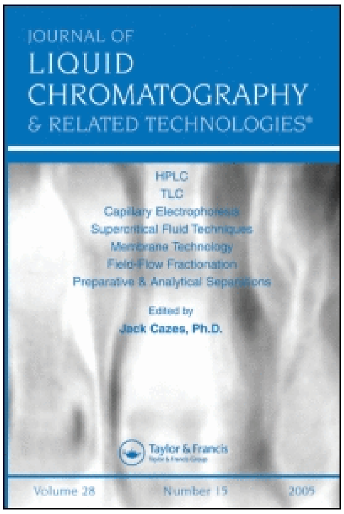


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Ion Chromatographic Separation on Silica Grafted with Benzo-18-C-6 Crown Ether

M. Lauth[a]; Ph. Gramain[a]
[a] Institut Charles Sadron (CRM-EAHP), Strasbourg-Cedex, France

To cite this Article Lauth, M. and Gramain, Ph.(1985) 'Ion Chromatographic Separation on Silica Grafted with Benzo-18-C-6 Crown Ether', Journal of Liquid Chromatography & Related Technologies, 8: 13, 2403 — 2415
To link to this Article: DOI: 10.1080/01483918508076578
URL: http://dx.doi.org/10.1080/01483918508076578

JOURNAL OF LIQUID CHROMATOGRAPHY, 8(13), 2403-2415 (1985)

ION CHROMATOGRAPHIC SEPARATION ON SILICA GRAFTED WITH BENZO-18-C-6 CROWN ETHER

M. Lauth and Ph. Gramain
Institut Charles Sadron (CRM-EAHP)
CNRS-ULP Strasbourg
6, rue Boussingault
67083 Strasbourg-Cedex, France

ABSTRACT

Benzo-18-C-6 crown ether has been grafted on silica gel modified with a spacer. By very carefull control of each step of the synthesis an exchanger for alkali and alkaline earth cations with high capacity and low equilibrium time has been prepared. The chromatographic behavior of alkali and alkaline earth metal halides on this benzo-18-C-6 crown ether modified silicas was investigated with water as the mobile phase. With alkali metal chlorides, very good separations are obtained in less than 30 minutes. With alkaline earth metal chlorides, very good separations are also obtained except for Ca^{2+}/Mg^{2+}. Separations are also observed with mixtures of alkali and alkaline earth cations. Moreover, a very efficient separation of anions is observed, partly as a result of the hydrophobic character of the exchanger.

INTRODUCTION

The application of crown ethers (C.E.) and cryptands in analytical chemistry have been extensively developed (1) and one of the most attractive applications is their use in liquid chromatography for cation separations (2,3). The best way to achieve this goal is the immobilization of the ligands on organic or inorganic supports. Inorganic materials such as silica gel seem to be preferable when high pressure is required in liquid chromatography. Blasius et al. (4) prepared benzo-15-crown-5-silica and observed good separation for alkali cations

0148-3919/85/0813-2403$3.50/0

in methanol. Igawa et al. (5) prepared silica gel coated by polyamide-type crown ether and obtained a good separation only for various anions. Better results have been published by Kimura et al. (6) with poly(crown-ether)-modified silicas. Rather good separations for alkali and alkaline earth cations are obtained by elution with water or mixtures of water-methanol. Those studies show that the quality of the cation separations strongly depend on the chemical structure of the bound crown ether and on the preparation of the exchanger.

In this paper the preparation of one exchanger with benzo-18-crown-6 supported by modified silica gel is described and the chromatographic behavior of this exchanger on separation of alkali and alkaline earth metal salts and of anions in water is presented. Particular attention has been paid to the method of preparation in order to optimize the quality of the separations.

RESULTS AND DISCUSSION

The synthesis route is composed of four steps :

