MEASUREMENT OF SOIL CHLORIDE BY SPECIFIC ION ELECTRODE

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SUMMARY

Highly significant differences were found between soil chloride values determined by potentiometric titration and those determined by specific ion electrode in aqueous soil suspension. The presence of very small particles in the suspension was found to be responsible for the differences.

A simple, rapid and accurate method for the direct determination of chloride by specific ion electrode in aqueous soil suspension is presented. The differences were eliminated by the addition of potassium alum.

A correlation coefficient of 0·999 between the presented electrode method and the potentiometric titration method was obtained.

I. INTRODUCTION

In the Agricultural Chemical Laboratory of the Queensland Department of Primary Industries, soil chloride determinations have been done using a modification of the potentiometric method described by Piper (1950).

The measurement of soil chloride is a routine determination in the laboratory, and is carried out on a 1:5 soil water suspension in conjunction with NO_3-, pH and conductivity determinations, which are all done by direct electrode readings on the one suspension.

An initial investigation into some 200 suspensions on routine samples, using a direct chloride determination by electrode, revealed that, for a wide range of soil types and chloride levels, the electrode chloride value was higher than the titration value on the majority of the samples. In some cases this difference was as great as +40%. Interference due to small suspended clay particles appeared to be responsible.

A detailed study was then carried out on 11 test soils, selected to give a wide range of chloride values and clay percentages. The results of this investigation are presented in this paper.

II. EXPERIMENTAL

Potentiometric titration.—All potentiometric titrations were carried out with standard silver nitrate solution using the following indicating system. A silver/ silver chloride electrode was connected *via* an agar bridge, saturated with potassium nitrate to a platinum electrode immersed in a quinhydrone half cell, buffered at pH 3·2. The buffer consisted of 10·21 g potassium phthalate plus 148 ml of 0·1N H_2SO_4 made up to 1 litre with deionized water. The circuit was completed *via* a morse-type tapping key and a Cambridge spot galvanometer.

Specific ion determination.—All specific ion determinations were made using an Orion model 94-17 solid state chloride electrode in conjunction with an Orion Ionalyser double junction reference electrode, model 90-02, using 10% KNO_3 outer filling solution. A Townson model 1950 combination specific ion pH meter was used for all readings.

Standards.—Suitable standards were prepared from Analytical Reagent grade sodium chloride. In the case of specific ion determinations, when activities were being determined, standards of 10^{-3} activity molar and 10^{-2} activity molar Cl^- or 10^{-2} activity molar and 10^{-1} activity molar Cl^- were used. When concentration measurements were being used, standards of 10^{-3} molar and 10^{-2} molar Cl^- or 10^{-2} molar and 10^{-1} molar Cl^- were used. Suitable intermediates were used in both cases to check the reproducibility of the electrode response over the whole scale of the specific ion meter.

The standards were chosen in relation to sample weight, dilution and chloride levels in the soils being investigated.

III. METHOD

A preliminary check of the potentiometric and electrode methods was carried out. Suitable test solutions were titrated potentiometrically and read using the specific ion electrode. Good agreement was obtained in each case. For specific ion calculations, the activities and specific conductivities of the test solutions were determined and concentrations were calculated according to the relationship:

$$\text{Activity} = \gamma \times \text{Concentration},$$
$$\text{where} \quad \gamma = \text{Activity coefficient of } Cl^- \text{ ion.}$$

Samples.—Eleven test soils were selected for detailed investigation. They were chosen to provide a wide range of chloride values (108–4613 p.p.m.), as well as having a wide range of clay content (11–72%). All the test soils were dried for 24 hr at 32–38°C. They were then ground or sieved to pass a 2 mm sieve. Particle size distribution and some relevant chemical characteristics are given in Table 1.

Procedure.—The 11 soils were labelled A-K (Table 1). The first nine, A-I, were extracted and analysed in replicates of 5. In the case of J and K they were extracted in duplicate because there was only a small amount of sample available.

Sample weights of 20 g were weighed into an extraction vessel and 100 ml of deionized water was added to each. The samples were shaken for 1 hr on an orbital shaker at 100 r.p.m.

TABLE 1

SOME CHEMICAL AND PHYSICAL PROPERTIES OF THE TEST SOILS

Test Soil	C.E.C. (m.equiv./100 g)	pH (1:5)	Specific Conductivity (m.mho.cm^{-1}; 1:5 suspension)	Particle Size Analysis (%)			
				Clay	Silt	Fine Sand	Coarse Sand
A	21	6·4	1·17	47	5	40	8
B	22	6·3	3·29	54	19	28	0·3
C	20	6·6	0·63	49	17	36	0·8
D	25	7·4	0·24	45	9	44	5
E	21	6·9	1·64	38	12	48	6
F	38	7·2	0·74	62	20	16	2
G	41	7·2	0·53	72	19	11	2
H	7	5·4	0·18	11	57	22	7
I	23	7·3	0·41	35	8	42	9
J	16	6·8	0·45	29	19	32	20
K	13	8·6	0·45	14	13	31	42

Chloride determinations were carried out on the stirred soil/water suspensions using the specific ion electrode. Activities were determined and concentrations were calculated. The same extracts were then titrated.

