Short Communication

Cation exchange separation of calcium and magnesium at high ionic strength*

In the course of a general investigation of the cation exchange behavior of the elements in very high ionic strength media, a marked difference was found in the adsorbability of Mg (II) and Ca (II) which may be utilized for rapid and simple separation of these elements from each other.

Adsorbability of Mg (II) in HCl and $HClO_4$ solutions decreases with ionic strength qualitatively as expected from the usual mass action expressions. In 9 M $HClO_4$ and 9 M HCl, the distribution coefficients D (amount per kg dry resin/amount per liter solution) were *ca.* 4.0 and 0.65 respectively, for Dowex 50-X4 at 25°. These results are in general agreement with those published recently by MANN[1].

Adsorbability of Ca (II) in perchloric acid solutions first decreases with M $HClO_4$ as expected, shows a minimum distribution coefficient, $D =$ *ca.* 7 near 4 M $HClO_4$ and then increases rapidly to $D =$ *ca.* 10^3 in 11 M $HClO_4$. While strong adsorption of Ca (II) was also observed by CHOPPIN AND DINIUS[2], our results differ from theirs in that we find a very much steeper rise of distribution coefficients above 6 M $HClO_4$.

In hydrochloric acid, adsorbability of Ca (II) goes through a minimum near 5 M HCl ($D =$ *ca.* 2); it then increases moderately to $D =$ *ca.* 30 in 12 M HCl. These results are in substantial agreement with earlier observations by DIAMOND[3].

The differences in adsorbabilities and hence the separation factors between Mg (II) and Ca (II) are thus very much larger in $HClO_4$ than in HCl solutions of equal but high concentration. In concentrated perchloric acid solutions the difference is large enough and adsorption of Mg (II) small enough to permit concentration and isolation of trace amounts of Ca (II) from moderately large volumes of Mg (II) solutions.

Adsorbabilities of Ca (II) and Mg (II) in mixtures of HCl and $HClO_4$ of constant total acidity are intermediate between those in the pure acids as demonstrated in Fig. 1, a plot of log D *vs.* the fraction $HClO_4$ (F_{HClO_4}) in 9 M acid mixtures. The separation factor, D_{Ca}/D_{Mg}, computed from the data of Fig. 1, increases gradually from 8.2 in 9 M HCl to 75 in 9 M $HClO_4$ solution.

In the chromatographic application of high ionic strength cation exchange, difficulties are encountered from the slow exchange rates. However, sharp elution bands can be achieved with reasonable flow rates by use of very fine mesh resins and occasional operation at elevated temperatures. We have also observed that HCl–$HClO_4$ mixtures have somewhat more favorable rates than $HClO_4$ solutions of the same ionic strength.

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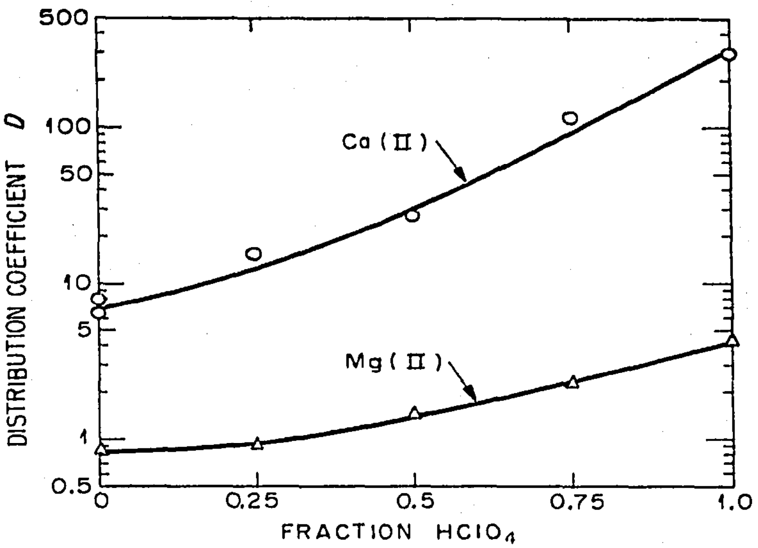

Fig. 1. Adsorption of Mg(II) and Ca(II) from 9 *M* HCl–HClO$_4$ mixtures (Dowex 50-X4, 25°).

