The determination of cation-exchange characteristics of saline and calcareous soils

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Summary

An improved method for the determination of cation exchange characteristics suitable for saline, calcareous and gypseous soils has been developed. The soil is saturated with a LiCl solution buffered at pH 8,2 with LiOAc, followed immediately by leaching with $Ca(OAc)_2$ at pH 8,2. Na, K, Ca, Mg and Li are determined in the extracts by direct flame photometry and complexometry. The necessity of washing the soil has been eliminated by assaying the remaining excess salts as Cl. Soluble ions are determined on a separate sample. The method can be used on non-saline or carbonatefree soils by adjusting the saturating and extracting solutions to pH 7.

1. Introduction

The determination of the cation exchange characteristics [1] of saline soils, which often are also calcareous and gypseous, entails numerous difficulties because of the interference from cations released by the soluble and slightly soluble salts. As yet no completely satisfactory method has been devised (U.S. DEPT. AGRICULTURE HANDBOOK, 1954; METSON, 1956; JACKSON, 1958; NIJENSOHN, 1960). Following the Riverside Salinity Laboratory study (BOWER, REITEMEIER and FIREMAN, 1952), the most commonly employed method uses ammonium extraction for soluble and adsorbed ions and a separate sodium saturation for cation-exchange capacity. Soluble ions have to be determined separately in a saturation extract and substracted from the amount of total extracted ions.

It is the aim of this paper to describe certain improvements of this procedure avoiding the drawbacks arising from the use of ammonium for saturation and due to lack of pH control during washing. The proposed procedure is simple and rapid and as it is subject to fewer inherent limitations, it is especially suitable for saline and calcareous soils.

2. Considerations in the choice of procedure

The considerations which led us to modify the commonly used procedures and to develop the new method were as follows:

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[1] The term "cation-exchange characteristics" comprises cation-exchange capacity and exchangeable cations values, similarly as the term moisture characteristics stands for a number of different determinations of moisture-capacity values.

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2.1. Saturating cation

The use of NH_4-salts which is presently employed in most procedures, is to be avoided because of the possibility of NH_4-fixation and release of fixed K. The use of polyvalent cations is also undesirable on the grounds that significantly higher exchange capacities may be obtained as a result of the formation of basic salts by hydrolysis (BOWER and TRUOG, 1940). In saline soils interference from the precipitation of insoluble carbonates and sulphates is also to be avoided. Lithium which is not normally present in soils is devoid of all these limitations and has the additional advantage of being easily and accurately determined by flame-photometry. Compared with other monovalent ions Li is small ($r = 0{,}68$ Å) and highly hydrated and it stands lowest in the series of relative replacing power. However, if a sufficiently large excess is available there is no difficulty in obtaining complete replacement.

The replacing of the saturating Li can be achieved with any cation provided it does not interfere in the Li determination. Calcium has been preferred in this case because of its high extracting power.

2.2. Choice of anions and pH of working conditions

For calcareous soils it is necessary to avoid the effect of possible dissolution of the $CaCO_3$ at pH 7 which is usually employed in extractions. Working conditions of pH 8,2 at which the solubility of $CaCO_3$ is negligible, were chosen and are obtained by buffering a 0,8 n LiCl-solution with an equal volume of 0,2 n LiOAc and adjusting the pH with dilute LiOH. The buffering capacity of this solution is sufficient to keep the pH constant during the extraction. At the same time, the concentration of the organic anion is kept sufficiently low so as not to interfere in the direct flame-photometric determination of the extracted cations.

2.3. Leaching procedure

The normally employed washing of the saturated soil with alcohol-water mixtures is considered unsound, as it may completely change the pH of the system. Also, this washing often causes difficulties due to the soil's hydrolysis and loss of the saturating cation (BOWER *et al.*, 1952). In our proposed procedure the Li saturated samples are leached, without any prior washing, with a 0,2 n $Ca(OAc)_2$-solution at pH 8,2. In appropriate aliquots of the leachate both Li and Cl are determined, the latter representing the amount of excess of saturating solution. The amount of adsorbed Li, equivalent to the cation-exchange capacity, is calculated from the difference. The idea of determining the accompanying anion to calculate excess electrolyte was already made use of by CHAPMAN and KELLEY (1930), although they worked in quite a different way.

