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SEPARATION OF METAL IONS ON A NEW AMIDE RESIN

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SUMMARY

The synthesis and characteristics of a new resin containing an amide functional group are described. The resin selectively retains uranium, thorium and zirconium from aqueous perchlorate solutions, and also strongly retains the noble metals from aqueous or methanolic hydrochloric acid solutions. Unlike conventional anion-exchange resins, the platinum-group metals and gold can be easily eluted with hydrochloric acid solutions containing sodium perchlorate and acetone, respectively. The chromatographic separation of thorium, uranium and zirconium, as well as that of some of the noble metals, has been demonstrated by using continuous spectrophotometric detection.

INTRODUCTION

Based on the encouraging results obtained in the liquid-liquid extraction of metal ions with *N,N*-di-*n*-octylacetamide¹, it was expected that an amide group incorporated into a resin would be advantageous. The use of such a resin in column chromatographic techniques combines the selectivity of the liquid amide with the multi-stage characteristics of chromatography. In addition, organic solvents can be employed with a resin to extend the scope of its application.

Orf and Fritz² have prepared amide resins either by reacting 4-chlorobutyl chloride with dibutylamine and then adding the resulting amide product to an XAD-4 polystyrene-divinylbenzene resin or by direct chloromethylation of the XAD-4 resin, followed by amination with butylamine and acylation with acetic anhydride. The latter resin was found to be inferior with respect to metal complexation, probably due to undesirable side reactions. The first resin was more successful, and was used in the selective separation of thorium, uranium and zirconium (in perchloric acid media) from many foreign ions. However, its synthesis was tedious, and it appeared to contain impurities that greatly reduced its efficiency.

It was the aim of the present investigation to produce a resin that would closely resemble liquid acetamides in selectivity, yet have the stability and charac-

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teristics useful in chromatographic separations. The following changes during the synthesis of the resin appeared to be appropriate. To inhibit secondary reactions during chloromethylation, it was decided to use zinc chloride³ instead of aluminium chloride as the catalyst. Further, XAD-1 was used instead of XAD-4 to increase the capacity of functional groups. For the intermediate amination step, the use of methylamine instead of butylamine was expected to favour interaction of the amide groups with metal ions, as there would be less hindrance by the smaller alkyl groups. Some applications of the new amide resin are demonstrated in this paper, and its use is compared with that of conventional anion-exchange resins. The elution of metal species was monitored during chromatographic separations by automatic, continuous photometric detection, both in the presence and absence of chromogenic reagents, with a Tracor 970 variable-wavelength detector.

EXPERIMENTAL

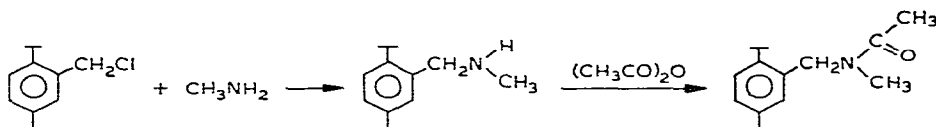
Liquid chromatograph

The chromatograph used in the experimental work has been described previously⁴. A sample loop of 59 μ l was employed, and a glass column (25 mm long and 5 mm wide) with uniformly restricted inlet and outlet pieces (each 20 mm \times 2 mm) was used unless otherwise stated.

The column was prepared by manually injecting a resin slurry until the column was tightly packed; a glass-wool plug was used to support the resin. Before chromatographic separations, the column was equilibrated with the first eluent to be used. Generally, a flow-rate of 1 ml/min was maintained.

Synthesis and characterization of the resin

The polystyrene-divinylbenzene XAD-1 (Rohm and Haas, Philadelphia, Pa. U.S.A.) macro-reticular resin (150–200 mesh) was used as starting material. The resin (15 g) was allowed to react with 30 ml of chloromethyl methyl ether in 105 ml of dichloromethane plus 11 ml of nitromethane with 8 g of zinc chloride as catalyst for 5.5 h at 45°. The secondary amine was formed by allowing the air-dried resin to react with liquified (liquid nitrogen) methylamine, followed by evaporation of the liquid overnight. From the nitrogen content of the resin (1.78%), the capacity was calculated as being 1.27 mequiv./g. Acylation of the secondary amine resin was achieved by treating the material with an excess of acetic anhydride on a boiling-water bath for 4 to 5 h; the product was washed with hydrochloric acid and methanol and air-dried.



