# Extraction chromatography with modified poly(vinyl chloride) and di( 2-ethylhexyl)dithiophosphoric acid

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## ABSTRACT

A method for the preparation of packed-bed columns made of gelled beads is described. The stable gelled beads composed of dialkyldithiocarbamate- or dialkyldithiophosphate-substituted poly(vinyl chloride) and di(2-ethylhexyl)dithiophosphoric acid were capable of the selective separation of metal ions. The stoichiometries of $Ag^+/H^+$ and $Cd^{2+}/H^+$ extraction were established to be 3:1 and 2:1, respectively. A simple model of Ag' extraction kinetics was correlated with the experimental data. The selectivity of metal separations in displacement and elution chromatography was demonstrated.

## INTRODUCTION

Extraction chromatography, or reversed-phase chromatography, is a method in which the support, *i.e.,* bed particles in the column, holds the organic phase as the stationary phase, while the aqueous phase is the mobile phase (eluent) [1]. The organic phase contains a specific extractant which is intended to be compatible with the support particles. A number of extractant–support systems have been reported [2]. In pioneering work, Small [3] proposed that a specific extractant should be incorporated in a physically stable gelled phase embedded in the packed beds. Using this idea, beads containing tributyl phosphate as an extractant were prepared from styrene-divinylbenzene copolymers as a support. Recently, we found that di(2-ethylhexyl)dithiophosphoric acid (DTPA) can form stable gelled phases in polymeric systems [4,5]. DTPA, an analogue of di(2-ethylhexyl)orthophosphoric acid, which is widely used in extraction chromatography [6], possesses a high extraction selectivity and distinguised kinetics.

In general, dialkyldithiophosphoric acids are a well studied class of extraction reagents [7]. DTPA is used commercially in processes for the recovery of zinc and nickel from residues in the hydrometallurgical industry [8]. Cardwell and coworkers demonstrated the possibility of HPLC separations of metal mixed-ligand chelates with dialkyldithiophosphates [9] and, owing to the volatility of some chelates, the possibility of their GC determination [10,11]. Complexes of metals with dialkyldithiophosphates could be determined by TLC [12,13]. A few attempts at extraction chromatography with dialkyldithiophosphates have been reported [14,15]. Bol'shova *et al.* [14] preconcentrated metal solutions using diisopropyldithiophosphate as the stationary phase supported by poly(ethylene tetrafluoride) particles as an inert column carrier. Turanov *et al.* [15] found very high distribution coefficients of trace metal impurities between macroporous resin impregnated with DTPA and aqueous acidic solutions. Their work might have resulted in an effective extractive process if the impreg-

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nated resin had been stable. However, owing to emulsification after complexation with metals, DTPA is readily washed out of macropores, hence a reproducible loading-elution process is doubtful.

In this work, we combined the excellent extraction properties of DTPA with its ability to form gelled phases to create a new extractant–support system that can be used in packed beds. The extractant is compatible with the modified polymer, leading to gelled phases. In recent papers [5,16], we described the synthesis of modified PVC capable of forming a gel with DTPA. As silver can be extracted preferentially over all other metals [17], we decided to study the recovery of silver from photographic waste waters. The stoichiometry and the kinetics of the extraction process were evaluated.

## EXPERIMENTAL

### Preparation of column materials

Di(2-ethylhexyl)dithiophosphoric      acid (DTPA) was synthesized from 2-ethylhexanol and phosphorus pentasulphide and then purified as described elsewhere [18]. The sodium salt of dioctyldithiocarbamate (DODTC) was prepared by reacting dioctylamine with carbon disulphide in the presence of NaOH [5]. Sodium salts of DTPA or DODTC were used to modify poly-(vinyl chloride) (PVC, 43 grade; Frutarom, Israel) by nucleophilic substitution of chlorine. The experimental details of the reaction have been given elsewhere [5,16].

The formulae of the modified polymers (MP) obtained are as follows:
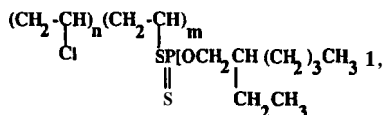


MP based on **di(2-ethylhexyl)dithiophosphate-substituted** PVC
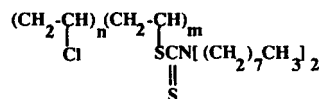


MP based on **dioctyldithiocarbamate-substituted** PVC

### Preparation of beads

#### Beads based on dioctyldithiocarbamate-substituted PVC

**System 1.** A mixture of modified polymer (MP) (S 4.9%, Cl 42.5%), PVC and DTPA in the mass ratio 1.0:2.3:3.4 was stirred in dioxane at 40°C until a clear solution was obtained. The concentration of dioxane in the solution was 83% (w/w). The viscous polymeric solution was then extruded into drops by means of a syringe and a needle into a stirred bath filled with the coagulation solution. To obtain beads of different sixes, needles of various inner diameter were used. The coagulation solution was 4% (v/v) of surfactant (polyethylene glycol, $M_w$ = 4000) in deionized water. An abrupt coagulation led to round-shaped bead formation. The coagulation solution was filtered off and the beads were dried under vacuum. The composition of the dried beads was S 7.7%, Cl 29.5%.

**System 1a.** The above mixture was dissolved in dioxane containing 5% (v/v) of dichloroethane. The concentration of the dioxane–dichloroethane mixture in the solution was 85% (w/w). The content of the beads obtained after coagulation was: S 7.2%, Cl 28.2%.

**System 2.** A mixture of MP (S 6.1%, Cl 36.6%), PVC and DTPA in the mass ratio 1.0:4.7:5.7 was stirred in dioxane as described above. The concentration of dioxane in the mixture was 81% (w/w). The composition of the resulting beads was S 8.3%, Cl 26.9%.

**System 3.** The composition of MP used was as described for system 2, PVC and DTPA were taken in the mass ratio 1.0:10.2:9.0. The resulting beads contained S 6.4%, Cl 32.9%.

#### Beads based on di(2-ethylhexyl)dithiophosphate-substituted PVC

**System 4.** A mixture of MP (S 4.10%, Cl 42.1%), PVC and DTPA in the mass ratio 1.0:0.9:1.1 was stirred in dioxane as described above. The beads contained S 7.0%, Cl 32.9%.

**System 4a.** The mixture as described in system 4 was dissolved in dioxane containing 5% (v/v) of dichloroethane. The resulting beads prepared as in system 1a contained S 6.1%, Cl 31.6%.

Blank material without any polymer modi-

fication was prepared by mixing 0.22 g of PVC and 0.22 g of DTPA in 5 g of dioxane at 40°C. Beads (S = 8.6%, Cl = 33.65%) were prepared as described above.

## Preparation of columns

A series of ion-exchange columns were prepared. Each column consisted of a polyethylene tube (I.D. 4.5 mm) closed at the end by a three-way stopcock connected to a syringe. A weighed amount (0.2-0.3 g) of beads was transferred in small increments into a column and pressed gently with a flat-ended rod to remove voids and to pack it uniformly. The bed height was set at 33-35 mm. The dried beads were preliminarily treated with 0.1 $M$ $H_2SO_4$ and then rinsed with distilled water.

