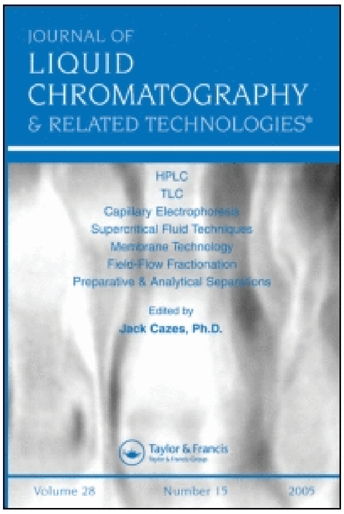


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Metal-Loaded Sorbents for Selective On-Line Sample Handling and Trace Enrichment in Liquid Chromatography

M. W. F. Nielen[a]; H. E. Van Ingen[a]; A. J. Valk[a]; R. W. Frei[a]; U. A. Th. Brinkman[a]
[a] Department of Analytical Chemistry, Free University, HV Amsterdam, The Netherlands

To cite this Article Nielen, M. W. F. , Van Ingen, H. E. , Valk, A. J. , Frei, R. W. and Brinkman, U. A. Th.(1987) 'Metal-Loaded Sorbents for Selective On-Line Sample Handling and Trace Enrichment in Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 10: 4, 617 — 633

To link to this Article: DOI: 10.1080/01483918708069013

URL: http://dx.doi.org/10.1080/01483918708069013

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(4), 617-633 (1987)

METAL-LOADED SORBENTS FOR SELECTIVE ON-LINE SAMPLE HANDLING AND TRACE ENRICHMENT IN LIQUID CHROMATOGRAPHY

M. W. F. Nielen, H. E. van Ingen, A. J. Valk,
R. W. Frei, and U. A. Th. Brinkman*
Department of Analytical Chemistry
Free University
De Boelelaan 1083
1081 HV Amsterdam, The Netherlands

ABSTRACT

Three different commercially available stationary phases containing a thiol, an 8-hydroxyquinoline (oxine), and a 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) functional group, were loaded with mercury (Hg(II)), platinum (Pt(IV)) and silver (Ag(I)) ions. The phases were packed in small precolumns and evaluated for their potential towards the selective on-line sample handling and trace enrichment of three model systems in liquid chromatography. The thiol 2-mercaptobenzimidazole was used to study trace enrichment on Hg(II)-loaded phases; the herbicide buturon, which contains an ethynic bond, was selected to study trace enrichment on Ag(I)-loaded phases. The on-line filter effect of Pt(IV)-loaded phases was investigated with 4-chloroaniline as a model compound.

The results indicate that the Hg(II)-ACDA phase should be preferred for the trace enrichment of thiols, a Pt(IV)-ACDA or a Pt(IV)-thiol phase for the anilines and the Ag(I)-oxine phase for the trace enrichment of ethynic compounds.

As environmental application, the selective on-line trace enrichment of buturon from river water samples, on a precolumn packed with Ag(I)-oxine, is shown.

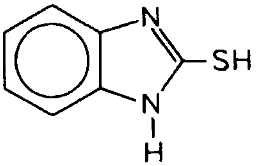
INTRODUCTION

Ligand-exchange phenomena (1) have been used for the liquid chromatographic separation of compounds of environmental and biomedical interest. Kettrup et al.

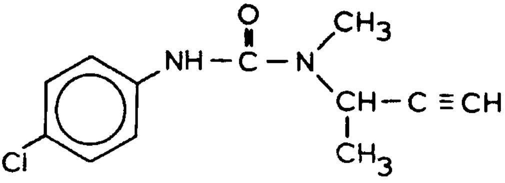
described chelating resins (2,3) and a silica-based 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) phase (4) and investigated the sorption and elution behaviour for several metal ions. Takayanagi et al. (5) loaded an ACDA phase with either copper or silver ions for the separation of dialkyl sulphides. Iminodiacetate phases were loaded with nickel (6), zinc (7) and copper (8) for the separation of peptides, amino acids and proteins.

