

CHROM. 11,489

APPLICATION OF EXCHANGERS WITH CROWN ETHERS AS ANCHOR GROUPS IN ANALYTICAL AND PREPARATIVE CHEMISTRY

E. BLASIUS, K.-P. JANZEN, H. LUXENBURGER, V. B. NGUYEN, H. KLOTZ and J. STOCKEMER

Department of Analytical Chemistry and Radiochemistry, University of the Saarland, D-6600 Saarbrücken (G.F.R.)

SUMMARY

Exchangers with cyclic polyethers as anchor groups have been prepared by condensation, substitution and polymerization reactions. The exchangers show high resistance to chemicals, temperature and radiolysis. The selectivity for different salts depends on the cation, anion, solvent and size of the ring, and also on the type and basicity of the hetero atom (O, N, S).

The exchangers have wide application in analytical chemistry, such as in separations of cations with a common anion (*e.g.*, alkaline and alkaline earth metals, heavy and precious metals), anions with a common cation (*e.g.*, halides and pseudo-halides) and organic compounds, trace enrichment (*e.g.*, radionuclides) and the determination of water.

The preparative applications of the exchangers include salt conversions and the activation of anions for organic syntheses. A number of reactions can be carried out or improved in anhydrous solutions with the help of the exchangers. They can easily be recovered by filtration and the solvent is not contaminated.

INTRODUCTION

By incorporating cyclic polyethers with various ring diameters and various hetero atoms into a polymer matrix, it is possible to prepare special exchangers¹⁻⁷ that form complexes with a particular range of inorganic and organic compounds. The specific properties of these exchangers, which contain mainly crown compounds and cryptates as the anchor group, lead to various interesting applications. The structures of some exchangers that have been investigated thoroughly are shown in Fig. 1.

In this paper, the properties and applications of these exchangers are considered.

PROPERTIES AND APPLICATIONS

The advantageous properties of these exchangers in comparison with commer-

TABLE I
SELECTIVITY SERIES IN WATER AND METHANOL

Exchanger	Solvent	Alkali metal ions	Ions	Alkaline earth metal ions	Alkylammonium chlorides
§-B-15-C-5 (phenol)	Water	K ⁺ > Na ⁺ > Rb ⁺ > Cs ⁺ > Li ⁺	OH ⁻ > SCN ⁻ > I ⁻ PO ₄ ³⁻ > NO ₃ ⁻ > SO ₄ ²⁻ Br ⁻ > Cl ⁻ > F ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	
	Methanol	K ⁺ > Rb ⁺ > Na ⁺ > Cs ⁺ > Li ⁺	OH ⁻ > SCN ⁻ > I ⁻ PO ₄ ³⁻ > NO ₃ ⁻ > Br ⁻ Cl ⁻ > F ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	Methyl > ethyl- > <i>n</i> -propyl = <i>n</i> -butyl-substituted; mono- > di- > tri- > tetra-substituted for methyl- and ethylammonium chlorides
§-DB-18-C-6	Water	K ⁺ > Rb ⁺ > Na ⁺ > Cs ⁺ > Li ⁺	SCN ⁻ > I ⁻ > NO ₃ ⁻ Br ⁻ > Cl ⁻ > PO ₄ ³⁻ OH ⁻ > F ⁻ > SO ₄ ²⁻	Ra ²⁺ > Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	---
	Methanol	K ⁺ > Rb ⁺ > Na ⁺ > Cs ⁺ > Li ⁺	SCN ⁻ > I ⁻ > NO ₃ ⁻ Br ⁻ > Cl ⁻ > OH ⁻ PO ₄ ³⁻ > F ⁻	Ra ²⁺ > Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	Methyl- > ethyl- = <i>n</i> -propyl- > <i>n</i> -butyl-substituted; mono- > tetra- > di- > tri-substituted for methylammonium chlorides; mono- > tetra- > tri- > di-substituted for ethylammonium chlorides
§-C[2 _n ,2,2]	Water	K ⁺ > Na ⁺ > Rb ⁺ > Cs ⁺ > Li ⁺	SCN ⁻ = I ⁻ > Br ⁻ > Cl ⁻	No uptake	---
	Methanol	K ⁺ > Rb ⁺ > Na ⁺ > Cs ⁺ > Li ⁺	SCN ⁻ = I ⁻ > Br ⁻ > Cl ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺ for Cl ⁻ , Br ⁻ Sr ²⁺ = Ca ²⁺ > Ba ²⁺ > Mg ²⁺ for SCN ⁻ , I ⁻	No uptake
§-DB-21-C-7	Water	Rb ⁺ > K ⁺ > Cs ⁺ > Na ⁺ > Li ⁺	SCN ⁻ > I ⁻ > Br ⁻ > Cl ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	---
	Methanol	Rb ⁺ > K ⁺ > Cs ⁺ > Na ⁺ > Li ⁺	SCN ⁻ = I ⁻ > Br ⁻ > Cl ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	Only monomethyl- and monoethylammonium chlorides are taken up
§-DB-24-C-8	Water	Cs ⁺ > Rb ⁺ > K ⁺ > Na ⁺ > Li ⁺	SCN ⁻ > I ⁻ > Br ⁻ > Cl ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	---
	Methanol	Cs ⁺ > Rb ⁺ > K ⁺ > Na ⁺ > Li ⁺	SCN ⁻ > I ⁻ > Br ⁻ > Cl ⁻	Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺	No uptake