Significant differences were recorded between methods for all samples with the exception of sample H (Table 2).

In an attempt to eliminate these differences, thought to be due to the suspension effect, the following procedures were carried out:

(1) Vacuum filtration using a Whatman No. 50 paper followed by filtration through a Whatman No. 42 paper.

(2) Centrifuging at 4500 r.p.m. 30 min.

(3) Flocculation using a mixture of Superfloc N100 and Superfloc 127 at 5 p.p.m. concentration.

(4) Filtration using a 0·65μ Millipore filter, following pre-filtration through a Whatman No. 42 paper.

(5) Flocculation.—A 2 ml aliquot of a saturated solution of potassium alum was added to the soil/water suspension after extraction, and prior to the electrode reading. Alum was added to the standards at the same level as the soil. The electrode system was calibrated to read concentrations rather than activities. Readings were done on the stirred suspension and corrected for the volume of added alum.

As a check on the accuracy of the specific ion electrode method with added alum, recovery tests were carried out. Chloride was added in 200 p.p.m. increments up to 600 p.p.m. The suspensions were then analysed for Cl⁻ by specific ion electrode, followed by potentiometric titration.

IV. RESULTS

Comparison of titration and electrode values of chloride for the test soils is given in Table 2. The differences between the potentiometric titration values and the specific ion electrode values are highly significant for all the samples listed with the exception of H.

TABLE 2

COMPARISON OF CHLORIDE VALUES BY TITRATION AND ELECTRODE

Test Soil	Potentiometric Titration (mean p.p.m. Cl⁻)	Specific Ion Electrode (mean p.p.m. Cl⁻)	Electrode Value as % of Titration Value	" t " Test o f Paired Differences
A	108	96	89	7·2**
B	4,613	4,783	104	7·2**
C	676	732	108	18·3**
D	139	181	130	13·02**
E	2,478	2,727	110	18·9**
F	756	870	115	14·5**
G	350	447	128	22·7**
H	146	150	103	1·8
I	449	521	116	19·3**
J	892	980	110	..
K	472	550	116	..

** Signifies calculated " t " value greater than that required for 1% significance.

Values for J and K are means of two. For other samples, values are means of five.

5% significance level for $t_4 = 2·78$.

1% significance level for $t_4 = 4·60$.

Vacuum filtration followed by filtration through a Whatman No. 42 paper, centrifugation, and flocculation using Superfloc treatments all resulted in electrode values similar to those from untreated suspensions. Clear solutions were unobtainable using these methods.

In Table 3, chloride values for titrated suspensions are compared with electrode and titration values for Millipore filtrates, and with electrode and titration values of potassium alum suspensions. All 't' tests showed no significant differences between the titrated suspensions (second column) and the other methods, except for sample G, which showed that the Millipore electrode figure

TABLE 3

TITRATED SOIL SUSPENSIONS COMPARED WITH MILLIPORE FILTRATES AND POTASSIUM ALUM SUSPENSIONS

Test Soil	Titrated Suspensions (p.p.m. Cl⁻)	Millipore Filtrates				Potassium Alum Suspensions			
		Electrode		Titration		Electrode		Titration	
		p.p.m. Cl⁻	" t "	p.p.m. Cl⁻		p.p.m. Cl⁻	" t "	p.p.m. Cl⁻	" t "
A	108	110	0·62	107		102	1·5	99	2·6
B	4,613	4,600	0·67	4,580		4,554	1·0	4,625	0·9
C	676	672	0·37	660		683	1·0	672	0·6
D	139	143	1·07	147		134	1·2	132	2·6
E	2,478	2,479	0·08	2,485		2,468	0·3	2,489	1·0
F	756	755	0·14	750		741	2·4	746	1·8
G	350	364	3·7*	359		337	2·6	344	1·6
H	146	146	0·19	141		142	1·2	141	1·4
I	449	448	0·14	442		451	0·3	448	0·2
J	892	891	..	892		900	..	894	..
K	472	490	..	479		497	..	476	..

* Signifies calculated " t " value greater than that required for 5% significance.

Values for J and K mean of two. For other samples values are means of five.

was significantly higher by 14 p.p.m. (4%) than the original value in the second column. This sample was not visually clear after three Millipore filtrations through a $0 \cdot 65\mu$ filter.