The presence of an amide group on the resin was confirmed by IR spectrophotometry.

Metal solutions and detection

Whenever possible, stock metal solutions were prepared by dissolution of

reagent-grade chlorides or oxides in hydrochloric acid. Noble-metal solutions were always evaporated to dryness in the presence of sodium chloride, and the residue was treated repeatedly with concentrated hydrochloric acid; this ensured reproducible formation of noble-metal chloride species.

Separated metal ions in the eluent were detected automatically with a Tracor 970 variable-wavelength spectrophotometer fitted with a flow-through cell. Uranium, thorium and zirconium were detected at 595 nm by using aqueous 0.12 mM arsenazo I in the dye circuit of the chromatograph. The platinum-group metals were detected as chloride complexes at 225 nm by using 1 M hydrochloric acid in the dye circuit.

With the exception of rhodium, metal ions from gravity-flow columns were determined by standard spectrophotometric methods. Very small amounts of rhodium were found to form an intensely yellow complex with tin(II) chloride in the presence of methanol. The complex was formed rapidly at room temperature, and consequently this method was used for the detection of rhodium. The rhodium-tin (II) chloride complex has two peaks in the absorption spectrum (maxima at 305 and 420 nm), with an absorption coefficient of 2.3×10^4 at 305 nm.

RESULTS AND DISCUSSION

Extraction chromatography

During a preliminary investigation, reversed-phase extraction chromatography with N,N-di-*n*-octylacetamide (DOAA) adsorbed on Chromosorb W was employed to allow comparison to be made between DOAA and the amide resin. Amberlites XAD-4 and XAD-11 and various types of Chromosorb were tested as supporting material. Chromosorb W loaded with 38% of DOAA was found to be superior with respect to packing characteristics, and loss of extractant due to bleeding was negligible; columns (60 mm \times 4 mm) with gravity flow were used in all experiments. The retention of several elements from aqueous hydrochloric acid solutions was measured. The results resembled those obtained by liquid-liquid extraction¹, with the notable exception of some of the platinum-group metals. Thus, iridium (which is strongly extracted into a solution of DOAA in benzene from 0.1 M hydrochloric acid) was only weakly retained on the reversed-phase column. However, from 5 M hydrochloric acid, as in solvent extraction, iridium was strongly retained, and the capacity of DOAA-loaded Chromosorb was 0.12 mmole of iridium per g (*i.e.*, 0.3 mmole of iridium per g of DOAA). Iridium was effectively eluted with aqueous sodium perchlorate solution or dilute (0.5 M) nitric acid. The weak retention of iridium on the column from 0.1 M hydrochloric acid thus emphasised the major role played by the diluent in liquid-liquid extraction.

As in solvent extraction, uranium was found to be strongly retained from solutions > 1 M in sodium nitrate; in addition, thorium was retained from solutions > 2 M in sodium nitrate. The thorium could be easily eluted with 9 M hydrochloric acid, leaving the uranium on the column, from which it was easily eluted with aqueous solutions of ammonium sulphate.

It was further observed that, from 1 M sodium perchlorate solutions, only gold was retained strongly (together with thorium, uranium and zirconium); all the other metals tested passed through the column.

Chromatographic experiments with the amide resin

The amide resin was found to be extremely stable, and no deterioration in its performance was observed after 2 months of continuous use. Moreover, different batches of resin performed equally successfully.

Separation of uranium, thorium and zirconium. The separation of uranium, thorium and zirconium on an amide resin has been described by Orf and Fritz². A similar procedure was used in the present investigation in order to evaluate the performance of the amide resin. A sample containing the three metals was injected into an eluent stream of 1 M sodium perchlorate at a pH value of 3. As shown in Fig. 1, uranium and thorium (after the elution of foreign ions) were separated by decreasing the perchlorate concentration and the pH of the eluent. Zirconium, which was still strongly retained was subsequently eluted with 1 M hydrochloric acid. The relative positions of the metals tested was ascertained by injecting each element individually. Praseodymium was included in the separation scheme as an example of an un-retained species; also, it formed a coloured, if insensitive, complex with arsenazo I under the conditions chosen. Arsenazo I was preferred to arsenazo III as chromogenic reagent because of its lesser tendency to cause baseline shifts due to precipitation. Since it was the aim of this investigation to demonstrate the efficiency of the resin, no further attempt was made to improve the sensitivity, *i.e.*, the detection limit for the individual metals. However, this could be easily achieved by buffering the dye solution choosing more selective chromogenic reagents or further expanding the absorption scale.

