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# Comparison of the chelating ion exchange properties of dye coated cellulose and polystyrene substrates for the separation and determination of trace metals from aqueous media

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## Abstract

The following paper describes the comparison of a number of dye impregnated polystyrene resins and dye coated cellulose for the chelating ion exchange of metal ions. Dye loadings, capacity factors, metal adsorption capacity and selectivities were measured. The cellulose substrate was found to have a strong affinity for copper but had a very low capacity. Of the polystyrene resins, highly cross-linked macronets gave the highest metal adsorption capacities. For one of the resins, an example of a separation of a synthetic mixture of alkaline earth metals in high ionic strength media is described.

*Keywords:* Cellulose; Polystyrene; Sample treatment; Chelating agents; Dye coatings; Alkaline earth metals; Metal cations

## 1. Introduction

There are many techniques available for the analysis of trace metals in environmental samples. However, problems may be encountered when dealing with samples in "complex" matrices such as in sea-water and industrial brines. A form of pre-treatment before the analysis of trace metals is therefore required since the matrices may strongly interfere with the detection of the analytes. The matrix elimination steps which have traditionally been used to solve this problem such as solvent exchange can be laborious and also cause contamination of samples leading to erroneous results.

A commonly used technique for sample pre-treatment employs chelating ion exchange and has been known for some time [1]. Chelating column methods

have principally been used for pre-concentration and matrix elimination before the sample is analysed by techniques such as inductively coupled plasma (ICP)-MS [2]. The systems developed at Plymouth have gone a step further where pre-concentration, separation and determination can be carried out on-line in a self-contained system using a single chelating-exchange column [3]. These systems have exploited the use of physically adsorbed chelating dyes since unusual selectivities have been obtained for metal ions of interest. Studies of these physically adsorbed dyes on high-performance resins have been described previously by Jones et al. [4] and have been the precursors to investigations involving other types of dye coated substrates. Previous research by Paull et al. [5] using dye impregnated "high-performance" resins has shown that pre-concentration and gradient elution of five or more metals is possible achieving analytical quality separations.

Investigations have shown that the behaviour of

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“immobilised” chelating dyes, in some cases, is different from the behaviour of the “free” dyes in aqueous solutions. This may infer that interactions of the dyes with the substrates affect the metal chelating abilities of the functional coordinating groups. This is probably due to both steric and physicochemical effects such as dispersion forces and  $\pi$ - $\pi$  interactions between the aromatic groups in the dye and the styrene moieties of the polystyrene backbone. This of course will be different for various other substrates but factors such as the hydrophobicity and density of a substrate may affect the stability constants of chelating metal ions. Therefore, it is of particular interest to investigate a number of chelating dyestuffs immobilised on a wider range of hydrophilic and hydrophobic substrates in order to find more unusual selectivities.

Until now, studies have concentrated mainly on polystyrene-based substrates with relatively low levels of crosslinking. Recently, highly cross-linked polystyrene resins have become available. These highly cross-linked resins called “macronets” have much greater surface areas than other resins previously available and they have been little explored. Therefore, it would be very interesting to investigate dye coatings on the macronets and compare them with dye impregnated standard low cross-linked resins. The macronets are only available in large particle sizes so direct comparison with small particle size “high-performance” resins was not possible. However, the high level of cross-linking in the macronets may allow the particles to be crushed to smaller sizes. Another interesting comparison would be to investigate the properties of chelating dye coatings on very hydrophilic substrates such as cellulose. Simple physical adsorption is not possible with this kind of substrate, so chemical bonding is necessary. One simple way of achieving this is to use the same techniques of cloth dyeing as in the cotton industry using triazinyl-substituted azo dyes which can be attached simply in aqueous media. This paper describes a preliminary comparison of chelating dye coatings on a number of polystyrene substrates and cellulose by measuring several parameters, namely the capacity factor,  $k'$ , the percentage of dye loaded on the substrate and the total metal retaining capacity.

## 2. Experimental

### 2.1. Instrumentation

The basic instrumentation used for most of the high-performance chelation ion chromatography (HPCIC) work is shown in Fig. 1. An LKB 2150 HPLC titanium pump (Bromma, Sweden) was used as the eluent pump. A Constametric, Model III, HPLC pump (Laboratory Data Control, Riviera Beach, FL, USA) was used to deliver the post-column reagent (PCR). Injection of the sample was via a polyether ether ketone (PEEK)-lined six-port injection valve (Rheodyne, Cotati, CA, USA) fitted with a 100  $\mu$ l PEEK sample loop. The eluent and PCR were mixed at a zero dead volume T-piece followed by a 1.4 m $\times$ 0.3 mm internal diameter PTFE reaction coil. Detection was achieved using a spectral array detector (Dionex, Sunnyvale, CA, USA) set at 490 nm. A chart recorder (Labdata, Surrey, UK) was used to record chromatograms.