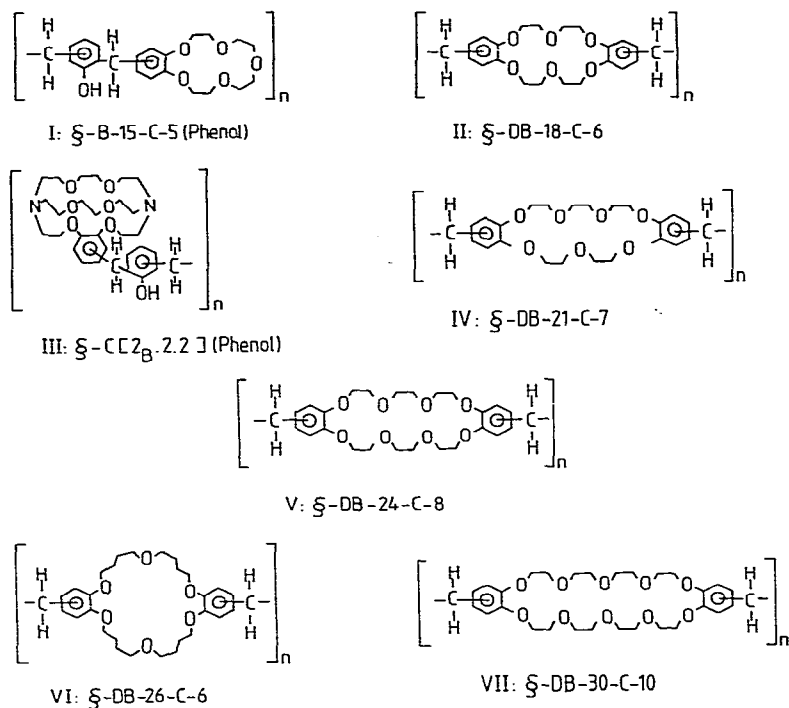


Fig. 1. Exchangers with cyclic polyethers as anchor groups. Hetero atoms: O, N. I = Benzo-15-crown-5; II = dibenzo-18-crown-6; III = cryptate [2_B.2.2]; IV = dibenzo-21-crown-7; V = dibenzo-24-crown-8; VI = dibenzo-26-crown-6; VII = dibenzo-30-crown-10.

cially available exchangers are as follows: high resistance to chemicals; temperature and radiolysis; neutral ligands as anchor groups; simultaneous uptake of cations and anions to maintain electrical neutrality; loosening or complete stripping of the shell of solvent molecules from the cations and anions; binding of ions is facilitated in solvents less polar than water, *e.g.*, methanol; stability of the polyether complexes depends on the cation, anion, solvent and size of the ring, and also on the type and basicity of the hetero atom (O, N, S); complexation with alkali metal cations; activation of anions, also of C-H acid compounds; results of separation and salt uptake are independent of pH if the anchor group contains only O as hetero atom; elution with pure solvents (*e.g.*, water or methanol); no contamination of the eluate.

Other properties are also significant. Firstly, maximum charge capacities and stabilities of the polyether complexes are parallel, and the acid-base theory of Pearson is generally valid. Maximum charge capacities in methanol are 1-2 mmole per gram of exchanger, whereas in water they are about half this value. Secondly, the stability sequences in methanol and water (Table I) correspond, apart from a few exceptions, with those of the monomer complexes. Thirdly, in the sequence of anions, the salt uptake increases in the order of their polarizabilities. In some instances OH⁻ has a special status (Table I).

Exchangers with cyclic polyethers have many possible applications in inorganic and organic chemistry. In radiochemistry they can be used to solve special

TABLE II
APPLICATIONS OF EXCHANGERS WITH CYCLIC POLYETHERS AS ANCHOR GROUPS

<i>Analytical chemistry</i>	<i>Preparative chemistry</i>
Separation of cations (<i>e.g.</i> , alkali and alkaline earth metals, heavy and precious metals)	Salt conversions (<i>e.g.</i> , preparation of iodides and thiocyanates)
Separation of anions (<i>e.g.</i> , halides and pseudo-halides)	Catalysis of organic reactions with activated anions: nucleophilic substitutions, eliminations, additions, saponifications, carbonyl reactions, (benzoin, Darzens, Cannizzaro, and malonic ester reactions), oxidations, reductions, Wittig reactions, organometal reactions, rearrangements, extrusions (CO ₂ , N ₂), isomerizations, polymerizations
Separation of organic compounds	
Trace enrichment (<i>e.g.</i> , radionuclides)	
Determination of water in inorganic and organic compounds	
Column chromatography, thin-layer chromatography	
Electrophoresis	
Ion-sensitive membranes	

problems. Table II shows problems that have been solved or are currently being investigated by us.