Five of the test samples were extracted in duplicate, and chloride was added at 200, 400 and 600 p.p.m. levels. Table 4 indicates the percentage recoveries. No statistical analyses were done as duplicates only were considered. All results are the means of duplicates.

TABLE 4

RECOVERY OF ADDED CHLORIDE

Test Soil	Titration Soil Suspension % Recovery			Electrode Potassium Alum Suspension % Recovery		
	+200 p.p.m.	+400 p.p.m.	+600 p.p.m.	+200 p.p.m.	+400 p.p.m.	+600 p.p.m.
C	107	98·5	99·9	99·5	99·8	100
D	102	98·5	96·8	100	100	99·7
G	100	104	98·5	100·5	100·2	100
H	100	98	97	99·5	98·9	99
I	100	102	100	100	98·9	99·3

A correlation coefficient and a regression line were calculated to compare the titration method without alum (Y) with the electrode method with added alum (X). Forty-nine pairs of values from the two methods were used in the calculations.

These same values were used to calculate the means listed in columns 2 and 6 in Table 3.

The calculated correlation coefficient ($r = 0 \cdot 999$) was highly significant ($1\% r_{45} = 0 \cdot 372$ from tables).

The calculated regression line is $Y = 1 \cdot 01 X - 1 \cdot 4$, where Y and X are expressed as p.p.m. Cl$^-$. A 't' test showed the slope to be just significantly different from $1 \cdot 0$ at the 95% level and the intercept to be not significantly different from zero.

V. DISCUSSION

Other workers (Hipp and Langdale 1971) have reported on the suitability of the chloride electrode for the direct determination of chloride in filtered soil extracts. The major advantage of specific ion electrodes in soil chemistry lies in the possibility of determining the ion concentration directly in the stirred soil/water suspension.

It has been reported by Mack and Sanderson (1971) that the nitrate electrode is subject to interference when NO_3^- is determined directly in soil/water suspensions. This interference resulted in a higher value which increased with clay content. Our results indicate a similar problem, though the detection principle involved in the solid state chloride electrode is different from that of the liquid membrane nitrate electrode.

A comparison of particle size distribution of the test samples (Table 1) with the electrode values for chloride as a percentage of titration values (Table 2) shows that generally higher values were obtained on high clay content soils.

Ordinary filtration methods failed to remove the interference, but filtration through a $0 \cdot 65\mu$ Millipore filter was successful. Thus the interference must have been caused by particles smaller than a Whatman No. 42 paper would retain. It is highly probable that the small suspended clay particles trapped by the $0 \cdot 65\mu$ Millipore filter were responsible for the interference.

The organic flocculants tried were only capable of flocculating some clay particles, and the best of these left a solution which was not clear, indicating again that small particles in suspension were causing the electrode to give higher results, since the electrode gave the same readings before and after flocculation by the organic polymer type agents Superfloc N100 and Superfloc 127.

Sample H showed no significant difference between titration and electrode methods (Table 2); however, this sample had only 11% clay and any suspension effect would be minimized.

Sample A had high levels of gypsum present, and the presence of relatively large amounts of divalent ions (e.g. Ca^{++} and $SO_4^{=}$) in soil suspension tends to have a similar effect to alum. Such solutions have a lower γ value than that used in calculations for Cl^-, which is a 1:1 electrolyte; thus a higher Cl^- value for sample A would have been obtained if the correct γ value had been used. This was impractical.

Since the interference is associated with the clay fraction of the soil it is possible that the small suspended clay particles which carry a residual charge are interfering with either (a) the $AgCl \rightleftarrows Ag^+ + Cl^-$ reaction at the membrane/liquid interface, or (b) the junction potential at the reference electrode/solution interface.

The use of the highly charged ionic flocculant potassium alum in these experiments provided an effective charge neutralization of the clay particles and this eliminated the interference as shown in Table 3.

Statistical analysis shows that, for the individual test soils, no significant differences can be found between the proposed electrode method with alum added, and the established titration method ('t' tests). Also, when all the results of the 11 soils are taken together a highly significant correlation coefficient is found.

The calculated regression line indicates both methods are almost equivalent.

The recoveries of added chloride shown in Table 4 are good, and indicate the electrode method to be comparable to the titration method.

It must be pointed out, however, that the specific ion electrode method is not as precise as the titration method and has higher standard deviations. Accuracy decreases at increasing chloride concentration as a logarithmic relationship exists between the total electrode potential and chloride ion activity.

The method presented consists of adding an aliquot of saturated potassium alum directly to the stirred soil/water suspension immediately prior to electrode reading.

VI. ACKNOWLEDGMENTS

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