

POLAROGRAPHIC DETERMINATION OF CALCIUM IN LEPIDOLITES AND MUSCOVITES

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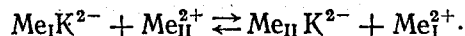
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In the calcium method of establishing the age of micas it is necessary to determine calcium in amounts which vary, as in the case of lepidolites, within the limit 0.001–0.2% [1].

The photometric method of determining calcium with murexide, despite its high sensitivity (1–8 μ g Ca in 10 ml), possesses low selectivity, as our experiments showed; colored compounds are formed by Fe, Co, Ni, Mn, Cu, Zn, Ba, Mg, Sr, etc. Accordingly, we established the possibility of using a polarographic method of determining calcium by means of sodium ethylenediaminetetraacetate (EDTA-Na).

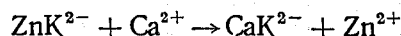
One of the methods of using complexons in polarography indicated by Pribil [2] is based on the exchange reactions:



The equilibrium of the exchange reaction is determined by the following equation:

$$K = \frac{[\text{Me}_{II}\text{K}^{2-}][\text{Me}_I^{2+}]}{[\text{Me}_I\text{K}^{2-}][\text{Me}_{II}^{2+}]} = \frac{K_I}{K_{II}}$$

(where K_I and K_{II} are the corresponding instability constants of the complexes of both metals). This equation is applicable to rapidly reacting complexes, so-called "equilibrium complexes" [3]. Such reactions have been fairly thoroughly studied [4]. It is possible to choose conditions such that, using the various rates of reaction of the exchange, there can occur quantitative displacement of the cations from the complexes by another cation, which forms a complex with a higher instability constant than that of the complex with the replaced cation. For example, Pribil and Vicenova [5] have shown that in an ammoniacal medium it is possible to expel zinc ions from zinc complexonate ($\text{pK}_{\text{ZnK}^{2-}} = 16.1$) by means of calcium ions ($\text{pK}_{\text{CaK}^{2-}} = 10.6$) according to the equation



and the liberated zinc ions determined polarographically. In this way Pribil et al. have determined calcium in solution [2,5] and in blood serum [6]. We have tried to use the method indicated for determining calcium in lepidolites and muscovites after removal of the main accompanying elements on KU-2 ion-exchange resin.*

EXPERIMENTAL

Measurements were carried out on a V 301 recording polarograph of the Heyrovsky type. The capillary characteristics were as follows: $m = 2.715 \text{ mg/sec}$; $t = 3.65 \text{ sec}$; $m^{2/3} \cdot t^{1/6} = 2.415 \text{ mg}^{2/3} \text{ sec}^{-1/2}$. The zinc

* See V. I. Baranov and Ch'en Yu-wei, Zhur. Anal. Khim. 15, 163 (1960) [See C.B. translation, p. 183].

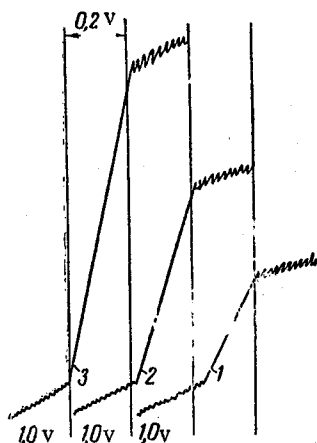


Fig. 1. 1) 1 ml of supporting electrolyte, 0.5 ml of conc. NH_4OH , and 7 drops of 0.5% gelatin; volume made up to 3 ml; 2) after addition of $28 \mu\text{g Ca}$; 3) after a second addition of $28 \mu\text{g Ca}$ ($56 \mu\text{g}$ of Ca in all).

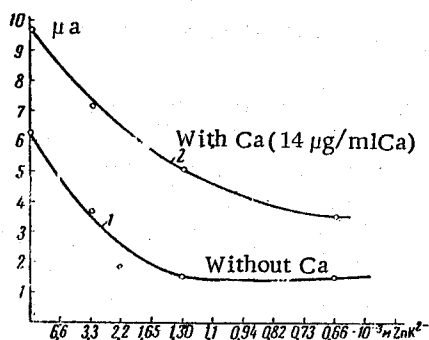


Fig. 2.

was added to a solution of EDTA-Zn. The relation between the diffusion current for zinc and the calcium concentration is shown in Fig. 3.

