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SELECTIVE CHROMATOGRAPHIC SEPARATION OF URANIUM(VI) ON DEAE-CELLULOSE LAYERS IN DILUTE ACETIC ACID MEDIA

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SUMMARY

In dilute acetic acid solutions, U(VI) shows a useful chromatographic distribution on DEAE-cellulose layers, while most other metal ions migrate upwards to the solvent front or remain at or near the start. This chromatographic behaviour of U(VI) enables a selective method for the separation of U(VI) by thin-layer chromatography to be developed. The R_F values on DEAE-cellulose and Avicel SF are quoted for 34 metal ions as a function of acetic acid concentration in the range 1–6 M. Results for two- and three-component separations by elution with 1 M acetic acid are given in order to illustrate the effectiveness and utility of the present method.

INTRODUCTION

Uranium(VI) is strongly adsorbed on DEAE-cellulose from mixed mineral acid–acetic acid media. R_F values for U(VI) on DEAE-cellulose have been reported to be 0.15 for 8 M HNO$_3$–HOAc (1:20, v/v)[1], 0–0.04 for 1–12 M HCl–HOAc (1:20, v/v)[2], 0–0.02 for 1 M HSCN–HOAc (1:3, v/v)[3] and < 0.05 for 0.01–1 N H$_2$SO$_4$–HOAc (1:3, v/v)[4]. This chromatographic behaviour of U(VI) is considered to be the result of the adsorption on DEAE-cellulose of nitrato, chloro, thiocyanato or sulphato complexes, respectively, of U(VI), stabilized by a low dielectric constant of acetic acid[1–4].

These ion-exchange systems, however, are not always suitable for the separation of U(VI), because there are many that exhibit similar behaviour on DEAE-cellulose in these mixed solvent media.

We found that in dilute acetic acid solutions, U(VI) exhibits a useful chromatographic distribution on DEAE-cellulose layers, while many other metal ions migrate upwards to the solvent front or remain at or near the start. This chromatographic behaviour of U(VI) provided the basis for its selective separation from a number of metals by thin-layer chromatography.

Some information is available on the separation of uranium by thin-layer chromatography[5–14]. Extraction chromatography, including thin-layer separations, of uranium has been reviewed by Brinkman[15], Shimizu and Ishikura[16] and Green[17]. Of methods previously reported, that described by Buchtela and Buchtela[8] seems to be most widely applicable with respect to the separation of uranium, allowing it

to be separated from about 50 metals. However, the eluent used was complex, consisting of hexone, tri-*n*-butyl phosphate and nitric acid.

EXPERIMENTAL

About 6 g of DEAE-cellulose (Cl⁻) (Serva, Heidelberg, G.F.R., for TLC use) was placed in a conventional column and treated with 100 ml of 0.5 M acetic acid; by this treatment, 52% of the DEAE-cellulose still remained in the chloride form. Another 6 g of DEAE-cellulose were treated in a similar manner. The combined DEAE-cellulose was slurried with 43 ml of distilled water and spread as a 250-μm layer on five 20 × 20 cm glass plates. The plates were dried in air for 1 h and then at 40° for 3 h, and were stored in a desiccator over saturated potassium bromide solution.

Thin-layer plates of microcrystalline cellulose Avicel SF (Avicel Dept., FMC Corp., Marcus Hook, Pa., U.S.A.), 250-μm thick, were also prepared and stored under similar conditions.

Metal chloride solutions (0.1 M) were prepared by dissolving the metal oxide or chloride in an appropriate concentration of hydrochloric acid, and 0.1 M Ag(I), Pb(II) and Tl(I) solutions were prepared by dissolving the nitrates in 0.1 M nitric acid. For Mo(VI), Se(IV), Te(IV), W(VI) and Re(VII), 0.1 M solutions were prepared by dissolving the sodium or ammonium salts in distilled water. The preparation of a stock solution of Nb(V) has been described earlier[2].

The metal ions (0.5 μl of solution) were developed for a distance of 15 cm in rectangular glass tanks with ground-glass lids. The solvents used were aqueous acetic acid solutions of concentrations 1.0, 2.0, 4.0 and 6.0 M.

The metal ions were detected mostly as described previously[3]. However, 2% oxine in alcohol was used for the detection of Be(II), Mg(II), Al(III), Ca(II), Ti(IV), Cr(III), Zn(II), Ga(III), Cd(II) and In(III), 0.1% 4-(2-pyridylazo)-resorcinol (PAR) in ethanol for the detection of Mn(II) and V(IV), and 10% SnCl$_2$·2H$_2$O in 3 M HCl for the detection of Ru(III).

