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ANION-EXCHANGE SEPARATION OF GOLD ON DEAE-CELLULOSE IN ACETIC ACID–HYDROCHLORIC ACID MEDIA

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SUMMARY

Gold(III) is strongly retained on DEAE-cellulose columns from acetic acid–hydrochloric acid mixtures. The distribution coefficients of gold(III) on DEAE-cellulose are given as functions of both acetic acid and hydrochloric acid concentrations. The adsorption becomes enhanced to a great extent in the mixed acid media as compared with those in aqueous hydrochloric acid media, reaching a distribution coefficient of 500 in acetic acid–0.5 *M* hydrochloric acid (9:1). The ion-exchange system allows separation of gold(III) from large quantities of many other metals on a short column. Results of the separation and determination of gold in an anode slime consisting of a complicated matrix are included.

INTRODUCTION

The weakly basic anion-exchanger DEAE-cellulose allows a limited number of metals to be adsorbed from aqueous mineral acid media[1–5]. Introduction of a protic solvent like methanol or acetic acid has been found to enhance the ion-exchange adsorption of chloro[6,7], nitrato[8,9] and thiocyanato[10] complexes of metals on DEAE-cellulose, permitting the development of effective chromatographic methods for these metal complexes.

We have previously reported that gold(III) can be adsorbed on DEAE-cellulose from dilute hydrochloric acid solutions[5]. However, the distribution coefficients were generally low, decreasing rapidly with increasing concentration of hydrochloric acid. This may somewhat hamper the utility of DEAE-cellulose for the separation of gold from large quantities of other metals which provide an excess of chloride ions.

We found that the adsorption of gold(III) on DEAE-cellulose could be enhanced to a great extent in mixed acetic acid–hydrochloric acid mixtures. This behaviour of gold(III) allowed us to develop an effective column chromatographic method for gold(III). The ion-exchange methods for the separation of gold(III) have been reviewed by Korkisch[11], Fritz and Millen[12], and Kuroda and Yoshikuni[5], and will therefore not be repeated here.

EXPERIMENTAL

Reagent and apparatus

DEAE-cellulose. DEAE-cellulose (Selectacel, 0.84 mequiv./g, Brown Co.) was obtained from Seikagaku Kogyo (Tokyo, Japan). The swollen DEAE-cellulose in the chloride form was dried at 40° for 20 h, and then stored in a desiccator over a saturated potassium bromide solution.

Stock solution of gold(III). An appropriate amount of $HAuCl_4 \cdot 4\,H_2O$ was dissolved in 1 *M* hydrochloric acid to give *ca.* 1.0 mg Au(III) per ml. The resulting solution was standardized chelometrically.

Ion-exchange column. One gram of the dried DEAE-cellulose was slurried with demineralized water and the mixture was poured into a column (1.0 cm I.D.) which was pulled to a tip and plugged with glass-wool at the outlet. Before use the column was pre-treated with *ca.* 30 ml of an acetic acid–hydrochloric acid mixture of desired composition. The resulting bed was about 6 cm long.

Determination of distribution coefficient for gold(III)

A batch equilibrium method was used to determine the distribution coefficient for gold(III). Portions of the DEAE-cellulose (0.5 g) were weighed and placed into glass-stoppered erlenmeyer flasks, which contained 20.0-ml portions of appropriate acetic acid–hydrochloric acid mixtures of varying composition and 1.00 ml of the gold(III) stock solution. The mixtures were shaken mechanically for 20 h at 25.0 ± 0.1° and then the two phases were separated by filtration. The filtrates were analyzed for gold spectrophotometrically with rhodamine B as reagent. The distribution coefficient, K_d, was calculated according to the following formula:

$$K_d = \frac{\text{amount of Au(III) in DEAE phase per gram of DEAE}}{\text{amount of Au(III) in solution phase per millilitre of solution}}$$

For lower adsorption ($K_d < 20$) an elution method was used to measure K_d. A short column containing 1 g DEAE-cellulose was used, so that the coefficient is simply given as $V_{max.} - V_i$, where $V_{max.}$ and V_i are the retention and interstitial volumes, respectively.