It is known that during the polarographic determination of calcium on the basis of the zinc wave, interference from magnesium can be eliminated by adding ammonium phosphate to the solution. There is no published information regarding the effect of manganese* on the determination of calcium by this method. Accordingly, experiments were carried out on the determination of calcium in which manganese was masked with ammonium phosphate (in the same way as magnesium is masked). For this purpose to several test tubes, each containing 1 ml of $6.6 \cdot 10^{-3} \text{M}$ EDTA-Zn, was added 0.1 ml of a 70% ammonium phosphate solution, an equal volume of calcium chloride, and varying amounts of manganese sulfate; ammonia solution was finally added until its concentration was 4–7 M, and then 7 drops of a 0.5% gelatin solution, and the volume made up to 5 ml with water. The solutions were transferred to the electrolyzer, purged with nitrogen, and polarograms were taken. In parallel, polarograms were taken of solutions containing exactly the same components, but with ammonium phosphate left out. Similar experiments were carried out with magnesium. The results obtained are shown in Fig. 4. As is evident from Curves 1 and 2, manganese and magnesium also liberate zinc from EDTA-Zn, thereby leading to high results for calcium. By binding Mn^{2+} and Mg^{2+} with ammonium phosphate it is possible to eliminate interference on the part of these metals completely** (Fig. 4, Curves 3 and 4). However, when magnesium is present in amounts five times that of calcium, the precipitate of magnesium phosphate adsorbs small amounts of calcium, and the calcium results are somewhat low (Curve 4). Barium and strontium, when present in amounts

ethylenediaminetetraacetate solution (EDTA-Zn) was prepared by dissolving (EDTA-Na) and 1.917 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in a small volume of twice-distilled water, after which 572 ml of concentrated ammonia (prepared by saturating twice-distilled water with ammonia from a cylinder) was added and the volume made up to one liter. The concentration of the solution was $6.6 \cdot 10^{-3} \text{M}$ with respect to EDTA-Zn and 8 M with respect to ammonia.

Solutions of calcium, barium, manganese, magnesium, strontium and other chlorides were prepared from the chemically pure salts after recrystallization of the latter; a 70% solution of diammonium hydrogen phosphate was prepared by dissolving the chemically pure salt (Merck). A 0.5% gelatin solution was used.

In Fig. 1 are shown polarograms for the supporting electrolyte and for zinc liberated by calcium from EDTA-Zn in ammonia solution.

In order to establish the extent of the liberation of zinc from EDTA-Zn by calcium, as a function of the ammonia concentration, polarograms were taken for solutions whose concentrations of EDTA-Zn and calcium chloride were constant, but whose ammonia concentrations varied.

Experiments showed that within the range 4–9.6 M ammonia quantitative replacement of zinc from EDTA-Zn by calcium ions occurs.

In Fig. 2 are shown results which demonstrate the effect of EDTA-Zn concentration on calcium determination. As Fig. 2 shows, the difference in the currents between curves 2 and 1 decreases at high and low concentrations of EDTA-Zn. The optimum EDTA-Zn concentration lies within the limits $1.2 \cdot 10^{-3}$ – $2.2 \cdot 10^{-3} \text{M}$. In order to establish the possibility of carrying out a quantitative determination of calcium in lepidolites and muscovites, from 1 to $8 \mu\text{g}$ calcium/ml

* Using a spectrographic method, about 0.07% Mn was found in the lepidolites, while about 0.03% Mn was found in the muscovites.

** The ammonium phosphate present in solution lowers the zinc diffusion current slightly.

Determination of Calcium in Micas

Mica	Location from which the samples were taken	Calcium found, %	Mean Ca content, %	Deviation from the mean, %
Muscovite	White Sea	0,022 0,021 0,022	0,0213	+3,2 -1,4 +3,2
Lepidolite	Voron'ya	0,0150	0,0175	-12,6
Muscovite	Tundra	0,0200	0,0175	+16,6
Muscovite	Chupa, Kareliya	0,028 0,026	0,027	+3,6 -3,5
Muscovite	Ukraine	0,035 0,035	0,035	— —

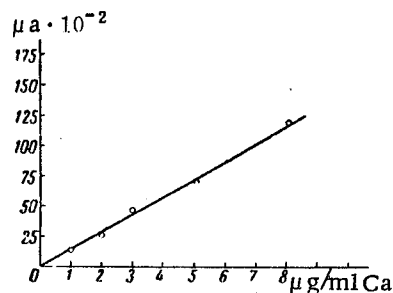


Fig. 3. Relation between the calcium concentration of the solution and the zinc current.

