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Donnan Dialysis of Transition Metal Ions Using Anion Exchange Membrane Modified with Xylenol Orange

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Abstract

A chelating ion-exchange membrane was obtained by modification of a PTFE-based anion-exchange membrane with Xylenol Orange. Its utility for dialysis of Cu(II), Ni(II), Mn(II), and Zn(II) was investigated by using receiver solutions without and with iminodiacetate, 1,2-diaminocyclohexanetetraacetic acid, and tetraethylenepentamine. In comparison to commercial PTFE cation-exchange membranes, modified chelating membranes exhibit for the metal ions investigated a larger differentiation of retention in the membrane phase and transport-to-receiver solution depending on the modifier used and the composition of the receiver solution.

INTRODUCTION

Since the pioneering work by Blaedel and Haupert (*1*) and Wallace (*2*), Donnan dialysis with the use of ion-exchange membranes has gained numerous analytical applications. They include preconcentration of the ions to be determined, separation of mixtures of ions for analytical purposes, and replacement processes that enable the use of the most advantageous indirect analytical detection. Each of those processes can be carried out in static conditions, where constant volumes of donor and receiver solution contact the membrane, or in flow conditions, where tubular membranes are most convenient.

Dialysis performed in static conditions allows for preconcentration of cations (*1–3*) and anions (*5*). In a carefully optimized receiver solution composition or an appropriate chemical modification of a sample solution,

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selective preconcentration of a given species can be achieved (*6–9*). Dialysis was utilized for the investigation of heavy metal speciation in waters with anodic stripping voltammetry (*10*) and for the preconcentration of nitrate in voltammetric determination with simultaneous elimination of interference of surfactants, chloride, and sulfate (*11*). By using a cation-exchange membrane, the effect of surfactants, complexing agents, and electroactive organic compounds on anodic stripping voltammetry and differential pulse polarography of transition metal ions was removed (*12*).

Flow dialyzing systems with tubular ion-exchange membranes were used for the preconcentration of the species to be determined with the elimination of matrix interferences in analytical voltammetry (*13*), potentiometry (*14*), conductometry, and atomic spectrometry (*16–18*). A flow-through dialyzer with a flat anion ion-exchange membrane was successfully utilized for the elimination of ammonia interference in the enzymatic potentiometric determination of urea (*19*).

Another broad area of application of tubular membranes is in high performance ion chromatography. The use of Donnan dialysis for the suppression of eluent conductivity was comprehensively reviewed by Dasgupta (*20*). A tubular membrane bathed in an appropriate solution can be utilized for replacement ion-chromatography where eluted, resolved species are replaced by the same indicator component. This concept was exploited with flow-through AAS (*21*), spectrophotometric (*22*), and potentiometric (*23*, *24*) detectors.

The authors of numerous papers mentioned above conclude that the efficiency of dialytic separation can be influenced by the presence of complexing ligand in the receiver (*1*, *2*, *6*, *7*, *13*) or the sample solution (*8*, *9*). However, the use of anion membranes modified with complexing ligands, which can transform them into cation chelating membranes, has not been explored. The transport mechanism of a particular species during dialysis significantly depends on the structure of the ion-exchange membrane. Until now, only chelating resins, either with complexing groups built in the resin structure or modified with ligand molecules adsorbed or chemically bonded on the resin surface, have been broadly used for preconcentration and the separation of cations. They usually offer more differentiated selectivity than conventional cation-exchange resins.

In this study the dialysis of several transition metal ions was investigated with the use of a commercial Teflon-based anion membrane with the sulfonated aromatic organic complexing agent Xylenol Orange. This compound was previously utilized for modification of a macroreticular anion-exchange resin for the separation of metal ions (*26*). Our preliminary work on modification of anion membranes with sulfo derivatives of aromatic complexing agents showed interesting properties of modified membranes (*27*).

EXPERIMENTAL

The anion-exchange membranes were PTFE-based type R-1030 and R-1035 obtained from Rai Research Corporation (Hauppauge, New York, USA). The cation-exchange membrane used for comparison was R-1010 from the same manufacturer.

