

THE DETERMINATION OF ADSORBED Na, K, Mg AND Ca ON SEDIMENTS CONTAINING CaCO₃ AND MgCO₃

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Abstract—A method for the determination of the cations of Na, K, Mg and Ca adsorbed on clay minerals mixed with CaCO₃ and MgCO₃ is described. An ethanolic solution of LiCl–CsCl is used to displace the exchangeable cations. Blank determinations performed using either a second ethanolic leach or a second LiCl–CsCl leach, are used to correct for carbonate dissolution. Details of the methods development are given.

The method has been tested using mixtures of homoionic forms (Na, K, Mg, Ca) of smectite and kaolinite with either CaCO₃ or MgCO₃. The smectite and kaolinite were found to have total CECs (with standard deviations) of 765 (4.4) and 39.8 (0.52) mequiv kg⁻¹, respectively. The amount of cation exchanged was found to vary directly with the proportion of clay mineral in the mixture; regression coefficients consistently greater than 0.997 were obtained.

Other tests with smectite–CaCO₃ mixtures in sea-waters of various salinity vindicated the use of the method with heteroionic forms of smectite. These tests also suggest that the phenomenon of fixation observed in most other studies of clay minerals in estuarine conditions might be redundant. It is contended that there is an urgent need for this suggestion to be tested.

INTRODUCTION

This paper describes a new method for determining the exchangeable Na, K, Ca and Mg cations on calcareous sediments. The method employs lithium and caesium as displacing cations in ethanolic solution. This combination allows one to utilize the advantages of most of the existing methods without having to suffer the associated disadvantages. Thus, the method amalgamates four major advantages. First, carbonate dissolution is suppressed by the use of ethanol (Chapman and Kelly, 1930; Tucker, 1954, 1971), thereby allowing work to be conducted on sediments contaminated with the carbonates of Mg and Ca. If these carbonates were to dissolve in the leaching reagent used to displace adsorbed cations the amount of adsorbed Mg and Ca would be in error. With some existing procedures, e.g. Bischoff *et al.* (1975), it is possible that this error could be large and hidden. Second, the problem of carbonate precipitation inherent in the use of divalent cations, e.g. Ba²⁺ (Carpena *et al.*, 1972) is avoided by the use of Li and Cs as displacing cations. Third, the use of 'neutral' LiCl and CsCl as displacing salts overcomes the problems encountered in the use of hydrolysable salts such as NH₄Cl and CH₃COONH₄. With the latter two salts, there is the likelihood that the buffering capacity of the salt solution is sufficiently high to change both the cation exchange capacity of pH sensitive sorbers, e.g. amorphous aluminium silicate, and the carbonate equilibria in the solution. Moreover, the carbonate equilibrium will also be changed when any carbonate contaminant is added with the alkali that is needed to raise the pH of the NH₄Cl reagent. In this case,

the amount of exchangeable Mg and Ca is underestimated. Fourth, the four major exchangeable cations on natural sediments can be determined using a single cation-displacing leach and its blank.

EXPERIMENTAL

Materials

All reagents were of Analar grade unless stated otherwise. The IMS was 64° over-proof. Distilled water was obtained from a Manesty cast-iron still. Precipitated CaCO₃ (calcite), natural MgCO₃ (magnesite), smectite (Fullers earth, bentonite) and kaolinite (English china clay) were obtained from B.D.H. Ltd.

The Na, K, Mg and Ca homoionic forms of each clay were prepared by treating 100-g portions of the dry clays with 1.0 liter of a 1.0 M solution of the appropriate metal chloride. The suspensions were stirred overnight. After settling for 2 h, the supernatant liquor was decanted and the clay was filtered on to a Whatman GFC 15 cm filter circle. The clay was then washed several times with 50-ml aliquots of 60 vol % IMS (industrial methylated spirits) until the filtrate gave no detectable chloride precipitate on addition of acidified AgNO₃ solution. This entire procedure was repeated four times more before each 'homoionic clay' sample was dried in an air-circulation oven at 20°C and stored in stoppered bottles. Subsamples of these clays were mixed thoroughly with calcite and magnesite, to give clay-carbonate mixed standards of 0, 25, 50, 75 and 100 wt % clay, and stored in tightly-capped specimen bottles prior to analysis.