Because of its rapidity the centrifuge method is recommended for saturation and extraction (BOWER *et al.*, 1952). Only one 5 to 10 grams of sample containing about 2 me of exchange capacity is required in the method proposed here. The centrifugation is repeated four times to obtain complete saturation and replacement.

2.4. Soluble cations

Soluble salts are usually determined on saturation extracts. However, because of the small volume of the extracted solution it is often impossible to perform a total analysis. For clayey soils high in Na and Mg it is therefore preferable to use a 1 : 2 soil-water extract. In gypseous soils there is the additional limitation in the use of the saturation extract as it does not permit the dissolution of a similar amount of gypsum as dissolves during leaching. In highly gypseous soils in which not even the 1 : 2 water extract completely dissolves all the gypsum present, sulphate is determined in the cation extract. Experience shows that during the extraction with Li-salts according to the proposed procedure a maximum of 580 mg $CaSO_4$ is dissolved, or 11,6 % if 5 g of soil are used.

2.5. Analytical methods

The supernatant liquid after centrifuging is collected in measuring bottles and aliquots are analysed after suitable dilution. Na, K and Li can be determined flame-photometrically without any additional treatment, and Ca and Mg by EDTA-complexometric titration. Cl and SO_4 can be determined by any standard method.

3. Procedure adopted

3.1.

Five to 10 g of soil containing about 2 me of exchangeable cations are placed into 50 ml centrifuge tubes and mixed with 30 ml of the Li-salts solution (see 2.2.). After shaking for half an hour the tubes are centrifuged for 20 minutes at about 2000 rpm and the clear supernatant liquid is poured into 150 ml measuring bottles. This manipulation is repeated altogether 4 times. The measuring flask is then made up to volume with the extracting Li-solution.

3.2.

A suitable aliquot of the extract is diluted 5 to 20 times, depending on the amounts of Na and K present. The amounts of Na and K are determined flame-photometrically using the "Kurvenschar" method (SCHUHKNECHT, 1961) and $Al(NO_3)_3$ to exclude Ca interference. Ca and Mg are determined in the undiluted extract by complexometric titration with EDTA; calcium with calceïn as the indicator (VAN SCHOUWENBURG, 1961) and Mg after separation of Ca with sodium tungstate (MIDDLETON, 1961). A possible phosphate interference can be suppressed in both cases either with ammonium molybdate (MIDDLETON, 1961) or with zirconyloxychloride (DERDERIAN, 1961). Sulphate is determined in cases where the abundant gypsum could not be completely dissolved (see 3.5).

3.3.

To the Li-saturated soil containing some remaining Li-solution 30 ml of 0,2 n $Ca(OAc)_2$ at pH 8,2 is added, and after shaking for half an hour the suspension is centrifuged as above. The same treatment is repeated altogether four times and the supernatant liquid is collected in a 150 ml measuring bottle. The flask is then made up to volume with the replacing solution. Ten ml are diluted to 100 ml with water and Li is determined flame-photometrically to give Li (p) which is composed of adsorbed Li and excess Li present as chloride and acetate. Chloride is determined in an aliquot by the $Hg(NO_3)_2$-diphenylcarbazone complexometric titration (HYDÉN, 1959) or by other standard methods. By multiplication with the Li/Cl-ratio of the extracting solution (about 5/4; see below, 3.4) the amount of Li equivalent to the chloride- and acetate ions is obtained (q). The difference of these values (p - q) is adsorbed Li, giving the CEC.

3.4.

It is necessary to determine the exact Li/Cl-ratio in the Li-salt extracting solution by analysis to obtain the multiplication factor for the calculation of the Li-content in the $Ca(OAc)_2$-replacing solution. As the Li-, Ca- and Al-salts generally used in the analysis are fairly impure, it is necessary to run blanks and to prepare new sets of standard curves for the Na and K determination after each renewal of the stock solutions.

3.5.

The 1 : 2 soil-water extract is prepared by mixing 100+m g of air-dry soil (m = per cent moisture on an oven-dry basis) with 200—m ml of distilled water. This mixture is left standing for two days, with occasional shaking for 15 minutes, in order to allow the gypsum to dissolve completely. The suspension is then centrifuged at 2000 rpm and the clear supernatant liquid poured off. In this extract Na and K are determined by flame-photometry and Ca and Mg by complexometric titration as above. Sulphate can be determined either by titration with $Ba(ClO_4)_2$ in alcoholic medium with thorin as the indicator (FRITZ and YAMAMURA, 1955) or colorimetrically with Ba-chloranylate (BARTOLACINI and BARNEY, 1957; PROCHÁZKOVÁ, 1961). Moreover, although not necessary for the determination of exchangeable cations, but necessary for other purposes, Cl^-, HCO_3^- and CO_3^{-2} can be determined (U.S. DEPT. AGRICULTURE HANDBOOK, 1954).