## Procedure

In chromatographic experiments, an aqueous solution of the corresponding metal acetate or nitrate was passed through the resin bed (in some experiments until the breakthrough point). The percolation of the solution was then discontinued and the bed was rinsed with three bed volumes of distilled water. The solutions were eluted from the columns at room temperature at a flow-rate of 7-15 ml/min (if not stated otherwise).

Waste solutions from a photographic process were obtained from photofinisher using Kodak developers and contained 1.4 m$M$ silver, 1.3 $M$ $Na_2S_2O_3$, 0.12 $M$ $Na_2SO_3$ and 10 m$M$ NaBr. The solutions were carefully filtered before use.

Metal ion concentrations in the effluent were monitored with a Perkin-Elmer Model 5100 PC atomic absorption spectrometer, pH values were measured on a Corning Model 240 pH meter. Scanning electron microscopy (SEM) was performed on a Philips Model 50.5 scanning electron microscope using a MicroScan Tracor energy-dispersive spectroscopy attachment.

Partition measurements were made in the following manner: weighed amounts of the beads were vigorously stirred with definite volumes (10–12 ml) of metal solutions of known concentrations in tightly closed flasks in which the pH

and metal concentrations (collecting samples of 0.1 ml each) were periodically measured. In some experiments the kinetics of sorption were interrupted by separating the beads from the solution. The beads were filtered off, kept for 1 day in air-dry conditions and then replaced in the same solution.

The extent of sorption of metal ions into the resin was calculated from the difference in metal concentrations in solution before and after sorption by the resin. The sorption was also measured by stripping the sorbed metal from the resin and determining the metal concentration in the stripped solution. The metal uptake ($U$) was obtained using the equation $U = 1 - (C_t/C_\infty)$, where $C_t$ and $C_\infty$ are the concentrations of metal in the solution at a given time $t$ and at equilibrium, respectively.

## RESULTS AND DISCUSSION

### Method of preparation

Preliminary experiments were performed in order to establish the stability of the gel with the specific extractant (DTPA). Mixtures of the modified polymer and DTPA were dissolved in tetrahydrofuran (THF), resulting in clear solutions. The solutions were then dried by keeping them in a closed box containing silica gel. After drying, the resulting mixtures were checked to see if homogeneous gel was formed. Polymeric materials such as PVC, poly(vinyl acetate), diethyldithiocarbamate-substituted PVC, dibenzyldithiocarbamate-substituted PVC and their mixtures were investigated. These materials do not form gelled phases with DTPA. The gel formation was observed only when dioctyldithiocarbamate or diisooctyldithiophosphate was used to substitute chlorine in PVC. The reason for this may lie in the fact that the nucleophiles used are compatible with the extractant and chemically closely resemble one another.

Many techniques were attempted in order to obtain round, non-agglomerated beads stable in packed-column chromatography. The optimum requirements were found to be as follows: the modified polymer and DTPA should form a homogeneous solution in a specific solvent; the

solution formed from MP and DTPA should be heavier than water so that a drop will sink immediately after it enters the coagulation bath; the solvent in which MP and DTPA are dissolved should 'be completely removed from the beads during their coagulation in the aqueous solution; the surface of the beads formed should be non-"sticky"; and the beads formed should contain a large amount of DTPA in order to achieve a high capacity,.

In order to meet the above requirements, we attempted' to' use solvents giving homogeneous solutions with MP and DTPA, such as THF, dimethyl sulphoxide (DMSO), dioxane and their mixtures; Attempts to precipitate the beads from THF solution resulted in an irregular-shaped polymer precipitate floating on the water (as THF is lighter than water). On the other hand, DMSO appeared to be a poor solvent for the polymeric mixture. Dioxane was found to be an appropriate solvent. To prevent bead agglomeration, we replaced some of the MP with PVC. By doing so we lowered the MP concentration leaving the DTPA concentration constant. The resulting technique for bead preparation (see Experimental) was found to be optimum. This

approach differs substantially from conventional methods for the preparation of impregnated resins in which the beads are swollen in a solution of modifier, then washed (or dried) and micellized in water [19,20].

## Structure of the beads

Beads consisting of several polymeric systems were studied using SEM. Fig. 1 shows a typical photomicrograph of internal and external parts of the cross-cut bead composed of system 4 (see Experimental). It can be seen that the bead of about 1 mm diameter was round with a de-veloped external surface. The internal part had a well defined wall and a very friable central part. However, a cross-cut resulted in marked smooth-ing of the flexible wall. The use of a very thin needle allowed the bead to be opened without damaging the wall (Fig. 2). This illustrates the fine internal structure of the bead. Microscopic examinations suggest that the beads are actually hollow spheres or spheroid membranes.

The origin of the spheroids can be explained as follows. Viscous DTPA-containing solution being extruded through the needle shows very
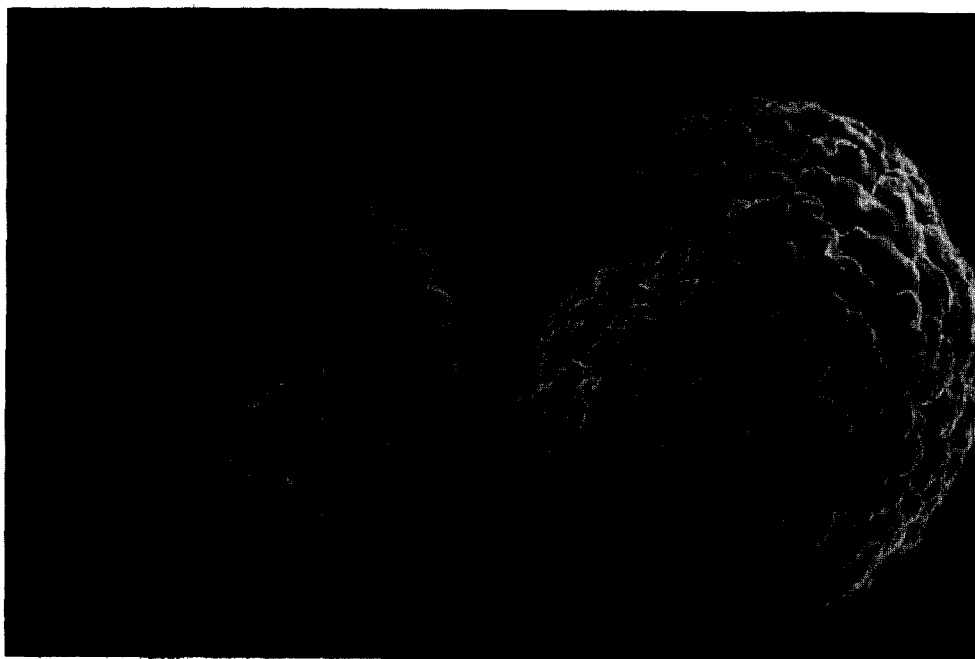


Fig. 1. External (right) and internal (left) parts of a cross-cut bead composed of system 4; magnification ×70.