The dialysis cell was constructed from a Teflon tube. A membrane of 2.5 cm diameter was used to close one end of the tube and was held in place by a threaded Teflon sleeve. The dialysis cell, containing 5 mL of receiver solution, was placed in a 100-mL magnetically stirred sample solution. After dialysis, the receiver chamber content was transferred to a 10-mL volumetric flask to eliminate the error, if any, from osmotic dilution. The concentrations of the metals in that solution and in the residual sample solution were determined by flame atomic absorption spectrometry by using an AAS-1 spectrometer from Carl Zeiss (Jena, East Germany).

Xylenol Orange (XO) was obtained from POCh (Gliwice, Poland), Eriochromcyjanine R was from Chemopol (Czechoslovakia), the sodium salt of iminodiacetic acid (IDA) was from POCh (Gliwice, Poland), and the salt of 1,2-diaminocyclohexanetetraacetic acid (DCTA) was from International Enzymes Ltd. (England). Tetraethylenepentamine (Tetren) was recrystallized as a sulfate before use. All other chemicals used were Reagent Grade. Triply distilled water was used for preparing all solutions.

The modification of the membrane was performed by immersing the dialysis cell containing 5 mL of 0.5 *M* ammonium sulfate as a receiver into 100 mL of 1 m*M* dye solution for 2 h. Then the dialysis cell was taken out of the solution, washed with distilled water, and used for the dialysis solution of given metal ions.

The data reported below are in terms of enrichment factor EF (defined as the ratio of metal concentration of the receiver electrolyte after dialysis to the initial sample concentration) and percent of the metal retained in the sample or in the membrane phase after dialysis. The latter was determined by the difference between the initial and the final sample solution concentrations.

RESULTS AND DISCUSSION

Membrane Modification with Xylenol Orange

The preparation of a chelating ion-exchange resin by the modification of conventional anion-exchange resins with complexing agents, which display a high affinity for anion-exchange sites, has often been utilized in analytical separations in recent years. The appropriate choice of ligand provides resins of greatly differentiated selectivities. The application of XO for the modification of commercial anionite Amberlyst A-26, mentioned above, allowed separation of several mixtures of metal ions (*26*).

On the same principle, chelating ligands can be attached to the surface of a Teflon-based anion membrane with vinylbenzyl-ammonium groups in its structure when ion-pairing between those membrane groups and sulfonic groups of the ligand molecule could occur. Firm bonding of the ligand of the anion membrane surface changes its properties to cation-exchange behavior.

Modification of the anion membrane is carried out by performing a dialysis process with a sample solution containing ligand XO and a receiver solution of high ionic strength. The influence of several experimental parameters on the efficiency of that process was examined for the R-1035 membrane. As shown in Fig. 1, the extention of dialysis to more than 1.5 h does not affect the amount of retained copper(II) during its dialysis with such a membrane. Either pH changes from 2 to 8 of 1 m*M* XO solution or changes of XO concentration from 0.4 and 2.0 m*M* does not affect modified membrane behavior.

Dialysis in the Absence of Complexing Agents

As the result of a dialysis process with a modified membrane, the distribution of dialyzed metal ions among donor sample solution, receiver

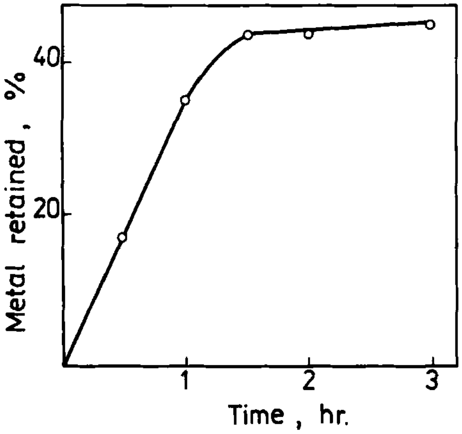

FIG. 1. Effect of modification time of R-1035 membrane with XO on the uptake of copper from 3 mg/L copper solution after 30 min dialysis. Receiver solution, 0.5 *M* $(NH_4)_2SO_4$ + 20 m*M* DCTA; pH 6.0.

solution, and membrane phase was expected. As widely already discussed in the literature, the efficiency of metal ion dialysis depends on such factors as the concentration of electrolyte in the receiver solution (*3*, *6*), the kind of cations present in the receiver solution (*6*, *13*), the presence of other cations in the sample solution (*3*), the pH of the receiver solution (*4*, *6*, *10*, *28*), and the charge of counterions in the receiver electrolyte (*25*). The importance of some of those factors for metal ion dialysis of Cu(II), Mn(II), Ni(II), and Zn(II) was verified in this study for XO-modified anion membrane.