Column separation procedure

A 95-ml volume of acetic acid was added to 7–8 ml of sample solution, which was adjusted to be <0.5 *M* in hydrochloric acid. The nitrate was present in a concentration of less than 1 *M*. The column was pre-treated with 30 ml of the same mixture of acetic acid and hydrochloric acid as used for the sample preparation. The mixture was loaded onto the top of the column and allowed to percolate. When the sample solution reached the top of the column bed, non-adsorbable metal ions were removed by elution with about 50 ml of the acetic acid–hydrochloric acid mixture as used for sample preparation. Gold(III) was removed from the column with about 25 ml of acetone–2 *M* hydrochloric acid (9:1).

When gold(III) was accompanied by Cr(III), Fe(III), Ga(III) and/or U(VI), the latter metal(s) were eluted first as above and subsequently with 20 ml of methanol–0.1 *M* hydrochloric acid (9:1); gold(III) was then eluted with acetone–2 *M* hydrochloric acid (9:1).

With Pd(II) and/or Pt(IV) present, the gold(III) was first eluted with 50 ml of acetic acid–2 *M* hydrochloric acid (9:1), and then the platinum metals were removed with 50 ml of acetone–2 *M* hydrochloric acid (9:1).

To separate gold(III) from Te(IV), gold(III) was first eluted with 50 ml of acetic acid–2 *M* hydrochloric acid (9:1), and then Te(IV) with 25 ml of acetone–12 *M* hydrochloric acid (9:1).

A flow-rate of about 1 ml/min was used throughout. Analytical methods used for effluent analysis are listed in Table I.

TABLE I

ANALYTICAL METHODS USED

EDTA = Ethylenediaminetetraacetate; NN = 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid; PAN = 1-(2-pyridylazo)-2-naphthol; Cu–PAN = mixture of Cu-EDTA and PAN.

Ion	*Method*
Au(III)	Back-titration of liberated nickel equivalent to gold with Mn(II) in excess of EDTA, eriochrome black T indicator; traces determined colorimetrically with rhodamine B
Cu(II)	Titatration with EDTA, PAN
Al(III), Co(II), Ga(III), In(III), Ni(II)	Titration with EDTA, Cu–PAN
Mg(II), Mn(II), Zn(II)	Titration with EDTA, eriochrome black T
Cr(III)	Back-titration with Mn(II) in excess of EDTA, eriochrome black T
U(VI)	Back-titration with Th(IV) in excess of EDTA, xylenol orange
Fe(III)	Titration with EDTA, variamine blue B
Ca(II)	Titration with EDTA, NN
Pd(II)	Titration of liberated nickel equivalent to palladium with EDTA, murexide
Se(IV), Te(IV), Pt(IV)	Colorimetrically with $SnCl_2$

RESULTS AND DISCUSSION

K_d values for gold(III) on DEAE-cellulose in acetic acid–hydrochloric acid media are illustrated in Fig. 1 as functions of hydrochloric acid and acetic acid concentrations. In general the coefficient decreases with increasing concentration of hydrochloric acid at a given concentration of acetic acid. Increasing concentration of acetic acid also favours the adsorption of gold(III) to a great extent. In an acetic acid–0.5 *M* hydrochloric acid (9:1) mixture a distribution coefficient as high as 500 can easily be obtained, while in aqueous hydrochloric acid media a comparable adsorption is only found below a concentration of 0.01 *M*[5]. The addition of formic acid or methanol was also examined to improve the adsorption of gold(III), but much less effective adsorption resulted as compared with the acetic acid.

