

## ION-EXCHANGE PROCEDURES

## VIII. SEPARATION OF SILVER FROM A NUMBER OF ELEMENTS BY PARTITION CHROMATOGRAPHY\*,\*\*

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HANDLEY AND DEAN<sup>2</sup> reported that trialkyl thiophosphates, *e.g.* tri-iso-octyl thiophosphate (TOTP) and tri-*n*-butyl thiophosphate (TBTP) are particularly selective extractants for Ag(I) and Hg(II) in HNO<sub>3</sub> solutions. Of some 35 elements tested in HNO<sub>3</sub> solutions, only Ag(I) and Hg(II) were significantly extracted by these reagents. As a typical example of the selectivity of these compounds, HANDLEY AND DEAN<sup>2</sup> isolated Ag(I) from a fission product mixture by batch extraction. WISH AND FOTI<sup>3</sup> also used one of the reagents (TOTP) for separating tracer Ag(I) from Cd(II) and Rh(III).

It would appear that partition chromatography, wherein the extracting agent is held on a suitable supporting material in a column, should give even better separation of Ag(I) and Hg(II) from other elements than batch extraction since partition chromatography is a multiplate technique. Separations of this type have received increasing attention in recent years particularly since a variety of new water-insoluble extracting agents have become available; the field was recently reviewed by CERRAI<sup>4</sup>.

In this paper, adsorption behavior of Ag(I) on small columns of supporting materials impregnated with a tri-iso-octyl thiophosphate (TOTP)-CCl<sub>4</sub> solution is described and a procedure is presented for separating Ag(I) from many non-extractable elements. Although the method does not involve ion exchange, it is included in the present series of procedures because partition chromatography is a related technique. Also, in a separation scheme under development at this laboratory, a method was needed for separating Ag(I) from certain elements *e.g.* the alkali metals, Be, Mg, Ba, Ra, V, Cr, Mn, Ni, Cu, Al, In, Rh and Pb. Except for silver, this group of elements can be separated into smaller subgroups by an anion-exchange procedure<sup>5</sup> employing citrate solutions. In the citrate media used, silver precipitates as an insoluble Ag(I) citrate if present at appreciable concentration and behaves erratically when present at tracer concentrations, presumably because it adsorbs irreversibly on the surfaces of containers. The present procedure permits separation of macro or tracer Ag(I) from the elements of interest prior to carrying out separations in citrate media.

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\*\* For Part VII see ref. 1.

## EXPERIMENTAL

The tri-iso-octyl thiophosphate (TOTP)\* was purified by diluting the reagent approximately four-fold with  $\text{CCl}_4$  and passing the resulting solution through a column of Fisher Chromatographic grade alumina as described by HANDLEY AND DEAN<sup>2</sup>. The pure reagent has a density of 0.934 g/ml and contains 2.23 moles TOTP per l. A 0.5 M TOTP solution (22 vol. % TOTP) in  $\text{CCl}_4$  was used for distribution and separation experiments.

Of the materials tested as supports for the organic phase, microporous polyethylene (30–40 mesh)\*\* and a polyfluorocarbon, "Fluoropak" (20–80 mesh)\*\*\* seemed promising. The latter is marketed as a support for gas-liquid chromatographic applications. Small columns were prepared from sections of  $\frac{1}{4}$  in. (i.d.) polyethylene tubing about 6 in. in length. The tubing was heated, pulled to a tip on one end and a porous "Teflon" plug inserted to retain the finely divided support. The dry supports were tamped in the columns in layers 2 to 3 mm deep to form uniformly-packed beds 1 cm in length.

The dry beds were "wetted" with 0.5 M TOTP in  $\text{CCl}_4$  and centrifuged 5 min to remove excess liquid. The amount of organic solvent retained by the beds was determined from the difference in weight of the dry columns and the weight of the "wetted", centrifuged columns.