A majority of our experiments were carried out by using 0.5 *M* ammonium sulfate as the receiver solution. This electrolyte has not previously been utilized in the dialysis of cations. From their comparison study of different receiver solutions, Cox and DiNunzio (*3*) selected magnesium sulfate with the addition of $Al_2(SO_4)_3$ as the best one. This solution, however, was not applied in our study because of a possible side complexation equilibria between XO and Mg (*29*) and Al (*30*), and also because of complex formation of those metal ions with the ligands used in the receiver solution. The results of the retention of metal ions in the membrane phase after 30 min dialysis with XO-modified R-1035 membrane are shown in Table 1. In none of those cases were the dialyzed metal ions found in the receiver solution. Similarly to dialysis with a nonmodified cation membrane (*3*), the most effective retention of metal ions in the membrane phase was

TABLE 1
Effect of the Receiver Solution on Metal Uptake by the XO-Modified R-1035 Membrane from 3 mg/L Metal Solutions. Dialysis Time: 30 min

Receiver	Metal dialyzed	Metal retained in the membrane phase (%)[a]
0.1 *M* Li_2SO_4	Cu	0
0.3 *M* Li_2SO_4	Cu	5
0.1 *M* LiCl	Cu	0
0.5 *M* $MgSO_4$	Cu	18
0.2 *M* $MgSO_4$ + 0.5 m*M* $Al_2(SO_4)_3$	Cu	20
	Mn	5
	Ni	5
	Zn	22
0.5 *M* NH_4NO_3	Cu	6
0.5 *M* $(NH_4)_2SO_4$	Cu	20 (11)
	Mn	16 (4)
	Ni	18 (11)
	Zn	11 (10)

[a] The values in parentheses were obtained for a R-1030 membrane modified with XO.

obtained for $MgSO_4$ or $MgSO_4$ with $Al_2(SO_4)_3$ solutions. The use of 0.5 *M* ammonium sulfate as a receiver solution for a R-1035 membrane resulted in a comparable uptake and in even a larger amount of retained Mn(II) and Ni(II). More limited retention of metal ions, except for Zn(II), was observed for a modified R-1030 membrane. After 30 min dialysis, 5 to 13% of the initial amount of metal ions was found in the membrane phase, whereas no transport of dialyzed cations to the receiver solution was observed within the pH range from 2 to 10.

Dialysis in the Presence of Complexones in Receiver Solution

Aminopolycarboxylic acids commonly used in chemical analysis form stable complex compounds with all transition metal ions. Because of the different relative stabilities of those complexes, the complexes formed by the metal ions investigated with XO, and due to the different charges of the complex species formed, the presence of such ligands either in the sample solution or in the receiver may significantly alter a dialysis process. This has already been observed for iminodiacetate (*6*) and EDTA (*1*, *2*, *13*) in the dialysis of transition metal ions using commercial cation-exchange membranes. The effectiveness of the dialysis of anionic chlorocomplexes of platinum group metals by using an anion membrane was affected by the type of anion present in the receiver solution, or more precisely, of the stability of the complex compounds formed (*7*).

In the case of an anion-exchange membrane modified with XO, the addition of IDA or DCTA results in an increase in the metal ions uptake in the membrane (Table 2) and in the transport of a certain amount of dialyzed metal ions to the receiver solution. A larger increase of metal ion retention in the membrane phase for all the metal ions examined was found

TABLE 2

Effect of the Presence of 20 m*M* Complexing Ligands in 0.5 *M* $(NH_4)_2SO_4$ Receiver Solution of pH 6.0 on the Retention of Metal Ions in the Membrane Phase after 30 min Dialysis Using XO-Modified R-1030 Membrane from 3 mg/L Metal Solutions

Ligand in receiver	Metal retained in membrane phase (%)			
	Cu(II)	Ni(II)	Mn(II)	Zn(II)
—	12	12	5	10
IDA	14	13	10	12
DCTA	44	30	26	22
Tetren[a]	52	18	15	20

[a]Receiver solution with pH 8.0.

for DCTA than for IDA, which is consistent with the stability of the complex compound formed.