The exchangers considered can be applied according to three groupings:

(a) §-B-15-C-5 ($\varnothing = 1.7\text{--}2.2 \text{ \AA}$), §-DB-18-C-6 ($\varnothing = 2.6\text{--}3.2 \text{ \AA}$), §-C[2_B.2.2] ($\varnothing = 2.8 \text{ \AA}$) and §-DB-21-C-7 ($\varnothing = 3.4\text{--}4.3 \text{ \AA}$) ($\varnothing =$ ring diameter). All four exchangers have comparable properties, with ring diameters ranging from 2 to 4 Å. §-DB-18-C-6 has the widest application, and its synthesis is simple. §-C[2_B.2.2] is especially advantageous for aqueous solutions; however, its synthesis is difficult. The first three exchangers prefer potassium of the alkali metal cations. §-DB-21-C-7 binds Rb⁺ more strongly (Table I).

(b) §-DB-24-C-8 ($\varnothing > 4 \text{ \AA}$). This exchanger shows selectivity for Cs⁺ and serves for its separation (Fig. 3).

(c) §-DB-26-C-6 ($\varnothing > 4 \text{ \AA}$) and §-DB-30-C-10 ($\varnothing > 4 \text{ \AA}$). These large polyether rings show only little tendency to form complexes with metal cations. However, they can be used for the separation of large organic molecules. §-DB-30-C-10 is the most versatile exchanger.

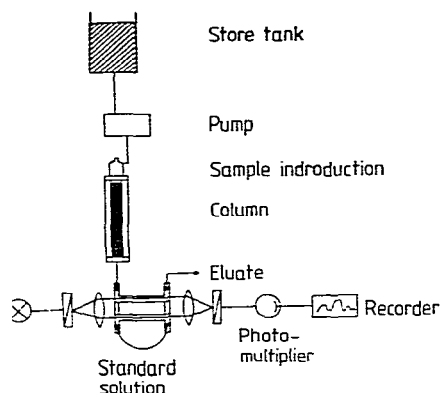
SEPARATIONS

As always in column chromatography, very carefully packed columns are a prerequisite for good separations (Fig. 2).

Columns A–D are used for trace and micro-scale analysis with a differential refractometer or a well-type scintillation counter as a detector. As in all other chromatographic methods, the detection and determination limits depend on the detector used in the separation; in this instance they range from the microgram to picogram level. For preparative purposes, column E is used in combination with a differential refractometer and a fraction collector.

ANALYTICAL APPLICATIONS

The exchangers considered have wide analytical applications, including the



Parameter	Column				
	A	B	C	D	E
Height (cm)	10	15	20	30	60
I.D. (cm)	0.4	0.4	0.4	0.4	2.5
Column volume (cm ³)	1.3	1.9	2.5	3.8	295
Flow-rate (cm ³ /h)	2-20	2-20	2-20	2-20	20-100
Working pressure (bar)	3-15	3-15	3-15	3-20	3-20
Temperature (°C)	25	25	25	25	25

Differential refractometer with photomultiplier

Fig. 2. Procedure for liquid chromatography using exchangers with cyclic polyethers as anchor groups with a differential refractometric detector.

separation of cations with a common anion, the separation of anions with a common cation, the separation of organic compounds and the determination of water.

Separation of cations with a common anion and separation of anions with a common cation

Separations of the alkali and alkaline earth elements, halides and pseudo-halides, heavy and precious metals and radionuclides, and substituted methyl- and ethylammonium chlorides in water and methanol have already been described^{6,7}. They proceed in accordance with the selectivity sequences given in Table I.

As additional examples, the separation of caesium(I) from a simulated medium-active waste solution, 1 M in nitric acid (Fig. 3), and the separation of sodium sulphate-sodium chloride (Fig. 4) by elution with water, can be mentioned.

The spent fuel elements are cut into small pieces, treated with nitric acid and submitted to the Purex process. During this process, large amounts of medium-active waste solutions are produced. After neutralization with sodium carbonate they contain, among other fission products, ¹³⁷Cs, which is difficult to retain in final storage. Its prior selective separation without addition of compounds that interfere later facilitates the glass fixation process of the medium-active waste solutions. A typical composition of a medium-active waste solution is shown in Fig. 3.

The determination of sodium sulphate in the presence of large amounts of sodium chloride (Fig. 4) is very important in rock salt analysis.

Separation of organic compounds

§-DB-30-C-10 serves for the separation of organic compounds in methanol, and a number of examples are given below.

Sulphur-containing compounds. Compounds containing sulphur are usually bound very strongly, as shown in the example urea-thiourea⁶. The separation of benzene from water and thiophene is also possible (Fig. 5).

Fig. 6 shows the separation of diphenyl disulphide and thianthrene, which is important for the investigation of the reaction of aryl mercaptans with sulphur tetrafluoride.