Distribution coefficients,  $D_v$  (amount of Ag(I) per liter bed/amount of Ag(I) per liter solution), were determined by the band elution method. The columns were pretreated with appropriate  $\text{HNO}_3$  solutions and small aliquots containing  $^{110}\text{Ag}$  tracer in  $\text{HNO}_3$  solution added. Elution was continued with the same  $\text{HNO}_3$  solution used in pretreating the columns. The number of column volumes (c.v.) of effluent at which  $^{110}\text{Ag}$  appeared in maximum concentration is numerically equal to  $D_v$ , after subtraction of the fractional interstitial volume of the columns. The latter depended on the degree of compaction of the support. The peak position of a typical non-adsorbed element, Cs(I), usually appeared in the region 0.1–0.3 c.v., and hence an average fractional void volume of 0.2 c.v. was assumed in computing  $D_v$  values.

Liquid-liquid extraction coefficients for Ag(I),  $E_v$  (amount per liter organic phase/amount per liter aqueous phase), were measured by equilibrating equal volumes of 0.5 M TOTP in  $\text{CCl}_4$  and aqueous  $\text{HNO}_3$  solutions containing  $^{110}\text{Ag}$  tracer. The organic and aqueous phases were analysed radiometrically for  $^{110}\text{Ag}$  and  $E_v$  was computed from these data. Most measurements were carried out at 25°; for those at 60° the solutions were equilibrated and sampled in a bath of controlled temperature.

Column separations were carried out with samples containing radioisotopes of the elements of interest in  $\text{HNO}_3$  solution, and the effluent fractions were analysed radiometrically. For those elements for which tracers were not conveniently available (Li(I), Mg(II) and Al(III)) appropriate spot tests were carried out on the effluent fractions to establish elution behavior.

Most measurements of  $D_v$  and separations were carried out at 60°. Temperature was controlled by placing the columns in a water jacket through which thermostated water was pumped.

\* From Peninsular Chem. Research Inc., Gainesville, Florida.

\*\* From E. S. B. Reeves Co., Glenside, Pennsylvania.

\*\*\* From Wilkens Instrument and Research, Inc., Walnut Creek, California.

## RESULTS AND DISCUSSION

(a) *Extraction coefficients,  $E_v$* 

The extraction coefficient,  $E_v$ , for tracer Ag(I) in 0.25 to 8 M HNO<sub>3</sub> was measured by batch extraction with 0.5 M TOTP in CCl<sub>4</sub>. For 0.25, 1.0, 4 and 8 M HNO<sub>3</sub>,  $E_v$  was 1, 2, 24 and 840 respectively, at 25°. With 4 M HNO<sub>3</sub> at 60°  $E_v$  was 9, *i.e.* extractability of Ag(I) decreases with increasing temperature at this HNO<sub>3</sub> concentration.

The extraction coefficients we observe for tracer Ag(I) are slightly higher than those reported by HANDLEY AND DEAN<sup>2</sup> for *ca.* 0.1 M AgNO<sub>3</sub> in HNO<sub>3</sub> solutions. However, our values of  $E_v$  at low M HNO<sub>3</sub> disagree by orders of magnitude with the results of WISH AND FOTI<sup>3</sup>, who observed  $E_v > 10^2$  with 20% TOTP–80% CCl<sub>4</sub> solutions and tracer Ag(I) in 1–3 M HNO<sub>3</sub> solutions. Since WISH AND FOTI did not purify the TOTP they used, the difference between our measurements and theirs may be caused by impurities in their reagent.