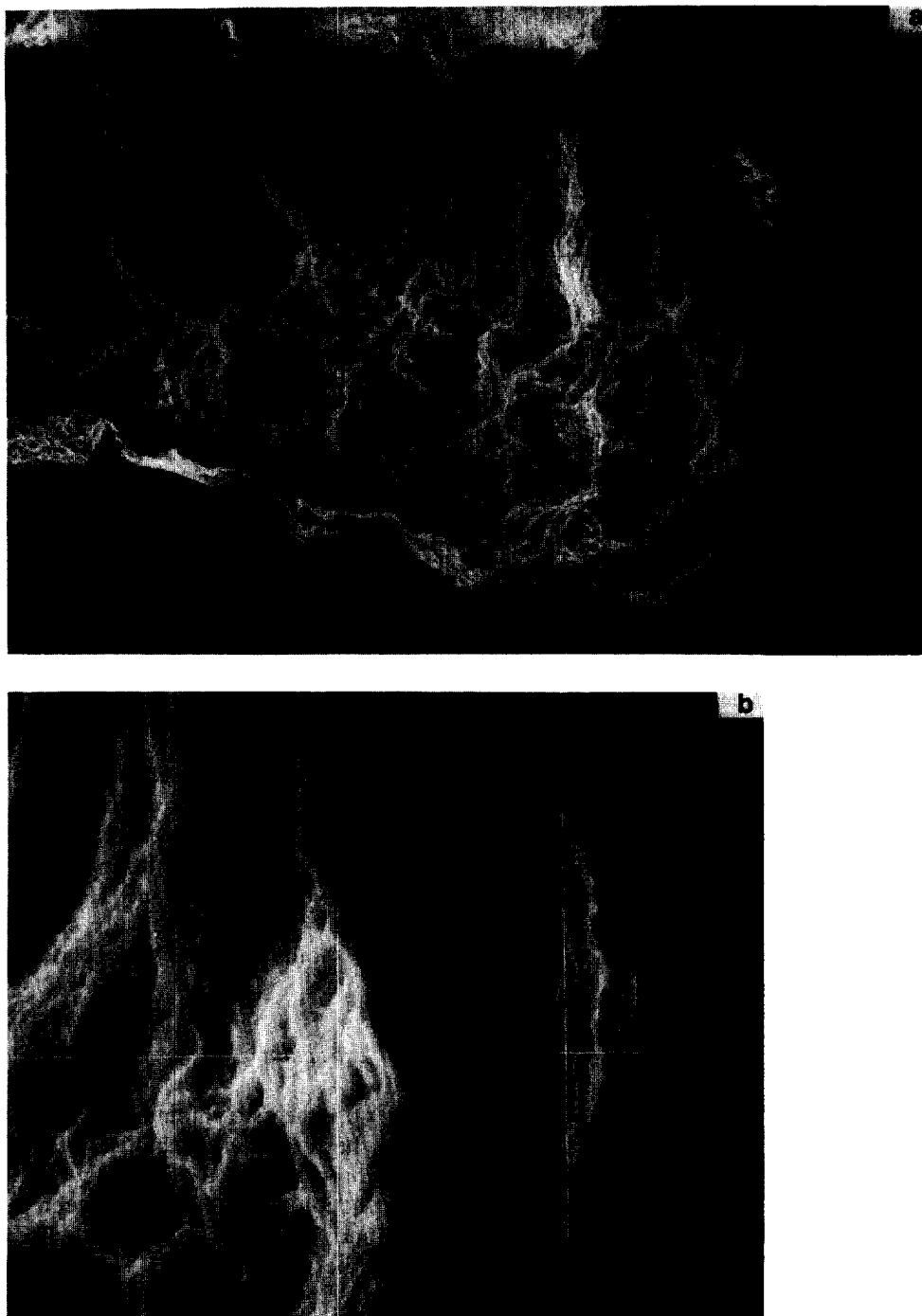**Fig. 2. Internal structure of the bead (system 4). (a) Magnification X120; (b) magnification ×1100.**

high adhesion to the walls of the needle. A hollow "tube" is formed, which on dropping into the water coagulates and produces spheres. The thickness of the wall is $10$–$20$ $\mu$m. The external surface contains small specks of the extractant (Fig. 3). SEM using energy-dispersive X-ray
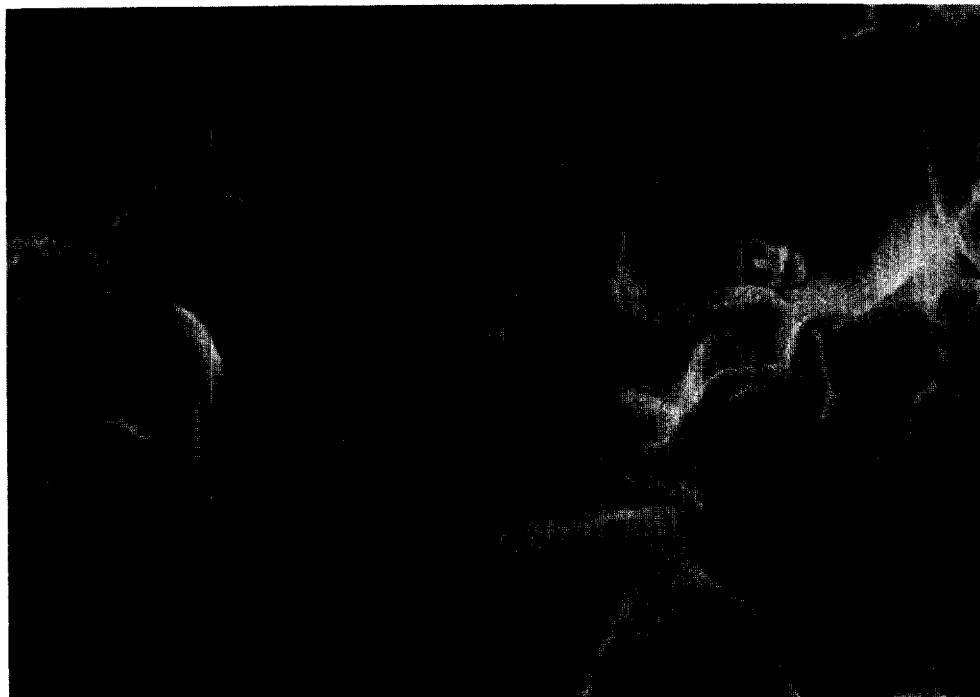
Fig. 3. External surface of a bead (system 1); magnification ×250.

analysis showed that the surface of the wall is enriched by sulphur and phosphorus and thus contains a high concentration of DTPA (Fig. 4). Addition of water-insoluble dichloroethane to the dioxane solution before the coagulation results in a more friable structure of the beads, which was also shown to contain pores (Fig. 5).