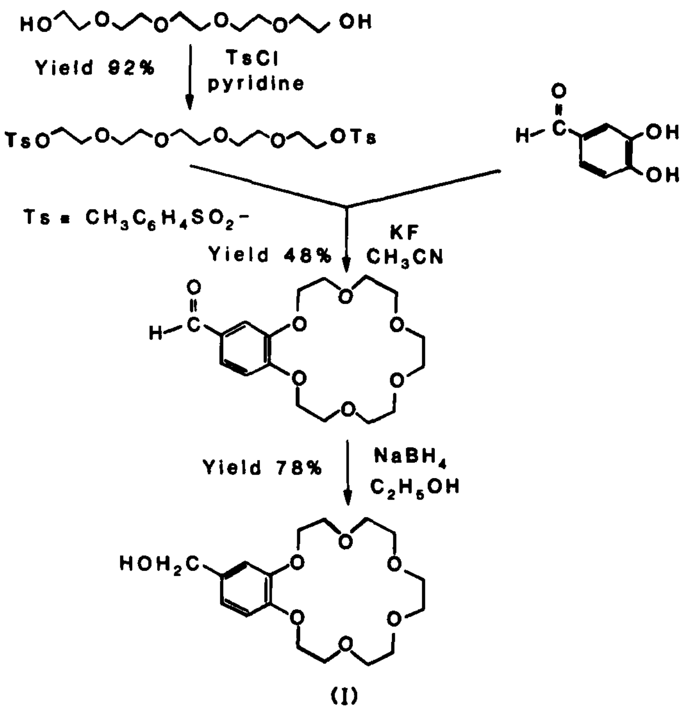
- synthesis of a functionalized crown ether
- activation of the selected silica gel
- grafting of a spacer on silica
- grafting of the C.E. on the modified silica

The result of each step is carefully analyzed by NMR and elemental chemical analysis.

Synthesis of 4'-(Hydroxymethyl)benzo-18-C-6 (I)

The scheme of the synthesis of (I) is illustrated in figure 1. 4'-formylbenzo-18-C-6 is obtained with 48% yield by using the general method described by Reinhoudt (7). Another method consisting to prepare first the benzo-18-C-6 with subsequent formylation (8,9) gives only 16% yield. Reduction of the formyl derivative with $NaBH_4$ in ethanol leads to (I) with 78% yield.

The binding properties of (I) for K^+, Sr^{++} and Ba^{++} in water has been determined by an original competition method which will be described elesewhere using the protonable C.E. dimethyl-diamine [22] (10).



(I)

FIGURE 1. Synthesis of 4'-(hydroxymethyl)benzo-18-crown-6

TABLE 1

Stability Constants in Water of some Crown Ether Complexes

Crown Ether	pK in water		
	K^+	Sr^{2+}	Ba^{2+}
18-C-6 (11)	2.03	2.72	3.87
DB-18-C-6 (12)	1.67	1.0	1.95
$HOCH_2B$-18-C-6 (I)	1.83	1.89	2.73

Results are collected in table 1 and compared with stability constants of complexes of DB-18-C-6 and 18-C-6 obtained by calorimetry and NMR (11,12). As expected, the binding properties of ligand (I) are between those of the two preceeding ligands.

Synthesis of Modified Silicas

The synthesis of spacer-modified silicas is depicted in figure 2. In a first step the silica gel (Lichrosorb SI 100, 30 and 10µm Merck) was activated by refluxing in concentrated HCl for 4h followed by washing with water and dried overnight under vacuum (0.01mbar) at 180°C. This leads to about 8 µmoles of OH by m^2 (13). In the second step the silica is grafted with 3-aminopropyltriethoxysilane leading to a monolayer grafting of 1.0mmole/g. The third step consists of completing the spacer by reacting 4-(chloromethyl)benzoyl chloride on the aminated silica. A 90% yield is obtained leading to a silica containing 0.80mmole of Cl per gramme. Finally the residual silanol groups are substituted

TABLE 2

Binding Characteristics of Benzo-18-C-6-silicas

Silica	Capacity (mmole/g) Calculated	Capacity (mmole/g) Experim.	Salt	Solvent	Equilibrium time (min)
30µm	0.27	0.26	KSCN	CH_3OH	10
		0.24	KSCN	CH_3OH-H_2O 90/10	"
		0.23	$Ba(SCN)_2$	"	"
		0.10	KCl	H_2O	"
		0.09	$BaCl_2$	H_2O	"
10µm	0.27	0.22	KSCN	CH_3OH-H_2O	15
		0.22	$Ba(SCN)_2$	90/10	"
		0.16	$Ca(SCN)_2$	"	"
		0.15	NaSCN	"	"
		0	LiSCN	"	"
		0.12	$BaCl_2$	H_2O	"
		0.05	$SrCl_2$	"	"
		0	$CaCl_2$	"	"