RESULTS AND DISCUSSION

U(VI) exhibits a useful chromatographic distribution on DEAE-cellulose over the acetic acid concentration range tested (Fig. 1), which is useful with regard to its separation. Because U(VI) is not adsorbed on Avicel SF to any great extent, the chromatographic distribution of U(VI) on DEAE-cellulose can be regarded as being due to the ion exchange of a strongly anionic acetato complex of U(VI).

Although not illustrated in Fig. 1, Be(II), Mg(II), Al(III), Ca(II), Sc(III), V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) do not appear to be adsorbed on either DEAE-cellulose or Avicel SF over the acetic acid concentration range tested. In addition to these metal ions, Ga(III), Sr(II), Y(III), Cd(II), In(III), Ba(II), the rare earths, Tl(I), Pb(II) and Th(IV) are not retained on DEAE-cellulose, as can be seen in Fig. 1.

These non-adsorbable metal ions can be separated very easily from U(VI) on DEAE-cellulose over a wide range of acetic acid concentrations.

Ti(IV), Zr(IV), Sn(IV), Sb(III), Te(IV) and Bi(III) tailed markedly on both

DEAE-cellulose and Avicel SF, probably because of hydrolysis. Ru(III) and Rh(III) streaked considerably on DEAE-cellulose, but not on Avicel SF.

Van den Winkel et al.[18] have reported that Sc(III), V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Ge(IV), As(III), Y(III), Cd(II), In(III), Sn(IV), Sb(III), the rare earths and Pb(II) show an almost rectilinear distribution function on Dowex 1 in acetic acid media, which intersects the abscissa and rises steeply with increasing acetic acid concentration. This group of metal ions obviously belongs with most of the metal ions that are not adsorbed on DEAE-cellulose in dilute acetic acid solutions. An insufficient concentration of acetic acid in our DEAE-cellulose–acetic acid system perhaps results in incomplete association of these metal ions with acetate ions to form the adsorbable acetato complexes.

In contrast to the metal ions mentioned above, Nb(V), Mo(VI), Pd(II), Ag(I), W(VI), Re(VII), Ir(IV), Pt(IV), Au(III) and Hg(II) were found to be retained strongly on DEAE-cellulose layers. Therefore, separations of U(VI) and these metal ions are feasible over a wide range of acetic acid concentrations.

Regarding the retention of Hg(II) and ions of the precious metals, there is a strong possibility that their adsorptions are caused by the ion-exchange of their chloro complexes, because these metal ions, except Ag(I), were applied to DEAE-cellulose (half in the chloride form) layers from hydrochloric acid solutions. In addition, Lederer and Ossicini[19] have already demonstrated that Pd(II), Os(IV), Ir(IV), Pt(IV), HAuCl$_4$, Hg(II), etc., are strongly retained on DEAE-paper in dilute hydrochloric acid solutions. Therefore, in order to establish the contribution of chloro complexes, Hg(II) was applied from both 0.1 M hydrochloric acid and 1 M nitric acid to the DEAE-cellulose layers, which had been carefully prepared in the acetate form, completely free of chloride. Hg(II) was chosen because the other precious metal ions, except Ag(I), are unstable in nitric acid solutions. R_F values obtained are given in Table I, in which the effect of the form of DEAE-cellulose on the R_F value is also illustrated for Ag(I) and Bi(III). Evidently, Hg(II) is not retained when the DEAE-cellulose is completely in the acetate form and the Hg(II) is in nitric acid solution. When the Hg(II) is in hydrochloric acid and the DEAE-cellulose is in the mixed chloride–acetate form, it is retained close to the start. Similarly, Ag(I)