Fig. 6 shows spot analyses of silver bound to the beads kept for 48 h in 1 $M$ AgNO$_3$ solution. It can be seen that the external surface of the beads (a) contains much more silver than the
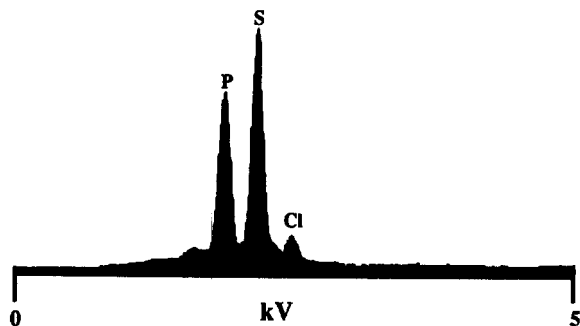


Fig. 4. Spot analysis on an external surface of a bead (system 4).

internal surface (b). Hence the extraction of the metal ions results in a thin layer of the metal ion bound to the extractant in the external wall of the beads. This layer is probably thinner than even the wall itself (i.e., <10–20 $\mu$m). Hence it can be predicted that the overall velocity of the extraction process should be only surface reaction limited.

### Stoichiometry of extraction

Consideration of the stoichiometry of the extraction yields the retention mechanism of the chromatographic process. Based on analogy with liquid-liquid extraction, the reaction between a metal ion $M^{n+}$ and DTPA adsorbed on gelled MP and PVC can be written as

$$a M^{n+}_{aq} + an HSR_{gel} \rightleftharpoons (MSR,),,,,, + an H^+_{aq} \qquad (1)$$

with an equilibrium constant

$$K = \{[(MSR_n)_{a,gel}][H^+]^{na}_{aq}/[M^{n+}]^a_{aq}[HSR]^{na}_{gel}\}_{eq}$$

$$= D[H^+]^{na}_{aq}/[HSR]^{na}_{gel} \qquad (2)$$

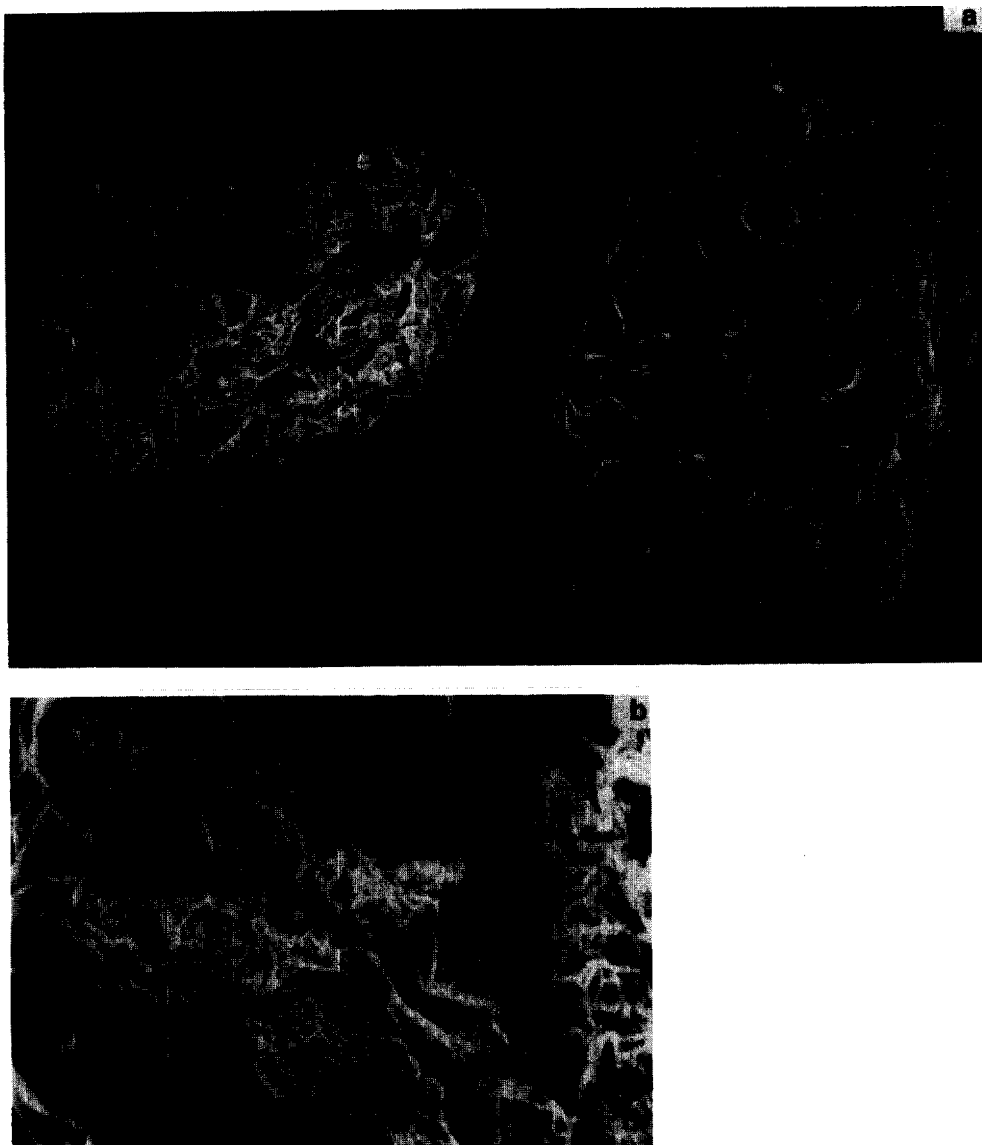where $D$ is the effective distribution coefficient

Fig. 5. (a) External (right) and internal (left) parts of a cross-cut bead composed of system 4a; magnification x95; (b) internal surface of a bead composed of system la; magnification X185.

of the metal between the beads and the aqueous phase and a is the degree of association of DTPA.

When a stripping agent (ligand) is used in aqueous solution, the $K$ value should be modified as follows:

$$K_1 = K \bigg/ \left(1 + \sum_{i=1}^{n} \beta_i c_1^i\right)$$

where $\beta_i$ is the stability constant of the metal–

ligand complex and $c_1$ is the concentration of the **ligand** .

The mechanisms of liquid extraction (reaction 1) in which DTPA participates have been investigated by a number of workers (for a review, see ref. 7). We shall limit ourselves by the extraction of silver and cadmium.

