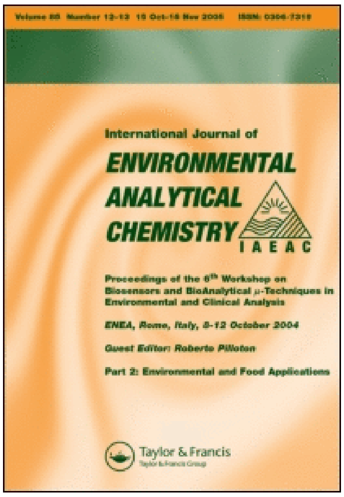

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ION EXCHANGE SEPARATION Ag(I) FROM WASTE WATERS

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In photographic industry and for preparing silver films, waste waters are rich with silver. Some of the silver is elecroanalytically regenerated, but low concentrations (0.5 $\mathrm{g\,dm^{-3}}$) stay in waste waters. In our work, we separated and concentrated the silver by ion exchange resin.

Fixing baths and stop baths are polyvalent solutions, therefore we examine synthetic solutions. For exchange of silver, Amberlit IRA – 120 and Dowex 50 × 4 were used. The batch method was used to obtain a static equilibrium. The optimum medium concentrations and the time for sorption were determined: $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ HNO_3 and 1 hour.

Silver elution from cation exchanger is based on silver transformation to a stable anion complex. Reference data determined the use of CN^- and $S_2O_3^{2-}$ for forming stable complexes. By varying the ligands, pH and eluant concentrations, optimum elution has been in 1 hour, 2 M KCN and 1 M $Na_2S_2O_3$.

KEY WORDS: Silver concentration, cation ion exchanger, silver sorption and elution.

INTRODUCTION

In photographic industry and for preparing silver film,[1] waste waters are rich in silver. Some of the silver is regenerated electroanalytically, but low concentrations 0.5 $\mathrm{g\,dm^{-3}}$ remain in waste waters.

ANS (8-amino naphtalene-2-sulphonic acid) immobilized on Amberlit A-26 transforms it into a kind of selective silver ions exchanger towers. As a result, the conditions for the selective separation of Ag(I) from the following metals: Pb, Zn, Co, Fe and Cd were in 0.05 M HNO_3.[2,3]

Dowex 2 × 9 (strong) and AG 3 × 4A (weak) exchangers were converted to oxalates by passing through 1% potassium oxalate. The sorbed Ag(I) ion was eluted with 1 M HNO_3. Sorption of Ag as oxalate on weak and strong anion exchangers has been studied.[4]

On the sulphonic cation exchanger Duolite C 263 used here, with a $AgNO_3/Cu(NO_3)_2$ mixture, silver is more strongly fixed by the resin at 15 °C than 60 °C.[5]

In our work, we separated and concentrated the silver by ion exchange resin. Fixing baths and stop baths in photography are polyvalent solutions, therefore we examine synthetic solutions. The batch method was used to obtain a static

Table 1 Parameters of silver sorption and elution

$c(HNO_3)$	D	$t(h)$	D
5.00	0.0096	24	1.2115
1.00	0.0096	12	1.2109
0.10	0.2526	6	1.2108
0.001	1.2115	3	1.2110
0.0001	1.2070	1	1.2114
H_2O	1.1067	0.5	0.9800

equilibrium. For separation of silver, Amberlite IRA - 120 and Dowex 50 × 4 were used.

EXPERIMENTAL

The conditions of silver binding and silver elution have been determined by batch method by means of synthetic solutions and silver concentrations have ranged between 10^{-1} and $10^{-5}\,\mathrm{mol\,dm^{-3}}$. Strong cation exchangers Dowex 50 × 4 and Amberlite IRA 120 polystyrene ring in H^+ forms were used. The results obtained with each of the two exchangers are identical. A great practical problem is the sensitivity of silver to light, so experiments were done in the absence of light and in infra red light.

Silver binding to a strong cation exchanger was tested in the range of 10^{-4} to $5\,\mathrm{mol\,dm^{-3}}$ of nitric acid. The dependence of silver adsorption on concentration and time are given in Table 1.