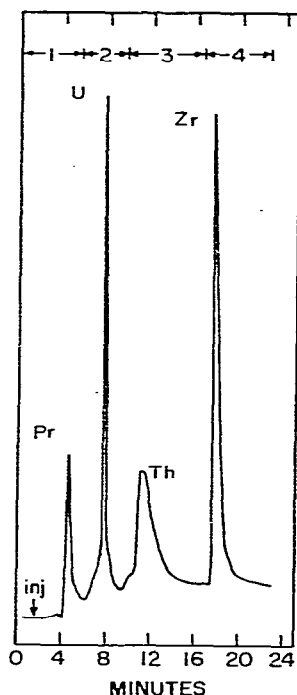


Fig. 1. Separation of praseodymium (75 μg), uranium (59 μg), thorium (3 μg) and zirconium (29 μg). Eluents: 1, 1 M NaClO_4 ; 2, 0.1 M NaClO_4 + 1% HClO_4 ; 3, 0.1 M NaClO_4 + 2.5% HClO_4 ; 4, 1 M HCl .

Basically, the separation of uranium, thorium and zirconium resembled that obtained by Orf and Fritz². However, it appeared that the new resin showed increased column efficiency, and no tailing of zirconium was observed. Manual collection of the fraction containing the zirconium followed by spectrophotometric determination showed a recovery of 98% of the zirconium (100 μg) added.

Separation of noble metals. The retention of some noble metals on an amide resin was studied by Orf and Fritz², who found that gold and palladium were strongly retained and that rhodium and platinum were not retained from 1 and 5 *M* hydrochloric acid.

From previously obtained data in liquid-liquid extraction and reversed-phase chromatography involving the use of DOAA, it appeared a reasonable prediction that all noble metals, with the possible exception of rhodium, should be retained on the amide resin from dilute hydrochloric acid solutions; this was confirmed experimentally. Although rhodium was only partially retained, all other noble metals were strongly adsorbed by the resin from 0.1 *M* hydrochloric acid, whereas base metals [*i.e.*, manganese(II), iron(III), cobalt(III), nickel(II), tellurium(VI), copper(II), zinc(II) and lead(II)] passed through the column. The addition of methanol to the eluent (ratio of methanol to 1 *M* HCl 9:1) resulted in the complete retention of rhodium(III) as well as the other noble metals, while all base metals tested were eluted. The elution of the retained rhodium(III), ruthenium(IV), palladium(II), platinum(IV) and iridium(IV) as a group from the resin was easily achieved with 1 *M* hydrochloric acid containing 0.5 *M* sodium perchlorate or perchloric acid; gold was then eluted with acetone.

Stepwise addition of perchlorate ion to the eluent lowered the retention of the platinum-group metals sufficiently to allow the individual separation of some of these metals. The eluent concentration was kept constant at either 1 *M* sodium chloride or hydrochloric acid to prevent hydrolysis of the noble metals. The separation of rhodium and ruthenium (Fig. 2), of rhodium, ruthenium and iridium (Fig. 3) and of rhodium, palladium and iridium (Fig. 4) under similar conditions is demonstrated. The baseline shift observed was due to increasing absorption with increasing perchlorate concentration at 225 nm.

Difficulties were encountered in the separation of a mixture of palladium and platinum on the very small column used. However, when a longer column (350 mm \times 2 mm) was used, the resolution was much improved and almost complete separation of platinum and palladium was obtained (see Fig. 5). When 1 *M* sodium chloride was used instead of 1 *M* hydrochloric acid, the separation of platinum and palladium was possible on the smaller column (see Fig. 6); however, tailing was much more pronounced. From the chromatograms shown, it is obvious that separation of all five platinum-group metals tested cannot be achieved by stepwise elution, because ruthenium would be eluted with palladium, and platinum with iridium. It appears, however, that by using a gradient, *i.e.*, by increasing the perchlorate concentration of the eluent in a continuous manner, complete resolution of all noble metals would be possible.