Assuming that DTPA is trimerized while contacted with silver [21], we obtain from eqns. 1 and 2 the following expression:
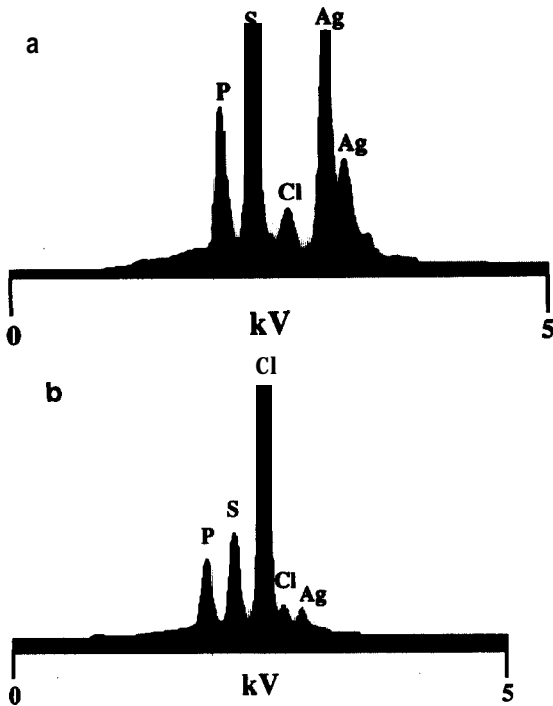
Fig. 6. Cross-section analysis of the beads (system 4) saturated by Ag. (a) Analysis of the external surface of the bead; (b) analysis of the internal surface of the bead.

$$K = D(1 + D)^2[H^+]_{aq}^3/([Ag^+]_{aq}^{in})^2[HSR]_{gel}^3 \qquad (3)$$

where $[Ag^+]_{aq}^{in}$ is the initial silver concentration in the aqueous phase set in the experiment.

It can be seen from the definition of $D$ that

$$[Ag^+]_{gel}/[Ag^+]_{aq}^{in} = D/(D + 1) \qquad (4)$$

Therefore, for a given concentration of DTPA in the beads, using eqns. 3 and 4 one can obtain the following equation:

$$\log D + 2 \log(D + 1) = -3 \log[H^+]_{aq} + \text{constant} \qquad (5)$$

Fig. 7 shows a plot of the left-hand side of eqn. 5 *versus* log(sulphuric acid concentration). $D$ was obtained by dividing the silver concentration per gram of beads by the silver concentration per gram of aqueous solution of $H_2SO_4$ containing 0.4 $M$ thiourea. Yukhin et al. [21] used solvent extraction experiments to show that thiourea is an excellent stripping agent for silver. In order to measure $D$ accurately, we lowered its value by adding thiourea to the solution. The
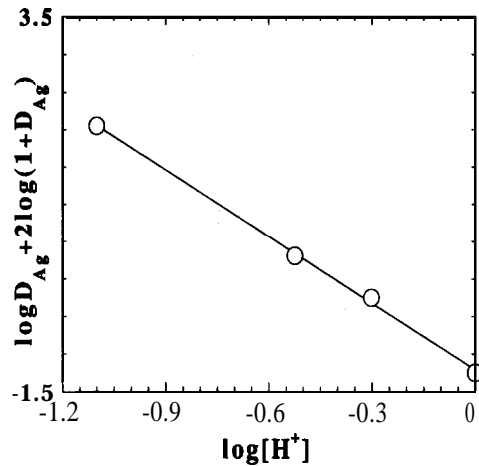


Fig. 7. Relationship between the distribution coefficient ($D_{Ag}$) for silver and $H_2SO_4$ concentration. Beads (system 3; loading 15.0 g $l^{-1}$; temperature 22°C) were equilibrated with $AgNO_3$ (initial concentration 1.0 m$M$) solutions of $H_2SO_4$ containing 0.4 m$M$ thiourea.

slope of the straight line in Fig. 7 of 2.95 fits fairly well the assumptions made in eqn. 3. These data strongly correlated with membrane transport experiments in which silver diffused through gelled phases containing DTPA and PVC [4]. The dependence of the distribution coefficient on the **DTPA** concentration in the membrane indicated trimerization of DTPA taking place in the gelled membrane phase [4].

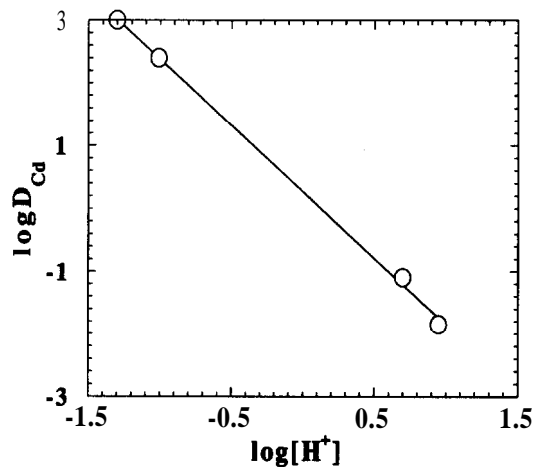It can be seen from Fig. 8 that silver can be



Fig. 8. Relationship between the distribution coefficient ($D_{Cd}$) for cadmium and HCl concentration. Beads (system 2; loading 14.0 g $l^{-1}$; temperature 20°C) were equilibrated with $Cd(NO_3)_3$ (initial concentration 0.1 m$M$) solutions of HCl.

effectively stripped from the beads by acidic solutions saturated with thiourea.

As cadmium-dialkyldithiophosphate complexes have been reported to be non-associated in dilute solutions of hydrocarbons [22], we consider the expression

$$K = D[H^+]^2_{aq}/[HSR]^2_{gel} \qquad (6)$$

to be relevant in the extraction of $Cd^{2+}$. Fig. 8 shows a **logarithmic** plot of $D$ versus the concentration of hydrochloric acid in the stripping solution. The slope is close to 2 and fits eqn. 6. A 9 *M* HCl concentration almost completely strips cadmium from the beads.

### Kinetics of extraction

Eqn. 1 can be expressed as follows:

$$3Ag^+_{aq} + 3HSR_{gel} \overset{K}{\rightleftharpoons} [(AgSR)_3]_{gel} + 3H^+_{aq} \qquad (7)$$

where $K = k_1/k_2$ is the equilibrium constant. **K** is extremely high ($2 \cdot 10^{41}$ [21]). Considering that **interruption** of the extraction process had no influence on the kinetic curves (see Experimental), we assume the process to be reaction controlled [23]. This assumption is in accordance with the SEM data showing the presence of DTPA as a thin layer on the wall of the beads (see Fig. 6).

In this case the overall reaction rate according to eqn. 7 is described by

$$\partial q / \partial t = k_1[q^3_{Ag,aq}q^3_{HSR} - (1/K)qq^3_{H,aq}] \qquad (8)$$

where $q$ is the effective DTPA-complexed silver concentration in the beads, $q_{HSR}$ is the effective concentration of DTPA in the beads, $q_{H,aq}$ is the proton concentration in the aqueous solution appearing as a result of the reaction (eqn. 7) and $q_{Ag,aq}$ is the silver concentration in the aqueous solution.