A more detailed study of dialysis in the presence of DCTA was carried out for copper(II) ions. Because of protonation of ligand and formation of copper(II) hydrocomplexes, the pH value of the solution may influence the dialysis results. For the pH range from 4 to 10, an increase in pH causes stronger Cu(II) retention in the membrane, whereas the amount transported to the receiver solution decreased above pH 6.0 (Fig. 2). Figure 2 also shows the influence of pH on Cu(II) retention in the membrane phase in the absence of DCTA in the receiver solution.

Distribution of dialyzed cations among all three phases depends essentially on the dialysis time. The amount of Cu(II) retained in the membrane phase increases only during the first 30 min (Fig. 3A). After a longer time period, transport to the receiver solution predominates. This was observed for both the modified membranes used. For the R-1030 membrane, a marked enrichment of Cu(II) (EF > 2) in the receiver solution was observed after 2 h dialysis. An increase of DCTA concentration in the receiver was not effective for larger Cu(II) enrichment.

Dialysis in the Presence of Tetren in Receiver Solution

Larger differences in the stabilities of complexes formed by transition metal ions are observed for polyamines than for complexones, hence one can expect an improvement of selectivity of dialysis performed in the pres-

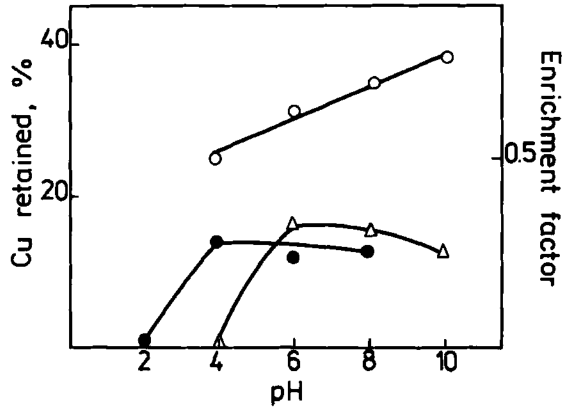

FIG. 2. Effect of pH on the amount of metal retained in the membrane phase (○, ●), and the enrichment factor (△) in 30 min dialysis of copper with an XO modified R-1030 membrane using as receiver a 0.5 *M* $(NH_4)_2SO_4$ solution without (●) and with 20 m*M* DCTA (○, △) from 3 mg/L copper solutions.

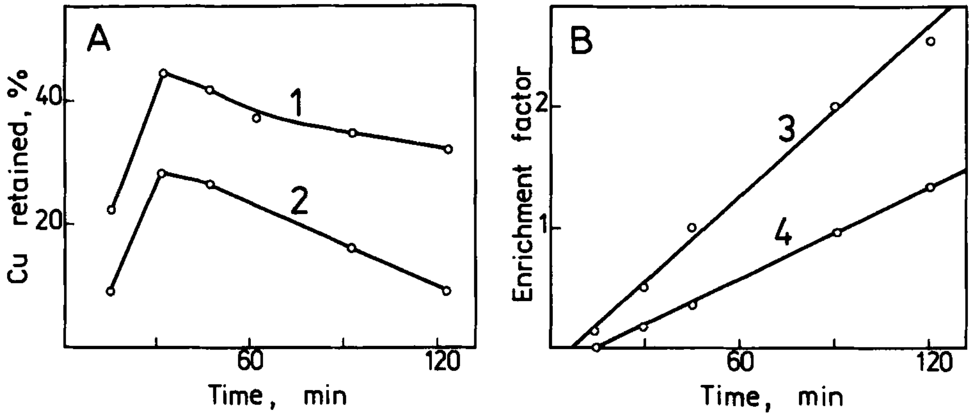

FIG. 3. Effect of time of dialysis from 3 mg/L copper solutions on the amount of metal retained in membrane phase (A) and enrichment factor (B) for XO modified R-1030 (2, 3) and R-1035 (1, 4) membranes using as receiver a solution of 0.5 *M* $(NH_4)_2SO_4$ with 20 m*M* DCTA at pH 6.0.

ence of polyamines in the receiver solution. This was examined for Tetren by using an XO-modified R-1030 anion membrane. A study carried out for copper(II) showed a strong dependence of the amount of Cu(II) retained in the membrane phase on the Tetren concentration in the receiver solution in the absence of a strong electrolyte (Fig. 4). However, in the presence of 0.5 *M* ammonium sulfate at only a 20-m*M* concentration of Tetren, 52% of Cu(II) was retained in the membrane phase. Because of amine protonation equilibration, an increase in the pH of the receiver

