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THE CHROMATOGRAPHY OF METALS ON DEAE-CELLULOSE LAYERS IN PHOSPHORIC ACID MEDIA

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SUMMARY

The adsorption behaviour of forty-eight metals on DEAE-cellulose thin layers has been examined in aqueous phosphoric acid media. R_F values are given as a function of phosphoric acid concentration over the range 0.01–1.0 *M* and are compared with those obtained in a similar manner with a crystalline cellulose, Avicel SF. Particularly strong retention on DEAE-cellulose occurred for Mo(VI), W(VI), Re(VII), the platinum group metals, Au(III) and Bi(III). Weak to moderate retention was also observed for several metals, such as V(V), Fe(III), Se(IV), In(III), the rare earths and U(VI), at lower concentrations of phosphoric acid (<0.1 *M*).

INTRODUCTION

Comparatively little attention has been paid to the ion exchange of metal ions in phosphoric acid solutions. A systematic study of the analytical aspects of anion-exchange resins in phosphoric acid was undertaken by Freiling *et al.*¹, who reported the distribution of Cs, Sr, Ce(III), Ce(IV), U(VI), Np(IV), Zr, Nb, Mo(VI) and Te(IV) between Dowex 2 resin and various concentrations of phosphoric acid solutions. Further studies on the adsorption and separation of uranium on strongly basic anion-exchange resins in phosphate media have also been reported^{2,3}.

The general application of the weakly basic anion exchanger DEAE-cellulose for the sorption of metals from phosphoric acid has not been undertaken so far. The purpose of the present work was to investigate systematically the analytical potential of DEAE-cellulose for the separation of metals in phosphoric acid solutions. Thin-layer chromatography (TLC) was used with DEAE-cellulose as the adsorbent.

EXPERIMENTAL

Metal solutions of 0.1 *M* concentration were prepared as stock solutions. These solutions were mostly 1 *M* in nitric acid, but 3 *M* in nitric acid for Zr, In and Bi(III), 1 *M* in hydrochloric acid for Ru(III), Rh(III), Pd(II), Ir(IV), Pt(IV), Au(III) and Ge, and 3 *M* in hydrochloric acid for Ti(IV), Hf(IV), Sn(IV), Sb(III) and As(III). Pure aqueous solutions were prepared for V(V), Mo(VI), W(VI), Re(VII), Se(IV) and Te(IV).

A cellulose anion exchanger, DEAE-cellulose (diethylaminoethylcellulose, Serva, for TLC use) was used as the adsorbent. The DEAE-cellulose was treated with 1 *M* phosphoric acid and washed with water by centrifugation until the pH of the supernatant was 2.5. The DEAE-cellulose was then spread to a thickness of 250 μm on 20 \times 20 cm plates. The plates were dried in air for 1 h and at 40° for 3 h and stored in a desiccator over saturated potassium bromide solution. Plates of the microcrystalline cellulose Avicel SF (Avicel Sales Division, FMC Corp.) were also prepared in a similar manner.

Metal ions (0.5 μl of solution) were developed for a distance of 15 cm in rectangular glass tanks with ground-glass lids.

The solvent systems tested were aqueous phosphoric acid solutions with various concentrations (0.0103, 0.1030 and 1.030 *M* H_3PO_4). We examined 48 metals, for which the detection reagents are summarized in Table I.

TABLE I

DETECTION METHODS USED

<i>Metal</i>	<i>Spraying agent</i>
Mo(VI), W(VI), Re(VII), Ru(III), Rh(III), Pd(II), Ir(IV), Pt(IV), Au(III), Se(IV), Te(IV), Fe(III), Co(II), Ni, Cu(II), Ag(I), Hg(II), Ti(I), Pb(II), Bi(III)	10% SnCl_2 in 3 <i>M</i> HCl
Sc, Y, La, Sm, Yb, Th, U(VI), Zr, Hf	Dilute sodium sulphide solution
Mg, Ca, Zn, Cd, In	0.1% aq. Arsenazo III solution
Ge, Sn(IV), Sb(III)	2% oxine in ethanol, followed by NH_3 ; UV
V(V), Cr(III), Mn(II)	0.05% phenylfluorone in ethanol
	0.1% alkaline PAR solution, followed by 1 <i>M</i> NaOH
Nb, Ti(IV)	0.1% tannic acid solution
Sr, Ba	0.1% sodium rhodizonate solution, followed by NH_3
Be, Al	0.1% morin in ethanol; UV
Ga	0.5% Rhodamine B in 6 <i>M</i> HCl
As(III)	Saturated SnCl_2 in 3 <i>M</i> HCl, followed by 5% $\text{Na}_2\text{S}_2\text{O}_3$

RESULTS AND DISCUSSION

R_F values of 41 metals on DEAE-cellulose in aqueous phosphoric acid solutions are shown in Fig. 1 as a function of phosphoric acid concentration. For the sake of comparison R_F values of the metals on Avicel SF were measured in the same solutions and are also shown in Fig. 1. It was often difficult to detect metals developed on the plates in phosphate media. With the reagents given in Table I, the detection of Mg, Ca, Sc, Zr, Hf, Nb and Sn(IV) of the 48 metals tested was unsuccessful.