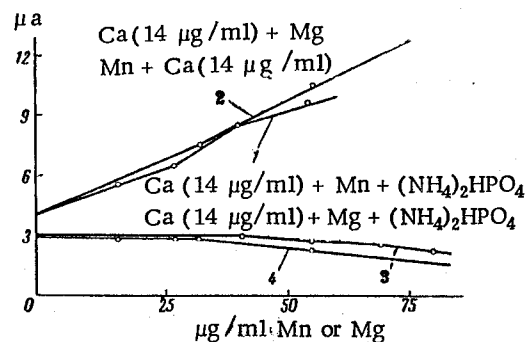


Fig. 4. Effect of manganese and magnesium on calcium determination in the absence and in the presence of ammonium phosphate.

which are twice that of calcium, do not affect the polarographic determination of calcium by the method indicated; when they are present in greater amounts, high results are obtained. When phosphate is present in the solution, barium and strontium do not affect calcium determination.

We also tried EDTA-Co* . $pK_{CoK^{2+}} = 16.1$, instead of EDTA-Zn and found that calcium liberates cobalt from EDTA-Co in an equivalent amount ($CoK^{2+} + Ca^{2+} \rightarrow CaK^{2+} + Co^{2+}$).

Consequently, the calcium concentration of the solution can also be determined from the wave height for cobalt. Our experiments showed that manganese and barium do not essentially affect the results for calcium determinations based on the cobalt wave. Magnesium and strontium interfere with the determination of calcium based on the cobalt wave. When, however, phosphate is added, interference from strontium can be eliminated but magnesium leads to a deterioration in the shape of the curve and makes it difficult to measure.

On the basis of this work, the following method has been developed for the determination of calcium in lepidolites and muscovites: 1 g of sample is decomposed with 40 ml of concentrated pyrophosphoric acid, phosphoric and silicic acids are then removed on the cation exchange resin KU-2 (the rate at which the solution is passed through the resin column should be 2 ml/min). The aluminum is first eluted from the column by means of concentrated ammonia until the eluate gives no reaction with alizarin S; calcium and the other cations are then eluted from the column with 3 N HCl at the rate of 2 ml/min. The hydrochloric acid solution is evaporated on the water bath to dryness; the residue is dissolved in water, adding the latter

in small portions. The solutions are poured into a test tube with a capacity of 5 ml, and the volume made up to the mark with water. Two ml of the solution is transferred to a 10 ml standard flask, 2.5 ml of $6.6 \cdot 10^{-3} M$ EDTA-Zn solution, 1 ml of concentrated ammonia solution, 0.1 ml of 70% diammonium hydrogen phosphate, and 7 drops of a 0.5% gelatin solution are added, and the volume finally made up to 10 ml.

The solution is placed in the electrolyzer and is purged with nitrogen (or hydrogen) for 5-10 minutes, then polarograms are taken. The calcium concentration is determined by comparing it with a standard solution containing the same components as the test solution, or by means of a calibration curve. Several samples of lepidolites and muscovites were analyzed by the method indicated. The results obtained are given in the table.

* 2.48 g of EDTA-Na and 1.9588 g $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in a small volume of twice-distilled water, 572 ml of concentrated ammonia was added, and the volume made up to one liter with water.

SUMMARY

A method is suggested for the determination of calcium in lepidolites and muscovites; it is based on removing a number of the accompanying elements (P, Si, Al, etc.) on a KU-2 ion exchange resin, and subsequently determining calcium in the eluate by a polarographic method, on the basis of the wave for zinc which is obtained as a result of an exchange reaction between EDTA-Zn and calcium ions.

Interference from manganese, barium, strontium (and magnesium) during the polarographic determination of calcium on the basis of the zinc wave, can be eliminated by adding ammonium phosphate to the solution.

It has been shown that on replacing EDTA-Zn by EDTA-Co, satisfactory results can also be obtained for calcium when the latter is determined on the basis of the cobalt wave. In this case manganese and barium do not essentially affect the determination of calcium; strontium does not interfere with the determination of calcium in the presence of phosphate, while magnesium interferes by spoiling the shape of the curve.

LITERATURE CITED

1. L. H. Ahrens and R. D. Evans, *Phys. Rev.* **74**, 279 (1948).
2. R. Pfabil, *Complexons in Chemical Analysis* [Russian translation] (IL. Moscow, 1955).
3. G. Schwarzenbach, *Angew. Chem.* **62**, 218 (1950).
4. H. Ackermann and G. Schwarzenbach, *Helv. chim. acta* **35**, 485 (1952).
5. R. Pfabil and E. Vicenova, *Chem. Listy* **46**, 535 (1952).
6. R. Pfabil and Z. Roubal, *Chem. Listy* **47**, 189 (1953); *Coll. Czech. Chem. Comm.* **19**, 252 (1954).