Chemical analysis

Leachable Na, K, Mg and Ca were determined using a Pye Unicam SP 90 Atomic Absorption Spectrophotometer with an air-acetylene flame. For Ca, Na and K determinations, a standard absorption burner-head was used to give a 10-cm flame path-length; for the Mg determination an emission-head was used to give a flame path-length of approximately 1 cm.

In all cases, the matrix of the standards had the same composition as that of the samples under analysis. Further, lanthanum chloride (LaCl_3) (10.0 g l^{-1}) was added to each sample before analysis, to suppress Al and P interferences in the flame (Slavin, 1968). Na, K, Mg, Ca and La working-standards were prepared by dilution of stock atomic-absorption standards (BDH Ltd). During analysis, sub-samples of either standards or samples were run in batches of 40. Calibration was effected both at the beginning and end of each batch, and additional standards were placed after eight samples so that a check could be kept on any drift. Samples and distilled water wash were aspirated alternately for durations of 35 and 40 s, respectively. The response of the spectrophotometer was displayed on a Smith's Servoscribe RE 511 potentiometric recorder.

METHOD DEVELOPMENT

Preliminary studies of the amounts of exchangeable cations on calcareous sediments were made using His-sink's (1923) approach, but with LiCl instead of NaCl. In this way, it seemed that the four major exchangeable cations might be determined using a single leach. However, the dissolution of calcium carbonate was found to be a major problem. To suppress carbonate dissolution, ethanol was added to the leaching reagent (Chapman and Kelly, 1930). This change in the solvent seemed likely to alter the degree or solvation of the lithium cation, and therefore the ability of lithium to displace cations from their adsorption sites on the sediment. To compensate for this change, and to provide a most efficient leaching agent, a mixed LiCl-CsCl leach was chosen to allow competition both between Li^+ and small cations, and between Cs^+ and the larger cations.

In further studies, it was first necessary to establish the relative concentrations of lithium and caesium chloride that are required to displace adsorbed cations from clay minerals; most previous work had already vindicated the value of 1.0 M solutions for individual displacing salts. Afterwards, an optimum sediment to reagent ratio, and a representative 'blank' procedure had to be found. In this work, the 60% ethanolic solution recommended by Tucker (1954) was used without further investigation. With the lithium-caesium combination, it was expected that divalent cations would be more difficult to displace than monovalent cations (Grim, 1968). Therefore, to test the lithium-caesium mixtures under the most

adverse conditions likely to be encountered in routine work, Ca and Mg homoionic forms of smectite were used. In the final part of the method development, the behavior of the method toward mixtures of carbonates and homoionic forms of clay minerals, was investigated.

The choice of an appropriate lithium to caesium ratio

To obtain a satisfactory combined lithium-caesium reagent 1.00 M solutions of LiCl and CsCl in 60% IMS were mixed to give solutions with various known ratios of lithium-caesium concentration. Each solution was boiled to remove dissolved carbon dioxide, cooled in a CO_2 -free atmosphere, and made up to its initial volume with CO_2 -free 60% IMS solution. Approximately 0.1000-g portions of Ca and Mg homoionic forms of smectite were weighed in separate 50-ml stoppered glass bottles and to each a 50-ml aliquot of the LiCl-CsCl solution was added. The mixtures were shaken vigorously and left at room temperature for 20 h to equilibrate. The supernatant liquids were decanted, filtered through separate Millipore® membrane filters ($0.2 \mu\text{m}$ average pore dia.); portions were treated with LaCl_3 solution and stored in stoppered glass bottles. Ca and Mg were determined using atomic adsorption spectrometry. The experiment was repeated with storage times of 2 h and 4 days.