So far, only a few authors have used the potential of ligand-exchange phenomena for selective sample handling purposes. Veuthey et al. (9) developed a bis-dithiocarbamate-copper and a cyclam-copper phase and demonstrated their applicability for the on-line preconcentration of amino and carboxylic acids. Andersson et al. (10) used a cation-exchanger in its silver form for the selective isolation of ethynyl steroids from urine and our group applied a Pt(IV)-ACDA phase to the selective removal of interfering anilines from a phenylurea herbicide mixture (11). More recently, we used a precolumn packed with Hg(II)-oxine for the selective on-line trace enrichment of 2-mercaptobenzimidazole (12). Excellent selectivity, even when using ordinary UV absorbance detection at 254 nm, was demonstrated at low-ppb levels.

The aim of the present study was to evaluate various commercially available packings, e.g., an ACDA, an oxine and a thiol phase for the selective on-line sample handling and trace enrichment of three model systems: 2-mercaptobenzimidazole



on Hg(II)-loaded phases, 4-chloroaniline on Pt(IV)-loaded phases and buturon



(a herbicide containing an ethynic bond) on a Ag(I) phase.

Special attention was given to the Ag(I)-loaded phases, which were studied in more detail because of the relatively low complexation constants of Ag(I)-ethynic bonds. In addition, the environmental applicability of these Ag(I) phases will be shown.

EXPERIMENTAL

Apparatus

A Kontron (Zürich, Switzerland) LC system consisting of two Model 410 pumps was used in combination with a Perkin-Elmer (Norwalk, CT, U.S.A.) LC-75 variable-wavelength UV absorbance detector, a home-made six-port switching valve and a Rheodyne (Berkeley, CA, U.S.A.) Model 5011 six-way solvent selection valve. Breakthrough curves and chromatograms were analog recorded on a Kipp & Zonen (Delft, The Netherlands) BD 8 recorder and processed manually.

Stationary phases and columns

8-Hydroxyquinoline-modified hydroxyalkyl-methacrylate gel, Spheron Oxine 1000 (25-40 μm), and thiol-modified hydroxyalkyl-methacrylate gel, Spheron Thiol 1000 (40-63 μm) were obtained as a gift from Lachema (Brno, Czechoslovakia). 2-Amino-1-cyclopentene-1-dithiocarboxylic acid-modified silica, ACDA (40 μm) was synthesized on request and donated by Analytichem (Harbor City, CA, U.S.A.). The structures of these stationary phases are given in Fig. 1.

Trace enrichment was carried out on 2 x 4.6 mm I.D. home-made precolumns (13) which were hand-packed with the metal-loaded (see below) stationary phase with a microspatula and using a thick slurry of the packing material in methanol.

For reasons of comparison, some experiments were performed using 40 μm octyl-bonded silica (Baker, Deventer, The Netherlands).

The analytical column was a 100 x 3.1 mm I.D. stainless-steel column home packed with 10 μm Spherisorb ODS-2 (Phase Separations, Queensferry, U.K.).

Chemicals

HPLC-grade methanol, HPLC-gradient grade acetonitrile and analytical-grade sodium acetate, acetic acid, mercury(II) acetate, sodium chloride, sodium hydroxide, nitric acid and silver(I) acetate were obtained from Baker; cysteine was obtained from Merck (Darmstadt, F.R.G.) and EDTA from Sigma (St. Louis, MO, U.S.A.).

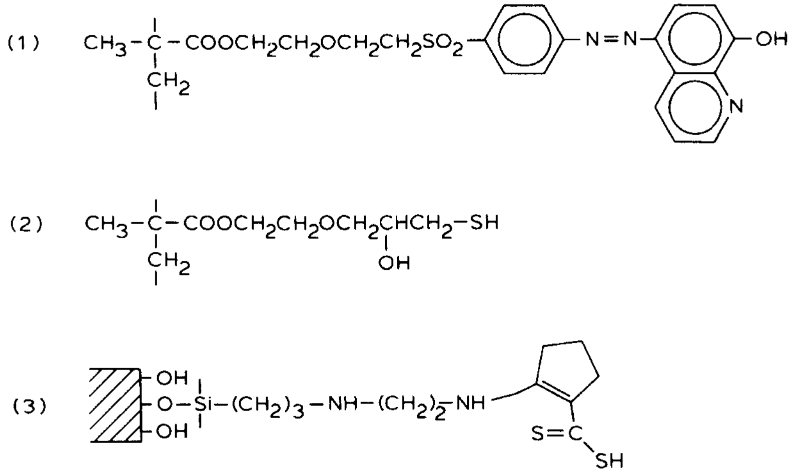


FIGURE 1. Structure of the sorbents under investigation. (1) 8-Hydroxyquinoline-modified hydroxyalkyl-methacrylate gel, Spheron Oxine; (2) thiol-modified hydroxyalkyl-methacrylate gel, Spheron Thiol; (3) 2-amino-1-cyclopentene-1-dithiocarboxylic acid-modified silica ACDA.