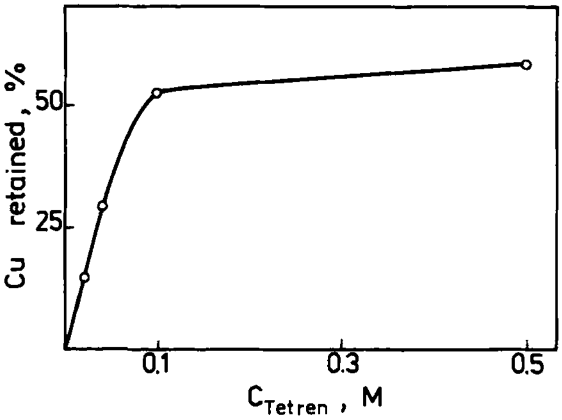

FIG. 4. Effect of the concentration of Tetren solution of pH 8.0 on the uptake of copper in the membrane phase after 30 min dialysis using an XO modified R-1030 membrane.

solution results in increasing uptake of metal ions into the membrane phase [except for Mn(II)] and an increase in selectivity of Cu(II) uptake in comparison to other metal ions (Fig. 5). This selectivity deteriorates for longer dialysis times in spite of a favorable increase of metal uptake in the membrane phase. After 30 min, the dialysis amount of Cu(II) retained was 3.3, 2.8, and 2.5 times larger than of Mn(II), Ni(II), and Zn(II), respectively, whereas after 2 h dialysis those ratios were equal to 2.3, 1,8, and 1.3, respectively (Fig. 6). In all the experiments with Tetren, metal ions were not transported to the receiver solution. Because the indirect spectrophotometric test shows an adsorption of approximately 30% of Tetren present in the receiver solution on the membrane surface, it seems that in such conditions dialysis through an XO-modified membrane with adsorbed Tetren does not occur, but only a preconcentration in the membrane phase.

Dialysis with a Commercial Cation-Exchange Membrane

In order to compare the properties of a Teflon-based anion membrane modified with XO, the same dialysis experiments were performed by using the commercial cation membrane R-1010. The enrichment factor values obtained are shown in Table 3. For a receiver solution either containing or not containing Tetren, certain amounts of dialyzed metal ions were retained in the membrane phase. In the absence of Tetren, it was 10, 28,

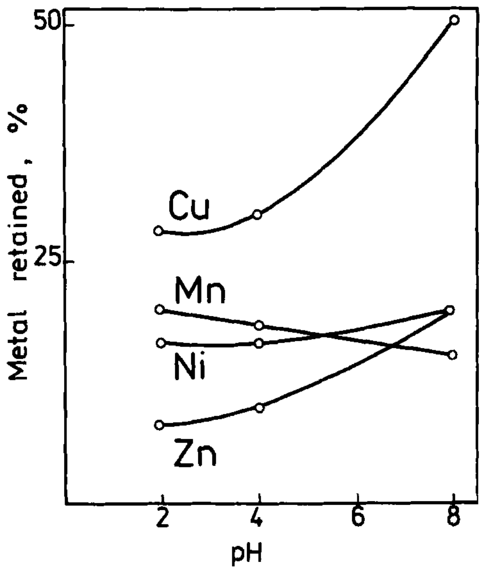

FIG. 5. Effect of pH on amount of metal ions retained in the membrane phase after 30 min dialysis using an XO modified membrane and 0.5 *M* $(NH_4)_2SO_4$ with 20 m*M* Tetren as the receiver solution. Initial metal concentration: 3 mg/L.

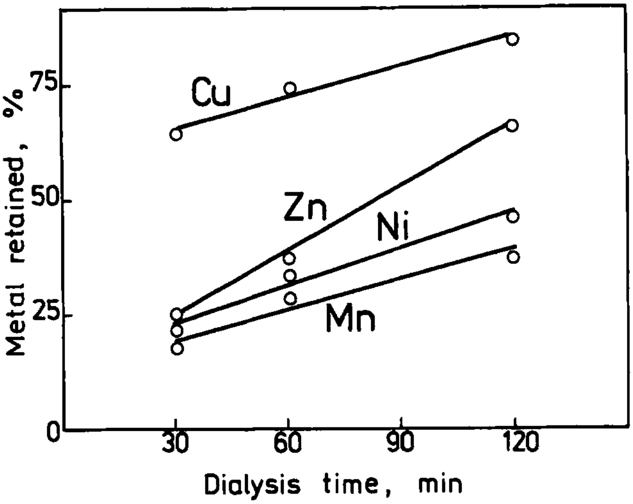

FIG. 6. Effect of dialysis time on amount of metal ions retained in the membrane phase by using an XO modified R-1030 membrane and 0.5 *M* $(NH_4)_2SO_4$ with 20 m*M* Tetren of pH 8.0 as the receiver solution.