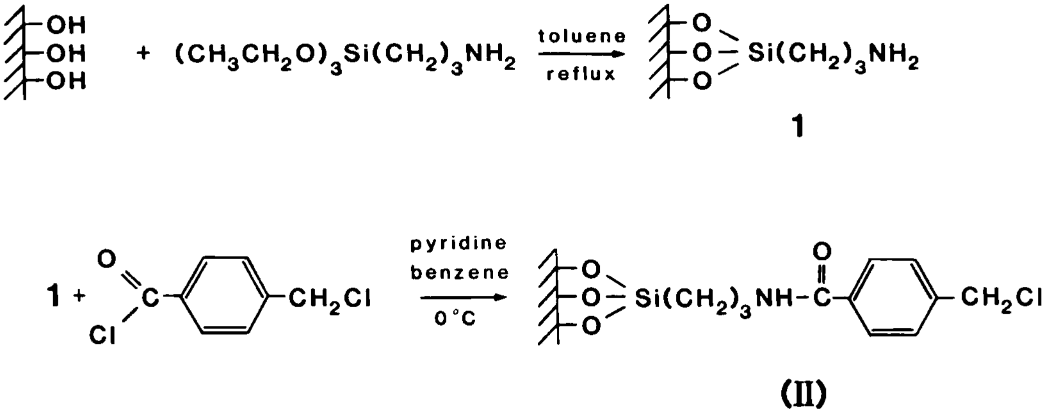


FIGURE 2. Synthesis of spacer-modified silicas

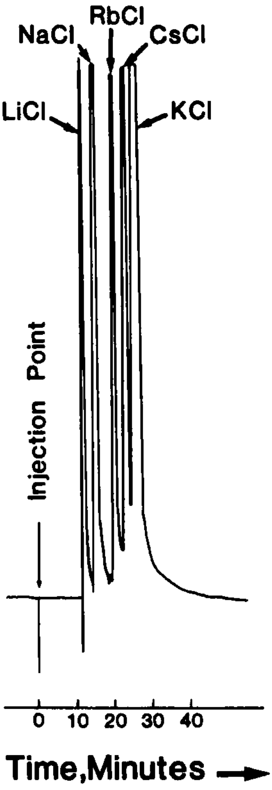


FIGURE 3. Separation of alkali metal chlorides ; mobile phase, water

by treatment with trimethylsilyl chloride (TMCS) at room temperature. Based on the percentage increase of carbon, it appears that 0.5µmole OH/m^2 have been substituted ; this demonstrated that even after TMCS treatment, many OH groups are present but not accessible.

Grafting of the Crown Ether

By formation of the alcoolate of (I) and nucleophilic substitution in THF, the final C.E.-grafted silica is obtained with a theoretical capacity of 0.27mmole/g. This relatively low yield (35%) is first explained by a nucleophilic breaking of some siloxane bonds (10%) and secondly by steric reasons.

Binding Characteristics

The binding characteristics of two grafted silicas (10 and 30µm) have been determined by equilibration with different metallic chlorides and thiocyanates in water and water/CH_3OH mixtures. Results are collected in table 2 together with the time necessary to obtain 90% of the equilibrium capacity.

The following is observed :

- the maxima capacity as determined by chemical analysis is effectively attained with KSCN in pure CH_3OH
- the capacity depends on the solvent and on the type of anion as generally observed with supported crown ether. The reason of these dependence is clearly explain by the hydrophobic nature of the material
- the capacity depends on the type of the cation and is in agreement with the binding properties of the ligand in water solution. K^+ and Ba^{++} are best retained, Li^+ and Ca^{++} show no retention
- the equilibrium times are short and independent of the nature of the solvent and of the salt. This indicates that the accessibility of the ligands is good. Shorter times are obtained with the 30µm silica, probably due to higher porosity.

In summary, by carefully choice of the synthesis route it is relatively easy to get a benzo-18-C-6 modified silica with good binding characteristics. The maximum capacity obtained in this study compares well with that obtained in other studies. The observed capacity limit is attributed to the non reactivity of many hydroxyl groups present on the silica and to an effect of steric hindrance.

CHROMATOGRAPHIC BEHAVIOUR

We use the grafted silica previously described with an average size of 10µm, except when mentioned, and a theoretical capacity of 0.27mmole per 1g of dry material. The silica is packed in a stainless column (l=13cm, i.d.=0.48cm) using a suspension in CCl_4 injected at high pressure (300 bars). Chromatographic experiments were performed with a classical chromatograph system with detection by conductivity measurements. The water flow rate used is 0.24ml per minute.