### 2.2. Cellulose column preparation

Procion Violet P-3R (Zeneca Colours, Huddersfield, UK) was chemically bonded to cellulose fibres (0.02–0.15 mm in length) (Fluka, Glossop, UK) using industrial dye methods (Zeneca Colours). A 1.32 g weight of the dye coated cellulose fibres was slurry packed in a 10.0 cm $\times$ 0.46 cm PEEK HPLC column (Alltech Chromatography, Carnforth, UK).

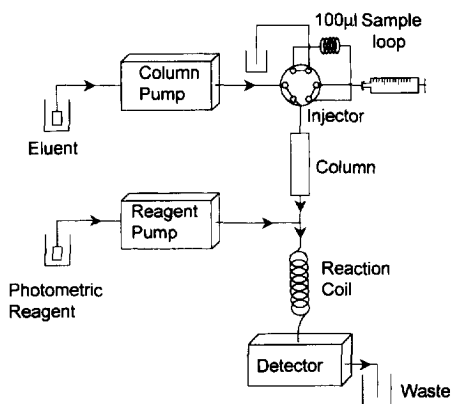


Fig. 1. A basic HPCIC system

### 2.3. Polystyrene column preparations

The chelating columns used were prepared as described in several recent papers [6,7]. 4-(2-Pyridylazo)-resorcinol (PAR) (Fluka) was used to impregnate four different macroreticular polystyrene resins: Amberlite IRA 904, a strong basic anion exchange resin; Amberlite XAD-2, a neutral resin; Purolite MN100, a weak basic anionic exchange macronet resin and Purolite MN200, a neutral macronet resin.

Initial dye loading investigations were performed on resins with a particle size range of 125–250  $\mu\text{m}$ . MN200 was further investigated after crushing the resin to a mean particle size of 25  $\mu\text{m}$ .

### 2.4. Reagents

The post-column photometric reagent used in these studies was PAR–zinc–ethylene–diaminetetraacetic acid (EDTA). A 0.5 or 1.0 mol  $\text{dm}^{-3}$  potassium nitrate solution containing 0.05 mol  $\text{dm}^{-3}$  lactic acid was used as an eluent and adjusted to the required pH. The eluent and PCR were delivered at 1 ml  $\text{min}^{-1}$ .

All reagents used were of AnalR grade (Merck, Poole, UK) with the exception of Zn–EDTA (Fluka). Solutions were prepared using distilled-deionised water (MilliQ, Millipore, Milford, MA, USA) and degassed using helium.

### 2.5. Procedures

The dye loadings on the substrate were calculated using UV–Vis spectrophotometry. The absorbance of the dye solutions were determined before and after the dyeing processes, the difference being directly proportional to the concentration of the dye coated on the substrates. The capacities of the columns were calculated from the midpoint of the s-shaped breakthrough curves. Known quantities of buffered zinc or copper solution were pumped through the columns. The capacity factors for each dye coated substrate was obtained from the retention times of metal ions at various pH values.

## 3. Results and discussion

### 3.1. Cellulose substrate

The dye loading of the cellulose substrate was 2.5% (w/w). Unfortunately, the exact structure of the dye is not available since it is of commercial interest to the suppliers to maintain confidentiality. However, it is known that the dye is an azo dye with an  $\alpha$ - $\alpha'$ -dihydroxy group for strong chelation with metal ions and also has a mono-chlorotriazinyl reactive group for linking to the cellulose matrix by a condensation reaction.

The metal retaining capacity of the column was found to be 17.3  $\mu\text{mol}$  of  $\text{Zn}^{2+}$  per gram of dry substrate. The s-shaped breakthrough curve for the capacity test was very sharp and probably indicates fast kinetics of exchange with metal ions in the column. Thus, the hydrophilic properties of the substrate may allow the possibility for fast flow-rates through the column with relatively low back pressures.

