Some examples of the use of amphoteric ion-exchange resins for inorganic separations

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Abstract

The usefulness of the amphoteric ion exchange resin Retardion 11A8, as well as, the chelating ion exchanger Chelex 100 for the separation of inorganic ions is demonstrated. The ion exchange method for selective separation of cadmium from other elements exploiting both anion- and cation-exchange function of Retardion 11A8 is presented. Conditions which should be met in order to retain, as well as, remove cadmium from the column are discussed. The ion exchange behaviour of about 20 elements on Chelex 100, depending on pH, as well as, concentration of HCl and NH_3, respectively was studied. Results of the above investigations allowed the development of several interesting separations of some metal ions, where not only cationic (chelating) but also anionic function of the resin was employed.   © 1997 Elsevier Science B.V.

Keywords: Stationary phases, LC; Ion exchangers; Inorganic cations

1. Introduction

Ion-exchange chromatography is a well known and widely used method for the separation and preconcentration of inorganic ions. The innumerable separation procedures published so far are almost exclusively based on the use of monofunctional ion exchangers, mostly strongly basic anion exchangers with quaternary ammonium groups and strongly acidic exchangers with sulfonic acid groups [1–5]. The presence of groups other than the above mentioned functional groups in the resin was usually considered to cause undesirable [6] or at least unexpected effects [7].

Amphoteric ion exchangers in contrast to conventional monofunctional exchangers contain anionic and cationic exchange sites. Under appropriate conditions, amphoteric resins can retain simultaneously anions and cations from external solutions [8–11].

Some of these amphoteric ion exchangers are chelating resins with functional groups able to form complexes with several cations and are used for the preconcentration of trace elements or radionuclides from large volumes of natural waters, sea water, and other solutions [9,12–19]. Because these complex-forming groups contain basic nitrogen atoms that can be protonated, the resins may also act as weakly basic anion exchangers.

Although it was surmised long ago [20], that simultaneous presence of anion and cation exchange groups may offer new interesting separation possibilities, very few attempts to exploit these possibilities in practice can be found in literature [8,9].

In recent years, studies of amphoteric ion-exchange resins for inorganic separations were carried out in our laboratory [10,11,20–23]. Some interesting observations were made. For instance, the elution order of elements, e.g. of the Ga-ion pair, can be reversed by switching from the cation to the anion-exchange function of the same resin [10,20]. Many

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separations of binary and multicomponent mixtures were achieved by elution chromatography [10,11,20–23]. Of special interest is the possibility of keeping an element on the column during stepwise elution, while switching the exchange function of the resin. Very selective separation of an element from almost all other elements can be obtained in this way [21–23].

In this paper, the results of a study with the goal to find and explain conditions under which separations of cadmium from other elements based on switching the exchange function of the Retardion 11A8 resin are possible, are presented. In addition, several new separations of individual ions obtained with the Chelex 100 while exploiting cation- (chelating) and anion-exchange function of the resin are reported, and potential possibilities of other separations are indicated.

2. Experimental

2.1. Ion exchange resins, radioactive tracers, reagents

The methods for grinding and fractionating of the amphoteric ion exchange resin Retardion 11A8 (Bio-Rad Labs.) were described earlier [25]. The fraction with particle size: 23–46 μm was used in this work. The resin was purified by sequentially passing 1 mol l^{-1} NaOH, water, and 1 mol l^{-1} HCl through the column. Finally it was washed with deionized water until free from chloride ions.

Chelating resin Chelex 100 (Bio-Rad Labs., 200–400 mesh) was of analytical grade and in the sodium form.

The following radioactive tracers were used: ^{115}Cd–^{115m}In (53.5h–4.5h), ^{65}Zn (245d), ^{24}Na (15h), ^{60}Co (5.26y), ^{59}Fe (44.6d), ^{203}Hg (46.9d), ^{64}Cu (12.8 h), ^{110m}Ag (253d), ^{99}Mo–^{99m}Tc (66.0h–6.0h), ^{114m}In (50d), ^{140}La (40h), ^{134}Cs (2.1y) ^{46}Sc (83.8d), ^{122}Sb (66.0h), ^{186}Re (90.6h), ^{72}Ga (14.3h), ^{75}Se (121d), ^{197}Pt (18.3h), ^{199}Au (3.4d), ^{109}Pd (13.5h), ^{54}Mn (313d), ^{131}Ba (11.7d). ^{54}Mn and ^{131}Ba were supplied by the Centre for Production and Distribution of Isotopes (Świerk, Poland). All other tracers were prepared by neutron irradiation of spectrally pure salts or oxides in the Polish reactors 'EWA' and 'MARIA' (Świerk, Poland).