The reproducibility of separation of mixtures of platinum metals was very good; Fig. 2 shows, for example, the reproducibility obtainable in two separations of rhodium and ruthenium. The chromatographic separations achieved appear to be complete. However, no quantitation of the individual platinum metals was attempted

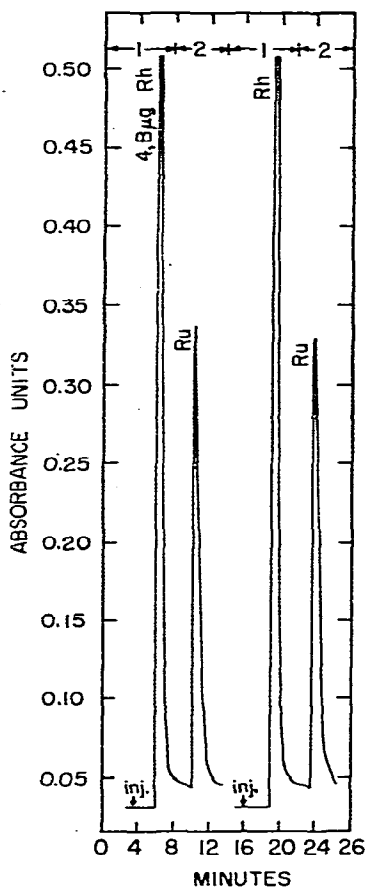


Fig. 2. Separation of rhodium (4.8 μg) and ruthenium (4.8 μg). Eluents: 1, 1 M HCl-0.01 M NaClO₄; 2, 1 M HCl-0.10 M NaClO₄.

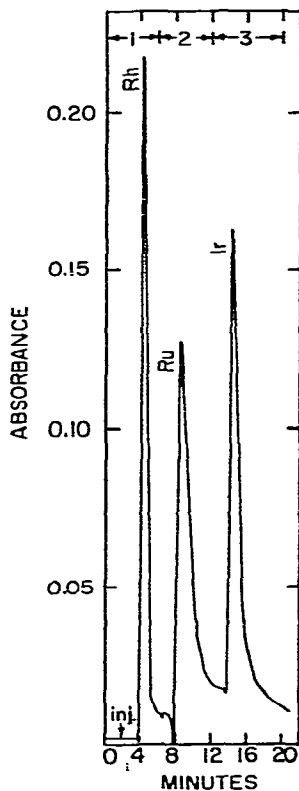


Fig. 3. Separation of rhodium (1.18 μg), ruthenium (2.36 μg) and iridium (5.9 μg). Eluents: 1, 1 M HCl; 2, 1 M HCl-0.025 M NaClO₄; 3, 1 M HCl-0.5 M NaClO₄.

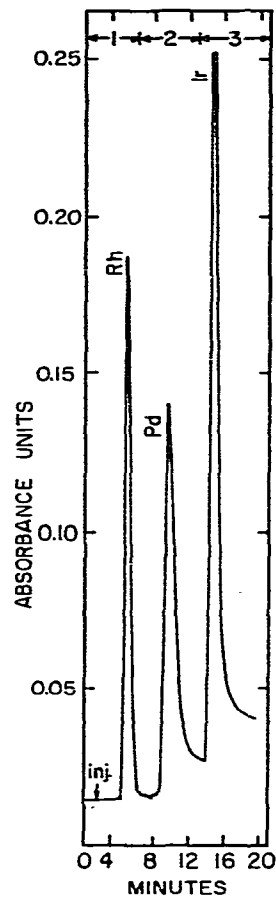


Fig. 4. Separation of rhodium (1.18 μg), palladium (1.18 μg) and iridium (5.9 μg). Eluents: 1, 1 M HCl; 2, 1 M HCl-0.05 M NaClO₄; 3, 1 M HCl-1.0 M NaClO₄.

because the absorbance of the eluted metals is species-dependent and changes considerably, depending on the history and previous treatment of the sample.

Separation of gold. Gold is strongly adsorbed on the resin from all concentrations of hydrochloric acid solution and could be eluted only with difficulty with any mineral acid. Moreover, gold retained from a hydrochloric acid medium could be left for 6 days on the column without any visible signs of reduction. The capacity of the resin for gold was found to be in the range of 0.63 mmole (124 mg) of gold per g of resin.