A typical separation illustrating the use of high ionic strength media is shown in Fig. 2. A small aliquot of a mixture of tracers of Mg(II) and Ca(II) (^{28}Mg, $T_{1/2}$ = 21 h; ^{47}Ca–^{47}Sc, $T_{1/2}$ = 4.7 d–3.4 d) in 6.0 *M* HClO$_4$–2.6 *M* HCl was added to a small column (0.25 cm^2 × 6 cm) of Dowex 50-X4 at 25°; resin of mesh size 270 to 325 was used. Effluents were analyzed by gamma spectrometry.

On elution with 6.4 *M* HClO$_4$–2.6 *M* HCl, Mg(II) appeared rapidly in the effluent with maximum concentration near 1 column volume. The band was free of calcium (and scandium) activity and was symmetrical at the flow rate used (0.3 cm/min). Ca(II) can readily be eluted with *ca.* 5 or 6 *M* HCl, *i.e.*, a medium in which it shows minimum adsorption. In the experiment portrayed in Fig. 2, elution was carried out with 5 *M* HCl. Ca(II) appeared in maximum concentration after *ca.* 1.5 column volumes; the daughter activity ^{47}Sc was slightly more retained than Ca(II) under these conditions and its elution band followed that of Ca(II) with some overlapping.

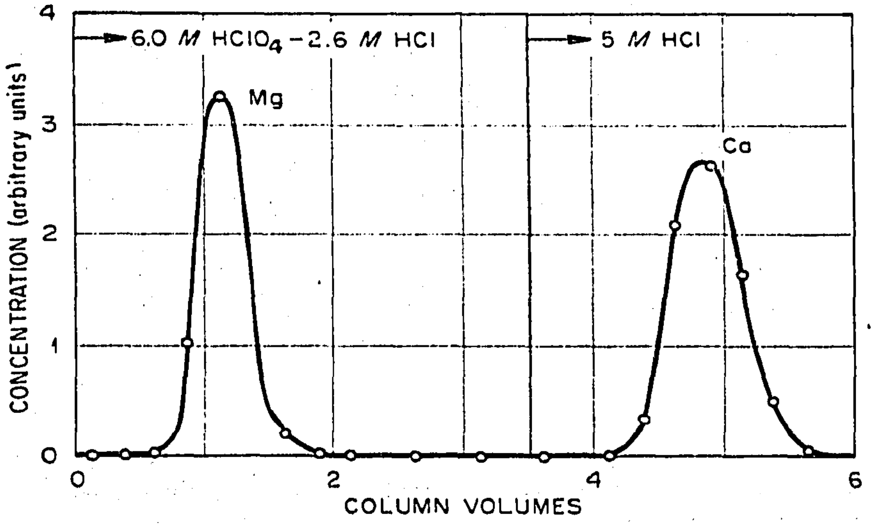

Fig. 2. High ionic strength cation exchange separation of Mg(II) and Ca(II); Dowex 50-X4, 25°, 6 cm column.

Although this separation was carried out with trace concentrations of Ca(II) and Mg(II), the method has been applied equally successfully to macro amounts (0.1 *M*) of these elements. The method should also be readily adaptable to the analysis of natural waters containing reasonable amounts of sodium chloride as well as such other ions as carbonates and sulfates.

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Notes

Chromatographic separation of *Rauwolfia serpentina* and opium alkaloids on thin layers of alumina

The chromatographic separation of alkaloids constitutes a problem that has been studied extensively. This is due above all to the wide distribution of these substances in natural materials, in which they mostly occur in low concentration accompanied by large amounts of impurities. Use has been made of paper chromatography for the separation of alkaloids, but one of the drawbacks of this method is that separation is only obtained after 5 to 12 h[1]. Moreover, the separation is not so clear specially in the case of *Rauwolfia* alkaloids. These alkaloids are located by means of ultra violet light, and ajmaline becomes visible only after spraying the developed chromatogram with sodium acetate solution[1]. In studies on the composition of complexes or crude products as regards their individual basic constituents, specially in the case of *Rauwolfia* alkaloids a need was felt for a suitable and quick method for their chromatographic analysis.

We have succeeded in achieving further progress in the chromatography of *Rauwolfia* and opium alkaloids by applying the method described by MOTTIER AND POTTERAT[2] for the separation of some synthetic fat-soluble pigments.

Materials and methods

0.5 % solutions of the following alkaloids were prepared: reserpine, serpentinine, serpentine, ajmaline, ajmalicine, morphine, narcotine, codeine and papaverine.

The *Rauwolfia* alkaloid solutions were dissolved in chloroform, narcotine in acetone, codeine, papaverine and morphine in ethyl alcohol.