Acetate, phosphate and ammonia buffer solutions were prepared by mixing appropriate volumes of the following solutions: 0.1 mol l^{-1} CH$_3$COOH and 0.1 mol l^{-1} CH$_3$COONa, 1/15 mol l^{-1} Na$_2$HPO$_4$ and 1/15 mol l^{-1} KH$_2$PO$_4$, 12 mol l^{-1} or 1 mol l^{-1} NH$_3$ and 4.0 mol l^{-1} NH$_4$Cl.

All reagents were of analytical grade. Doubly distilled water served as solvent.

2.2. Procedures

Mass distribution coefficients, λ (mass of analyte per g of dry ion exchanger/mass of analyte per ml of solution) were determined by batch equilibration or from elution curves [2,25] at room temperature.

Column experiments were carried out with glass columns of 3–5 mm I.D. and a resin bed 5–15 cm high supported on a plug of quartz wool. The effluent was collected in fractions of several drops in test tubes employing the fraction collector Redifrac (Pharmacia, LKB), and radioactivity of individual fractions was measured by gamma-ray spectrometry.

Concentrations of chloride ion and pH in the fractions were determined potentiometrically with a combined chloride-ion-selective electrode 96–17B and pH electrode 81–15 (Orion) connected to a pH-meter model 720A (Orion). The electrodes were standardized before each series of measurements with pH solutions and standard solutions of chloride.

All radioactivity measurements were done with the aid of γ-ray spectrometer consisting of a 213-cm^3 HPGe coaxial detector (Ortec, resolution 2.1 keV for 1332 keV ^{60}Co line, efficiency ca. 40%) and Ortec analog line coupled to the multichannel analyzer TUKAN (Institute of Nuclear Problems, Świerk, Poland).

3. Results and discussion

3.1. Ion exchange behaviour of cadmium on Retardion 11A8

Retardion 11A8 is a so called 'snake in cage' amphoteric ion exchanger, which contains strongly

basic quaternary ammonium groups ($>$CH-C_6H_4-CH_2-$N^+(CH_3)_3Cl^-$) and an equivalent amount of weakly acidic carboxylate groups [26]. Linear polyacrylic chains with carboxylate groups (snake) are intricately intertwined with the crosslinked styrene–divinylbenzene matrix (cage), and are firmly enmeshed in the matrix.
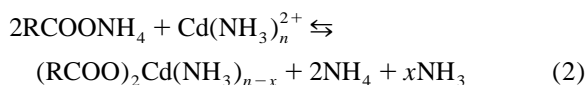
The presence of both, cation and anion exchange groups, creates the possibility of retaining cations or cationic complexes, as well as, anions or anionic complexes, depending on the nature of the external solution in contact with Retardion 11A8. The ion exchange behaviour of twenty elements in HCl solutions (0.01–12 mol l^{-1}) and in 0.1 mol l^{-1} NH$_4$Cl + y mol l^{-1} NH$_3$ (y = 0.01–12) solutions was studied in this laboratory by batch equilibration and the results were published [22–24]. These data together with recent results for additional 13 elements seemed to indicate, that cadmium could be selectively retained on the column and separated from many other elements when the cation and anion exchange functions of the resin are exploited.

In the system: Retardion 11A8–HCl aq. Cd is relatively strongly ($\lambda_{Cd} > 10^2$) retained in the HCl concentration range: 0.2–8 mol l^{-1} with the maximum (λ = 680) at 2 mol l^{-1}. In ammoniacal solutions, relatively high mass distribution coefficients of cadmium were observed in the range from 0.01 mol l^{-1} NH$_3$ + 0.1 mol l^{-1} NH$_4$Cl (λ_{Cd} = 4400) up to 2 mol l^{-1} NH$_3$ + 0.1 mol l^{-1} NH$_4$Cl (λ_{Cd} = 125).

The ion exchange reactions in the two systems can be written as:

$$(i - 2)\text{RCl} + \text{CdCl}_i^{2-i} \leftrightarrows \text{RCdCl}_i^{2-i} + (i - 2)\text{Cl}^- \quad (1)$$

where: R denotes cationic rest of the resin, and:

$$2\text{RCOONH}_4 + \text{Cd(NH}_3)_n^{2+} \leftrightarrows$$
$$(\text{RCOO})_2\text{Cd(NH}_3)_{n-x} + 2\text{NH}_4 + x\text{NH}_3 \quad (2)$$

where this time R denotes resin matrix.