The results (Table 1) show no significant difference between 20-h and 4-day equilibration. However, the 2-h equilibration period led to variable results with between only 60–80% exchanges of Mg and Ca. In later experiments, therefore, an equilibration period slightly greater than 20 h was adopted. The results also show that the mixed lithium-caesium reagent removed more Mg and Ca than either a lithium or a caesium solution alone. With each of the homoionic forms of the smectite, mixtures having a Li^+/Cs^+ concentration ratio between 0.33 and 3.00 yielded a constant amount of exchangeable cation. The apparent difference in exchange capacity between the Mg and Ca homoionic forms of the smectite was due to a slight CaCO_3 impurity in the smectite; in a proper determination of exchangeable Mg^{2+} and Ca^{2+} the 'blank' correction would have removed the anomaly. Although a wide range of Li and Cs ratios could be used, here a solution with a ratio of 3.00 was chosen so that both the effect of Na impurity in the CsCl and the cost of reagents could be minimized.

Table 1. The amounts (uncorrected for blank) of Ca^{2+} and Mg^{2+} displaced from calcium and magnesium homoionic forms of smectite on treatment with a 1.00-M mixture of LiCl and CsCl in 60% IMS

LiCl (M l^{-1})	CsCl (M l^{-1})	Ca^{2+} leached (mequiv kg^{-1})			Mg^{2+} leached (mequiv kg^{-1})	
		2 h	20 h	4 days	20 h	4 days
1.00	0.00	700	895	900	750	765
0.75	0.25	690	940	920	770	770
0.50	0.50	700	940	940	760	765
0.25	0.75	690	940	920	770	765
0.00	1.00	600	705	715	720	715

Table 2. The effect of suspension loading on the amounts of Ca^{2+} and Mg^{2+} displaced from calcium and magnesium homoionic forms of smectite and kaolinite on treatment with the Li-Cs reagent

Homoionic form of clay	Suspended load	
	0.1000 g/50.0 ml	0.5000 g/50.0 ml
Ca smectite	756	770
Mg smectite	765	768

Homoionic form of clay	Suspended load	
	0.5000 g/50.0 ml	2.5000 g/50.0 ml
Ca kaolinite	39.5	40.0
Mg kaolinite	39.0	39.0

The choice of the sediment suspension load

In preliminary work, sediment loadings of 0.1 and 0.5 g in 50.0 ml of solution were arbitrarily chosen for use with the smectite and kaolinite, respectively. In later work, these loadings were increased five-fold so as to reduce the magnitude of the blank relative to that of the exchanged cations. This also reduced reagent costs. The increase in sediment loading did not significantly affect the results yielded by the method (Table 2).

The blank procedure

A blank procedure is required to give a correction for residual calcium or magnesium carbonate dissolution. The error from this source is greatest in the analysis of a carbonate-rich mixture containing a clay-mineral of low cation exchange capacity (CEC). The blank procedure recommended here is satisfactory for all calcium carbonate-clay mineral mixtures, but is unsatisfactory for the measurement of the amount of exchangeable Mg in a mixture of MgCO_3 and a clay mineral with a low CEC. However, this is unlikely to be a serious disadvantage, as these latter mixtures are rarely found. In the recommended blank procedure, 60% IMS is substituted for the lithium-caesium displacing solution. Although this procedure can never be a truly representative blank, because the ionic strength of the IMS does not match that of

the displacing solution, the error was found to be negligible in the case of mixtures of CaCO_3 and clay-minerals. Thus, the amount of Ca leached from pure CaCO_3 (precipitated) by both IMS and IMS containing LiCl and CsCl was less than $0.6 \text{ mequiv kg}^{-1}$. In a similar experiment with MgCO_3 (naturally occurring magnesite), the IMS leached less than $0.6 \text{ mequiv kg}^{-1}$ of Mg but the displacing solution leached $16 \text{ mequiv kg}^{-1}$. Thus, with MgCO_3 the ionic strength difference introduces a significant error and it is necessary to avoid using this procedure. Instead, with mixtures rich in MgCO_3 which contain a clay mineral with a low CEC the alternative but longer blank procedure for Mg, in which a second lithium-caesium leach is performed, is recommended. Using this alternative blank procedure on the aforementioned MgCO_3 the appropriate correction of $16 \text{ mequiv kg}^{-1}$ was obtained.