4-Chloroaniline was purchased from Fluka (Buchs, Switzerland); buturon was a gift from the Food Inspection Service (Amsterdam, The Netherlands) and 2-mercaptobenzimidazole was a gift from Dr. F. Iverson (Health Protection Branch, Ottawa, Canada).

Demineralized water was purified in a Milli-Q (Millipore, Bedford, MD, U.S.A.) filtration system to obtain LC-grade water for use in eluents and standard solutions. Eluents were degassed in an ultrasonic bath under vacuum prior to use.

Preparation of the metal-loaded sorbents

1 g of Spheron Oxine, Spheron Thiol or ACDA-bonded silica was suspended in 25 ml of a 0.05 M Hg(II) acetate solution in LC-grade water and each mixture was mechanically shaken for 2 h. The Hg(II)-loaded phases were collected on glass filters and washed with 30 ml of LC-grade water and dried for 2 h at 100°C.

Ag(I)-loaded phases were prepared in a similar way by using a 0.05 M Ag(I) acetate solution in 1 mM acetic acid. 0.5 g of Spheron Oxine, Spheron Thiol or ACDA-bonded silica was suspended in 25 ml of a 0.025 M sodium hexachloroplatinate(IV) solution (adjusted to pH 5 with NaOH) and further processed similar to the mercury phases.

Procedures

Stock solutions of the model compounds were prepared by weighing and dissolving in methanol; they were stored at -20^{o}C. The solutions were diluted with methanol-water mixtures to obtain standard solutions at the ppb level. Solutions of 2-mercaptobenzimidazole and cysteine were freshly prepared each day, degassed in an ultrasonic bath, purged with nitrogen and stored in the dark to prevent oxidation to disulphides.

The capacity of the metal-loaded sorbents was calculated by determining the amount of metal ion remaining in solutions and wash solvents after the preparation of the phases. Hg(II) was determined with a complexometric back titration of an excess of EDTA by zinc sulphate (14); Ag(I) was titrated with bromide (15) and Pt(IV) was determined by ICP-AES.

Breakthrough studies were carried out (in triplicate) according to the procedure reported in ref. 16, using 250 ppb standard solutions of the model compounds in water-methanol (7:3), at a flow-rate of 1 ml min^{-1}.

Elution profile studies were carried out following the procedures reported in the Results and Discussion section.

River water samples were filtered over a 0.8 µm membrane filter prior to their trace enrichment onto the Ag(I)-oxine phase.

RESULTS AND DISCUSSION

Capacity

Data concerning the capacity of the various metal-loaded sorbents are summarized in Table I. The preparation of these phases was carried out in triplicate and the results were found to be reproducible within 5-10%. Metal-loaded ACDA-bonded silica provided highest capacity in all cases; however, for Hg(II)--loaded phases differences are relatively small. Pt(IV) could not be effectively loaded on the oxine phase and the loadability for Ag(I)-thiol is relatively poor. The data for the Pt(IV)-ACDA phases were taken from another study (11) and are not directly comparable. According to these data, no limitations show up for selecting a stationary phase to be loaded with Hg(II). Pt(IV) loading should be performed on either thiol or ACDA stationary phases and Ag(I) preferably on ACDA or oxine phases.

TABLE I

Capacity of Metal-Loaded Sorbents (mMol g^{-1})*

Sorbent	d_p (µm)	Hg(II)	Ag(I)	Pt(IV)
Spheron Oxine	25-40	0.31	0.18	0.03
Spheron Thiol	40-63	0.29	0.10	0.16
ACDA-Silica	40	0.40	0.32	0.52**

*For determination, cf. Experimental section.
**Data from ref. 11.

Retention characteristics of the metal-loaded precolumns

The retention of the model compounds on the various metal-loaded phases will be governed by at least two different mechanisms. Firstly, strong complexation will occur between the metal ion and the functional group of the test solute. Secondly, carbon chains and aromatic rings of the stationary phases may be expected to display a distinct hydrophobic interaction with the aromatic system of the model compounds. In retention studies we always prepared the sample solution in water-methanol (7:3). That is, trace enrichment was carried out under conditions in which retention will be predominantly due to ligand-exchange phenomena, while hydrophobic interaction will be suppressed.