As was shown by us earlier [22], $x \approx 2$ for practically the whole range of NH$_3$ concentrations, when ammonium ion concentration in the mobile phase is not lower than 2 mol l^{-1}. For lower ammonium ion concentrations e.g. at $C_{NH_4^+}$ = 0.5 mol l^{-1} and C_{NH_3} > 1 mol l^{-1}, the value of x is close to unity.

The principal idea underlying the use of am-

photeric resin for increasing the selectivity of separations of inorganic ions is to find conditions in which an ion could be firmly kept on the column during changing from acidic to basic solution and vice versa, whereas other ions would be eluted.

Numerous column experiments have shown that when cadmium is retained by Retardion 11A8 from ammoniacal solution, the action of 2 mol l^{-1} HCl does not remove this metal ion from the column. As is known, Cd forms anionic CdCl$_3^-$ and CdCl$_4^{2-}$ complexes [27,28] which are strongly retained by the quaternary ammonium functional groups [2,3,22]. Cd is also strongly taken up by Retardion 11A8 from NH$_4$Cl solution with λ_{Cd} > 100 in the NH$_4$Cl concentration range from 0.1 to 4 mol l^{-1} [24].

The situation is much more complex when it is desired to keep on the column Cd, retained from HCl solution, when changing to cation exchange function of the resin. As follows from Eq. (2), in ammoniacal solutions mass distribution coefficient of cadmium should depend both on ammonium ion and ammonia concentration in the mobile phase. Mass distribution coefficients of cadmium were determined by elution technique with ^{115}Cd as radioactive tracer employing as mobile phases solutions with fixed concentration of ammonia and changeable concentration of ammonium chloride. The results are shown in Fig. 1.

One can see, that λ_{Cd} decreases with the increasing concentration of both ammonia and ammonium ion in the mobile phase. In this case retention of cadmium ion is not exclusively due to electrostatic forces. Carboxylate functional groups displace ammonia molecules from the inner coordination sphere of cadmium cation, and therefore according to mass action law the increase of C_{NH_3} in solution brings about the decrease of λ_{Cd} (Eq. (2)).

In order to better understand the processes occurring when cadmium retained on Retardion 11A8 from HCl solution is eluted with ammonia, experiments with radioactive tracer ^{115}Cd were carried out. The column was first eluted with 2 mol l^{-1} HCl, then with NH$_3$ solution of different concentrations. The effluent was collected in fractions in which Cd radioactivity (which is proportional to cadmium concentration), C_{Cl^-} and pH were determined. Selected results are shown in Figs. 2–4.

When the ammoniacal solution reaches the top of the column, hydrochloric acid in the interstitial space
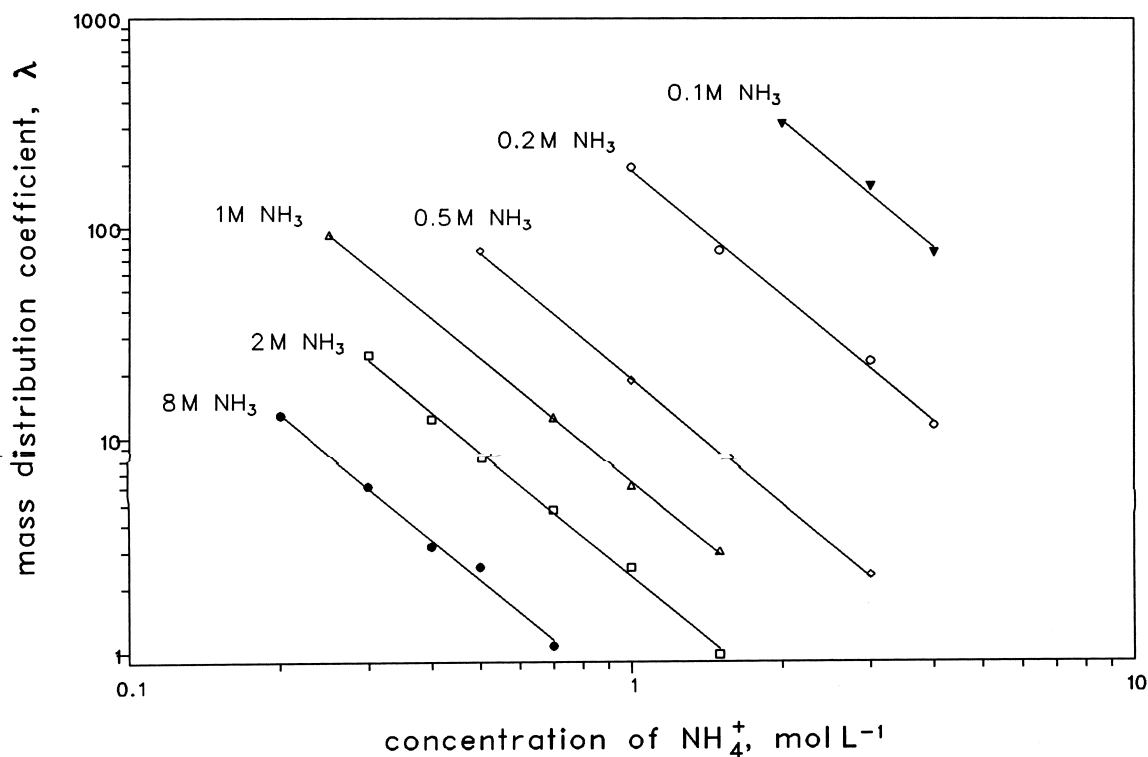
Fig. 1. Mass distribution coefficients of cadmium as a function of the concentration of ammonium cation at constant concentration of ammonia as determined by elution. Column: 8.5 cm×0.0707 cm^2; Retardion 11A8 (23–46 μm); temperature 25°C; flow-rate: 0.9–1.4 cm min^{-1}.