(b) *Support*

The choice of support for the solvent is important in partition chromatography; some of the organic and inorganic materials used and methods of impregnating the support with extracting agents are described by CERRAI<sup>4</sup>. Since Ag(I) at tracer concentrations would be less likely to adsorb irreversibly on certain organic supports than on porous inorganic materials, *e.g.* diatomaceous earth, fire brick, etc., only high non-reactive organic supports were tested such as porous polyethylene and a polyfluorocarbon, "Fluoropak". These materials have a fairly large adsorptive capacity for TOTP–CCl<sub>4</sub> solution (0.2 to 0.3 ml/ml bed) and are resistant to attack by HNO<sub>3</sub>. Presumably other similar materials such as finely-divided "Kel-F"<sup>6,7</sup> or "Corvic", a poly-(vinyl chloride–vinyl acetate) polymer<sup>8</sup>, could have been used.

Columns prepared from "Fluoropak" and porous polyethylene contained 1.1 and 0.15 g of dry support per ml bed, respectively, when compacted. In preparing the relatively small columns, it was important to compact the supports firmly. With loosely compacted columns or columns prepared by settling the material by gravity, erratic elution behavior resulted, presumably because of channelling.

Preliminary column experiments showed that elution bands for Ag(I) were extremely broad and tailed at 25° with both the "Fluoropak" and porous polyethylene supports which contained *ca.* 0.25 ml of 0.5 M TOTP per ml bed; no significant improvement resulted when a finer fraction (60–80 mesh) of the Fluoropak support was used. Elution kinetics was also unsatisfactory with more concentrated solutions (0.1 M Ag(I)). At 60°, however, the elution bands of Ag(I) were considerably sharper with both supports, presumably because of increased rates of diffusion of the Ag(I) species. Sharper elution bands and minimum tailing might be expected at even higher temperatures, but troublesome gas bubbles formed in the columns at temperatures above 60°, particularly at high HNO<sub>3</sub> concentrations. Hence most measurements of  $D_v$  and separations were carried out at 60°.

(c) *Distribution coefficients,  $D_v$* 

Typical distribution data for tracer Ag(I) are shown in Fig. 1, a semilog plot of  $D_v$  vs. M HNO<sub>3</sub>. The data were obtained at 60° by the band elution method with

a small column of 20–80 mesh "Fluoropak" impregnated with 0.5 M TOTP in  $\text{CCl}_4$  (0.26 ml/ml of bed). As shown in Fig. 1,  $D_v$  of Ag(I) increases rapidly with increasing  $\text{HNO}_3$  concentration from  $D_v = 0.6$  near 1 M  $\text{HNO}_3$  to  $D_v = 15$  near 6 M  $\text{HNO}_3$ . Similar results were found with porous polyethylene columns loaded with organic solvent approximately to the same extent. With "Fluoropak" however, the elution bands usually tailed less severely and the columns did not gas as badly and hence this material seemed preferable.

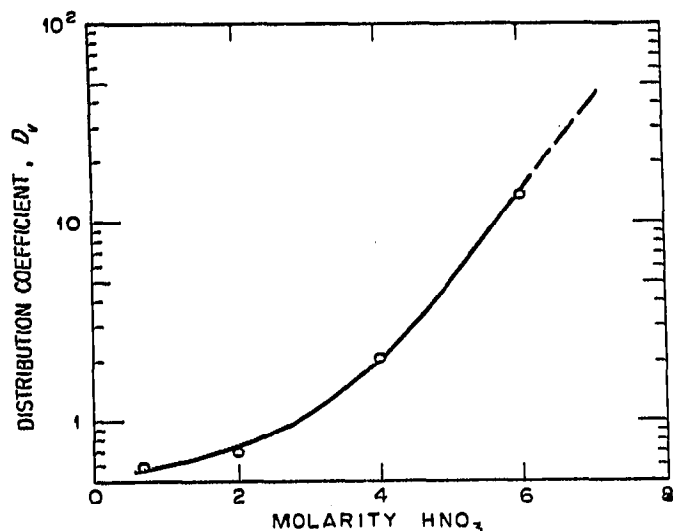


Fig. 1. Adsorption of tracer Ag(I) from aqueous  $\text{HNO}_3$  solutions (0.5 M TOTP on "Fluoropak",  $60^\circ$ ).