The addition of aprotic solvents such as acetone or butanol to hydrochloric

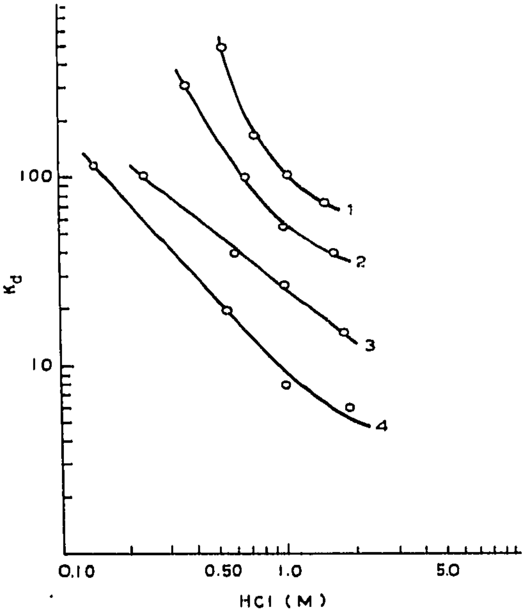

Fig. 1. Distribution coefficients for gold(III) on DEAE-cellulose as functions of hydrochloric acid and acetic acid concentrations. The HCl concentration represents that for the aqueous portion with which the acetic acid portion is mixed. Acetic acid concentrations: 1 = 90.5%; 2 = 85.7%; 3 = 76.3%; 4 = 47.6%.

acid solution resulted in a marked decrease in adsorption, the distribution coefficient for acetone/or butanol–0.14–1.45 *M* hydrochloric acid being actually zero over the organic solvent concentration range 50–90%. Based on these observations a mixture of acetone–2 *M* hydrochloric acid (9:1) was used as the effective eluent for gold(III) adsorbed on DEAE-cellulose. A similar eluent has also been used by Fritz and Millen[12] for the elution of gold(III) adsorbed on a special acrylate resin column.

As a possible ion-exchange medium other than those involving hydrochloric acid, the adsorption of gold(III) on DEAE-cellulose in the thiocyanate form from thiocyanic acid or mixed methanol–thiocyanic acid was then examined. The results are quoted in Table II. The K_d values obtained in thiocyanic acid are of the same order of magnitude as those in aqueous hydrochloric acid[5]. As can be seen, the addi-

TABLE II

DISTRIBUTION COEFFICIENTS OF GOLD(III) ON DEAE-CELLULOSE (SCN^-) IN THIOCYANIC ACID AND METHANOL–THIOCYANIC ACID MEDIA

Thiocyanic acid		*Methanol–thiocyanic acid (24:1)*	
HSCN (M)	*K_d*	*HSCN (M)*	*K_d*
0.028	318	0.028	154
0.056	150	0.056	66
0.112	76	0.112	51
0.280	45	0.280	35

tion of methanol does not facilitate the adsorption of gold(III) from thiocyanic acid.

Enhanced adsorption of gold(III) on DEAE-cellulose in mixed acetic acid–hydrochloric acid solutions may be caused by ion-exchange of its chloro complex, $AuCl_4^-$. Van den Winkel *et al.*[13] have surveyed the adsorption of 65 elements in water–acetic acid media on Dowex 1-X8 in the region 2–17 *M* acetic acid, and found the strongest adsorption ($>10^5$) with gold(III) over the acetic acid concentration range tested. Assuming that the selectivity scale of Dowex 1 was valid in moderate or even concentrated acetic acid solution, they noted that the affinity of gold(III), as well as other precious metals, is attributable to the strong adsorption of their chloro complexes originally present in their stock solutions. In contrast to the anion-exchange behaviour, gold(III) has been found not to be retained on Bio-Rad AG 50W cation-exchange resin from 1–17 *M* acetic acid media to any great extent ($K_d < 2$)[14]. Therefore, the adsorption of gold(III) on organic networks seems not to play any significant role in the retention of gold(III) in acetic acid media involving the $AuCl_4^-$ anion. With respect to cellulose anion exchanger, Lederer and Ossicini[15] demonstrated that the adsorption of many anions is mainly one of anion exchange, with a relatively small "adsorption" effect in aqueous hydrochloric acid. These observations, together with the dependence of K_d on the chloride concentration, suggest that the anion exchange of the stable $AuCl_4^-$ may therefore account for the behaviour of gold(III) in mixed acetic acid–hydrochloric acid media.

Separation

In the mixed acid media the adsorption of gold(III) is sufficiently high to allow its separation on columns: $K_d \approx 500$ in acetic acid–0.5 *M* hydrochloric acid (9:1) and $K_d \approx 300$ in acetic acid–0.4 *M* hydrochloric acid (85:15). Decreasing the concentration of hydrochloric acid will tend to improve further the adsorption of gold(III). The results for the separation of gold(III) and various foreign metal ions under varying conditions are listed in Table III. Except when the foreign metal concentration was large, quantitative separation and recovery of gold(III) were obtained. The recovery of gold(III) decreases with increasing amounts of copper(II), zinc and iron(III). This can be attributed to the increasing concentration of nitrate ions introduced with the metals which subsequently competed with gold(III) for the ion-exchange sites. In order to have a quantitative recovery of gold(III), it seems necessary to have a nitrate concentration of less than 1 *M* with respect to the aqueous portion in around 90% acetic acid media.