Distribution coefficient D is the measure of successful sorption or elution of silver. The greater value D means a shift of the exchange balance toward the solid phase—resin.

$$D = \frac{c(Ag)\text{ in resin}}{c(Ag)\text{ in solution}}.$$

Method: 10 ml of standard Ag(I) solution and 10 ml of the given concentrations are balanced with 0.05 g resin. This mixture is stirred for 0.5, 1, 3, 6, 12, 24 hours. After the equilibrium has been reached, silver in an aliquot is determined by titration (Volhard).

Silver elution from a cation exchanger is based on silver transformation to a stable anion complex. Reference data determined the use of CN^- and $S_2O_3{}^{2-}$ for forming stable silver complexes. The change of hydroxonium ion concentration changes the selectivity of ion exchanger,[6] and the silver is released by means of solutions of different concentrations. The resin has been converted to Ag^+ form. The resin particle size 0.1–0.2 mm, was suspended in methanol. After the methanol, a mixture of chloroform and methanol (2:3) was used for washing, followed again by pure methanol. The material was filtered and dried at 80 °C overnight. The dry ion exchanger was mixed with 5% silver nitrate solution for 24 hours. The resin was then washed with distilled water and finally with methanol. It was found that

1 ml of swelled resin corresponded to 1.8 mol of Ag^+. The ion exchanger in Ag^+ form was used recently for the separation of optical isomers.[7]

Method: Light-proof containers were filled with 0.05 g resin each, to which 25.00 ml different concentration of solutions were added by pipette (Figures 1, 2 and 3).

Equilibrium was achieved by stirring the mixture for periods of 1, 2, 6, 12 and 24 hours.

After mixing, silver was determined in aliquots by means of AAS–method. The apparatus was Perkin-Elmer 603, wavelength 328.1 μm, optic slit 0.7 and oxy-acetylene burner.

RESULTS AND DISCUSSION

The selectivity of Dowex 50×4 and the resultant distribution coefficient are influenced by the anion presence in the solution, which, together with the silver ion, makes complexes of various stability.

The difficulty in experimenting can be illustrated by pointing out cases when the data can best be explained by assuming that the resin species is not the coordinatively saturated one. One case is the silver chloride system, where the resin species is most probably $AgCl_3{}^{2-}$, although $AgCl_4{}^{3-}$ can exist in the aqueous phase. Other examples are that of silver thiosulphate where $AgS_2O_3{}^-$ seems to be the resin species, compared with $Ag(S_2O_3)_3{}^{5-}$ in the aqueous phase; and silver cyanide, where an infra-red investigation showed the predominant species in resin to be $Ag(CN)_4{}^{3-}$ predominant in solution.[8] Silver adsorbs strongly at low M HCl and distribution coefficients decrease with increasing M HCl. Adsorbability becomes negligible in concentrated HCl.

The anion exchange behaviour of Ag^+ is sufficiently unusual to permit rapid isolation of this element for most purposes in one adsorption-cycle, such as adsorption at low M HCl and elution at high M HCl. The relatively low solubility of Ag in chloride solutions does not appear to present difficulties at tracer concentrations.[9]

This implies that Ag(I) does not form undissociated complex acids to any large extent even in concentrated HCl, in agreement with the known acid insensitivity of the solubility of AgCl in chloride media. The creation of silver complexes with different ligands decreases in charge, e.g.

$$Ag^+ + Y^- \rightarrow AgY$$

and AgY connection to cation exchanger is weaker than that of Ag^+. The increased concentration of ligands changes the complex charge and it no longer binds to the cation exchanger.

$$AgY + Y^- \rightarrow [AgY_2]^-$$

The formation of negatively charged complex changes the selectivity of the exchanger according to Ag^+, i.e. the selectivity of the cation exchanger decreases.