It was found that all Hg(II)-loaded phases showed breakthrough volumes of at least 100 ml (the maximum volume tested) for a 250 ppb solution of 2-mercaptobenzimidazole, which does not contradict with the capacity data in Table I.

For Pt(IV)-loaded phases breakthrough curves are shown in Fig. 2. It can be seen that the Pt(IV)-oxine phase is not suitable for the trace enrichment of the model compound; complete breakthrough occurs almost instantaneously due to the low capacity of this phase (cf. Table I). The Pt(IV)-ACDA sorbent shows equal or better performance than the Pt(IV)-modified thiol phase.

Fig. 3 shows breakthrough curves of buturon on the Ag(I)-modified phases. Because of its lower capacity, the Ag(I)-thiol seems to be less suitable. However,

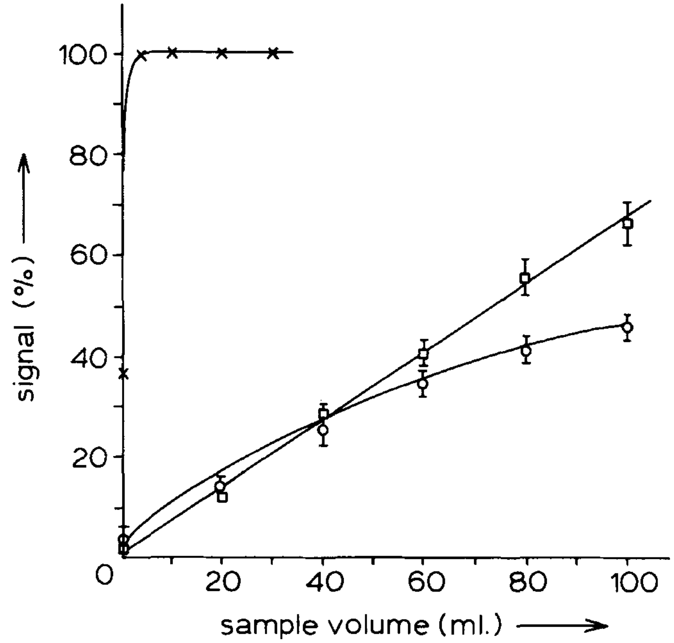


FIGURE 2. Breakthrough curves of 4-chloroaniline on Pt(IV)-loaded oxine (x), thiol ( ) and ACDA (o). Conditions: precolumn 2 x 4.6 mm I.D., flow-rate 1 ml min^{-1}; 250 ppb 4-chloroaniline in methanol-water (3:7). Detection at 245 nm.

contrary to the capacity data, the Ag(I)-oxine phase shows much better retention characteristics towards the model compound than Ag(I)-ACDA.

In general, one should notice the different shape of the breakthrough curves for Pt(IV) and Ag(I) phases as compared to the situation in e.g. ref. 16, where precolumns packed with hydrophobic materials were investigated. A slowly increasing partial breakthrough seems to occur starting with the first ml of sample. However, this was found not to influence the recovery or repeatability in the final application (cf. below). The observed differences are difficult to explain, but it is obvious that more than one complexation mechanism is involved. Metals have more than one coordination number, hence a mixture of different retention strenghts may be expected. Unfortunately, literature data concerning complexation usually refer to homogenic systems, which are not directly comparable with the present situation.

Because of the relatively low complexation constant (17) of the Ag(I)-acetylene bond as compared to, e.g., a Hg(II)-cysteine bond (K = 16 versus 10^{42}), silver phases were studied in more detail.

Retention on Ag(I)-loaded precolumns

Breakthrough curves were recorded using a 25 ppb solution of buturon. The retention characteristics were found to be essentially the same as in Fig. 3, although standard errors for each data point increased, because measurements had to be performed close to the detection limit. These results suggest that overloading is not a dominant factor in the explanation of the retention behaviour.

Fig. 4 shows the influence of the linear velocity on the breakthrough curve of buturon on the Ag(I)-oxine phase. It can be seen that up to 2 mm s^{-1} (ca. 2 ml min^{-1}) the retention is not influenced by the linear velocity. However, the use of a pulse damper connected to the sampling pump, was found to be essential for obtaining reproducible retention on Ag(I)-loaded precolumns.

