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Properties of Chelating Sorbents Prepared by Modification of LiChroprep RP-8 and LiChroprep RP-18 with Calconecarboxylic Acid

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ABSTRACT

Two new chelating sorbents for metal ions were prepared by the impregnation of chemically modified silicas LiChroprep RP-8 and RP-18 with ion pairs composed of the cation of Aliquat 336 and the anion of Calconecarboxylic Acid (CCA). The sorbents were compared with an analogous sorbent with a plain silica carrier containing the same ion pairs. A hypothetical molecular mechanism of binding this ion pair by the surfaces of the applied carriers was presented. A higher stability of the two sorbents in comparison with that of the plain silica chelating sorbent was demonstrated. The sorbents obtained were applied for chromatographic separations of some chosen mixtures of some metal ions and for additional purification of aqueous solutions of alkali metals from trace amounts of heavy metals. The multiple use of the sorbents based on RP-8 and RP-18 in sorption–desorption processes of metal ions without deterioration of their sorption capacities was demonstrated.

Key Words. Calconecarboxylic acid (CCA); Liquid anion exchanger; Aliquat 336; Chelating sorbents; LiChroprep RP-8, LiChroprep RP-18, Purification of alkali metal salts

INTRODUCTION

The determination of trace amounts of heavy metals in various materials often requires their preconcentration and separation from macroamounts of other metals for elimination of the matrix effect (1). One of the most commonly used methods for the preliminary concentration of metals from aqueous solutions is based on the utilization of chelating sorbents; many such materials containing various groups have been proposed. Besides commercial chelating resins used for these purposes, other chelating sorbents have recently found increasing popularity (2), and especially interesting are silica gels modified with various chelating reagents (3). The sorbents derived from silica, in contrast to polymeric ion exchangers, have higher mechanical stability; i.e., they can be used at high pressures in high-performance liquid chromatography (HPLC).

In analytical chemistry, including trace analysis of metal ions, chemically modified silicas have also found wide applications (4–6). Chelating sorbents can be obtained in a very simple manner by the impregnation of silica with ion pairs formed by an alkylammonium cation of a liquid anion exchanger such as Aliquat 336 (methyltrioctylammonium chloride) and the anion of a sulfonated chelating reagent (7). In this way, a number of new chelating sorbents have been prepared and investigated for numerous metal cations (8).

The application to trace analyses for some metals of a chelating sorbent obtained by impregnation of silica with a mixture of Aliquat 336 and Calconecarboxylic Acid (CCA) was reported in a previous paper (9).

Earlier unpublished data indicated the high stability of sorbents formed by impregnation of chemically modified silica (RP-8 and RP-18) with mixtures of Aliquat 336 and sulfonated chelating reagents. Therefore the experiments on the preparation of sorbents by modification of RP-8 and RP-18 with CCA and their comparison to the common unsilanized silica gel modified with CCA were undertaken. The present paper relates the results of the performed investigations.

EXPERIMENTAL

All experiments were performed at room temperature (20 ± 1°C).

Reagents and Solutions

Calconecarboxylic acid (POCh, Poland) was used as a chelating reagent. Aliquat 336–methyltrioctylammonium chloride (Merck, Darmstadt, Germany) was purified from iron as described previously (9).

LiChroprep RP-8 and LiChroprep RP-18 (0.040-0.063 mM) (Merck) were used as supports for the stationary phase.

Aqueous solutions of metal salts were prepared by dilution of Titrisol standard metal salt solutions (Merck). Working solutions were freshly prepared from standard metal salt solutions by dilution with doubly distilled water (previously adjusted to an appropriate pH value with 1 mol L^{-1} hydrochloric acid, acetate buffer, or tetraborate buffer).

Freshly distilled chloroform of analytical-reagent grade was used as diluent of Aliquat 336.

Solutions of $HClO_4$ and HCl (Suprapur, Merck) were used as eluents.

KCl of analytical-reagent grade (POCh, Poland) and Suprapur grade (Merck) were used for purification from heavy metals.

Apparatus

A Pye Unicam (Cambridge, UK) single-beam atomic absorption spectrometer was used for the determination of the metal ions, except Al^{3+}, which was determined by spectrophotometry with Alizarin Red S at 500 nm, with the use of a Spekol 11 visible spectrophotometer (Zeiss, Jena, Germany).