Chromium(III), iron(III), gallium and uranium(VI) exhibited adsorption on the DEAE-cellulose column from around 90% acetic acid media, so that they remained partly adsorbed after elution with 50 ml of acetic acid–0.05 *M* hydrochloric acid (19:1). However, the additional 20 ml of methanol–0.1 *M* hydrochloric acid (9:1) was found to be effective enough to remove the partially retained portion of them while gold(III) was kept retained tightly.

Palladium(II), platinum(IV) and tellurium(IV)[7] were adsorbed on DEAE-cellulose to a great extent. Gold(III) was allowed to pass down the column before eluting palladium(II), platinum(IV) or tellurium(IV). The chromatographic separation of copper(II), gold(III) and palladium(II) was accomplished, as illustrated in Fig. 2. As can be seen, very effective quantitative separation, without tailing, can be conducted on a 1-g DEAE-cellulose column (1.0 cm I.D.).

TABLE III

SEPARATION OF GOLD(III) FROM OTHER METAL IONS

Au(III) (mg)		*Foreign metals (mg)*			*Sample composition**		
Taken	*Found*		*Taken*	*Found*	*Vol. (ml)*	*(Cl⁻)*	*(NO₃⁻) (M)***
1.045	1.058	Al(III)	54.0	52.0	8	0.16	0.75
1.045	1.032	Ca(II)	79.4	78.3	8	0.16	0.495
1.045	1.006	Co(II)	123.5	125.4	8	0.16	0.525
1.045	1.038	Cu(II)	220.0	227.0	7	0.18	0.99
1.045	1.006		220.0	216.0	7	0.18	0.99
1.045	1.038		220.0	217.0	7	0.18	0.99
1.045	0.644		660.0	645.0	9	0.14	2.31
1.045	0.355		1100	1082	11	0.11	3.15
1.045	1.045	In(III)	116.6	116.4	8	0.16	0.63
1.045	1.045	Mg(II)	42.6	42.3	8	0.16	0.44
1.045	1.045	Mn(II)	113.6	113.3	8	0.16	0.52
1.045	1.058	Ni(II)	198.0	198.7	8	0.16	0.84
1.045	1.045	Sc(IV)	158.0	162.6	8	0.16	—
1.045	1.045	Zn(II)	150.0	149.0	7	0.18	0.65
1.045	0.555		600.0	595.0	10	0.13	1.83
1.045	0.229		1200	1198	14	0.09	2.62
1.045	0.882	Cr(III)	85.0	85.5	8	0.16	0.61
1.045	1.045	Fe(III)	97.0	96.5	8	0.16	0.65
1.045	0.980		242.5	237.0	11	0.11	1.18
1.045	0.784		485.0	482.0	16	0.08	1.63
1.045	1.025	Ga(III)	24.0	21.0	8	0.31	—
1.045	1.032	U(VI)	243.6	234.6	8	0.16	0.26
1.045	1.050	Pd(II)	3.52	3.70	8	0.29	—
1.045	1.050	Pt(IV)	15.08	14.65	8	0.24	—
1.045	1.015	Tc(IV)	2.11	2.00	7	0.26	—

* Each sample mixed with 95 ml of acetic acid and loaded.