The dissociation of the silver-DTPA complex **is** negligible, so a reasonable **approximation** is

$$q_{H,aq} = q_{HSR} = q_{SH} - q;$$
$$q_{Ag,aq} = q_\infty \text{ at } 0 \leqslant r \leqslant r_0 \qquad (9)$$

where $q_{SH}$ is the effective **concentration** of the reactive SH groups in the beads, $q_\infty$ is the concentration of silver in the bead phase at

equilibrium with the silver in the bulk solution and $r_0$ is the average external radius of the beads.

Initial and boundary conditions are given as follows:

$$q_H = q_{SH}; \quad q = o; \quad t = O \qquad (10)$$

$$r = r_0 \qquad (11)$$

where $q_H$ is the proton concentration in the beads.

The fractional attainment of equilibrium is given by

$$U = q/q_{SH} \qquad (12)$$

Substituting eqns. 9 in eqn. 8, we have

$$\partial q / \partial t = k_1(q_{SH} - q)^3(Kq^3_\infty - q)/K \qquad (13)$$

Solving eqn. 13 with the use of eqns. 9-12, we obtain

$$[1/2(1 - U)^2] - [1/(KB - 1)(1 - U)]$$
$$+ [1/(KB - 1)^2]\ln[(KB - U)/K(1 - U)]$$
$$= k_1q^3_{SH}r^2_0(KB - 1)\tau/KD_e$$
$$= k_1q^2_{SH}(Kq^3_\infty - q_{SH})t/K \qquad (14)$$

where $B = q^3_\infty/q_{SH}$, $t = D_e\tau/r^2_0$ and $D_e$ is the effective diffusion coefficient of silver in the beads. Assuming $K \rightarrow \infty$, eqn. 14 becomes

$$1/(1 - U)^2 = 2k_1q^2_{SH}q^3_\infty t \qquad (15)$$

Experimental and theoretical uptake data are shown in Fig. 9. Note that the $U$ values obtained for small ($r_0 = 0.05$ mm) and large ($r_0 = 0.5$ mm) beads are almost identical. This is additional evidence for the **assumption** that the kinetics are reaction limiting. Had it been a diffusion-limiting process, we should have obtained a strong dependence of $U$ on $r_0$ [23]. *The* theoretical uptake dependence calculated using eqn. 15 is shown as a solid line. In calculations the following values were used: $q_\infty = 12.3$ mol $m^{-3}$, $q_{SH} = 700$ mol $m^{-3}$ and $k_1 = 4.2 \cdot 10^{-11}$ $m^{15}$ $mol^{-5}$ $s^{-1}$. The $q_\infty$ and $q_{SH}$ values were found experimentally and $k_1$ was calculated. It can be seen (Fig. 9) that the **experimental** and theoretical uptake data agree fairly well.
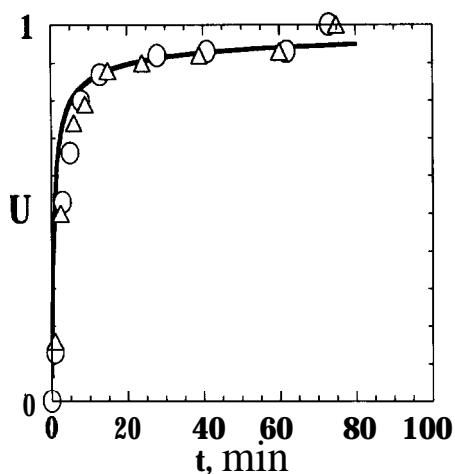
Fig. 9. Rate of uptake of silver under vigorous agitation. Initial concentration of $AgNO_3$ in water, 0.74 m$M$; initial pH, 7.2; bead loading, 14.3 g l$^{-1}$; temperature, 18°C. 0= Data obtained with the beads made of system 3, average diameter 1.0 mm; A = data obtained with the beads made of system 4a, average diameter 0.1 mm; solid line = theoretical dependence.

## *Zon separations*

Frontal separations give information about the equilibrium separation factor $\alpha$:

$$\alpha = (1 - N)n/(1 - n)N \qquad (16)$$

where N and $n$ are the mole fractions of a certain ion relative to the sum of the ions to be separated in the resin and in solution, respectively.

Value of $\alpha$ can be characteristic of the selectivity of the extraction by the beads. Figs. 10–12 show typical output curves obtained in the frontal separation of metal ion mixtures. The equilibrium degree of retention was obtained using the difference between the amounts of a certain ion entering and leaving the column:

$$N = \left[ \sum_{i}^{j} (V_i - V_v)C_{in} - \sum_{i}^{j} V_i C_i \right] \Big/ Q \qquad (17)$$

where $V_i$ is the volume of ith sample, $V_v$ is the void volume of the column estimated in the separate experiments to be 10–15% of the column volume, $C_{in}$ is the concentration of the initial solution, $C_i$ is the concentration in the ith sample, $j$ is the number of the sample after the removal of which the initial solution emerges
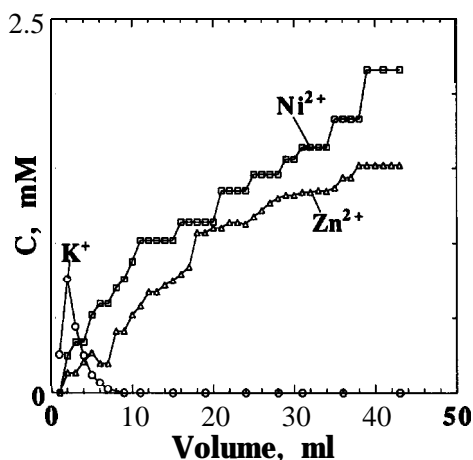


Fig. 10. Output curves obtained by displacement of K$^+$ by Ni" and Zn$^{2+}$ ion mixture. Column (beads of system 4, $r_0 = 0.05$-0.1 mm) was saturated with KNO,, then Ni(CH$_3$COO)$_2$ and Zn(CH$_3$COO)$_2$ solution was run. For initial composition of the eluent, see Table I.
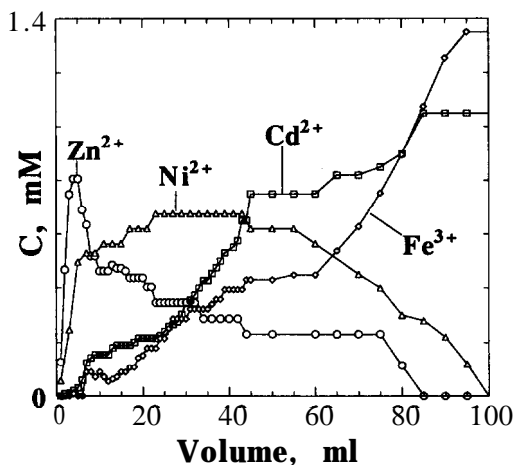


Fig. 11. Output curves obtained by displacement of Ni$^{2+}$ and Zn$^{2+}$ ton mixture in the column by Cd(CH$_3$COO)$_2$- and Fe(NO$_3$)$_3$-containing eluent. See Fig. 10 and Table I.

from the column and Q is the amount of all ions extracted by the resin on equilibration.