All pH measurements were performed with a Mera-Elwro N517 direct-reading pH meter (Wroclaw, Poland), with a glass–silver/silver chloride combination electrode.

A UPE-2a voltammetric analyzer (Radius, Gdańsk, Poland) was used in the determination of trace amounts of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} in KCl by anodic stripping voltammetry. A graphite electrode, impregnated with epoxy resin and coated with a mercury film in situ, was used as a working electrode, having a working area of 12.5 mM^2.

Procedure

The impregnating solution was prepared by shaking an appropriate volume of a 0.01 mol L^{-1} solution of Aliquat 336 in freshly distilled chloroform with 10 volumes of a 0.001 mol L^{-1} aqueous solution of CCA. After separating the phases, the organic phase was passed through a cellulose filter to remove the residual aqueous phase. Amounts of 10 g of the sorbents were prepared by mixing a 100-mL portion of the organic solution containing 1 mmol of CCA (0.46 g) and 1 mmol of Aliquat 336 (0.442 g) with 9.1 g of LiChroprep RP-8 or LiChroprep RP-18. The diluent (chloroform) was then evaporated with the use of a vacuum evaporator on a water bath. One gram of the chelating sorbents obtained contained 0.1 mmol of CCA and 0.1 mmol of Aliquat 336.

Elution of CCA from the sorbents with aqueous solutions of mineral acids was performed in the following manner. A 0.1-g amount of the obtained sorbents was shaken for 10 min with 5 mL of an appropriate acid solution in small tubes. The solution was subsequently centrifuged, and the dye was then determined by spectrophotometry at 539 nm with reference to a calibration graph.

Small polypropylene columns (55 × 5 mM) (J. T. Baker, Phillipsburg, NJ, USA) were packed with 0.1 g of dry sorbents and used to measure the relative capacity of the sorbents towards different metal ions. A 3-mL portion of each solution (previously adjusted to an appropriate pH), containing 0.3 mg of the metal to be determined, was passed through each column for 5 min. Each percolate was analyzed to determine the residual metal-ion concentrations.

Columns (65 × 13 mM) packed with 5 g of dried sorbents were used to study the separation of metal-ion mixtures. After conditioning the column with 1 mL of Michaelis buffer solution at pH 7.0, 10 mL of the synthetic solutions (the mixtures prepared from Titrisol standard solutions of metals) at pH 7, containing 100 μg of each separate metal ion, were passed through the column. The metals were then eluted with $HClO_4$ solutions, and the eluate was collected in 5 mL fractions.

Voltammetric determination of the metals was performed in the following manner. Volumes of 10 mL of 0.5 mol L^{-1} KCl analytical-reagent grade to which mercuric nitrate was subsequently added [the concentration of $Hg(NO_3)_2$ in the resulting solution was 10^{-4} mol L^{-1}] were passed through columns packed with 1 g of the sorbents. Two microliter volumes of standard solutions of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} ions of 100 ppm concentration were introduced into 10 mL of 0.5 mol L^{-1} KCl (analytical-reagent grade) (the concentration of each metal ion added in the solution was then 20 ppb). Oxygen was removed from the analyzed solutions with a stream of argon of special purity. The solutions were electrolyzed for 3 min at −1.3 V. Anodic oxidation of the metal was subsequently performed with an amplitude 1.2 V and a potential change of 10 mV/s^{-1}.

RESULTS AND DISCUSSION

As discussed in the Introduction, chelating sorbents can be easily obtained by impregnation of silica by ion pairs composed of methyltrioctylammonium cation and sulfonated chelating reagent anion obtained by a static extraction process (7).

During the preparation of such sorbents, silica gel was impregnated with Aliquat 336 and chelating reagents from chloroform solutions in such proportions that the molar concentration of Aliquat 336 was twice a large as the concentration of the reagent containing a single sulfo group (or four times for reagents with two sulfo groups, e.g., Nitroso-R-Salt). It was found experimentally many times that the use of excess amounts of Aliquat 336 improved the quality of sorbents so that they became more resistant to elution of the chelating reagent or the whole ion pairs by the aqueous acid solutions (8).

Several questions arise: how the ion pairs are bound by the silica surface, the role of the two-fold excess of Aliquat 336, and the cause of the increased stability of the sorbents prepared with this excess.