Strong influences on the retention were found after the addition of 1 mM EDTA to the sample solution: breakthrough now occurred almost immediately. The same effect was found after the addition of saline (0.9% NaCl) to the sample. One can conclude that in the application of small Ag(I)-loaded precolumns to real environmental and biomedical samples - which usually contain trace metals, saline, added EDTA etc. - several precautions should be taken to prevent insufficient loading due to the presence of, e.g., competing trace metals in the sample, and to prevent overloading of the Ag(I) phase by competing ligands in the sample which may even precipitate (AgCl!) on the precolumn. The bulk of possible interferences is easily eliminated in practice, by using a dual-precolumn approach, as will be demonstrated elsewhere (18).

Elution characteristics of the metal-loaded precolumns

Pt(IV)-loaded precolumns are used for selective filtering only (cf. ref. 11) because efficient elution often requires high concentrations of mineral acids (3,4) which are not directly compatible with on-line sample handling systems. Consequently, we compared the elution profiles for different Ag(I)- and Hg(II)-loaded precolumns only.

In the case of Hg(II)-loaded precolumns, 6-20 ml of a 250 ppb 2-mercaptobenzimidazole solution in methanol-water (3:7) were loaded onto the

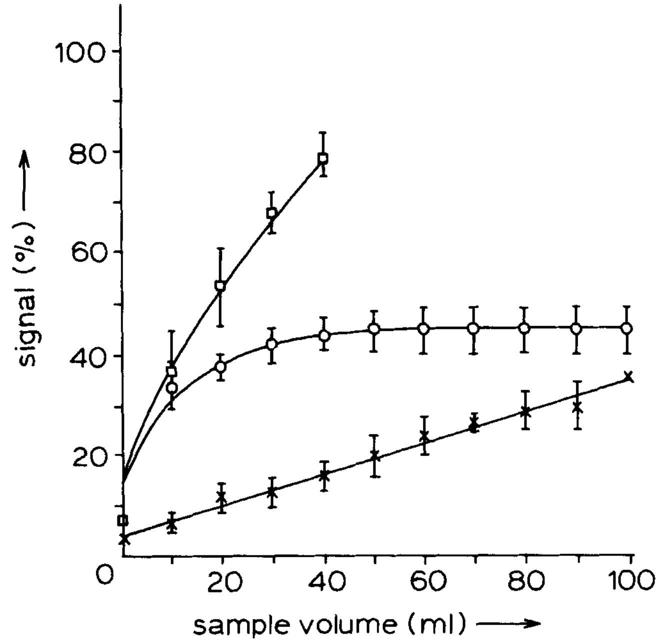


FIGURE 3. Breakthrough curves of buturon on Ag(I)-loaded oxine (x), thiol ( ) and ACDA (o). Conditions: 250 ppb buturon in methanol-water (3:7). Other conditions as in Fig. 2.

precolumn followed by a 5 ml flush with methanol-water (3:7) at 1 ml min^{-1}. Elution was performed by a 0.5 ml plug of 0.1 M cysteine in methanol-water (3:7) without reconcentration on the top of the C18 analytical column (contrary to ref. 12), in order to be able to study the contribution of the metal-loaded sorbent to the total band broadening. Each experiment was carried out in triplicate. The results expressed in terms of plate number and asymmetry (at 10% of the peak height), are presented in Table II. Although capacity (cf. Table I) on the various Hg(II) precolumns was found to be comparable, the elution profiles certainly favour the use of the Hg(II)-ACDA phase.

In the case of Ag(I) precolumns 10 ml of a 10 ppb buturon solution in methanol-water (3:7) was loaded onto the precolumn followed by a 2.5 ml flush at 0.5 ml min^{-1}. Elution to the C18 analytical column was accomplished with a mobile phase consisting of acetonitrile-water (35:65), acidified with nitric acid to pH 2.