An amide resin was prepared from Bio-Rad chloromethylated beads by amination with methylamine followed by acylation with acetic anhydride. Although the final gel-type resin contained 3.30% of nitrogen, it hardly took up any gold at all. This suggests that the macroporous nature of the previous resin (prepared from

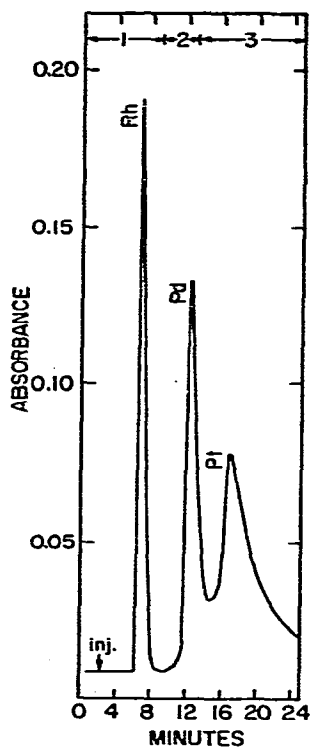


Fig. 5. Separation of rhodium ($1.18 \mu\text{g}$), palladium ($1.18 \mu\text{g}$) and platinum ($11.8 \mu\text{g}$) in the presence of HCl. Eluents: 1, 1 M HCl ; 2, $1 \text{ M HCl}-0.05 \text{ M NaClO}_4$; 3, $1 \text{ M HCl}-0.15 \text{ M NaClO}_4$.

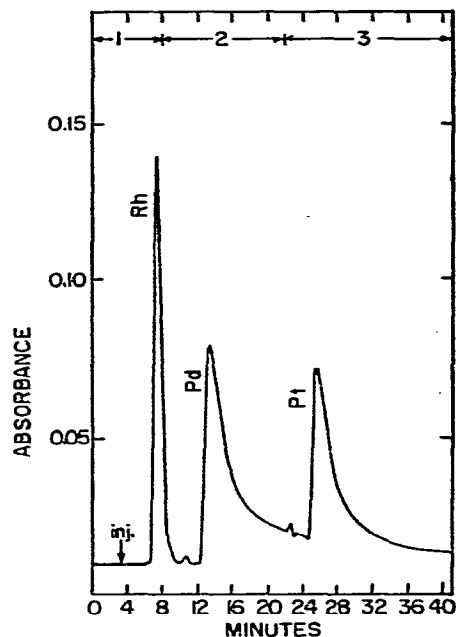


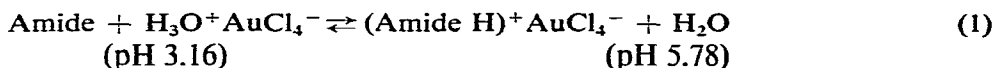
Fig. 6. Separation of rhodium ($1.18 \mu\text{g}$), palladium ($1.18 \mu\text{g}$) and platinum ($11.8 \mu\text{g}$) in the presence of NaCl. Eluents: 1, $1 \text{ M NaCl}-0.1 \text{ M HCl}$; 2, $1 \text{ M NaCl}-0.025 \text{ M NaClO}_4$; 3, $1 \text{ M NaCl}-0.15 \text{ M NaClO}_4$.

XAD-1) is very important to the successful uptake of metal ions from aqueous solution.

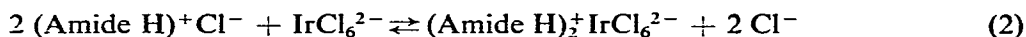
Various solvents were tested for the desorption of gold; desorption was achieved with 0.1 M sodium cyanide, dimethylformamide and acetone, but not with methanol, acetonitrile, ethyl acetate or isopropyl ether. Thus, it appears that, with the exception of cyanide, only those solvents containing a carbonyl group can successfully compete with the forces binding the gold to the resin.