Considerable differences in adsorption between DEAE-cellulose and Avicel SF were observed for Y, the rare earths, Th, U(VI), V(V), Mo(VI), W(VI), Re(VII), Fe(III), Ru(III), Rh(III), Pd(II), Ir(IV), Pt(IV), Au(III), In(III), Bi(III) and Se (IV). These metals favour the DEAE-cellulose phase to a great extent in comparison with Avicel SF.

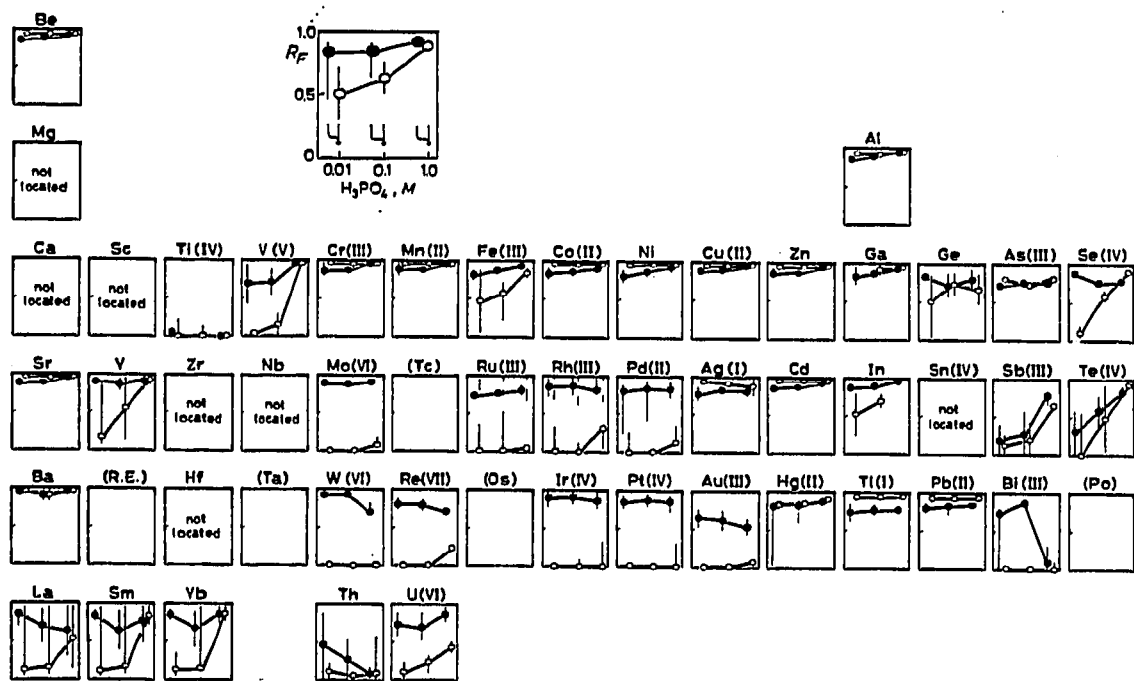


Fig. 1. R_F values of metals chromatographed on DEAE-cellulose in phosphoric acid media. O, DEAE-cellulose; ●, Avicel SF. For convenience, R_F values on Avicel SF are shifted on the abscissa arbitrarily to the left.

Most of the metals tested did not exhibit marked adsorption on Avicel SF over the concentration range tested. Only a few metals are retained to a moderate extent, including Sb(III), Te(IV), Au(III), Bi(III) and Th.

The R_F value of Ti(IV) on both Avicel SF and DEAE-cellulose is virtually zero, perhaps because of the precipitation of titanium phosphate, a known inorganic ion exchanger⁴.