is neutralized and ammonium chloride is formed. It corresponds to increase of concentration of chloride ions as well as pH c.f. Figs. 2–4. At the moment when HCl has been completely neutralized and pH reaches slightly basic values, cadmium chloride species are transformed into amine ones, because the stability constants of the latter are of a few orders of magnitude higher [27,28]. Cadmium amine complexes react with the carboxylate groups of Retardion 11A8 which become practically completely dissociated in this medium. The elution behaviour of cadmium depends on the kind and concentration of species in the mobile phase zone and in particular on concentration of ammonia and ammonium ion.

It was found, that cadmium is firmly kept on the column when ammonia solution of the concentration lower than 3 mol l^{-1} is used. At higher concentrations of NH_3, the percentage of Cd eluted varies from approx. 5% when using 4 mol l^{-1} NH_3 to about 84% for 8 mol l^{-1} NH_3, c.f. Fig. 2. The reason for

this becomes evident when the changes of C_{Cl^-} and pH occurring in the course of elution are closer examined.

In the case of 4 mol l^{-1} NH_3, the pH in the external solution reaches weakly basic values (pH≈ 8–9) just when the concentration of C_{Cl^-} (and also $C_{NH_4^+}$) is approximately 0.5 mol l^{-1} and rapidly decreases. Under these conditions cadmium shows already moderate affinity towards Retardion 11A8 (c.f. Fig. 1) and so, only a small part of it is eluted. The use of more concentrated (8 mol l^{-1}) NH_3 yields more rapid neutralization of HCl and as a result, pH of about 8–9 in the interstitial liquid corresponds to much higher concentration of NH_4Cl (ca. 2.3 mol l^{-1}). Hence, a much larger fraction of cadmium appears in the effluent. It is worth mentioning, that even when using very concentrated (12 mol l^{-1}) NH_3 solution, the elution of Cd was not quantitative [21].