Hansen et al., (10) in their paper on dynamically modified silica have demonstrated that the H^+ ions are substituted by the tetraalkylammonium cation.

The cations of Aliquat 336 are assumed to be bound to the silica surface by a similar mechanism: The mode of binding of the ion pairs, namely tetraalkylammonium cation–sulfonated chelating reagent anion, with a double molar excess of Aliquat 336 is probably as follows: half of the Aliquat 336 is bound to the silica surface according to Fig. 1a. The adsorbent surface is covered by

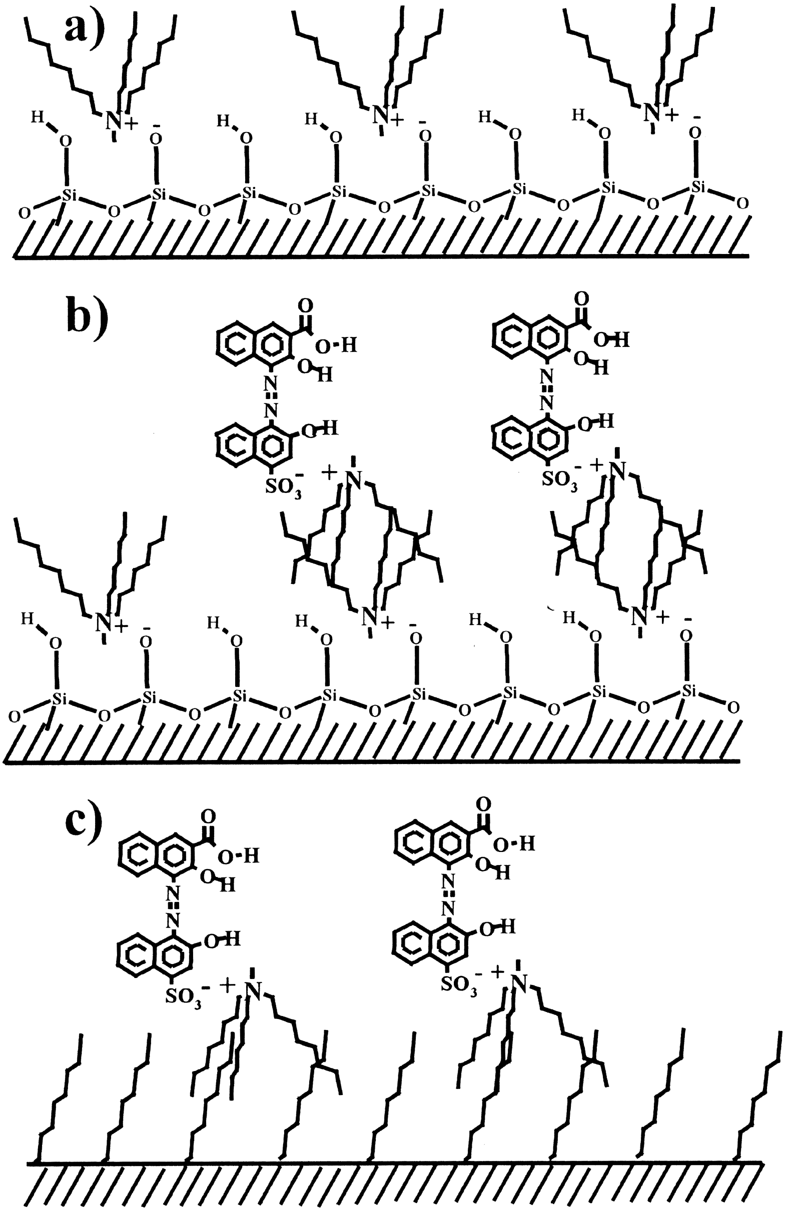

FIG. 1 (a) Silica impregnated with Aliquat 336; (b) silica impregnated with Aliquat 336 and modified with ion pairs composed of cation of Aliquat 336 and anion of CCA; (c) LiChroprep RP-8 modified with ion pairs composed of cation of Aliquat 336 and anion of CCA.