Some of the metals retained on DEAE-cellulose have been reported to be adsorbed on a strongly basic anion-exchange resin. Freiling *et al.*¹ found very strong adsorption on Dowex 2 of Zr, Nb, Mo(VI), U(VI) and Np(IV) ($K_d > 1,000$) and weak adsorption of Sr, Ce(III) and Ce(IV) ($4 < K_d < 10$) at lower phosphoric acid concentrations. Cs and Te(IV) did not favour the resin phase even in 0.1 N phosphoric acid. Wish³ found that the maximum adsorption for Te(IV) occurs in 0.1 N phosphoric acid, with a K_d value of 1.3; with increasing concentration of phosphoric acid, the coefficient decreases, reaching a value of 0.4 in 16 N phosphoric acid.

Unfortunately, the behaviour of Zr and Nb could not be established in our system because of the failure to detect these metals. However, Mo(VI), U(VI) and, to a lesser extent, Te(IV), are adsorbed on DEAE-cellulose at lower concentrations of phosphoric acid, the selectivity sequence being Mo(VI) > U(VI) > Te(IV). This is in accord with that measured in the Dowex 2-phosphoric acid system.

Molybdenum(VI) forms molybdophosphate, which provided a basis for the anion-exchange separation of Mo(VI) from Re(VII) in 2 M phosphoric acid with

Anionite EDE-10 (ref. 5). Extractable ion-association complexes of molybdophosphate and basic dyes have also been reported⁶. Like Mo(VI), the formation of heteropolyacids of W(VI), V(V), Nb, Ta and U(VI) has also been described⁷. The adsorption behaviour of some of these metals on DEAE-cellulose as well as on Dowex 2 is therefore considered to be due to the formation of heteropoly-acids with phosphorus as the hetero-atom.

In accordance with evidence on the formation of anionic phosphato complexes⁸, the rare earths, Th, Fe(III), Ir(IV), In and Bi(III) exhibit adsorption on DEAE-cellulose from phosphoric acid solutions.

Little is known about the phosphato complexes of the platinum group metals other than those of Ir(IV) and Au(III). It is likely that these metals are adsorbed on DEAE-cellulose by anion exchange of their chloro complexes, which are present in their stock solutions, because they are adsorbed strongly on to DEAE-cellulose from dilute hydrochloric acid solutions^{9,10}. Because Hg(II) is also adsorbed strongly on to DEAE-cellulose from dilute chloride⁹ or thiocyanate media¹¹, sufficiently to permit its column separation¹², we examined the adsorption behaviour of Hg(II) in phosphoric acid media to see whether the R_F value varies with the type of acid used for the preparation of the stock solutions. The results obtained are given in Table II. It can be seen that when Hg(II) is in hydrochloric acid solution, it is partially retained near the start, but most of it migrates upwards, with an R_F value similar to that in nitric acid. This result suggests that the adsorption of the platinum group metals and perhaps of Au(III) may be largely controlled by the ion exchange of some complexes involving phosphate, although a partial contribution of chloro complexes from the stock solutions must also be taken into account. Similarly, we obtained R_F values of 0.10 and 0.09 for Th with DEAE-cellulose in 0.010 *M* phosphoric acid, when it was contained in 1 *M* nitric acid and 1 *M* hydrochloric acid, respectively. In this instance there is nothing to indicate the significance of the type of acid used, although Th is retained strongly on DEAE-cellulose columns from nitric acid-methanol media, thus permitting column separation¹³.

TABLE II

VARIATION OF R_F VALUES OF Hg(II) ON DEAE-CELLULOSE IN PHOSPHORIC ACID MEDIA WITH THE TYPE OF ACID USED FOR THE PREPARATION OF STOCK SOLUTIONS

Stock solution	H_3PO_4 concentration (<i>M</i>)		
	1.0	0.10	0.010
HNO ₃ (1 <i>M</i>)	0.92	0.88	0.84
HCl (0.1 <i>M</i>)	0.26, 0.66	0.10, 0.76	0.04, 0.67

Even though the behaviour of several metals on DEAE-cellulose could not be determined in the present study, it is evident that phosphate media will prove useful in TLC and probably also in the column chromatography of some metals. Several TLC separations were conducted on DEAE-cellulose in 1.0 *M* phosphoric acid:

Re(VII) (0.17–0.28)–Mn(II) (0.97–1.0)

Mo(VI) (0.12–0.28)–U(VI) (0.51–0.67)

Pd(II) (0.10–0.35)–Ni(0.95–1.0)

Bi(III) (0–0.12)–Pb(II) (0.93–0.98)

The values in parentheses indicate the range of the R_F values.

The development time depended on the adsorbent and the concentration of phosphoric acid used. With 1.0, 0.10 and 0.010 M phosphoric acid, it took 4.0, 3.5 and 3.5 h, respectively, for the front to travel 15 cm on the DEAE-cellulose layer at 25°.

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