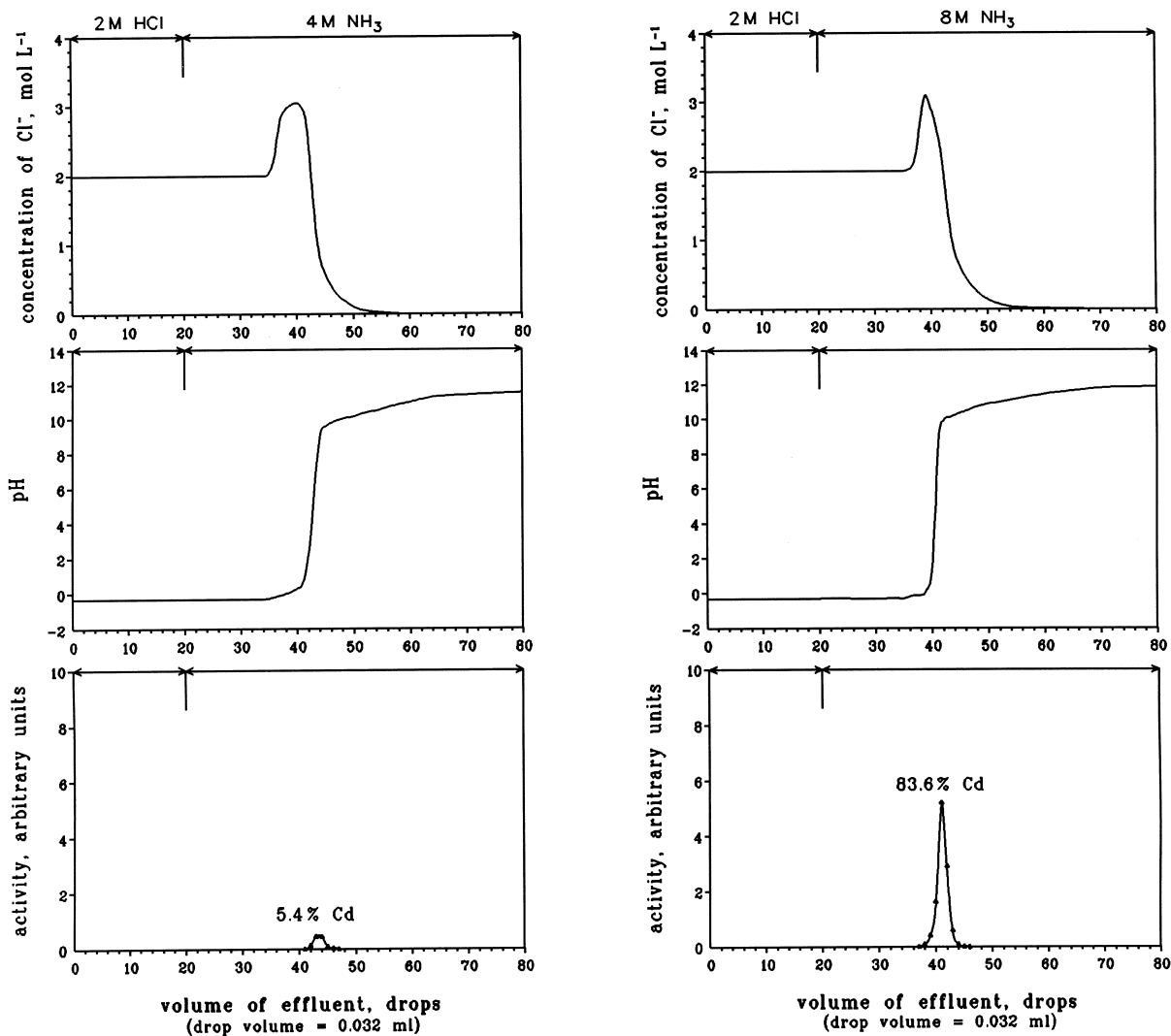When it is desired to keep cadmium firmly on the

Fig. 2. Elution behaviour of cadmium (retained as chloride complexes on Retardion 11A8) with ammonia solutions, and accompanying profiles of chloride ions concentration and pH in the effluent. Column: 8.5 cm×0.0707 cm^2; Retardion 11A8 (23–46 μm); temperature 25°C; flow-rate: 1.1 cm min^{-1}.

resin, the pH of 8–9 should be attained after the NH$_4$Cl concentration in the interstitial liquid had dropped to appropriately low value, as is the case of elution shown in Fig. 3. In these conditions several sequential changes of eluent from 2 mol l^{-1} HCl to 1.0 mol l^{-1} NH$_3$ + 0.1 mol l^{-1} NH$_4$Cl do not cause any leakage of cadmium from the column.

When, in turn, the complete recovery of cadmium from the resin bed is desired, the use of ammonia solution containing appropriate concentration of neu-