Fig. 2 illustrates the variation of capacity factor with pH for six metals:  $\text{Mg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . The height of a line on the graph is a measure of the column's affinity for a metal ion. The low lines on the graph indicate a strong affinity e.g. the copper line and the higher lines indicate a weaker affinity of the column substrate for metal ions e.g. the magnesium line. The selectivity order is broadly as expected for chelating dyes ( $\text{Cu}^{2+} > \text{Zn}^{2+}$ ,  $\text{Pb}^{2+} > \text{Mn}^{2+}$ ,  $\text{Cd}^{2+} > \text{Mg}^{2+}$ ) with the affinity being especially strong for copper. The slopes of the lines also indicate a very rapid change in retention times with pH which could assist the isolation of one metal from another even though the  $k'$  values are quite close. The graph may be utilised to determine the optimum pH values for separation of the metal ions.

### 3.2. Polystyrene substrates

Table 1 shows the dye loadings of PAR on the four different polystyrene substrates. XAD-2 has the highest dye loading but was not found to possess the highest capacity for metal ions. This is because many of the dye molecules adsorbed to the polystyrene backbone may be sterically hindered either by the

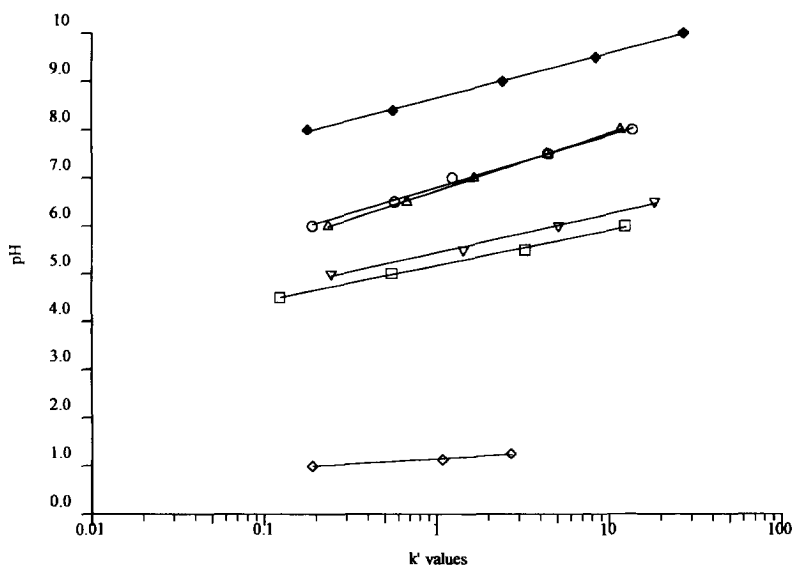


Fig. 2. The variation of capacity factor with pH for cellulose fibres coated with Procion Violet:  $\blacklozenge$  =  $\text{Mg}^{2+}$ ;  $\circ$  =  $\text{Cd}^{2+}$ ;  $\triangle$  =  $\text{Mn}^{2+}$ ;  $\nabla$  =  $\text{Pb}^{2+}$ ;  $\square$  =  $\text{Zn}^{2+}$ ;  $\diamond$  =  $\text{Cu}^{2+}$ .

polystyrene itself or by other dye molecules. The macronet resins, MN100 and MN200, have dye loadings less than that for XAD-2 but their capacities for metal ions are much greater. The strong basic anion exchange resin, IRA-904, had both low dye loading and a low capacity for metal ions. The greater number of sites for metal chelation of the dyes on the macronet resins could be related to their large surface areas (1000–1500  $\text{m}^2$  per g of dry resin) which are comparatively greater than those of other resins (<400  $\text{m}^2$  [8]).

Fig. 3 illustrates the variation of the capacity factors with pH for the four dye coated resins. Data for Zn and Mg is presented. Evidently the capacity factors for IRA-904 are much lower than those of the other three resins for both Mg and Zn. No clear

significant differences are apparent when the three remaining resins are compared for the Zn and Mg sets of data. However, since the data given in Table 1 shows that the actual capacity for XAD-2 is much lower than those for MN100 and MN200, the choice of resin used for further work was between the macronets. It was considered that MN200 was the most suitable as it is a neutral resin, thus eliminating interferences from functional groups in the resin backbone.