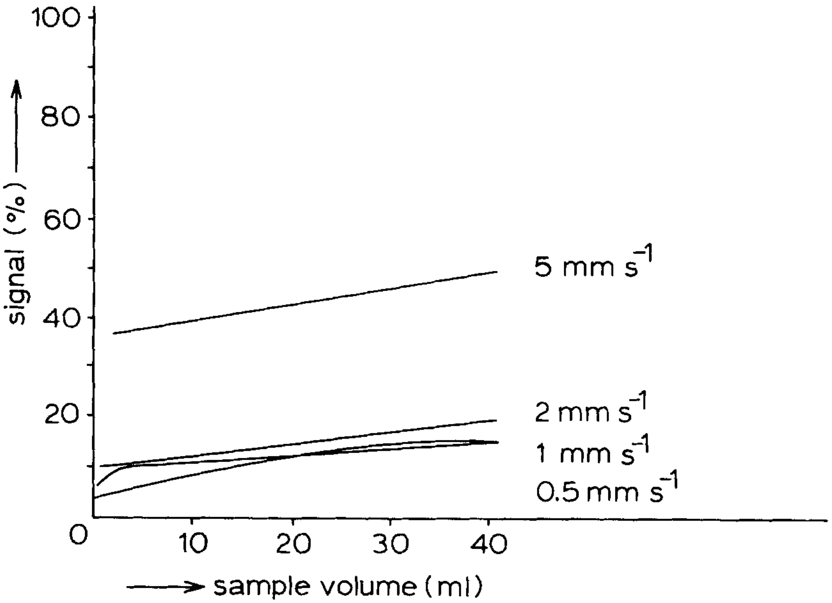


FIGURE 4. Breakthrough curves of buturon on Ag(I)-oxine at different linear velocities. Conditions: as in Fig. 3, except for flow-rate.

TABLE II

Elution Profiles for Different Hg(II)- and Ag(I)-loaded Precolumns

For conditions, see text.

	Plate number	Asymmetry (0.1 h)
Hg(II)-oxine	100 ± 15	5.8 ± 0.5
Hg(II)-thiol	700 ± 15	3.2 ± 0.2
Hg(II)-ACDA	1600 ± 450	1.7 ± 0.1
Ag(I)-oxine	275	-
Ag(I)-thiol	275	2.4 ± 0.3
Ag(I)-ACDA	-	-

-, Could not be determined.

From Table II it can be seen that the elution behaviour when using Ag(I)-oxine and -thiol is similar, although retention was found to differ significantly (cf. Fig. 3). Surprisingly, it was found impossible to obtain a buturon peak on the Ag(I)-ACDA phase, which prevents further application of this system. Possibly other, chemical, reactions play a significant role here promoting, e.g., silver sulphide formation. Generally spoken, the plate number of the peaks is not very impressive, which is obviously due to the strong interaction between the sample and sorbent. In practice this problem can be solved by applying peak-compression techniques on top of the C18 separation column, as was earlier demonstrated for 2-mercaptobenzimidazole (12).

Re-use of the metal-loaded precolumns

In order to investigate the possibilities of their re-use, the metal-loaded precolumns were treated with an excess (4 ml) of eluent and flushed with methanol-water (3:7) until baseline stabilization. Then a breakthrough curve was recorded as described under "Retention characteristics".

For all Hg(II)-loaded phases breakthrough occurred immediately. Obviously, the Hg(II) was removed from the sorbent by the cysteine-containing eluent, which is to be expected, considering the complexation constants for Hg(II)-oxine and Hg(II)-cysteine (10^5 and 10^{42}, respectively). The same results were obtained with the Ag(I)-loaded phases after treatment with 4 ml of the acetonitrile-water (35:65) eluent, acidified with nitric acid to pH 2.

The results reported in an earlier paper (11) that elution and regeneration using Pt(IV)-loaded precolumns can be performed by flushing with pure acetonitrile turned out to be too optimistic; we never obtained a satisfactory elution pattern with the present Pt(IV)-ACDA phases. Flushing these Pt(IV)-loaded precolumns with 4 ml of acetonitrile had no influence at all on the retention characteristics of the model compound 4-chloroaniline: exactly the same breakthrough curves were obtained as in Fig. 2. One may conclude that the Pt(IV)-thiol and -ACDA phases can be used for more than one sample; however, due to the absence of an eluent compatible with an on-line system, these platinum filters (11) may get saturated by (other) complexing species. The possibility of re-use will therefore be determined by the complexity and the volume of the samples under investigation.

As outlined in ref. 12, regeneration of metal-loaded precolumns is sometimes possible but in practice it is laborious and difficult to automate. In addition, it will be more economical to repack the small precolumns than to regenerate them with, e.g., an excess of a metal salt solution. Therefore, for metal-loaded sorbents, we generally recommend the use of an automated precolumn exchange device such as the AASP (Varian, Sunnyvale, CA, U.S.A.) or the automated cartridge exchanger described by Nielen et al. [19].