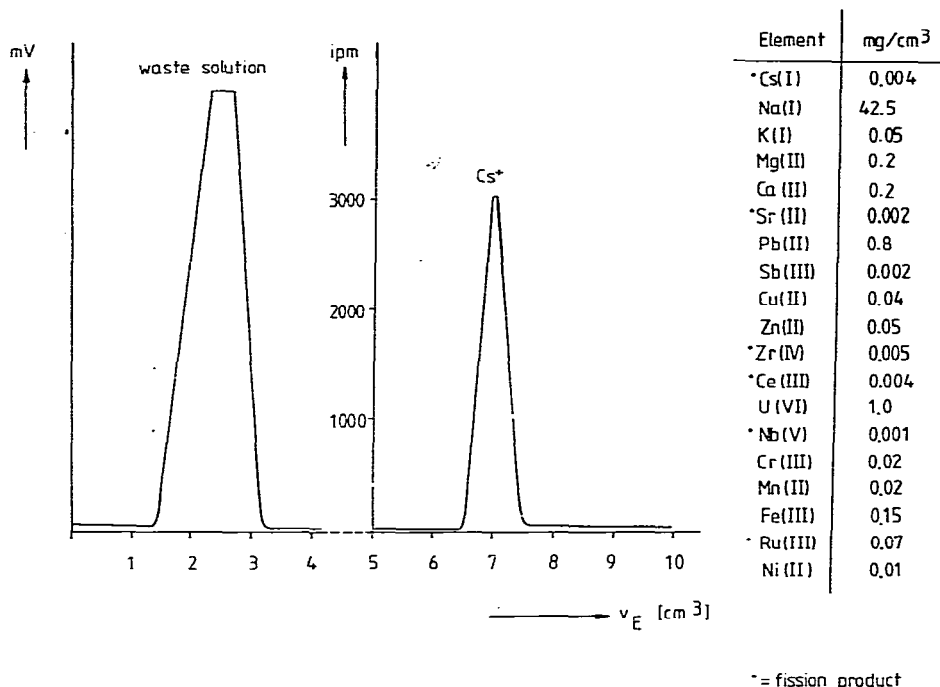


Fig. 3. Separation of 0.0004 mg of Cs^+ (labelled with $5 \mu\text{Ci}$ of ^{137}Cs) from a simulated 1 M nitric acid medium-active waste solution by elution with water, using an exchanger with dibenzo-24-crown-8 as anchor group produced by condensation. Column, D: resin mass, 1.8 g; particle size, $\leq 90 \mu\text{m}$; flow-rate, $2 \text{ cm}^3/\text{h}$.

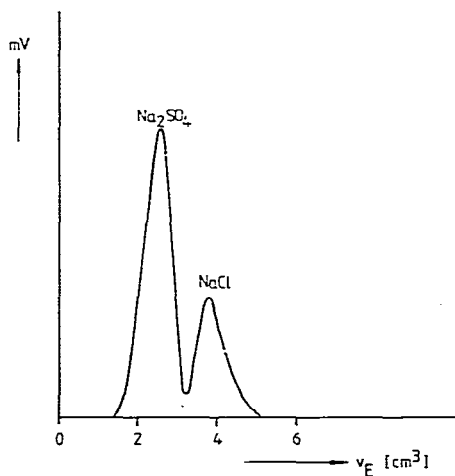


Fig. 4. Separation of 0.05 mg of sodium chloride and 0.07 mg of sodium sulphate by elution with water, using an exchanger with dibenzo-18-crown-6 as anchor group produced by condensation. Conditions as in Fig. 3, except resin mass = 1.6 g.

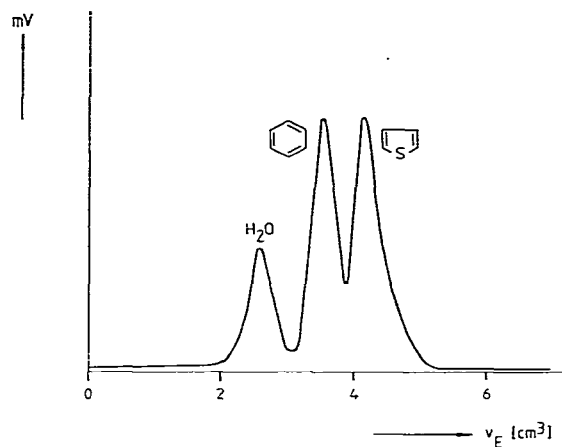


Fig. 5. Separation of 0.4 mg of benzene and 0.4 mg of thiophene by elution with methanol, using an exchanger with dibenzo-30-crown-10 as anchor group produced by condensation. Conditions as in Fig. 3, except resin mass = 2.8 g.