Tests with clay mineral-carbonate mixtures

Mixtures of four (Na, K, Ca, Mg) homoionic forms of kaolinite and smectite (taken individually) with either calcium or magnesium carbonate were analysed by the recommended procedure. The method was vindicated when plots of the amount of cation displaced against the proportion of clay in the mixture fitted a linear model well. In every case, the correlation coefficient exceeded 0.997 (Table 3). Further, in each case, the intercept, which as a measure of the amount of cation displaced from the carbonate was expected to be close to zero, did not differ significantly from zero at the 95% confidence limit. The fitted lines allow calculation of the amount of cation displaced from the clay mineral, that is for a homoionic form, the CEC. The agreement between these values was good since the mean CEC and standard deviation for the kaolinite and the smectite were 39.8 and 0.52, and 765 and $4.4 \text{ mequiv kg}^{-1}$, respectively.

RESULTS

As a preliminary to its field application, the method has been used in a study of the cation-exchange be-

Table 3. Regression lines for the exchange capacities of admixtures of carbonate with kaolinite and smectite, as clay content varies

System	No. of sample points	m	95% confidence interval for m	C	95% confidence interval for C	Multiple correlation coefficient	Calculated exchange capacity of clay (mequiv kg^{-1})
Na kaolinite + MgCO_3	5	0.406	± 0.023	-0.540	± 1.427	0.9988	40.1
Na kaolinite + CaCO_3	5	0.416	± 0.024	-0.900	± 1.450	0.9988	40.7
K kaolinite + MgCO_3	5	0.391	± 0.040	0.294	± 2.426	0.9980	39.4
K kaolinite + CaCO_3	5	0.391	± 0.040	0.294	± 2.436	0.9980	39.4
Mg kaolinite + MgCO_3	5	0.400	± 0.017	-0.200	± 1.028	0.9996	39.8
Mg kaolinite + CaCO_3	5	0.388	± 0.046	0.600	± 2.808	0.9973	39.4
Ca kaolinite + MgCO_3	5	0.392	± 0.013	0.200	± 0.786	0.9998	39.4
Ca kaolinite + CaCO_3	5	0.404	± 0.017	0.000	± 0.104	0.9997	40.4
Na smectite + MgCO_3	5	7.604	± 0.410	-0.68	± 2.51	0.9989	760
Na smectite + CaCO_3	5	7.630	± 0.262	-4.12	± 16.28	0.9995	762
K smectite + MgCO_3	5	7.590	± 0.449	7.45	± 27.48	0.9993	767
K smectite + CaCO_3	5	7.610	± 0.323	6.46	± 19.92	0.9996	768
Mg smectite + MgCO_3	5	7.564	± 0.562	11.20	± 34.39	0.9989	768
Mg smectite + CaCO_3	5	7.640	± 0.170	-4.00	± 9.65	0.9999	760
Ca smectite + MgCO_3	5	7.584	± 0.320	2.40	± 19.64	0.9997	761
Ca smectite + CaCO_3	5	7.692	± 0.589	2.20	± 36.08	0.9989	771

Table 4. The exchangeable cations on smectite (Wyoming bentonite) after equilibration with sea-waters of various known salinity

(a) Smectite-calcium carbonate mixtures in 35‰ sea-water						
% smectite	% CaCO ₃	Exchangeable cations (mequiv kg ⁻¹)				
		Na	K	Mg	Ca	Total (CEC)
100	0	623	9	344	56	1031
90	10	575	8	303	50	936
80	20	509	5	266	45	825
70	30	476	7	228	40	751
60	40	383	4	196	34	616
50	50	327	5	162	28	522
40	60	254	4	129	21	408
30	70	167	4	105	18	294
20	80	117	3	72	10	202
10	90	70	1	39	5	115
0	100	0	0	0	0	0

(b) Smectite in sea water 0–35‰ S (no added carbonate)					
Salinity (‰)	Na	K	Mg	Ca	Total
0	930	6	32	88	1056
5	521	4	408	90	1023
15	554	11	356	74	995
25	646	5	334	63	1048
35	623	9	344	56	1031

havior of smectite in sea-waters of various known salinity (0–35‰ S). This study was particularly interesting as it allowed the method to be tested in a regime other than that of the homoionic clays that was essential for the method's development. While, in one set of experiments, mixtures of smectite (Wyoming bentonite) and calcium carbonate of various known proportions were equilibrated with sea-water of 35‰ S, in another, the same smectite was equilibrated with sea-waters with salinities ranging between 0 and 35‰ S. In each case, the ion-exchange equilibrium between solid and sea-water phases (5.0 g l⁻¹) was assumed to have been attained after 6 months soaking with continual re-suspension.