The appearance of a negatively charged complex decreases the share of silver ions that the exchanger can bind, and this decreases the distribution coefficient (K) expressed as:

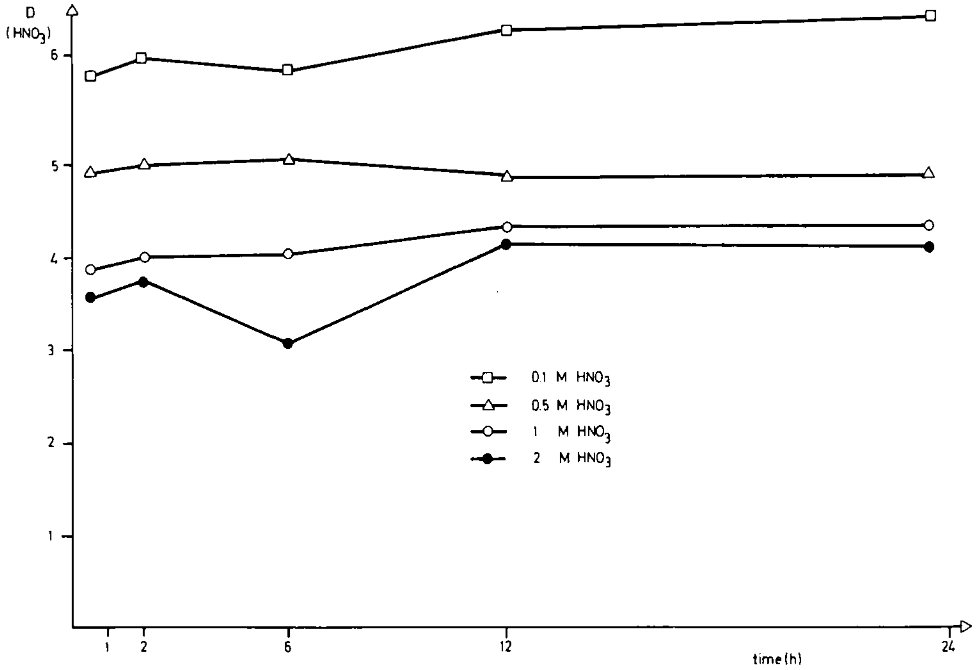

Figure 1 Variation of D with HNO$_3$ concentrations and the time.

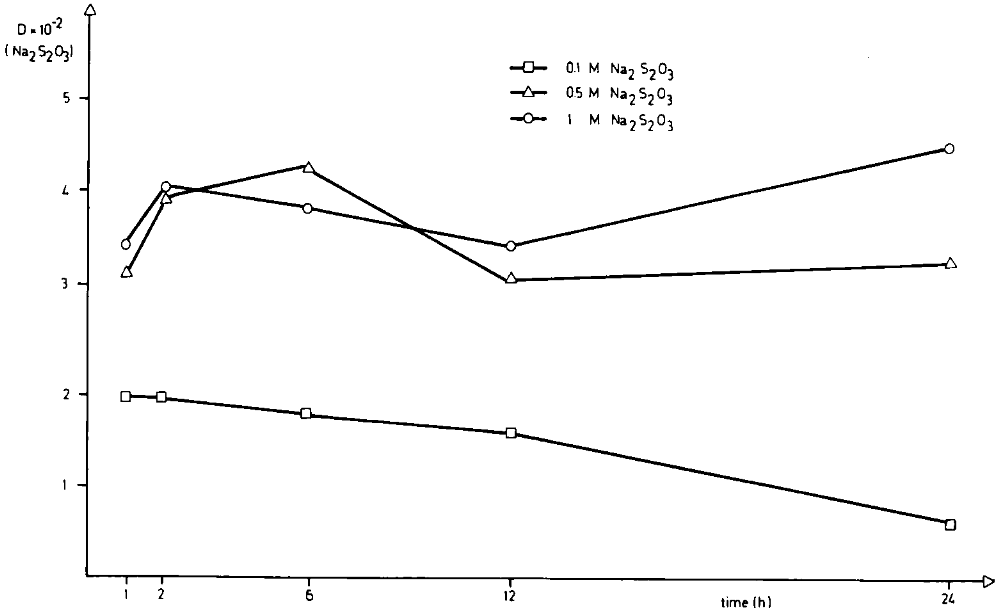

Figure 2 Variation of D with the thiosulfate concentration and the time.