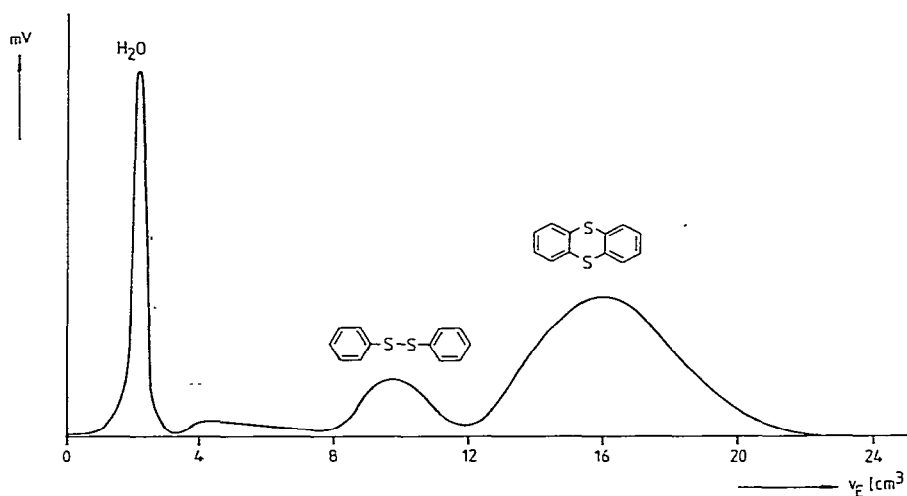


Fig. 6. Separation of 0.5 mg of diphenyl disulphide and 1 mg of thianthrene by elution with methanol, using an exchanger with dibenzo-30-crown-10 as anchor group produced by condensation. Conditions as in Fig. 5.

Nitrogen-containing compounds. Fig. 7 shows the increase in the binding forces to the exchanger with increasing number of nitrogen atoms in the six-membered ring.

Fig. 8 shows the separation of furan, thiophene and pyrrole. The elution volumes of these analogously structured compounds increase as the hetero atom changes from O to S to N.

Analgesics. Fig. 9 shows the separation of the active substances of an analgesic. Such separations are interesting for the investigation of the efficiency and the residence time of analgesics in the human body, and also for the purity tests and analyses of analgesics.

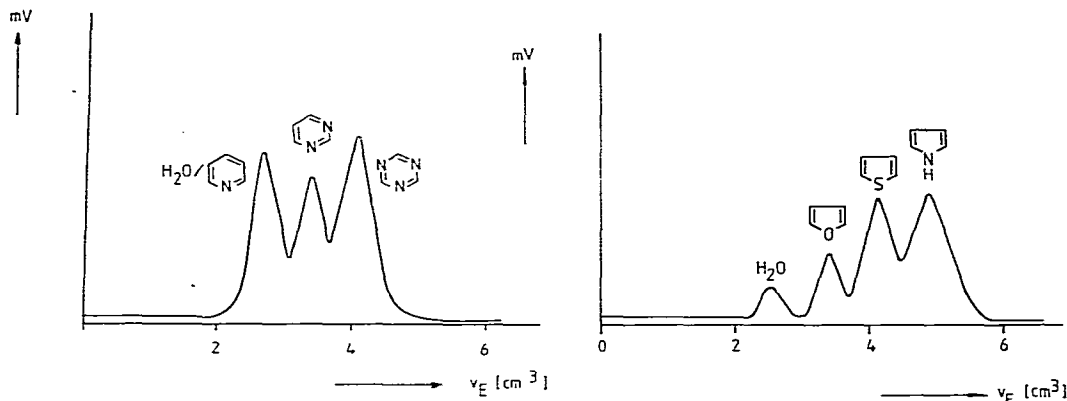


Fig. 7. Separation of 0.07 mg of pyridine, 0.15 mg of pyrazine and 0.25 mg of triazine by elution with methanol, using an exchanger with dibenzo-30-crown-10 as anchor group produced by condensation. Conditions as in Fig. 5.

Fig. 8. Separation of 0.2 mg of furan, 0.2 mg of thiophene and 0.2 mg of pyrrole by elution with methanol, using an exchanger with dibenzo-30-crown-10 as anchor group produced by condensation. Conditions as in Fig. 5.

Vitamins and antibiotics. Fig. 10 shows the separation of some vitamins. The separation of the vitamin B complex is valuable for establishing which micro-organisms are able to produce or consume a particular B vitamin on a culture medium. The separation of antibiotics is also possible.

Determination of water

The determination of water in methanol as a solvent serves as an example of the quantitative application of elution chromatography using exchangers with cyclic polyethers as anchor groups. Analytically pure methanol from Merck (Darmstadt, G.F.R.) itself contains a maximum of 0.01 % of water. This does not disturb the measurement, however, as a differential refractometer is used as a detector.

Additional traces of water in methanol and other organic solvents lead to a water band. In this way water of crystallization and association in salts and organic compounds can be determined. Fig. 11 shows the behaviour of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

With quinone as the sample (Fig. 12), an impurity peak is found next to the water peak.

By quantitative evaluation of the area of the water peak, it is now possible to determine contents down to 1 ppm. This method can be recommended when gas chromatography or other methods permit the water contents of compounds to be determined with only low accuracy or not at all. Copper(II) salts and quinone, for example, react with components of Karl-Fischer solution.

In addition, it has been shown experimentally that the water of solvation and crystallization in most salts is quantitatively stripped during complex formation.