The results for the first experiment (Table 4a) showed that the method works well in sea-water even when calcium carbonate is present in the sediment. The amount of each cation displaced from the clay mineral-calcium carbonate mixture seemed to vary directly with the proportion of the clay mineral present in the mixed sediment. Regression of the data for each cation, as well as for the total, on to a linear model confirmed this (Table 5). The correlation coefficients were generally greater than 0.998; the results for potassium were exceptional probably because of the small amount of exchangeable potassium on the clay mineral. The amounts of the exchangeable

cations associated with the calcium carbonate did not differ significantly from 0.0 mequiv kg⁻¹, at the 95% confidence limit.

As expected the results for the second experiment (Table 4b), which simulated the estuarine behavior of smectite (Wyoming bentonite), showed that the relative proportions of the exchangeable cations upon the clay mineral changed as the clay mineral was exposed to waters of different salinity. Little significance can be attached to the individual exchangeable cations measured at zero salinity (distilled water) as these mainly reflect an unknown pore-water composition existing at the time the clay mineral was collected. However, for the salinity range 5–35‰, the amount of exchangeable sodium increased at the expense of exchangeable magnesium and calcium, as would be expected with most clay minerals. No significant variation was observed in the exchangeable potassium which, as in the previous experiment, was low. The total amount of exchangeable cations (CEC) did not change significantly with salinity between 0 and 35‰. A mean and standard deviation of 1031 and 24 mequiv kg⁻¹ were obtained. This constancy is similar to that obtained with the four homoionic forms of the other smectite (fuller's earth) used during the method's development. These results contrast markedly with most earlier ones (e.g. Weaver, 1958; Keller, 1963; Russell, 1970; Roberson, 1974), where usually a decrease in total exchange capacity accompanied any increase in salinity. Previous workers invoked ion-fixation (principally potassium) to account for the loss of exchangeable sites (Berner, 1971). It is possible that the difference in fixation exhibited by the two smectites used here and those clay minerals studied by the previous workers results from differences in structure, as Berner (1971) might have maintained. It is noted in this context that the Wyoming bentonite had a lower affinity for potassium than did the clay minerals studied by previous workers. Equally, however, it is possible that the 'fixation' effect is an artifact introduced by the methods that hitherto have been used to determine exchangeable cations. The fact that the leaching solution used here incorporates lithium in an ethanolic solution adds substance to this argument. Thus, it is suggested that this combination is able to replace ions sorbed on to less accessible sites because the unhydrated lithium ion is small. It is a matter of some urgency to find whether or not this hypothesis is correct.

Table 5. Regression of the amount of exchangeable cation on the mixed sediment, on the percentage of clay mineral in the mixture

Exchangeable cation	No. of sample points	Gradient (mequiv kg ⁻¹) (% clay) ⁻¹	Intercept (mequiv kg ⁻¹)	Correlation coefficient
Na	11	6.42 (±0.31)*	-2.56 (±17.8)*	0.9979
K	11	0.06 (±0.02)	1.09 (±1.3)	0.8904
Mg	11	3.34 (±0.12)	0.74 (±7.0)	0.9989
Ca	11	0.56 (±0.01)	-0.37 (±0.9)	0.9994
Total (CEC)	11	10.39 (±0.22)	-1.26 (±13.0)	0.9994

* Numbers in parentheses indicate 95% confidence interval.

CAUTIONARY NOTE

Recently, Sayles and Mangelsdorf (1977, in press) have reopened the discussion on the merits of the washing procedures used in preparing clay minerals for marine studies. As a result of their new work, they contend that most of the earlier work with clay minerals in marine systems is erroneous; as a result of the Donnan equilibrium theory, the dilution that occurs during washing leads to selective removal of sodium from the clay mineral; exchangeable magnesium is thereby grossly overestimated while exchangeable sodium suffers a concomitant underestimation. Unfortunately, insufficient time has been available for this work to be fully digested, and it is probably premature to dismiss the earlier work outright. With this type of study, it seems especially worthwhile to be cautious as the experimental systems are heterogeneous. Indeed, I believe that there are serious problems inherent in the approach used by Sayles and Mangelsdorf details of which will be published elsewhere. Nevertheless, it is recommended that any worker who intends to apply the method reported here to marine systems should be aware of any controversy over the problems of washing.