TABLE I

VARIATION OF R_F VALUES WITH THE TYPE OF ACID USED FOR THE PREPARATION OF STOCK SOLUTIONS AND THE FORM OF DEAE-CELLULOSE

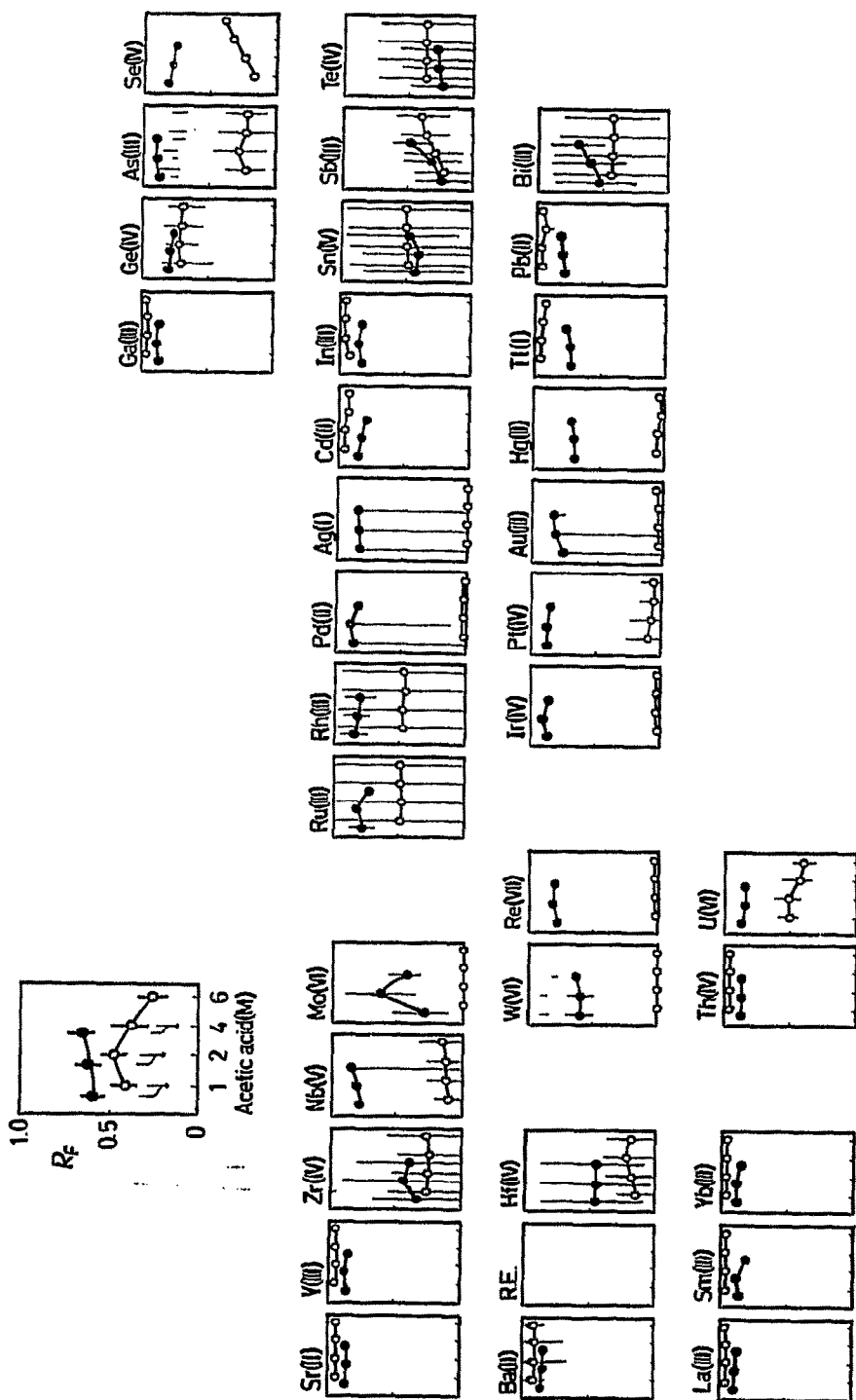| Metal ion	Form of DEAE	Stock solution	Acetic acid (M)			
			1.0	2.0	4.0	6.0
Hg(II)	OAc⁻	1 M HNO₃	0.63–0.79	0.66–0.83	0.70–0.87	0.69–0.84
	OAc⁻	0.1 M HCl	0.06–0.70	0.03–0.65	0.03–0.74	0.02–0.70
	Cl⁻/OAc⁻	0.1 M HCl	0.0 –0.14	0.0 –0.13	0.0 –0.07	0.0 –0.11
Ag(I)	OAc⁻	0.1 M HNO₃	0.0 –0.43	0.0 –0.52	0.0 –0.45	0.0 –0.50
	Cl⁻/OAc⁻	0.1 M HNO₃	0.0 –0.04	0.0 –0.05	0.0 –0.04	0.0 –0.06
Bi(III)	OAc⁻	3.0 M HCl	0.0 –0.89	0.0 –0.89	0.0 –0.90	0.0 –0.86
	Cl⁻/OAc⁻	3.0 M HCl	0.0 –0.88	0.0 –0.87	0.0 –0.84	0.03–0.80

Fig. 1. R_F values of metals chromatographed on DEAE-cellulose (OAc^-/Cl^-) and Avicel SF in acetic acid media. O, DEAE-cellulose; ●, Avicel SF. For convenience, the R_F values on Avicel SF are shifted on the abscissa arbitrarily to the left.

migrates upwards to about $R_F = 0.5$ with tailing when the DEAE-cellulose is in the acetate form. For Bi(III) there is no indication of the significance of the form of the DEAE-cellulose.