The water and the anchor group interact, as shown in the elution diagrams in Fig. 13. In this way, lithium, manganese and chromium(III) chlorides are eluted from the column before the water.

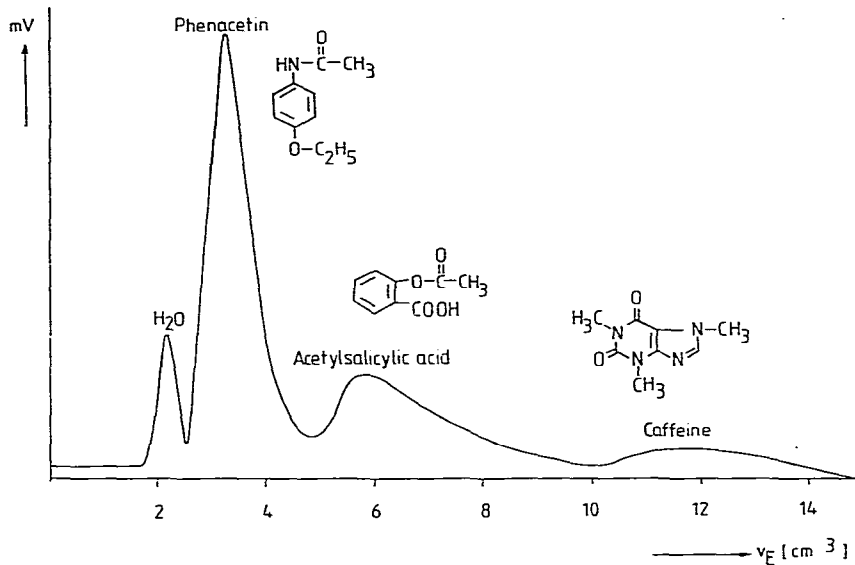


Fig. 9. Separation of active substances of an analgesic (0.015 mg of acetylsalicylic acid, 0.004 mg of phenacetin and 0.0001 mg of caffeine) by elution with methanol, using an exchanger with dibenzo-30-crown-10 as anchor group produced by condensation. Conditions as in Fig. 5.

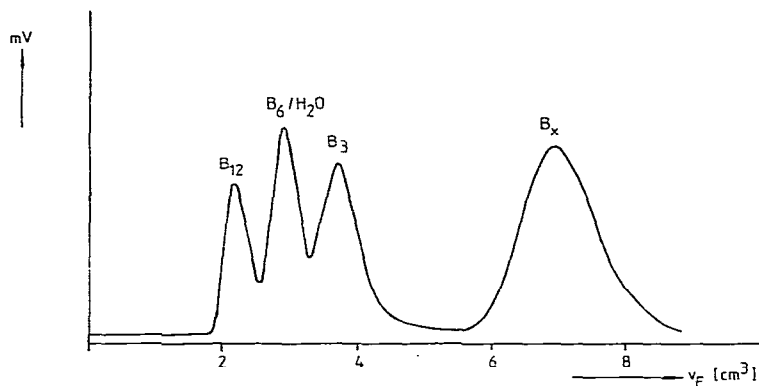


Fig. 10. Separation of 0.1 mg of vitamin B₁₂, 0.03 mg of vitamin B₆, 0.01 mg of vitamin B₃ and 0.3 mg of vitamin B_x by elution with methanol, using an exchanger with dibenzo-30-crown-10 as anchor group produced by condensation. Conditions as in Fig. 5.

PREPARATIVE CHEMISTRY

The preparative applications of the exchangers include salt conversions (exchange of partners of anions and cations) and the activation of anions for organic syntheses.

Salt conversions

According to this method, gram amounts of the following salts were prepared in

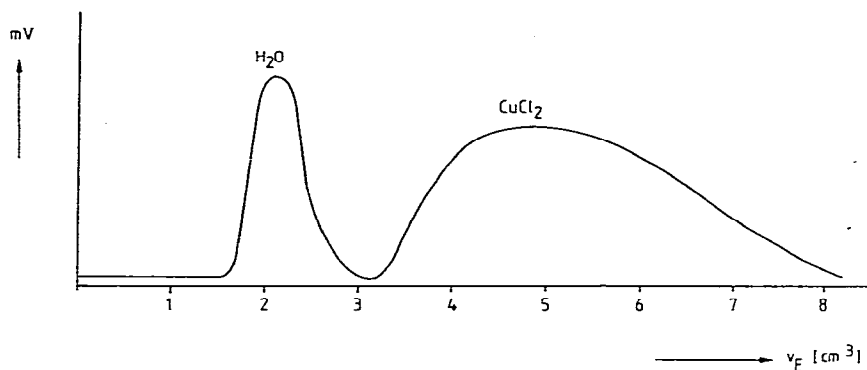


Fig. 11. Determination of water in 0.168 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ by elution with methanol, using an exchanger with dibenzo-18-crown-6 as anchor group produced by condensation. Column, C; resin mass, 1.3 g; particle size, 40–63 μm ; flow-rate, 4 cm^3/h .