The mechanism for gold(III) uptake by the resin appeared to be different from that of the platinum metals. It was tentatively assumed that gold was retained as chloroauric acid (HAuCl_4) and it was further reasoned that, by largely excluding hydrogen ions from the resin, the uptake of HAuCl_4 would result in an increase in the pH value of the eluent. To verify these assumptions, the resin column was washed thoroughly with aqueous sodium perchlorate to remove chloride and much of the hydrogen ions. Next, a gold solution ($\approx 200 \mu\text{g/ml}$) containing a minimum of hydrochloric acid (pH 3.16) was prepared by evaporation of a gold-hydrochloric acid solution to incipient dryness, followed by dilution with water to a volume of approximately 20 ml. To minimise hydrolysis of the gold complex, the solution was passed through the column within minutes of its preparation. The pH

value of the eluate was measured and found to have increased to 5.78. The decrease in hydrogen-ion activity can therefore be accounted for by sorption of predominately HAuCl_4 on the resin according to the equation:



Gold(III) was readily taken up by the amide resin whether the resin was in the chloride form (from washing with hydrochloric acid) or was completely deficient in chloride, as in the experiment just described. However, uptake of platinum-group metals occurred only when the resin was in the chloride form. When a solution containing H_2IrCl_6 was passed through a column that had previously been washed with hydrochloric acid and then with water, the chloride content of the eluate was qualitatively found to increase. This suggests that the platinum metals can only be taken up by the resin through formation of an ion pair:



A glance at eqns. 1 and 2 might lead to the conclusion that the mechanism for retention of gold(III) and the platinum metals is the same. However, the elution of most of the platinum metals from the resin by acids or salt solutions containing sodium perchlorate suggests a simple anion-exchange mechanism. Since gold(III) is not eluted by these solutions, it is possible that gold is attracted by the resin oxygen or nitrogen and therefore held by forces other than simple electrostatic attraction of positive resin ions for the AuCl_4^- anions.

Acetone easily elutes gold(III) from the amide resin (see Fig. 7), but the platinum metals are not readily eluted. The gold(III) anion, or ion pair, is undoubtedly solvated by the carbonyl group of the acetone, whereas the platinum-metal anions are not.

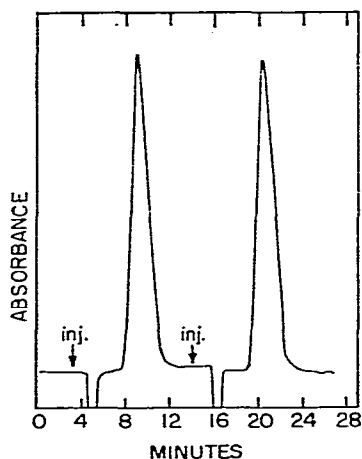


Fig. 7. Elution of gold(III) (11.6 μg) with acetone (repeated injection)

It is of interest that gold(III) is only eluted from the amide resin if chloride is present; acetone does not elute gold(III) from a resin that is deficient in chloride until hydrochloric acid is mixed with the acetone or the resin is washed with aqueous sodium chloride and then with acetone.

CONCLUSION

The separation of uranium, thorium and zirconium, and of the noble metals, from each other and from foreign metal ions has been demonstrated on the new amide resin. The high capacity of the resin for gold (0.63 mmole/g), as well as its excellent selectivity, suggest its possible use for the concentration and recovery of gold on a larger scale. An amide resin of higher capacity would be advantageous for such a purpose; probably a gel-type resin or another type of macroporous resin with higher capacity could be produced.

The new amide resin showed none of the irregular sorption patterns for zirconium or palladium that were observed for an earlier amide resin². For analytical purposes, the new resin is an improvement over ordinary anion-exchange resins for the concentration of noble metals in that no irreversible adsorption occurs. With the exception of gold(III), which can be simply eluted with acetone, all noble metals are easily eluted by increasing the perchlorate concentration of the hydrochloric acid eluent.

This investigation was intended as a survey of the characteristics and possible applications of the amide resin. Because of its ease of preparation, its stability and its selectivity, the amide resin appears to be a useful contribution to industrial and analytical separation procedures.

ACKNOWLEDGMENT

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REFERENCES

- 1 C. Pohlandt and J. S. Fritz, *Talanta*, in press.
- 2 G. M. Orf and J. S. Fritz, *Anal. Chem.*, 50 (1978) 1328.
- 3 S. Goldstein and G. Schmuckler, *Ion Exch. Membr.*, 1 (1973) 135.
- 4 J. N. King and J. S. Fritz, *J. Chromatogr.*, 153 (1978) 507.