Application of the Ag(I)-oxine precolumn

Contrary to the Pt(IV) and Hg(II) precolumns (11,12), the Ag(I)-loaded precolumn as yet has not been used for an environmental application.

We used the set-up of Fig. 5. 10 ml of a 10 ppb solution of the herbicide buturon in water were applied to the precolumn via pump A at 0.5 ml min^{-1}. After introduction of the sample, the precolumn was flushed with 2 ml of methanol-water (3:7). Then the valve was switched and the precolumn was eluted by acetonitrile-water (4:6), acidified to pH 2 with nitric acid, at a flow of 0.5 ml min^{-1}. The precolumn was repacked with fresh Ag(I)-oxine material after each analysis. Although this system was operated manually, it has been shown before that it can be easily automated using a microprocessor with a time-based valve- and solvent-switching program (11).

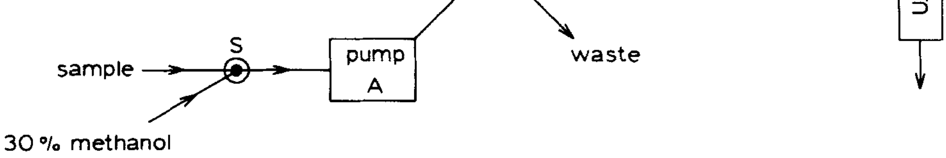


FIGURE 5. Experimental set-up for the selective on-line trace enrichment of buturon from water samples. S, low-pressure solvent selection valve; V, high-pressure switching valve. Precolumn 2 x 4.6 mm I.D. Ag(I)-oxine. Analytical column 100 x 3.1 mm I.D. packed with 10 μm Spherisorb ODS-2. M, acetonitrile-water (4:6) acidified to pH 2.0 with nitric acid. Flow rate of pumps A and B, 0.5 ml min^{-1}. Detection at 245 nm, 0.02 AUFS.

TABLE III

Analytical Data for the Selective On-line Trace Enrichment of Buturon on a Ag(I)-oxine Precolumn.

Conditions: 10 ml sample solutions analyzed according to the procedure in the text (cf. Fig. 5); data based on peak area measurements.

Criterion	Level	Results
Repeatability	10 ppb (n = 9)	± 3% RSD
Recovery	10 ppb (n = 9)	95 ± 3%
Linearity (r)	1-500 ppb (n = 7)	0.9994
Detection limit	S/N = 3/1	1.5 ng or 0.15 ppb

Table III summarizes the analytical data obtained by this procedure. The recovery, calculated by peak area comparison with the mean of four 100 µl loop injections directly onto the C18 analytical column, is in agreement with the 7% loss due to breakthrough, as predicted for a 10 ml sample by Fig. 4.

Fig. 6 shows chromatograms of (a) an LC-grade water standard solution and (b) a surface water sample (river Waal, Lobith, The Netherlands). Results for the blanks as well as samples spiked with 10 ppb of buturon are given. The selectivity of the ligand-exchange sample handling is already evident when we consider the similarity between the standard and the river water sample. It is even more nicely demonstrated by comparing chromatograms (b) and (c); the latter represents the on-line trace enrichment of the same spiked river water sample on a precolumn packed with non-selective octyl-bonded silica. In this case, retention was only due to hydrophobic interaction and the precolumn could only be flushed with water, which clearly results in a serious lack of selectivity.

The method was found to be selective for the herbicide buturon. After preconcentration of a mixture of nine different phenylurea herbicides, only buturon -