a monomolecular layer of octyl groups from Aliquat 336 so that the surface is hydrophobized and it binds by hydrophobic (and dispersive) interactions the second layer of Aliquat cations, forming chelating ion pairs with the sulfonated reagent. In the hydrophobic interactions, the octyl groups from both tetraalkylammonium cations are involved. In effect, the carrier surface is isolated from the aqueous bulk phase and the chelating groups are outside the double layer, and capable of binding metal ions from the bulk aqueous solution. The structure of the sorbent containing CCA can thus be represented as in Fig. 1b. During the elution of metal ions bound by sorbents of this type with aqueous solutions of mineral acids, the weaker or stronger accompanying elution of chelating reagents (or even whole ion pairs) is observed so that the properties of the sorbent are changed and its ion-exchange capacity is decreased. The anions of chelating reagents are displaced from the ion pairs by the anion of acids used (especially by ClO_4^- anions, which have greatest affinity to the tetraalkylammonium cations). The affinity of anions to the tetraalkylammonium cation and their displacement ability increases in the following order:

$$SO_4^{2-} < Cl^- < NO_3^- << ClO_4^-$$

On the other hand, the hydrogen ions from the acids applied in the eluent not only elute metal ions bound by the sorbent (which is advantageous), but also, at higher concentrations, can displace the whole hydrophobic layer in a process reverse to Fig. 1a and then the chelating sorbent is decomposed. This is especially true in cases when, for elution of some metal ions bound by the sorbent, aqueous acid solutions of high concentrations (0.5–1 mol L^{-1}) are used. Therefore, there was a need to look for other supports, which would bind the ion pairs more strongly so that a sorbent of higher stability would be obtained.

The experiments on the preparation of sorbents were carried out on the basis of modified silicas, RP-8 and RP-18 and the earlier investigated ion pair composed of Aliquat 336 and sulfonated chelating reagent CCA.

The investigations of such sorbents have shown that in this case the double excess of Aliquat 336 (as in the case of a plain silica support) is not necessary. The alkyl chairs ("brush") on the RP-18 or RP-8 surface bind directly the Aliquat–CCA ion pairs according to Fig. 1c.

The chelating sorbents thus prepared are more stable than those formed on the basis of plain silica.

This is illustrated in Fig. 2, which represent the amounts of eluted CCA (in the form of anion or whole ion pairs) plotted against the concentration of the acid applied. The higher stability of sorbents based on RP-8 and RP-18 could be explained by the fact that acidic solutions do not displace the ion pairs as in the case of sorbent prepared on a plain silica carrier. On the other hand, there is only a slight difference in the stability of sorbents based on RP-8 and RP-18 supports; the former is slightly better than the latter. CCA used alone,