3.6.

We use Li-salt and $Ca(OAc)_2$ solutions at pH 7 for the analysis of saline, non-calcareous soils, if the pH is lower than 7. Even when there is a non-calcareous horizon of near neutrality within a soil profile extracting and replacing solutions of pH 7 are used for this horizon.

Solutions adjusted to a pH of 8,2 are used for the analysis of calcareous non-saline soils.

4. Results

Some typical results obtained are given below. The samples were taken from selected horizons of soils of the Marau-Koembe coastal plain in the south-eastern part of New Guinea (TABLE 1).

TABLE 1. Soluble anions and cation-exchange characteristics of some horizons of salt-affected coastal plain soils

Nr.	pH		Soluble salts (me/100 g)		CaCO$_3$ %	Exchangeable cations in me/100 g of soil				Sum of cations	CEC (me/100 g)
	H_2O	sat. $CaSO_4$	Cl	SO_4		Ca	Mg	Na	K		
109	6,54	6,25	2,4	tr.	tr.	11,7	15,2	3,6	0,2	30,7	30,6
110	7,12	6,74	2,4	0,9	2,1	10,4	14,8	3,3	0,3	28,8	28,9
111	8,07	7,70	3,4	1,3	17,5	10,2	9,5	0,9	0,6	21,2	21,6
118	6,98	6,75	1,9	1,6	tr.	13,4	16,9	2,4	0,0	32,7	33,3
103	7,91	7,61	3,8	3,3	15,2	11,7	12,4	2,4	0,1	26,6	26,5
120	7,96	7,78	4,3	4,1	24,4	11,4	8,7	2,0	0,1	22,2	22,3

The soils belong to the coastal solonetz-like soils, part of which are still occasionally inundated (see: REYNDERS, 1961; SCHROO, 1961). As an example of a calcareous non-saline soil was taken a chernozem profile (near Ensheim, West Germany), developed on calcareous loess. The results are given in TABLE 2.

TABLE 2. Cation-exchange characteristics of a chernozem profile

Nr.	pH		$CaCO_3$ %	Exchangeable cations in me/100 g of soil				Sum of cations	CEC (me/100 g)
	H_2O	0,01 m $CaCl_2$		Ca	Mg	Na	K		
71	7,69	7,32	5,7	14,8	1,7	0,2	0,5	17,2	17,4
72	7,98	7,54	5,9	17,2	1,7	0,1	0,1	19,1	18,9
73	7,91	7,53	6,2	17,2	2,1	0,1	0,1	19,5	19,5
74	7,93	7,38	35,2	10,2	1,7	0,1	0,1	12,1	12,1
75	8,16	7,42	37,9	9,4	0,2	0,1	0,1	9,8	9,9

5. Discussion

The advantages of the outlined method over previous ones are:

a. that both the exchangeable cations and total exchange capacity are determined on the same sample at a controlled pH;

b. that the elimination of the alcohol-water washings speeds up the procedure and avoids serious errors due to hydrolysis;

c. that simple and rapid analytical procedures are used for the determination of the cations and anions which do not involve many analytical steps.

As no sufficiently standard criteria exist for the evaluation of cation-exchange characteristics of saline soils, no comparisons with other methods were made. The best check on the adequacy and accuracy of the method is by comparing the sum of cations with the total exchange capacity. The results of TABLE 1 indicate that good agreement (within 2 %) has been obtained in all cases. They also indicate that the choice of the 1 : 2 soil-water extract is suitable for calcareous and gypseous saline soils.

The extent of the shift in adsorption between monovalent and divalent cations due to the use of the 1 : 2-ratio instead of saturation extract is being studied further. It seems that it rather well expresses the ratio of exchangeable cations during the very early stage of reclamation of highly sodic soils.

The proposed method is also well applicable to calcareous non-saline soils, as is shown in TABLE 2. It is suggested that the method can also be used for the analysis of the cation-exchange characteristics of non-calcareous non-saline soils, though in this case the saturation and extracting solutions should be adjusted to pH 7.

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