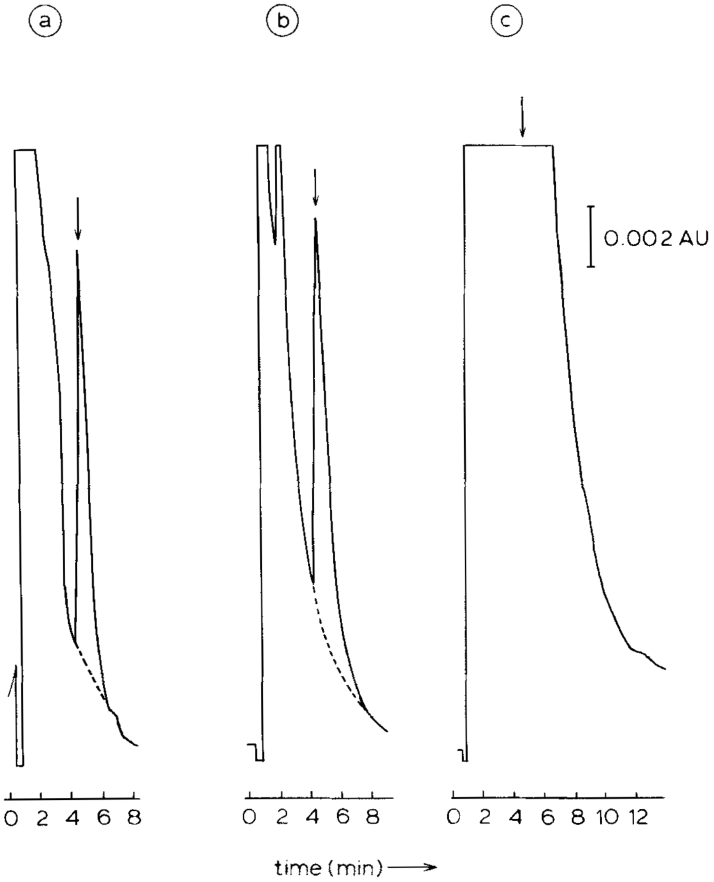


FIGURE 6. Chromatograms of 10 ml water samples spiked with 10 ppb of buturon and analyzed using the set-up of Fig. 5 and the procedure described in the text. (a) LC-grade water solution, (b) river Waal water, and (c) river Waal water, preconcentrated on an octyl-bonded silica precolumn. Blanks, ------. Other conditions as in Fig. 5.

being the only analyte to contain an ethynic bond - appeared in the final chromatogram.

CONCLUSIONS

Selective on-line sample handling and trace enrichment based on metal complexation can be successfully carried out using small precolumns packed with metal-loaded stationary phases. Three commercially available stationary phases, having a relatively large particle size and either based on silica or on a soft polymer, were easily and reproducibly loaded with Hg(II), Pt(IV) and Ag(I). After determining the capacity, one could conclude that Pt(IV)-oxine phases should be rejected and Ag(I)-thiol phases should be handled with caution because of their relatively low capacity.

Retention on the metal-loaded precolumns still is difficult to interpret. Breakthrough volumes for the Hg(II)-loaded precolumns were at least 100 ml but the breakthrough curves for the Pt(IV)- and Ag(I)-loaded precolumns were found to have a significantly different shape as compared to curves for precolumns packed with hydrophobic materials. Besides, the retention on Ag(I)-loaded precolumns was strongly influenced by, e.g., EDTA and chloride ion. Because of the very low complexation constant of the Ag(I)-ethynic bond, one should always consider the presence of these and other interferences in real samples.

The elution profiles obtained from metal-loaded precolumns were found to be rather inefficient; peak compression techniques on top of the separation column can, however, as a rule dramatically improve the final result.

On the basis of capacity, retention and elution behaviour, one can recommend a Hg(II)-ACDA phase for the selective trace enrichment of thiol compounds; the selective filtering of anilines should be done by means of a Pt(IV)-loaded ACDA or thiol phase and a Ag(I)-oxine phase should be recommended for the selective on-line trace enrichment of ethynic compounds.

On-line regeneration of metal-loaded precolumns was found to be laborious. In addition, the use of an excess of a metal salt solution for regeneration is not economical. Fortunately, the metal-loaded precolumns are inexpensive, and consequently they should be used only once. By using an automatic cartridge exchange device, fully automated procedures can be developed.

Although retention, elution and regeneration still present various experimental problems, three interesting applications of selective on-line sample handling and trace enrichment using metal-loaded precolumns have now been demonstrated (refs. 11 and 12, and this paper), one of these featuring the application of the rather labile Ag(I)-ethynic bond formation. Each of them shows good linearity and repeatability, low- or sub-ppb detection limits and an excellent selectivity with real samples even when using non-selective UV detection. This superior selectivity argues for the rapid development and commercialization of more types of selective sorbents for on-line sample handling and trace enrichment in liquid chromatography.

The conversion of an off-line method for the determination of ethynyl steroids in urine using Ag(I)-loaded precolumns (10) into an automated on-line procedure is presently being studied (18).

ACKNOWLEDGEMENTS

Lachema, Analytichem, Baker and Phase Separations are acknowledged for the gift of packing materials. Mr. J. Padmos of Delft Technical University is thanked for performing the ICP measurements.

This work was supported by the Dutch Foundation for Technical Sciences, grant no. VCH 44.0616.

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