Where comparison can be made, distribution coefficients of Ag(I) agree with batch extraction data. At 4 M  $\text{HNO}_3$  and  $60^\circ$ ,  $D_v = 2.1$  (Fig. 1); this value corresponds to an extraction coefficient,  $E_v = 8.1$ , when correction is made for the volume fraction of solvent in the column (0.26). The extraction coefficient at the same  $\text{HNO}_3$  concentration and temperature was found to be 9.0. The difference is within experimental error.

#### (d) Typical separations

Separation of Ag(I) at "macro" concentration (0.1 M) can be achieved with small columns of TOTP on porous polyethylene or "Fluoropak". In a typical experiment, 0.1 ml of 0.1 M  $\text{AgNO}_3$ –8 M  $\text{HNO}_3$  solution containing  $^{110}\text{Ag}$  and  $^{134}\text{Cs}$  tracers was added to a "Fluoropak" column containing 0.25 ml of 0.5 M TOTP in  $\text{CCl}_4$  and which had been pretreated with 8 M  $\text{HNO}_3$ . On elution with 8 M  $\text{HNO}_3$ ,  $^{134}\text{Cs}$  was eluted in a sharp band with peak concentration near 0.2 c.v. Then Ag(I) was removed with 1 M  $\text{HNO}_3$ , a medium in which its extractability is low.

A typical column separation of Ag(I) from a number of non-adsorbed elements is shown in Fig. 2. The sample composition was:  $^{110}\text{Ag}$ (I), 0.01 M  $\text{LiNO}_3$ ,  $^{22}\text{Na}$ (I),  $^{42}\text{K}$ (I),  $^{86}\text{Rb}$ (I),  $^{134}\text{Cs}$ (I),  $^7\text{Be}$ (II), 0.005 M  $\text{Mg}(\text{NO}_3)_2$ ,  $^{133}\text{Ba}$ (II),  $^{226}\text{Ra}$ (II),  $^{49}\text{V}$ (IV),  $^{51}\text{Cr}$ (III),  $^{54}\text{Mn}$ (II),  $^{65}\text{Ni}$ (II),  $^{64}\text{Cu}$ , 0.005 M  $\text{Al}(\text{NO}_3)_3$ ,  $^{114}\text{In}$ (III),  $^{102}\text{Rh}$ (III) and  $^{210}\text{Pb}$ (II) in 8 M  $\text{HNO}_3$ . The tracers were all less than  $10^{-4}$  M in metal ion. The sample also contained decay products of  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ .

A  $0.32 \text{ cm}^2 \times 1 \text{ cm}$  column of "Fluoropak" containing 0.25 ml of 0.5 M TOTP in  $\text{CCl}_4$  per ml bed was pretreated with *ca.* 4 c.v. of 8 M  $\text{HNO}_3$  and 0.2 ml of the sample added. The column was operated at  $60^\circ$ ; on elution with 8 M  $\text{HNO}_3$ , all elements except Ag(I) appeared in the effluent in a sharp band and were completely removed in the first 5 c.v. of effluent. On treatment of the column with 1 M  $\text{HNO}_3$ , Ag(I) was removed in a band which tailed somewhat; however, *ca.* 99% of the Ag(I) was removed