Separation of Akali Metal Chlorides

The chromatographic behavior of the stationary phase for alkali metal chlorides is illustrated in figure 3. Injected quantities are

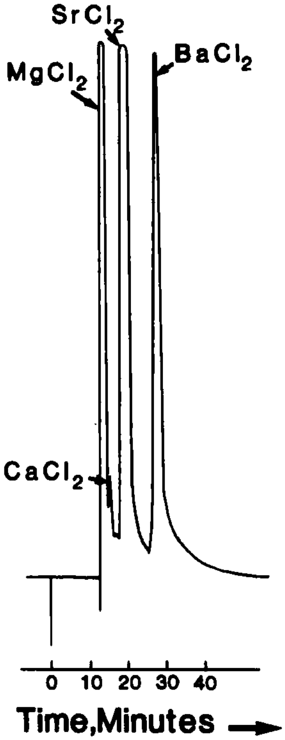


FIGURE 4. Separation of alkaline earth metal chlorides ; mobile phase, water

(in µ g) : Li, 25 ; Na, 35 ; Rb, 48 ; Cs, 67 ; K, 112. Complete separation of LiCl, NaCl, KCl, RbCl and CsCl is observed in 30 minutes by elution with pure water. The elution sequence is in agreement with the expected sequence except for Cs^+ which appears more retained than Rb^+ contrary to their relative size. A possible explanation is the formation of a sandwich complex with Cs^+ (two ligands for one cation).

Separation of Alkaline Earth Metal Chlorides

The separation of alkaline earth metal chlorides is illustrated in figure 4. A very good separation is obtained in a short time except for Mg^{2+}/Ca^{2+} even though these cations have different sizes (0.65Å

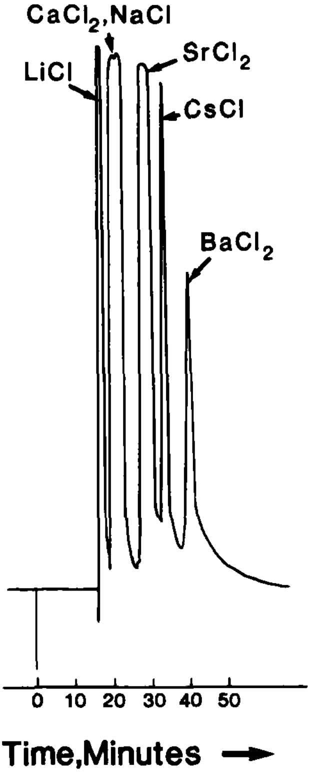


FIGURE 5. Separation of alkali and alkaline earth metal chlorides ; mobile phase, water

and 0.99Å respectively). This has already been observed with a similar system (14) and can be attributed to the strong hydration of these cations.

Injected quantities are (in µg) : Mg,29 ; Ca,11 ; Sr,95 ; Ba,208.

Separation of Mixtures of Alkali and Alkaline Earth Metal Chlorides

Simultaneous separation of alkali and alkaline earth metal chlorides is possible in pure water as shown in figure 5, without using a gradient elution.

In the typical example shown only the two components Ca/Na are not separated.

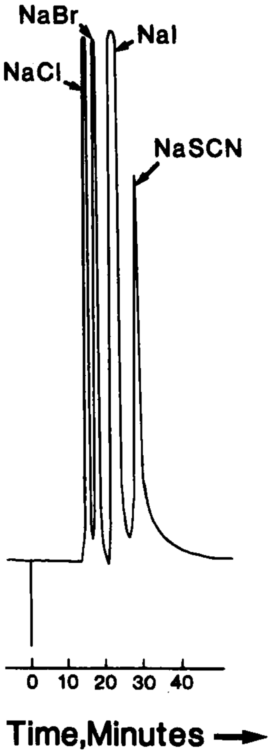


FIGURE 6. Separation of anions ; mobile phase, water

Injected quantities are (in μg) : Li,21 ; Ca,Na,33 ; Sr,48 ; Cs,84 ; Ba,208.

Separation of Anions

Figure 6 illustrates the chromatographic behavior of sodium salt mixtures with chloride, bromide, iodide and thiocyanate eluted with pure water. The anions are very well separated and the order of elution corresponds to the increase of polarizability of the anion. The hydrophobic character of the exchanger is probably the determining factor in obtaining such good separations.

Injected quantities area (in μg) : Cl,12 ; Br,21 ; I,90 ; SCN, 97
Modified silica of 30μm.

CONCLUSION

The presented results of the separation of alkali, alkaline earth cations, mixtures of these and of anions, illustrated the exceptional binding properties of crown ethers. However it is clear that such a good performance can only be obtained by a very careful synthesis of the exchanger together with a good choice of the silica support. More detailed results will be described soon. It is believed that such exchangers offer new separation possibilities.