19, and 6% of the total amount of dialyzed metal for Cu, Mn, Ni, and Zn, respectively. In the presence of 20 m*M* Tetren in the receiver solution, the retention of copper and zinc in the membrane was not changed, whereas for Mn and Ni it decreased to 5 and 8%, respectively. The negligible effect of Tetren on the enrichment of dialyzed metal ions and on the selectivity of dialysis makes this system very different from that with an XO-modified anion membrane. The distribution of metal ions among the three phases is disadvantageous for analytical applications where complete transport to the receiver solution or retention in the membrane phase is preferred.

Dialysis with a Anion-Exchange Membrane Modified with Eriochromcyjanine R

The selectivity properties of chelating membrane can be modified by the choice of ligand used for membrane modification. For comparison with

TABLE 3

Enrichment of Metal Ions Obtained after 30 min Dialysis by Using a Cation-Exchange Raipore R-1010 Membrane. Initial Metal Concentration 3 mg/L for Each Metal Ion

	Enrichment factor			
Receiver solution	Cu(II)	Ni(II)	Mn(II)	Zn(II)
0.5 *M* $(NH_4)_2SO_4$, pH 6.0	2.6	2.8	2.4	2.8
0.5 *M* $(NH_4)_2SO_4$, 20 mM Tetren, pH 8.0	2.6	2.9	2.9	3.0

the results obtained for Xylenol Orange, similar experiments were carried out for an R-1030 membrane modified with Eriochromcyjanine R, a chelating ligand with a structure similar to XO because it has one sulfonic group, but containing two carboxylic groups instead of two aminodiacetate groups. The results of dialysis with the Eriochromcyjanine R modified membrane and a receiver solution containing Tetren are presented in Table 4. The results for 30 min dialysis are not very different from those for the XO-modified membrane, except for Zn(II), which was practically not retained for the Eriochromcyjanine R-modified membrane. This membrane can be utilized for the separation of Cu(II) and Zn(II).

CONCLUSIONS

The modification of anion-exchange membranes with chelating ligands offers a new possibility for the selective preconcentration and separation of metal ions.

The different behaviors of modified membranes in comparison to commercial cation membranes were demonstrated by using Xylenol Orange as a membrane modifier. Dialysis performed with a modified membrane results in retention of metal ions in the membrane phase; however, in the presence of a complexing ligand in the receiver solution, the dialyzed metal ions are distributed among the three phases. This was observed without pronounced differences of retention for DCTA in the membrane phase for the metal ions examined. The use of Tetren is more advantageous because only metal uptake into the membrane phase was observed as a result of dialysis. Better separation by the XO-modified membrane can be obtained at a relatively short dialysis time (30 min). The selectivity of such processes

TABLE 4

Retention of Metal Ions on Eriochromcyjanine R Modified R-1030 Membrane Obtained by Using as Receiver Solution 0.5 M $(NH_4)_2SO_4$ with 20 mM Tetren of pH 8.0. Initial Metal Ion Concentration 3 mg/L

Metal dialyzed	Dialysis time (min)	Metal retained in membrane phase (%)
Cu (II)	30	52
	120	55
Mn (II)	30	11
	120	13
Ni (II)	30	19
	120	30
Zn (II)	30	0.5
	120	22

can be adjusted by the choice of chelating ligand for membrane modification as shown by comparison of the properties of membranes modified with Xylenol Orange and Eriochromcyjanine R. In the latter case, several transition metal ions can be separated from zinc(II). Preconcentration of metal ions with the use of tubular membranes in the modified membrane phase, in comparison to modified conventional ion exchangers or of nonionic sorbents, offers new possibilities for the design of a novel open tubular microreactor for selective preconcentration in flow sample processing for analytical purposes.

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