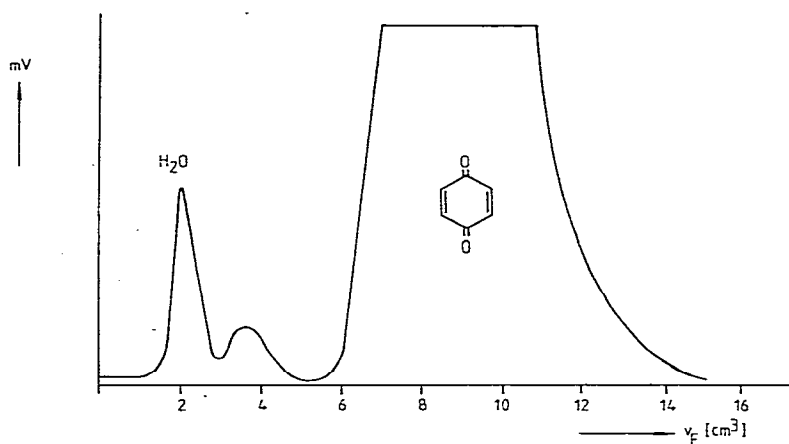
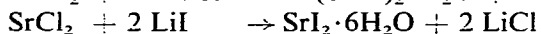
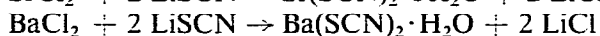
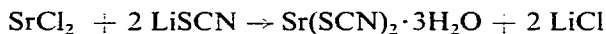


Fig. 12. Determination of water in 0.605 mg of quinone by elution with methanol, using an exchanger with dibenzo-18-crown-6 as anchor group produced by condensation. Conditions as in Fig. 11, except flow-rate = 2 cm^3/h .

aqueous solution:



Organic syntheses with activated anions

A number of reactions can be carried out or improved in anhydrous solutions by using anion activation with the help of cyclic polyethers. This is very important if water interferes in the reaction.

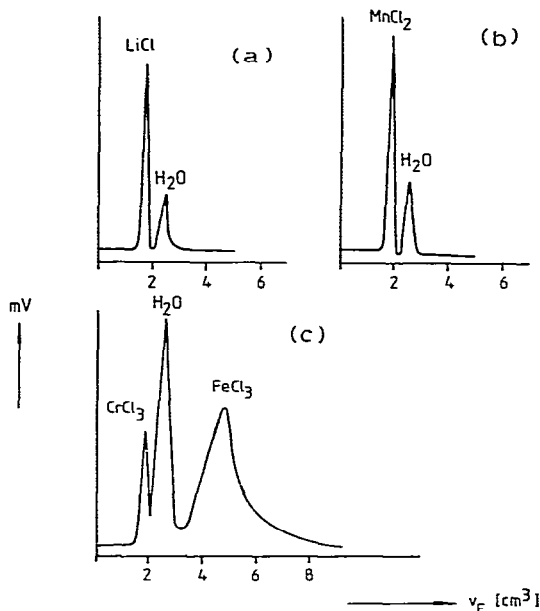


Fig. 13. Elution of (a) 0.02 mg of $\text{LiCl} \cdot x\text{H}_2\text{O}$, (b) 0.08 mg of $\text{MnCl}_2 \cdot 3\text{H}_2\text{O}$ and (c) 0.39 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.05 mg of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with methanol, using an exchanger with dibenzo-18-crown-6 as anchor group produced by condensation. Column, D (I.D. 0.34 cm); resin mass, 2.1g; particle size, $\leq 90 \mu\text{m}$; flow-rate, $5 \text{ cm}^3/\text{h}$.

The simple separation, recovery by filtration and renewed application is a great advantage in comparison with the application of monomeric cyclic polyethers, and the solvent is not contaminated. The extension of the reaction time is disadvantageous.

§-DB-18-C-6 is charged with a potassium salt (cyanide, thiocyanate, acetate) in methanol under reflux and filtered *in vacuo*. The reactions are carried out in carbon tetrachloride. When the reaction has finished, the charged exchanger is filtered, the solvent distilled off *in vacuo* and the residue identified and analysed by NMR and IR spectroscopy and by gas and thin-layer chromatography.

Some model investigations are described below. Application of the polymeric crown ether is compared with that of a monomeric crown ether and a classical method. They represent only the beginning of a comprehensive series of experiments, and the reactions carried out with charged exchangers can be improved further. The application of the charged exchangers particularly promotes nucleophilic substitutions.

Reaction of benzyl chloride with potassium thiocyanate to form benzyl thiocyanate and benzyl isothiocyanate (Table III). Benzyl isothiocyanate is formed together with benzyl thiocyanate; this does not occur when using monomer cryptates.

The production of benzyl isothiocyanate by classical methods is very difficult (four-fold distillation of benzyl thiocyanate at $250\text{--}260^\circ$). Using §-DB-18-C-6, benzyl isothiocyanate is formed even at 77° .

