

DETERMINATION OF THE CATION-EXCHANGE CAPACITY (LAYER CHARGE) OF SMALL QUANTITIES OF CLAY MINERALS BY NEPHELOMETRY

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(Received 24 April 1978)

Abstract—Nephelometric (light scattering) methods for the determination of Ca and Ba in the 0–30 ppm range, and their application to the estimation of the cation exchange capacity ($\pm 10\%$) of small (≤ 30 mg) samples of clay minerals, are described and evaluated.

Key Words—Exchange, Microanalysis, Nephelometry, Smectite.

INTRODUCTION

The cation exchange capacity (CEC) of a clay mineral may be determined by a variety of established methods (see, for example, Grim, 1968; Weiss, 1958), the choice of technique varying with, inter alia, the value of the CEC, the quantity of sample available, and the interlayer cation present. The most widely used methods involve the displacement of the interlayer ion into a known volume of solution, which is then analyzed by a standard technique such as flame photometry (Adams et al., 1977), atomic absorption or titrimetry. Such methods can, however, be difficult to employ when only a few milligrams of the clay are available, while if the clay has been exchanged with an ion which 'fixes' the clay, the necessary displacement reaction is no longer possible. (In such cases, it is more properly the layer charge resulting from lattice substitution which is required, rather than the CEC, this latter parameter being irreversibly reduced by such exchange. The two parameters remain, however, closely related.) If the cation is indeed one which cannot easily be displaced, its estimation must involve the dissolution of a sample of the clay as a whole. This can readily be achieved by fusion with sodium hydroxide (Bennett and Reed, 1971), but the subsequent determination of the cation—at the ppm level—in solutions containing both silicon and a considerable excess of sodium presents considerable difficulty to common techniques such as flame photometry and atomic absorption. However, nephelometry—an analytical technique in which the light scattered by a turbid solution at right angles to an incident light beam is measured—possesses considerable potential for such work, and despite being a long-established technique, described in some detail by, for example, Vogel (1961), it does not appear to have been exploited in this context. In this paper we describe how nephelometry may be used to estimate barium and calcium in the 0–30 ppm region, enabling CEC (layer charge) to be determined from clay samples weighing 30 mg or less. Nephelometric techniques should, however, prove applicable whenever a suffi-

ciently insoluble salt of the interlayer cation exists. The essence of the method is simply to precipitate the insoluble salt quantitatively and in a controlled fashion so that the fraction of the incident light scattered by the turbid solution is directly proportional to the original concentration of the cation concerned. Our procedures use barium sulfate (solubility product (s.p.) 1.08×10^{-10} mol² liter⁻² at 25°C) and calcium oxalate monohydrate (s.p. 2.57×10^{-9} mol² liter⁻² at 25°C): the minimum detectable concentration is in principle determined by the s.p. although in practice for solubilities in this range the residual turbidity of certain reagent solutions is a more significant limitation. The following procedures could easily be adapted to estimate barium and calcium present in the mineral matrix itself.

EXPERIMENTAL

The initial dissolution of the clay sample (~30 mg) was carried out as described by Bennett and Reed (1971), but on a reduced scale. 0.70 g NaOH was melted in a nickel crucible and allowed to cool. After distributing the finely ground sample over the surface of the alkali, it was then heated to a dull red heat for 10 min. When the melt had solidified, the contents of the crucible were leached out with warm water into a stainless steel beaker. The solution thus obtained was added (quantitatively) to 2.0 ml of concentrated HCl (slowly, with swirling) and, when cold, made up to 25 ml with deionized water. The determinations described below were conducted in duplicate to establish the reproducibility of the technique.

Nephelometric determination of barium

This method was adapted from one given for the determination of sulfate by Vogel (1961). A standard barium solution of ca. 30 ppm is required as are a chloride solution (60 g NaCl and 5 ml concentrated HCl in 250 ml deionized water) and a 1:2 mixture of glycerol and ethanol. This last mixture required filtration as it was appreciably turbid as mixed.

2.5 ml chloride solution and 5 ml of the glycerol/eth-

Table 1. Comparison of nephelometric and other determinations of cation-exchange capacities.

Clay	Ex-change-able cation	CEC by nephelometry/ meq/100 g	CEC by other techniques ¹ meq/100 g
Bentonite (Hopkin & Williams) (air-dry)	Ca	62 ± 4 (1.24% Ca)	66 ± 2 (FP, EDTA, C) (1.32% Ca)
Montmorillonite (Volclay, Wallasey, Cheshire) (air-dry)	Ba	74 ± 5 (5.07% Ba)	69 ± 2 (FP) (4.52% Ba)
Beidellite (ex G. Lagaly similar to that described by Weiss et al., 1955) (dried)	Ca	122 ± 15 (2.44% Ca)	119 (CA) (2.39% Ca)
Beidellite (as above) (dried)	Ba	119 ± 5 (8.19% Ba)	119 (CA) (8.15% Ba)

¹ FP = flame photometry (Adams et al., 1977).