Fig. 4 shows the separation of a 5 ppm  $\text{Ba}^{2+}$ , 5 ppm  $\text{Sr}^{2+}$ , 10 ppm  $\text{Ca}^{2+}$  and 10 ppm  $\text{Mg}^{2+}$  system using a 10 cm column of 25  $\mu\text{m}$  MN200 coated with PAR. The eluent was 0.5  $\text{mol dm}^{-3}$  potassium nitrate with 0.05  $\text{mol dm}^{-3}$  lactic acid adjusted to pH 10 with ammonia. The elution order of the metals from

Table 1

A comparison of the dye loadings and metal retaining capacities of polystyrene resins impregnated with PAR

Dye	Resin	mmol of dye per g of resin	mmol of $\text{Cu}^{2+}$ per g of resin	(%) Available sites for chelation
PAR	MN100	0.159	0.147	95.3
	MN200	0.202	0.140	72.4
	IRA-904	0.069	0.003	4.4
	XAD-2	0.382	0.028	7.9

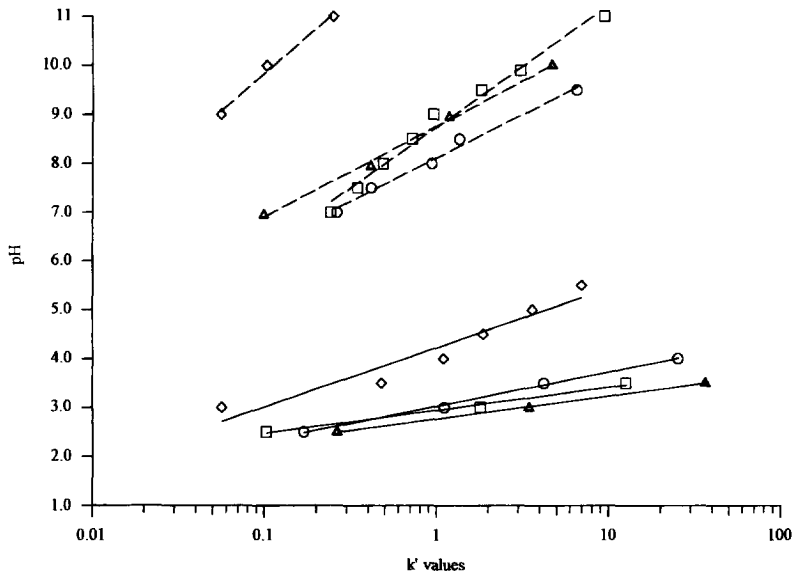


Fig. 3. The variation of capacity factor with pH for polystyrene resins impregnated with PAR:  $\square$ =MN100;  $\circ$ =MN200;  $\diamond$ =IRA=904;  $\triangle$ =XAD-2; —=Zn<sup>2+</sup>; ---=Mg<sup>2+</sup>.

the column is opposite to that observed with simple ion exchange. This will be of value for samples such as milk where using normal ion exchange, the high calcium concentrations will swamp the barium and strontium signals. The chromatogram shows rapid broadening of the peaks. This arises because the kinetics of exchange of the metal ions become slower as the value of the conditional stability

constant increases. The peak shapes can be greatly improved if gradient elution is employed [9].

#### 4. Conclusion

The cellulose dye coated substrate showed a surprisingly high affinity for copper which could assist in its isolation and removal from fairly acid solutions. However, the overall capacity was quite low and so the substrate may only be suitable for “polishing” of solutions such as fine chemicals or drinking water.

For the polystyrene resins, the strong base anion exchanger gave a much poorer performance than the other three, in terms of capacity and chelating strength. This is interesting because this type of resin is commonly used for chelating dye coatings for metal removal studies [10]. The results for the other three clearly support earlier findings showing that the amount of dye adsorbed could bear little resemblance to the actual metal adsorbing capacity. Thus, XAD-2 showed the highest dye loading but the lowest metal capacity, much lower than the other two. The very high surface area of the macronets could explain the higher capacities where the chelating groups may be

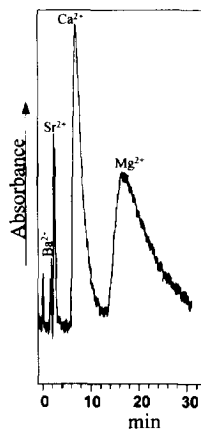


Fig. 4. A separation of 5 ppm Ba<sup>2+</sup>, 5 ppm Sr<sup>2+</sup>, 10 ppm Ca<sup>2+</sup> and 10 ppm Mg<sup>2+</sup> at pH 10 in 0.5 M KNO<sub>3</sub> with 0.05 M lactic acid. PCR was Zn-EDTA with detection at 490 nm.

less sterically hindered. Good separation of alkaline earth metals was achieved considering the particle size was 25  $\mu\text{m}$ . Further studies on the macronet series of substrates is underway focusing on low particle size for high-performance separation.

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