EXPERIMENTAL

Materials

2,3-[4-(Hydroxymethyl)benzo] -1,4,7,10,13,16-hexaoxacyclooctadec-2-ene(I)

14.3g(4.2×10^{-2}mole) of 4'-formylbenzo-18-C-6 is added to 2.23g (5.9×10^{-2}mole)$NaBH_4$ in dry ethanol at room temperature. After 48h, the mixture is poured in 250ml water, neutralized with acetic acid and extracted three times with $CHCl_3$. 13.4g of pure product is obtained after evaporating the solvent and recrystallization from ethyl ether (mp 60°C). Yield : 78%.

3-Aminopropyl-silica

In anhydrous conditions 17.0g of activated silica is added to 7.0g (3.2×10^{-2}mole) of 3-aminopropyltriethoxysilane in solution in 100ml toluene. After 1h refluxing, 25ml of solvent is evaporated and reflux is repeated 1h. This operation is repeated two times. The silica is recuperated and washed with toluene and THF/water and dried at 80°C for 16h at 0.05mbar giving 18.9g of 3-aminopropyl-silica.

3-[4-(Chloromethyl)benzamido]propyl-silica (II)

11.1g (1.2×10^{-2}mole) of 3-aminopropyl-silica, 6ml anhydrous pyridine are mixed in 40ml of benzene at 0°C. Drop by drop, 5.1g (2.7×10^{-2}mole) of 4-(chloromethyl) benzoyl chloride dissolved in 75ml benzene is introduced. Afer 8h the silica is washed and dried at 80°C giving 12.5g. Yield : 87%.

Grafting of (I) on (II)

(II) is first treated with TMCS and dried. Clean NaH 0.82g (3.4×10^{-2} mole) is introduced in 150ml anhydrous THF and 7.6g (2.2×10^{-2}mole) of (I). After 6h at 50°C, 20.0g (1.7×10^{-2}mole) of TMCS - silica is introduced and the mixture is refluxed for 120h with very slow stirring.

Silica is recuperated, washed with different solvents and dried under vacuum giving 20.7g. Yield : 35%.

Binding Determinations

Equilibrium time

250mg of silica is put in equilibrium with 5ml of a salt solution (0.25M) with slow stirring in a thermostated room. After 5,10,20,30 minutes and 1,6,24 hours, the solution is titrated by silver nitrate.

Capacity

We use the same method as before with different salt concentrations (25,50,75,100,200x10^{-3}M). After 12 hours, the solution is filtered and analysed.

Instrumentation

The chromatographic system consists of a water tank (desionizated and filtered on Millipore R pH=5), a Milton Roy pump, a sample injector Chromatem 70-10 with a volume of 20µl, a conductimetric detector Taccusel CD 6N, and a recorder Philips PM 8100. The thermostat in the room is set to 25°C.

REFERENCES

(1) Kolthoff, I.M., Anal.Chem., 51, 1R, 1979.

(2) Kimura, K. and Shono, T., J.Liquid Chromatogr., 5(Suppl.2), 223, 1982.

(3) Frère, Y. and Gramain, Ph., Makromol.Chem., 183, 2163, 1982.

(4) Blasius, E., Janzen, K.P., Klein, W., Klotz, H., Nguyen, V.B., Nguyen-Tien, T., Pfeiffer, R., Scholten, G., Simon, H., Stockemer, H. and Toussaint, A., J.Chromatogr., 201, 147, 1980.

(5) Igawa, M., Saito, K., Tsukamoto, J. and Tanaka, M., Anal.Chem., 53, 1942, 1981.

(6) Kimura, K., Nakajima, M. and Shono, T., Anal.Lett., 13, 741, 1980.

(7) Reinhoudt, D.N., de Jong, F. and Tomassen, H.P., Tetrahedron Lett. 2067, 1979.

(8) Wada, F., Hirayama, H., Namiki, H., Kikukawa, K. and Matsuda, T., Bull.Chem.Soc.Jpn, 53, 1473, 1980.

(9) Smith, W.E., J.Org.Chem., 37, 3972, 1972.

(10) Lauth, M., Frère, Y., Gramain, Ph., to be published.

(11) Izatt, R.M., Terry, R.E., Haymore, B.L., Hansen, L.D., Dalley, N.K., Avondet, A.G. and Christensen, J.J., J.Am.Chem.Soc., 98, 7620, 1976.

(12) Shchori, E., Nae, N. and Jagur-Grodzinski, J., J.Phys.Soc. Dalton Trans., 2381, 1975.

(13) Unger, K., Porous Silica, Elsevier, Amsterdam, 1979, pp. 83-130.

(14) Nakajima, M., Kimura, K. and Shono, T., Anal.Chem., 55, 463, 1983.