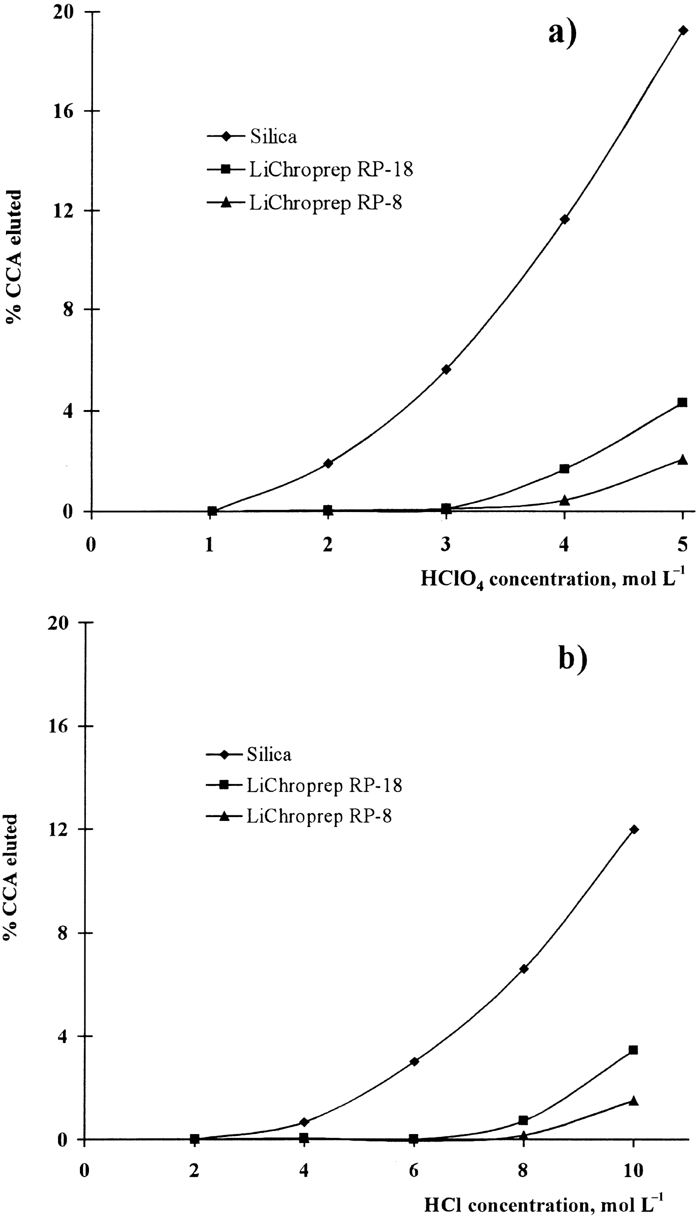

FIG. 2 Percentage of CCA eluted from silica, LiChroprep RP-8, and LiChroprep RP-18 modified with a mixture of Aliquat 336 and CCA as a function of concentration of (a) $HClO_4$ and (b) HCl acids used as eluents.

without Aliquat 336, to impregnate RP-8 or RP-18 did not give good results: it was easily eluted from the column by bi-distilled water. The ion-exchange capacities of the sorbents obtained were comparable to those obtained with a silica carrier [9].

This is understandable taking into account the equal amounts of chelating reagent (CCA) per 1 gram of each sorbent. Only very small differences in the concentrations of mineral acids ($HClO_4$ and HCl) necessary to elute the metal ions from the columns were observed. The sorbents prepared were successfully applied to analytical problems analogous to those described earlier for CCA sorbent on the basis of plain silica.

Figure 3 represents the separation of a synthetic mixture of some metal ions by column-extraction chromatography using stepwise gradient elution with a solution of chloric (VII) acid. The recovery of the separated metals was in the range of 98–99.5%. The sorbents do not bind the ions of alkali metals in a

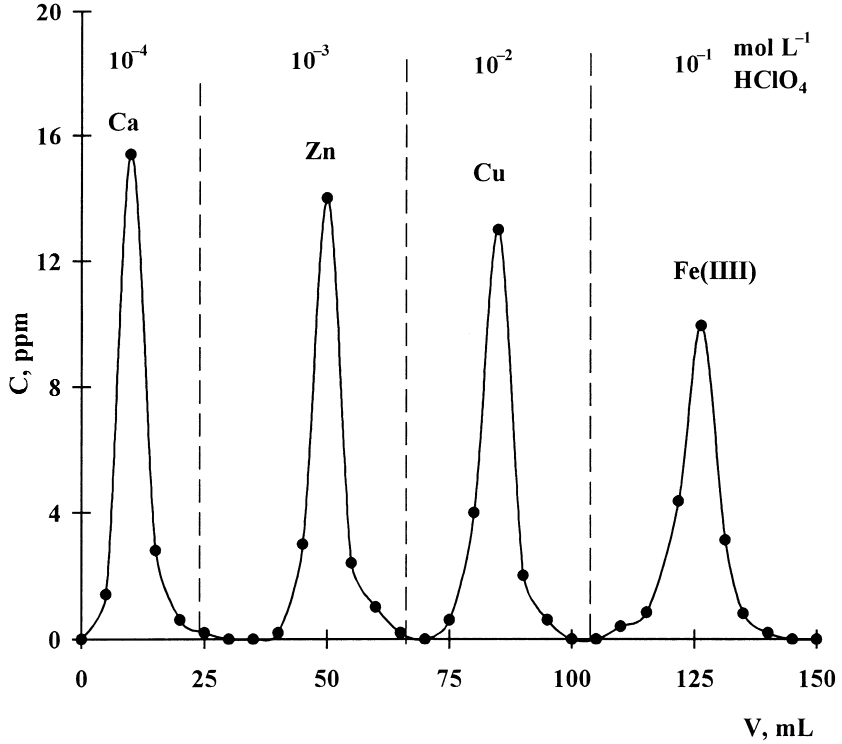

FIG. 3 Separation of metal-ion mixtures containing 100 µg of each metal ion, on LiChroprep RP-8 treated with a mixture of Aliquat 336 and CCA. Column packed with 5 g of sorbent. Mean flow rate: 1 mL min^{-1}.

wide pH range (1–9). The ions of calcium and magnesium are bound at pH 4.5, while other metals investigated were bound in the pH range 3–6. Therefore, the sorbents can be applied to remove trace amounts of heavy metals from aqueous solutions of sodium, potassium, and ammonium salts.