The main results of the experiments shown in Figs. 10–12 are given in Table I. It can be seen that the separation factor $\alpha$ is in excellent agreement with the extraction sequence of metals by DTPA [7], viz., Ag $\geqslant$ Hg > Pb > Fe(III) > Cd > Ni > Zn $\gg$ K. At equilibrium silver replaces all other metals in the column.
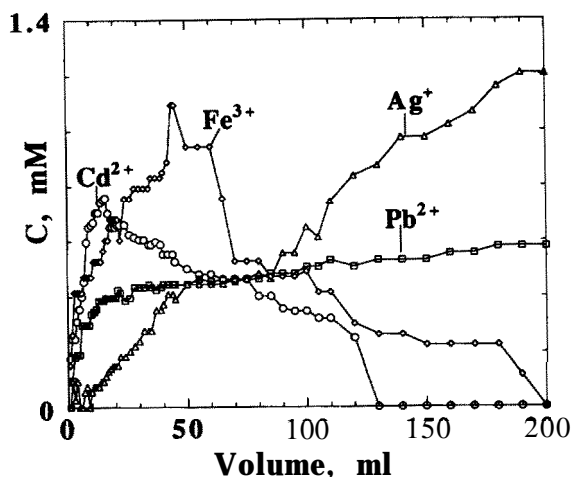
In the experiments with the blank material

Fig. 12. Output curves obtained by displacement of $Cd^{2+}$ and $Fe^{3+}$ ion mixture in the column by $Pb(CH_3COO)_2$- and $AgNO_3$-containing eluent. See Fig 11 and Table I.
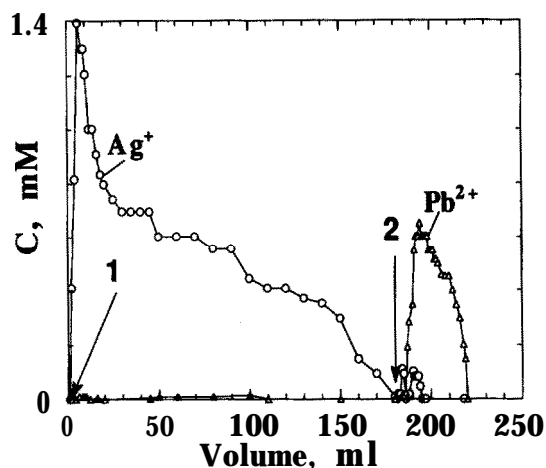


Fig. 13. Elution of Ag' and $Pb^{2+}$ from the column (see Fig. 12) by 1 $M$ $H_2SO_4$ saturated with thiourea (after arrow 1) and by 0.13 $M$ sodium ethylenediaminetetraacetate (after arrow 2).

composed of unmodified PVC and DTPA, the beads were dispersed into separated fibrils and almost entirely lost their ion-exchange capacity after the first extraction-stripping cycle. In contrast, the cation-exchange columns containing modified polymer gelled with DTPA and PVC demonstrated an ability to work satisfactorily during 20 or more extraction-stripping cycles without losing their ion selectivity. The ion-exchange capacity of the beads decreased by 20-30% during the first 5-10 cycles and then reached equilibrium. The composition of the beads after 25 cycles was S = 3–5%, Cl = 42.3-47.5%.

Figs. 13-15 illustrate the performance of the columns in elution chromatography. Fig. 13

represents the elution of $Ag^+$ and $Pb^{2+}$ from the column equilibrated in the experiment shown in Fig. 12.

Figs. 14 and 15 demonstrate the performance of the columns in the separation of micro-amounts of the metal ions. Mixtures of the corresponding cations which form strong neutral or anionic complexes were stripped off preferentially by passing through the beads eluent solutions containing the appropriate complexing anion. One cation after another could be stripped off by changing the eluent. Thus, $Ag^+$ and $Hg^{2+}$ were separated from many other metal ions by stripping with acidic solutions saturated with thiourea. The stripping sequences and conditions were found to be in accordance with

## TABLE I

### SEPARATION OF METAL IONS BY FRONTAL CHROMATOGRAPHY

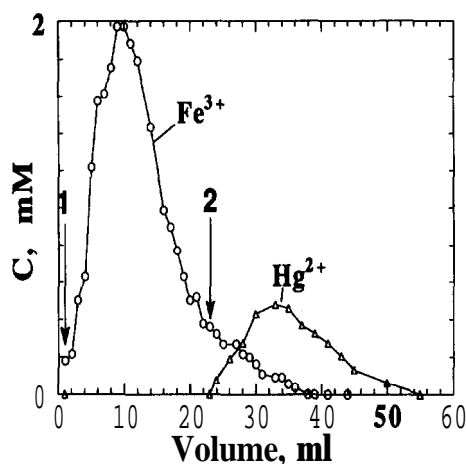| System | Metal ion | $C_{in}$ (m$M$) | $n_i$ | $N_i$ | $Q$ ($\mu$mol) | $\alpha$ |
|---|---|---|---|---|---|---|
| $Zn(CH_3COO)_2$, $Ni(CH_3COO)_2$ | $Zn^{2+}$ | 1.52 | 0.41 | 0.29 | 46.1 | 1.70 |
| [$KNO_3$] | $Ni^{2+}$ | 2.16 | 0.59 | 0.54 | | 1.23 |
| $Fe(NO_3)_3$, $Cd(CH_3COO)_2$ | $Cd^*+$ | 1.05 | 0.44 | 0.31 | 82.1 | 1.75 |
| [$Zn(CH_3COO)_2$, $Ni(CH_3COO)_2$] | $Fe^{3+}$ | 1.35 | 0.56 | 0.54 | | 1.08 |
| $AgNO_3$, $Pb(CH_3COO)_2$ | $Pb^{2+}$ | 0.58 | 0.32 | 0.09 | 68.7 | 4.76 |
| [$Fe(NO_3)_3$, $Cd(CH_3COO)_2$] | $Ag^+$ | 1.21 | 0.68 | 0.69 | | 0.95 |

Fig. 14. Elution of $Fe^{3+}$ and $Hg^{2+}$ from the column (beads of system 3) by 1 $M$ oxalate (after arrow 1) and by 1 $M$ $H_2SO_4$ saturated with thiourea (after arrow 2).
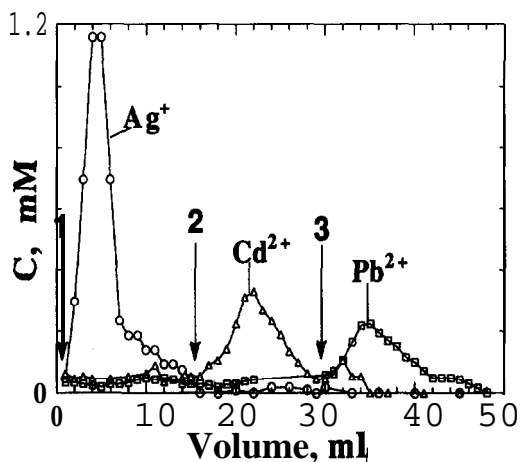