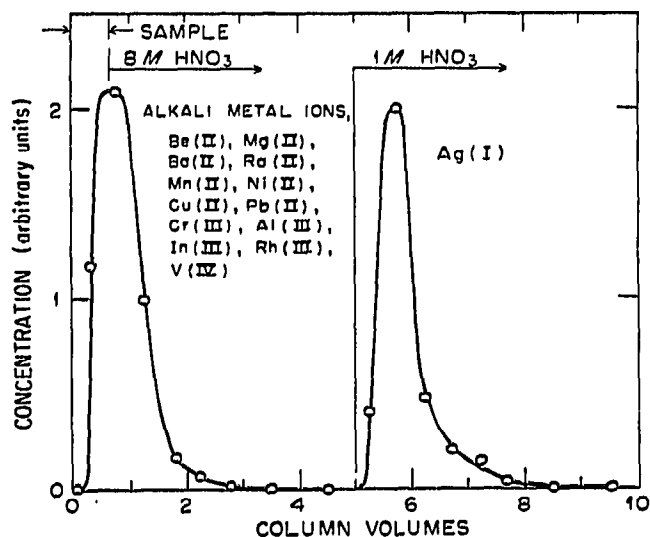


Fig. 2. Separation of Ag(I) from a number of elements by partition chromatography ( $0.32 \text{ cm}^2 \times 1 \text{ cm}$  column, 0.5 M TOTP on "Fluoropak",  $60^\circ$ ).

with 5 c.v. of 1 M  $\text{HNO}_3$ . To obtain satisfactory recovery of Ag(I), it is essential that the separation be carried out at elevated temperatures, at least with the supports used in these studies. When separation was repeated at  $25^\circ$ , the non-adsorbed elements were eluted quantitatively in a sharp band with 8 M  $\text{HNO}_3$  but only *ca.* 85% of the Ag(I) was removed with 5 c.v. of 1 M  $\text{HNO}_3$ .

## PROCEDURE

### (a) Materials and reagents

**Apparatus.** A section of plastic tubing, 0.64 cm i.d. and 12 cm in length, is used to prepare the column. The tubing is warmed, pulled to a tip at one end and a porous "Teflon" plug inserted to retain support. Other apparatus are plastic test tubes, plastic transfer pipets, "Teflon" evaporating dishes and syringes.

**Support.** "Fluoropak": 20–80 mesh.

**Extracting agent.** A 0.5 M tri-iso-octyl thiophosphate (TOTP) solution is prepared by dilution of TOTP (2.23 M) with reagent grade  $\text{CCl}_4$ . Impurities are removed by passing the solution through a column of Fisher chromatographic grade alumina.

**Column preparation.** The dry support, 20–80 mesh "Fluoropak", is packed in the column in layers 2–3 mm deep until a compact bed 1 cm in length is formed. A cylindrical glass rod, 0.6 cm in diameter, is convenient for compacting the support. The bed is "wetted" with TOTP solution and centrifuged 5 min to remove excess solvent.

**Eluents.** 8 M  $\text{HNO}_3$ , 1 M  $\text{HNO}_3$ .

*(b) Sample preparation*

The sample containing Ag(I) and non-adsorbable elements in HNO<sub>3</sub> solution is evaporated to near-dryness in a Teflon evaporating dish and taken up in 0.2 ml of 8 M HNO<sub>3</sub>.

*(c) Column operation*

The column of TOTP solution on "Fluoropak" is placed in a water jacket at 60°, pretreated with 4 c.v. of 8 M HNO<sub>3</sub>, and the sample added. Flow rate is controlled by air pressure to about 0.5 cm/min. Elution is continued with 5 c.v. (1.6 ml) of 8 M HNO<sub>3</sub>. This elutes the non-adsorbed elements. The column is then treated with 5 c.v. of 1 M HNO<sub>3</sub> (1.6 ml) to remove the Ag(I).

The column may be regenerated by treating it with 8 M HNO<sub>3</sub>. However, since the Ag(I) tails and about 1% of the Ag(I) is usually retained by the column in this procedure, a new column should be used for each separation. The column should not be allowed to remain in contact with 8 M HNO<sub>3</sub> for prolonged periods of time since TOTP is slowly decomposed by strong HNO<sub>3</sub> solutions.

The total column operation time is about 25 min.

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## SUMMARY

A procedure is described for separating silver from a number of elements by partition chromatography in nitric acid solutions. A small column of a finely divided polyfluorocarbon impregnated with a highly selective extractant for Ag(I) (tri isooctyl thiophosphate in carbon tetrachloride) is used to effect separation.

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