TABLE III

REACTION OF BENZYL CHLORIDE WITH POTASSIUM THIOCYANATE TO FORM BENZYL THIOCYANATE AND BENZYL ISOTHIOCYANATE, USING AN EXCHANGER WITH DIBENZO-18-CROWN-6 AS ANCHOR GROUP PRODUCED BY CONDENSATION
Activated anion: SCN⁻.

Method of preparation	Reactants	Solvent	Temperature (°C)	Reaction time (h)	Yields of benzyl thiocyanate/ benzyl isothiocyanate (%)		Reference
					With exchanger	Without exchanger	
With §-DB-18-C-6	5 g of exchanger + 43.5 mmole of benzyl chloride	Carbon tetrachloride	77	150	54.2/45.8	82.6/0	—
	10 g of exchanger + 43.5 mmole of benzyl chloride	Carbon tetrachloride	77	50	68.5/31.5	26/0	—
With C [2.2.2]*	1 mmole of Kryptofix [2.2.2] (Merck) + 100 mmole of benzyl chloride	Chloroform	25	144	80/0	80/0	—
Classical	Benzyl chloride Benzyl thiocyanate	Ethanol	78	No data	No data	No data	8
		Four-fold distillation of benzyl thiocyanate	250–260	No data	Mustard oil (70%) (23% of theory after working up)		9

* Cryptate N(CH₂·CH₂·O·CH₂·CH₂·O·CH₂·CH₂)₃N.

TABLE IV

REACTION OF α,p -DIBROMOACETOPHENONE WITH POTASSIUM ACETATE TO FORM p -BROMOPHENACYL ACETATE, USING AN EXCHANGER WITH DIBENZO-18-CROWN-6 AS ANCHOR GROUP PRODUCED BY CONDENSATION
 Activated anion: CH_3COO^- .

Method preparation	Reactants	Solvent	Temperature ($^{\circ}\text{C}$)	Reaction time (h)	Yield of p -bromophenacyl acetate (%)		Reference
					With exchanger	Without exchanger	
With δ -DB-18-C-6	15 g of exchanger + 5.4 mmole of α,p -dibromoacetophenone	Carbon tetrachloride	77	3.5	100	8	—
With 18-C-6	1 mmole of 18-C-6 + 20 mmole of α,p -dibromoacetophenone	Acetonitrile	80	0.25	100	100	10
Classical	No data	Water or dimethyl-formamide	No data	No data	No data	No data	11

Reaction of α,p -dibromoacetophenone with potassium acetate to form p -bromophenacyl acetate (Table II). The p -bromophenacyl esters of fatty acids permit the quantitative determination of fatty acids by using a UV detector, and the complete separation of the crown ether from the reaction mixture is therefore very important in this instance. The stated reaction time of 3.5 h can probably be shortened.

With classical methods, the formation of the ester is time consuming. Water present hydrolyses p -dibromoacetophenone and reduces the yield.

FUTURE PROSPECTS

At present, cyclic polyethers are fixed to a hydrophobic silica gel and their application in high-performance liquid chromatography for rapid quantitative determinations is being investigated.

In addition to exchangers with dibenzo-24-crown-8 as the anchor group, adducts of the crown ether with dodecamolybdato-phosphoric acid are suitable for the extraction of ^{137}Cs from medium-active waste solutions. Liquid exchangers can also be used to separate ^{137}Cs from medium-active waste solutions.

Further, exchangers with cyclic polyethers as anchor groups can be applied in thin-layer chromatography and as components of ion-sensitive membranes.

REFERENCES

- 1 E. Blasius, W. Adrian, K.-P. Janzen and G. Klautke, *J. Chromatogr.*, 96 (1974) 89.
- 2 E. Blasius and K.-P. Janzen, *Chem.-Ing.-Tech.*, 47 (1975) 594.
- 3 E. Blasius, K.-P. Janzen and G. Klautke, *Z. Anal. Chem.*, 277 (1975) 374.
- 4 E. Blasius and P.-G. Maurer, *J. Chromatogr.*, 125 (1976) 511.
- 5 E. Blasius and P.-G. Maurer, *Makromol. Chem.*, 178 (1977) 649.
- 6 E. Blasius, K.-P. Janzen, W. Adrian, G. Klautke, R. Lorscheider, P.-G. Maurer, V. B. Nguyen, T. Nguyen-Tien, G. Scholten and J. Stockemer, *Z. Anal. Chem.*, 284 (1977) 377.
- 7 E. Blasius, K.-P. Janzen and W. Neumann, *Mikrochim. Acta*, (1977) 279.
- 8 G. A. Barbaglia, *Ber. Deut. Chem. Ges.*, 5 (1872) 687.
- 9 H. Henicke, *Justus Liebigs Ann. Chem.*, 344 (1906) 24.
- 10 H. D. Durst, M. Milano, E. J. Kikta, S. A. Conelly and E. Grushka, *Anal. Chem.*, 47 (1975) 1797.
- 11 J. B. Hendrickson and C. Kandall, *Tetrahedron Lett.*, (1970) 343.