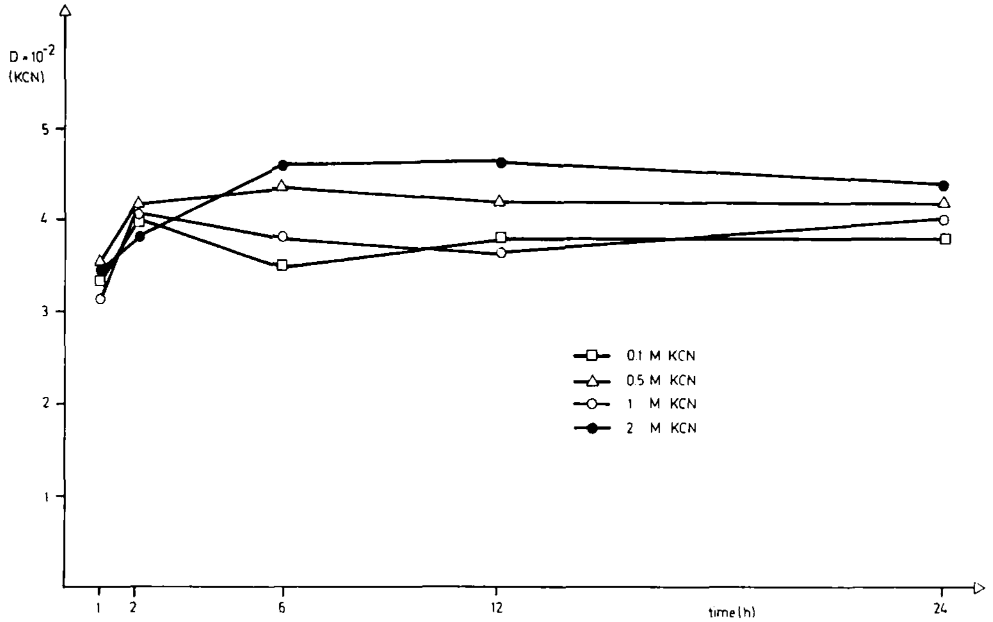

Figure 3 Variation of D with the cyanide concentrations and the time.

$$K_D = f \times \frac{(K_c Q^2)}{(A)^+ (Y)^n}$$

where:

K_c – distribution coefficient constant
Q – exchanger capacity
$(A)^+$ – cation concentration
(Y) – ligand concentration

The distribution coefficient constant depends on the concentration of the components of the complex and the stability of the new complex. In stable complexes, the K_D value decreases. The new complex ion does not bind to Dowex 50 × 4. If the ligand is also the anion of weak acid, its concentration will depend on pH solution. The change of pH solution or a change in ligand concentration (Figures 1, 2, 3) change the exchanger selectivity (D). The selectivity increases with the increase of complex ion charge and with the stability of the new complex. The change in concentration changes the concentration of new complexes in the solution, and also changes the distribution coefficient. The distribution coefficient defines the relationship between resin binded silver concentration and the total concentration of silver in the solution. Silver concentration on the resin can be very small, but can be very great in the solution if optimum elution conditions have been achieved. By varying the ligands and eluant concentrations, optimum elution has been achieved in 1 hour, as shown in Table 2.

Table 2 Distribution coefficients as a function of a media

$c(HNO_3)$ $mol\,dm^{-3}$	D	$c(KCN)$ $mol\,dm^{-3}$	D	$c(Na_2S_2O_3)$ $mol\,dm^{-3}$	D
0.1	6.0	0.1	4.00×10^{-2}	0.1	2.0×10^{-2}
0.5	5.0	0.5	3.50×10^{-2}	0.5	3.2×10^{-2}
1.0	3.8	1.0	4.24×10^{-2}	1.0	4.4×10^{-2}
2.0	3.8	2.0	4.97×10^{-2}		

The data points to the conclusion that the optimum distribution coefficient should be as small as possible, and its mathematical value about 1.

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