Fig. 15. Elution of $Ag^+$, $Cd^{2+}$ and $Pb^{2+}$ from the column (beads of system 1) by 1 M $H_2SO_4$ saturated with thiourea (after arrow 1), 9 $M$ HCl (after arrow 2) and 0.13 M sodium ethylenediaminetetraacetate (after arrow 3). The column was rinsed with 5-10 ml of distilled water before the eluent had to be changed. Rinsing is not shown.

the extractability of the corresponding complexes used in the stripping phases [4,16]. We hope that extraction chromatography based on the materials developed can be used for analytical purposes in the future. Obviously, DTPA with its extremely wide range of extraction constants for a variety of metal cations (from $10^{41}$ for mercury to $10^{-6}$ for $Mn^{2+}$ [24]) can be advantageously used compared with di(2-ethylhexyl)orthophosphoric acid, which possesses a much narrower

range of extractability. The disadvantages of DTPA are its unpleasant odour and its tendency to oxidize on contact with nitric or sulphuric acid [18]. These problems, however, can be overcome by the use of DTPA or even its oxidized products [25] stabilized by a gelled polymeric network.

### Recovery of silver from wash waters

Methods such as metal replacement, precipitation, ion exchange or extraction are used [26] to recover silver from dilute (1-50 $\mu M$) fixing baths after electrolytic purification. Conventionally, to recover silver from thiosulphate- and halide-containing solutions from photofinishers, a strongly basic anion-exchange resin is used. In this resin, chloride is the mobile ion and it exchanges with the silver thiosulphate to release a chloride ion while capturing the silver complex:

$$Resin\text{-}Cl + Ag_2S_2O_3^- \rightarrow Resin\text{-}Ag_2S_2O_3 + Cl^-$$
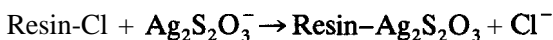
However, special efforts should be made to recover silver from the resin, which is usually burned to remove the metal, greatly increasing the expense of the process.

In order to extract silver from photographic waste waters, an extractant should possess an extremely high complexation ability. DTPA was
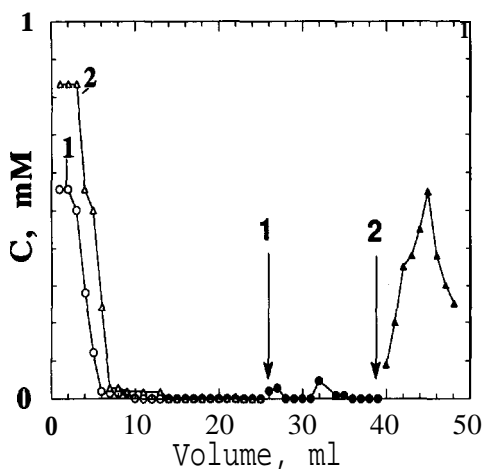


Fig. 16. Recovery of silver from aqueous solutions. Curve 1 represents the removal of silver by the beads of system 4 from $AgNO_3$ solution in distilled water and curve 2 the removal of silver from Kodak wastewater. Silver was eluted from the column by 1.3 $M$ $Na_2S_2O_3$ solution (after arrow 1) and 1 $M$ $H_2SO_4$ saturated with thiourea (after arrow 2).

found to be an excellent extractant for silver and may be embedded in a supported liquid membrane [17]. However, the membrane process has the drawback that it requires too long a time to recover silver at levels below 1-2 $\mu M$ because the driving force of the process, the membrane concentration gradient, then becomes very low, thus lowering the flow-rate through the membrane. The stability of the membrane may then become the main problem [4]. In contrast to the above method, extraction chromatography can be favourably applied, providing the possibility of recovering silver in a few cycles.

Fig. 16 demonstrates the performance of the column in the extraction and elution of silver, which was effectively removed from both $AgNO_3$ solution in deionized water (curve 1) and from Kodak waste silver solution containing sodium thiosulphate (curve 2). Then, 1.3 $M$ $Na_2S_2O_3$ solution was run through the column (after the first arrow). Virtually no silver was stripped off. In contrast, silver was effectively removed from the column by 1 $M$ $H_2SO_4$ containing 0.75 $M$ thiourea (after the second arrow).

The possibility of substantial purification of silver solutions is illustrated by Fig. 17. Curve 1 corresponds to the experiment shown in Fig. 16 (curve 1). Curve 2 in Fig. 17 represents the thorough analysis of curve 1 after the silver had

reached the ppb ($\leqslant 1$ $\mu M$) level After the first run (curves 1 and 2), the fractions containing micromolar concentrations were combined and then the solution was run again. The results of the second elution (curve 3) are compared with those for the first run (curve 2). It' can be seen that silver was removed from about 0.6 m$M$ to about 0.2-0.8 $\mu M$ in the first run and was further removed to a level of 0.1-0.5 $\mu M$ in the second run. Obviously, complete purification depends mainly on the quality of the column packing, which we believe can be improved by tightening the packing of the beads and by using smaller beads.

## CONCLUSIONS

Extraction chromatography based 'on modified poly(vinyl chloride) and di(2-ethylhexyl)-dithiophosphoric acid as a gelled phase was developed. The optimum method for the preparation of gelled beads for packed columns was elucidated. SEM investigations demonstrated that the beads obtained are spheroid: membranes. The stoichiometry of $Ag^+$ and $Cd^{2+}$ extraction was established. The kinetics of silver extraction by the beads were shown to be reaction controlled. Model considerations yielded the kinetic constant of the extraction reaction. Selective ion separations in frontal analysis 'and elution chromatography were achieved. The possibility of the use of the developed chromatographic material for the substantial purification of photographic waste waters was demonstrated.
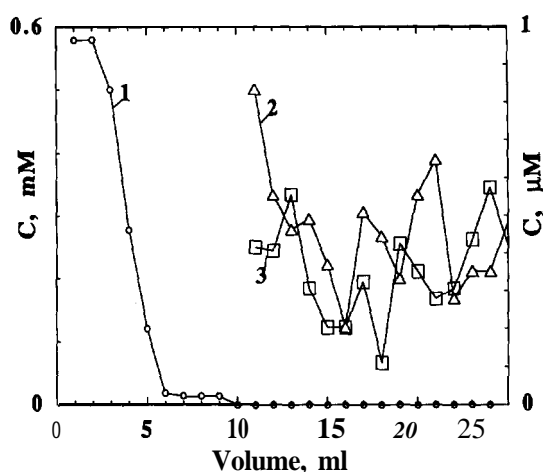
Fig. 17. Recovery of silver from aqueous solution. Curve 1 corresponds to curve 1 in Fig. 16. The rate of elution is 0.2 ml min$^{-1}$. Curve 2 represents the silver concentration in the first run below the micromolar level; curve 3 is the second run compared with the first run. For explanation, see text.

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