Figure 4, representing the voltamperograms of some solutions of salts purified in the described manner, confirms the useful properties of the prepared chelating sorbents.

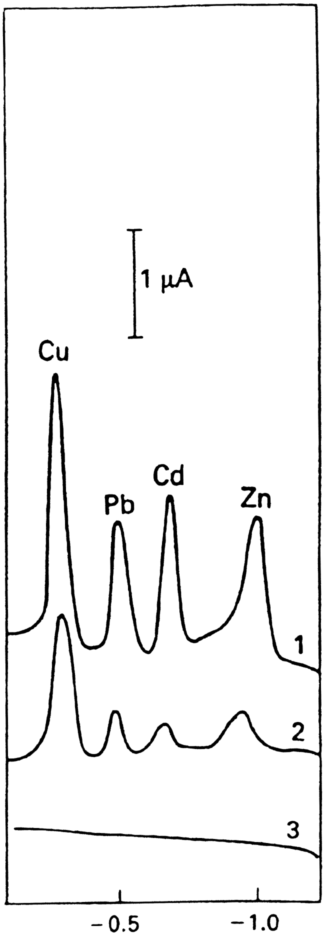

FIG. 4 Voltammograms for 10 mL volumes of 0.5 mol L^{-1} KCl solutions after 3 min electrolysis at −1.3V. Curves: (1) unpurified solution of analytical grade KCl to which Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} ions were added (the concentration of each metal ion was 20 ppb); (2) unpurified solution of analytical grade KCl; (3) sample 2 after passing through the column packed with LiChroprep RP-8 modified with CCA.

As discussed earlier, the sorbents containing ion pairs CCA–Aliquat 336 deposited on RP-8 or RP-18 are considerably more stable than an analogous sorbent based on plain silica. It has been demonstrated experimentally that in the case of a silica sorbent after a column was used five times the sorption capacity decreased gradually owing to bleeding of CCA such that the results could not be reliably reproduced. On the other hand, sorbents with RP-8 and RP-18 barely showed any changes under these conditions.

CONCLUSIONS

On the basis of RP-8 and RP-18, chelating sorbents with CCA have much better properties and better chances of practical use that the analogous sorbent with a silica carrier. Their disadvantages are higher cost and the possibility of partial hydrolysis of RP carriers at higher acidity of the aqueous eluent.

REFERENCES

1. J. Minczewski, J. Chwastowska, and R. Dybczyński, *Separation and Preconcentration Methods in Inorganic Trace Analysis,* Harwood Ltd., Chichester, 1982.
2. A. Mizuike, *Enrichment Techniques for Inorganic Trace Analysis,* Springer, Berlin, 1983.
3. M. A. Marshall and H. A. Mottola, *Anal. Chim. Acta, 158,* 369 (1984).
4. Z. Witkiewicz, *The Fundamentals of Chromatography,* WNT, Warsaw, 1992 (in Polish).
5. H. Niwa, T. Yasui, T. Ishizuki, A. Yuchi, H. Yamada, and H. Wada, *Talanta, 45,* 349 (1997).
6. G. D. Brykina, E. E. Lazareva, Uvarova, and O. A. Shpigun, *J. Anal. Chem., 52,* 969 (1997).
7. S. Przeszlakowski, E. Soczewiński, R. Kocjan, J. Gawecki, and Z. Michno, *Polish Patent 128743,* 1985.
8. R. Kocjan, *Chem. Anal. (Warsaw), 41,* 501 (1996).
9. R. Kocjan and S. Przeszlakowski, *Sep. Sci. Technol., 24,* 291 (1989).
10. H. Hansen, P. Helboe and M. Thomsen, *J. Pharm. Biomed. Anal., 2,* 165 (1984).

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