	3·2	7·9
23.	1·80	1572	6·3	0·63	7·17	8·1	0·36	4·2	1·2	8·1
24.	1·70	1470	9·6	1·53	0·53	9·1	0·86	1·4	0·2	7·7
25.	0·65	990	4·0	1·15	2·56	1·9	0·41	3·8	1·6	7·8
26.	1·70	1416	5·7	1·47	5·03	8·1	0·50	2·8	0·8	8·0
27.	1·30	1510	4·3	1·17	8·61	5·2	2·28	5·8	0·8	7·9
28.	0·60	526	3·8	2·10	0·96	1·3	1·54	3·8	1·2	8·1
29.	0·55	956	3·8	0·16	2·95	0·8	0·51	4·8	0·8	8·2
30.	0·75	916	3·2	0·16	4·81	2·2	0·57	4·6	1·2	8·5
31.	1·65	1916	4·0	0·81	8·41	6·9	1·54	4·4	0·8	7·7
32.	1·10	1000	2·9	1·87	6·30	4·4	1·27	5·0	0·4	7·9
33.	0·45	360	2·1	0·36	3·87	0·9	2·23	2·4	0·8	8·2
34.	0·50	250	2·3	0·54	2·67	0·6	0·51	4·2	0·2	7·6
35.	0·35	870	3·0	0·27	1·29	0·5	0·26	3·4	0·4	7·8
36.	0·50	416	2·0	1·26	3·54	0·8	1·20	3·2	1·6	7·9
37.	0·35	820	2·1	0·90	1·86	0·6	0·86	2·6	0·8	8·0
38.	1·60	966	3·0	1·91	11·02	5·1	1·63	9·2	—	7·4
39.	1·00	1004	3·3	0·81	3·56	3·2	1·27	3·4	0·8	7·8
40.	1·20	1260	4·1	1·67	3·17	3·8	0·34	4·6	0·8	8·0

Ions expressed as mlq./litre.

E. C. — in millimhos/cm.

TABLE III.

Statistical Analysis.

S. No.		Particulars		Correlation Coefficient	Regression Equation
I. *Simple Correlation:*					
1.	Electrical Conductivity (Y)	... Total Solids (ppm.)	(X)	0·84 ***	$Y = 0{\cdot}001\,X - 0{\cdot}025$
2.	Do.	... Calcium	(X)	0.82 ***	$Y = 0{\cdot}24 + 0{\cdot}24\,X$
3.	Do.	... Magnesium	(X)	0·31 *	$Y = 0{\cdot}745 + 0{\cdot}223\,X$
4.	Do.	... Chloride	(X)	0·91 ***	$Y = 0{\cdot}442 + 0{\cdot}177\,X$
5.	Do.	... Sulphate	(X)	0·46 ***	$Y = 0{\cdot}145 + 0{\cdot}0885\,X$
6.	Do.	... Bicarbonate	(X)	0·19	......
7.	Do.	... Sum of bicarbonates and carbonates	(X)	0·19	......
II. *Multiple Correlation:*					
1.	Electrical Conductivity (Y)	... Chlorides (X_1) and Sulphates (X_2)		0·98 ***	$Y = 0{\cdot}37 + 0{\cdot}18\,X_1 + 0{\cdot}047\,X_2$
2.	Do.	... Chlorides (X_1) and Bicarbonates (X_2)		0·93 ***	$Y = 0{\cdot}31 + 0{\cdot}18\,X_1 + 0{\cdot}029\,X_2$
3.	Do.	... Sulphates (X_1) and Bicarbonates (X_2)		0·49 ***	$Y = 0{\cdot}58 + 0{\cdot}058\,X_1 + 0{\cdot}087\,X_2$
4.	Do.	... Chlorides (X_1), Bicarbonates (X_2) and Sulphates (X_3)		0·98 ***	$Y = 0{\cdot}154\,X_1 + 0{\cdot}027\,X_2 + 0{\cdot}085\,X_3 + 0{\cdot}26$

Ions expressed as Mlq./litre.
E. C. expressed as millimhos/cm.

*** Significant at 0·1 % level
* Significant at 5·0 % level