METHODS

Reagents

Lanthanum chloride solution. This is obtained either as atomic absorption standard (BDH Ltd) or by dissolving 266.0 g of atomic absorption spectroscopy grade $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in 1.00 l. of distilled water. The solution contains 100.0 g l^{-1} of lanthanum.

Lithium chloride-caesium chloride leaching reagent. Dissolve 31.8 g Analar grade lithium chloride (LiCl) and 42.1 g Analar grade caesium chloride (CsCl) in a mixture of 600 ml IMS and 400 ml distilled water, and boil to remove any dissolved CO_2 . After cooling the solution in a stoppered flask protected with a Carbasorb guard-tube, transfer it to a volumetric flask and dilute it to 1.00 l. with CO_2 -free 60% IMS solution.

Na, K, Mg and Ca standard solutions. Dilute individual stock solutions (1.0000 g l^{-1} in the metal) of NaCl, KCl, MgCl_2 and CaCl_2 (atomic absorption spectroscopy standards, BDH) with distilled water to give a combined standard containing 50.0 mg l^{-1} of both Na and K and 100.0 mg l^{-1} of both Mg and Ca. Mix appropriate amounts of this combined standard with 10% lanthanum chloride solution, distilled water and either LiCl-CsCl leaching solution or 60% IMS to give working standards containing 0.00, 1.00, 2.00, 3.00, 4.00 and 5.00 mg l^{-1} of both Na and K; 0.00, 2.00, 4.00, 6.00, 8.00 and 10.0 mg l^{-1} of both Ca and Mg in a background of 1.00 g l^{-1} La and either LiCl-CsCl leaching reagent or IMS at the dilution appropriate to the samples being analysed.

Procedure

Preliminary treatment. Wash 2.0 g of sample several times with 25.0 ml portions of a solution containing

90% and 10% ethylene glycol (v/v) to separate the sediment from contaminating soluble salts (Tucker, 1971). Rinse the damp sediment with 100% IMS to remove excess ethylene glycol and dry the washed sediment at room temperature (approximately 20°C) in an air circulation oven.

Final treatment. For sediments with a high CEC ($>100 \text{ mequiv kg}^{-1}$), use approximately 0.1000-g portions of the pre-treated sediment; for those with low CEC, use 0.5000-g portions. To perform the salt-leaching, weigh a portion of the pre-treated sediment into a 14-ml stoppered centrifuge tube and add 10.0 ml of LiCl-CsCl leaching reagent. Stopper the tube, shake vigorously to 'disperse' the sediment, and leave for approximately 20 h (overnight) at 20°C (room temperature) to equilibrate. Decant the supernatant liquid, filter it through a GFC Whatman (5.5-cm) filter circle, add 2.00 ml of the stock La solution to 2.00 ml of the filtrate and dilute the mixture to 20.0 ml with distilled water. [The analyst might on occasions wish to change the dilution regime of 2.00–20.0 ml, to accommodate sediments with either intermediate ($\approx 40.0 \text{ mequiv kg}^{-1}$) or very high CECs]. Determine the concentration of Na, K, Ca and Mg in the cation-leaching solution. For all cases, except that of a mixed sediment containing magnesium carbonate and a clay mineral with a low CEC, repeat the entire procedure with 60% IMS in place of the salt leaching solution in order to obtain a blank.

In the exceptional case, obtain the blank by performing a second leach using a fresh 10.0-ml aliquot of the LiCl-CaCl reagent together with the sediment filtered from the first leach. For each ion, the amount of exchangeable cation (C) in mequiv kg^{-1} is

$$C = ZY(A - a)/EW$$

where Z is the initial volume (ml) of reagent added to W g of sediment, A and a are the concentrations (mg l^{-1}) of the cation in the salt leach and blank solutions, respectively, after they have been diluted y times (in this case 10 times). E is the equivalent weight (g) of the cation.

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