CA = chemical analysis (by G. Lagaly) together with thermogravimetric data.

EDTA = titration with EDTA.

C = conductivity method (Mortland and Mellor, 1954).

anol mixture were measured into each of five 25 ml volumetric flasks. 0, 5, 10, and 15 ml of the standard barium solution (30 ppm) were added to four of the flasks to provide calibration points, while 5 ml of the unknown (clay) solution were added to the fifth. After swirling, 2.5 ml of dilute (1.5 M) sulfuric acid were added to each and the flasks made up to volume with deionized water. The full turbidity developed over some 10 min; the light scattered by the samples was then measured (at right angles to the incident beam) in a Brice Phoenix Universal Light Scattering Photometer. Because the turbidity exhibited a slight time dependence (even after 10 min from mixing), calibrations using the first four solutions were performed both before and after the measurement of the light scattered by the unknown. The calibration plot was linear.

Nephelometric determination of calcium

A standard calcium solution of ca. 8 ppm, the 1:2 mixture of glycerol and ethanol, 3 M NH₄OH, and a solution containing 20 g/liter oxalic acid dihydrate are required.

4.0 ml of the glycerol/ethanol mixture, 1.5 ml 3 M NH₄OH and 4.0 ml of the oxalic acid solution were measured into each of five 25 ml volumetric flasks. After mixing, 0, 5, 10, and 15 ml of the standard calcium solution were added to the first four flasks, to provide calibration, while 5 ml of the unknown (clay) solution were added to the fifth. The flasks were made up to volume with deionized water and allowed to stand until

their full turbidity had developed (~15 min). The light scattered by each sample at right angles to a blue light beam was measured (twice) as described for barium above. The calibration plot was again linear. This determination appears to be somewhat pH sensitive; we have found the above procedure satisfactory for solutions prepared in the standard manner, but the inclusion of a suitable buffer may be desirable in other applications.

RESULTS

A summary of results obtained from microsamples of three clays previously well characterized by other techniques is given in Table 1. The degree of consistency between duplicate determinations (not shown) and between the nephelometric and standard methods suggests that the microtechnique may be considered accurate to ±10% in general.

CONCLUSIONS

The results in Table 1 demonstrate that CECs can be determined at a useful level of accuracy from 30 mg samples of Ca- or Ba-exchanged clays possessing CECs in the 70–100 meq/100 g range. However, since each determination required only one-fifth of the clay/NaOH solution the procedure described could be directly employed for samples as small as 5–10 mg with negligible loss of accuracy (using 15 ml of the fusion solution rather than 5 ml). Even smaller quantities of clay (≤1 mg) would probably suffice if additional precautions were taken to reduce the residual turbidity of the reagent solutions, in particular that of the glycerol/ethanol mixture.

The routine determination of CEC would probably be better undertaken using Ca-exchanged clay: we have recently obtained X-ray photoelectron spectra (to be described in detail elsewhere) which suggest that barium may adsorb on the surfaces of the clay particles. This could lead to the derivation of a high CEC from the barium analysis data. The figures in Table 1, however, suggest that such effects should usually remain within the overall experimental error.

ACKNOWLEDGMENTS

We thank Professor G. Lagaly (Kiel) for providing the specimen of beidellite of known composition, Professor J. M. Thomas for encouragement and the Science Research Council for support.

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Резюме—Описываются и оцениваются нефелометрические (использующие световое рассеивание) методы определения Са и Ва в пределах 0–30 ч/млн и их использование для оценки катионной обменной способности ($\pm 10\%$) малых (≤ 30 мг) образцов глинистых минералов.

Resümee—Nephelometrische (Lichtstreuung) Methoden für die Bestimmung von Kalzium und Barium von 0 bis 30 ppm und ihre Anwendung zur Bestimmung der Kationenaustauschkapazität ($\pm 10\%$) kleiner (≤ 30 mg) Proben von Tonmineralien werden beschrieben und beurteilt.

Résumé—Des méthodes néphelométriques (dispersion de lumière) pour la détermination de Ca et de Ba de 0–30 ppm et leur application à l'estimation de la capacité d'échange de cations ($\pm 10\%$) de petits (≤ 30 mg) échantillons de minéraux argileux sont décrites et évaluées.