Based on these observations, the apparent strong adsorption of Pd(II), Ag(I), Ir(IV), Pt(IV), Au(III) and Hg(II) on DEAE-cellulose can be attributed to the adsorption of their chloro complexes and the precipitation of Ag(I) (Fig. 1).

Similar observations have been reported in the Dowex 1–acetic acid system for the adsorption of the platinum group metals (via chloro complexes), Zr(IV), Hf(IV) and Ta(V) (fluoro complexes) and Tl(III) and Bi(III) (nitrato complexes)[18], indicating the significance of the type of acid used for the preparation of stock solutions.

In order to obtain good separations of U(VI) and metal ions such as Pd(II), Ir(IV), Pt(IV), Au(III) and Hg(II), the sample mixtures should be prepared in hydrochloric acid and the DEAE-cellulose should be in the mixed chloride–acetate or, perhaps, the chloride form.

TABLE II

SEPARATIONS ON DEAE-CELLULOSE

Metal ions separated (R_F) *	HOAc eluent concentration (M)
U(VI) (0.44–0.60)–Sc(III) (0.94–0.98)	1.0
U(VI) (0.41–0.57)–V(IV) (0.92–0.96)	1.0
U(VI) (0.43–0.60)–Fe(III) (0.93–0.99)	1.0
U(VI) (0.42–0.59)–Ni(II) (0.95–1.0)	1.0
U(VI) (0.41–0.56)–Zn(II) (0.96–1.0)	1.0
U(VI) (0.42–0.58)–Ga(III) (0.94–0.98)	1.0
U(VI) (0.54–0.69)–As(III) (0.13–0.43; 0.76–0.86)	1.0
U(VI) (0.25 . . . 0.42–0.55)–Se(IV) (0.18–0.28)	1.0
U(VI) (0.42–0.58)–Sr(II) (0.96–0.98)	1.0
U(VI) (0.48–0.62)–Y(III) (0.95–0.99)	1.0
U(VI) (0.33–0.48)–Nb(V) (0.0–0.17)	1.0
U(VI) (0.43–0.59)–Pd(II) (0.0–0.04)	1.0
U(VI) (0.40–0.57)–Ag(I) (0.0–0.02..0.08)	1.0
U(VI) (0.40–0.56)–Cd(II) (0.94–0.98)	1.0
U(VI) (0.48–0.60)–In(III) (0.94–0.98)	1.0
U(VI) (0.42–0.58)–Ba(II) (0.94–0.98)	1.0
U(VI) (0.43–0.59)–Re(VII) (0.0–0.06)	1.0
U(VI) (0.45–0.61)–Ir(IV) (0.0–0.08)	1.0
U(VI) (0.43–0.58)–Pt(IV) (0.0–0.02..0.32)	1.0
U(VI) (0.43–0.61)–Au(III) (0.0–0.03)	1.0
U(VI) (0.42–0.56)–Hg(II) (0.0–0.10)	1.0
U(VI) (0.43–0.59)–Tl(I) (0.94–0.97)	1.0
U(VI) (0.42–0.58)–Pb(II) (0.94–0.97)	1.0
Mo(VI) (0.0–0.03)–U(VI) (0.53–0.66)–La(III) (0.96–1.0)	1.0
Hf(IV) (0.0–0.25)–U(VI) (0.46–0.61)–Th(IV) (0.94–0.97)	1.0
Hg(II) (0.0–0.09)–Cd(II) (0.94–0.97)	1.0
Au(III) (0.0–0.07)–Se(IV) (0.32–0.42)–Cu(II) (0.95–0.97)	4.0

* . . represents a weak streak.

Van den Winkel et al.[18] suggested that for Ag(I), Hg(II), Th(IV) and U(VI), the formation of highly stable acetato complexes is responsible for their marked adsorption on Dowex 1 from acetic acid solutions (above ca. 5 M). However, we obtained no evidence in this work to suggest the formation of adsorbable acetato complexes for Hg(II) and Th(IV) over the concentration range of acetic acid used.

Judging from the chromatographic distribution of U(VI) and the extreme behaviour of many other metal ions (Fig. 1), it seems likely that U(VI) can be separated selectively from a number of metals. Representative pairs were chosen and separated on DEAE-cellulose layers by elution with 1 M acetic acid. The results are given in Table II, in which some three-component separations are also reported. The separation of U(VI) and Se(IV) was incomplete and W(VI) was hydrolyzed when mixed with the acidic U(VI) stock solution. The other separations were achieved successfully, as expected, simply by elution with aqueous acetic acid. It required about 2 h 50 min to complete the development (solvent front 15 cm high).

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