** — indicates the absence of nitrate.

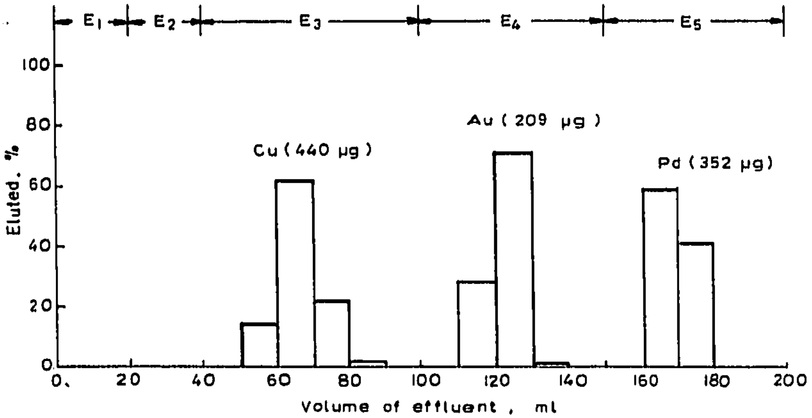

Fig. 2. Chromatographic separation of Cu(II), Au(III) and Pd(II). E_1 = Sample solution: a mixture was evaporated to dryness, taken up with 0.5 ml of *aqua regia* (HCl–HNO_3–H_2O = 4:1:1) and diluted to 25 ml with demineralized water. A 1-ml aliquot was taken, mixed with 19 ml of acetic acid and loaded; E_2 = CH_3COOH–0.05 *M* HCl (19:1); E_3 = CH_3COOH–0.5 *M* HCl (9:1); E_4 = CH_3COOH–2 *M* HCl (9:1); E_5 = CH_3COCH_3–6 *M* HCl (9:1). Column: 1.0 × 6 cm (containing 1 g DEAE-cellulose).

DETERMINATION OF GOLD IN ANODE SLIME

In order to examine the versatility of the present ion-exchange system for gold(III), an attempt was made to develop an analytical method for the separation and determination of gold in anode slime obtained in the electrolytic refinement of copper. The slime consisted of silver, lead, selenium, antimony, copper, tin and arsenic as major constituents, and bismuth, nickel and gold as minor constituents (see Table IV). Silver and lead were removed by precipitation with hydrochloric acid and sulphuric acid, respectively, and gold was subsequently separated by anion exchange on a DEAE-cellulose column in mixed acid media and determined spectrophotometrically with rhodamine B.

TABLE IV

DETERMINATION OF GOLD IN ANODE SLIME

The slime contained: Au, 0.26%; Cu, 4.94%; Ni, 0.33%; Sn, 2.30%; Sb, 5.30%; Ag, 25.85%; Se, 7.36%; Pb, 15.41%; As, 1.81%; Bi, 0.43%.

Sample taken (mg)	*Gold found (mg)*	*Gold content (%)*
51.0	0.150	0.294
50.7	0.136	0.268
51.3	0.136	0.265
		av. 0.276 ± 0.016

Procedure

About 50 mg of the slime was weighed out and placed in a beaker; 6 ml of *aqua regia* were added and the solution was heated on a hot plate. When the reaction ceased, the solution was evaporated down to about 1 ml, diluted to about 5 ml with demineralized water, and filtered through a filter paper to remove precipitated silver chloride. The precipitate was washed with small portions of 0.2 *M* hydrochloric acid; five drops of sulphuric acid (1:2) were added to the filtrate which was allowed to stand for about 3 h. After filtration and washing with water, the filtrate was evaporated nearly to dryness. The residue was moistened with *ca.* 1 ml of 6 *M* hydrochloric acid and 1 ml of water, and the solution was transferred with the aid of 18 ml of acetic acid to a column, and percolated. The column, which contained 1 g DEAE-cellulose in the chloride form (1.0 cm I.D.), was treated in advance with 30 ml of acetic acid–3 *M* hydrochloric acid (9:1), and washed with 40 ml of the same mixture, reserving all the effluents. The combined effluent was evaporated to dryness, and the residue was treated twice with a few millilitres of *aqua regia* to release the gold(III) completely. Finally, the solution was evaporated with 1 ml of hydrochloric acid, and a mixture of 5 ml of water and 95 ml of acetic acid was added to the residual syrup. The mixture was loaded on to an another 1 g DEAE-cellulose column (1.0 cm I.D.) and washed with 50 ml of acetic acid–0.05 *M* hydrochloric acid (19:1) discarding all the effluents. Gold(III) was eluted with 45 ml of acetic acid–2 *M* hydrochloric acid (9:1). An aliquot of the effluent, diluted to 50 ml, was used to determine gold colorimetrically with rhodamine B.

The analytical results obtained are indicated in Table IV. The agreement between our average result and the recommended value is satisfactory. The precision, expressed as the standard deviation, was, in comparison with the mean value of 0.276 %, relatively good.

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