tral salt (NH$_4$Cl) is necessary. As can be inferred from Fig. 1, at low NH$_4$Cl concentration e.g. 0.01 mol l^{-1}, cadmium has high affinity to the resin even in concentrated ammonia solution. Elutions with the use of 2 mol l^{-1} NH$_3$ + 1.0 mol l^{-1} NH$_4$Cl, as well as, 8 mol l^{-1} NH$_3$ + 1.0 mol l^{-1} NH$_4$Cl are presented in Fig. 4. As can be seen, when the concentration of NH$_4$Cl is sufficiently high (1.0 mol l^{-1}), cadmium is quantitatively eluted even by means of less concentrated (2 mol l^{-1}) ammonia solution. However, the
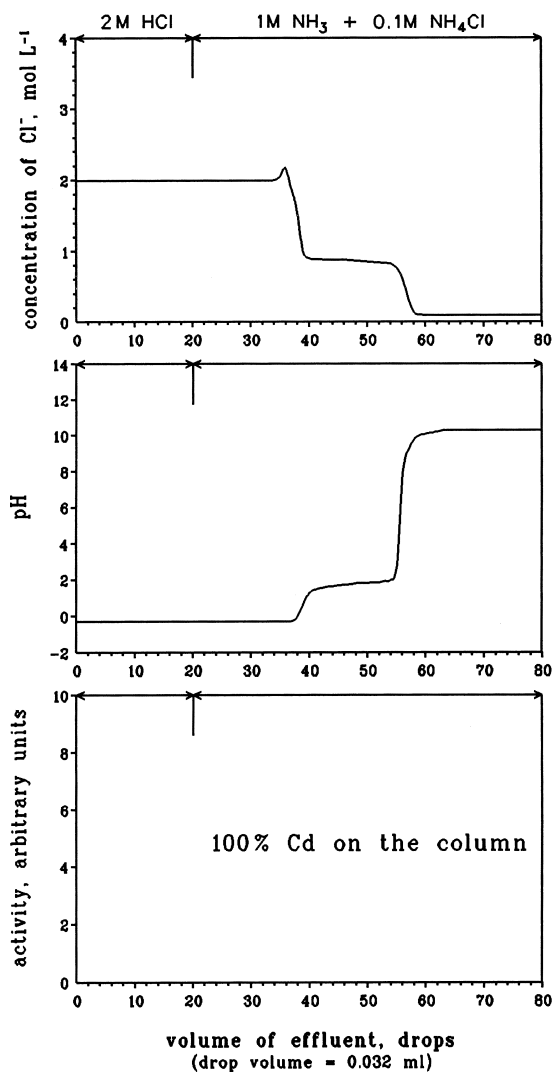
Fig. 3. Elution behaviour of cadmium (retained as chloride complexes on Retardion 11A8) with ammonia solutions, and accompanying profiles of chloride ions concentration and pH in the effluent. Column: 8.5 cm×0.0707 cm^2; Retardion 11A8 (23–46 μm); temperature 25°C; flow-rate: 1.2 cm min^{-1}.

use of a solution with higher concentration of NH$_3$ enables much faster stripping of Cd from the column.

3.2. Selective separation of cadmium from other elements using Retardion 11A8

On the basis of experiments described in the preceding section, a scheme for selective and quantitative separation of cadmium from many other elements was devised and is shown in Fig. 5. This scheme, originally was intended to be used as a component of a 'very accurate method' for the determination of trace amounts of cadmium in biological materials by radiochemical neutron activation analysis (NAA), was extensively tested with the use of radioactive tracers and its usefulness was confirmed during analysis of real samples (i.e. biological certified reference materials) [22]. Owing to the use of unique properties of amphoteric resin, cadmium can be efficiently separated on one column from all elements which form medium- and long lived radioisotopes and occur in the solution after wet-ashing of the neutron-irradiated biological samples.

It is perhaps worth mentioning that the scheme presented in Fig. 5 assures truly quantitative recovery of cadmium with very high decontamination factors (10^5–10^6) with respect to other elements. Also the separation from zinc, which shows similar ion exchange behaviour to cadmium, is substantially better than in the previous version of the method [21] where zinc was eluted (with some tailing) by means of 0.01 mol l^{-1} HCl+0.1 mol l^{-1} NH$_4$Cl solution.

3.3. The use of Chelex 100 for the separation of some metal ions by the ion exchange chromatography

Chelex 100 is a chelating ion exchanger, with iminodiacetic groups bonded to the styrene divinylbenzene polymer. They have strong complexing properties forming heterocyclic chelates with many metal ions depending on the pH of the mobile phase [2–4]. The stabilities of these species determine the ion-exchange affinity of particular cations towards Chelex 100 in neutral and slightly basic solutions.

The nitrogen atom of the iminodiacetic group which has a free electron pair, is protonated in acidic medium. Under these conditions, the carboxylic functional groups remain non-ionized and the resin can act as a weakly basic anion exchanger [29]. Consequently one can presume that it should be also capable of retaining anionic metal complexes (e.g. halide ones).

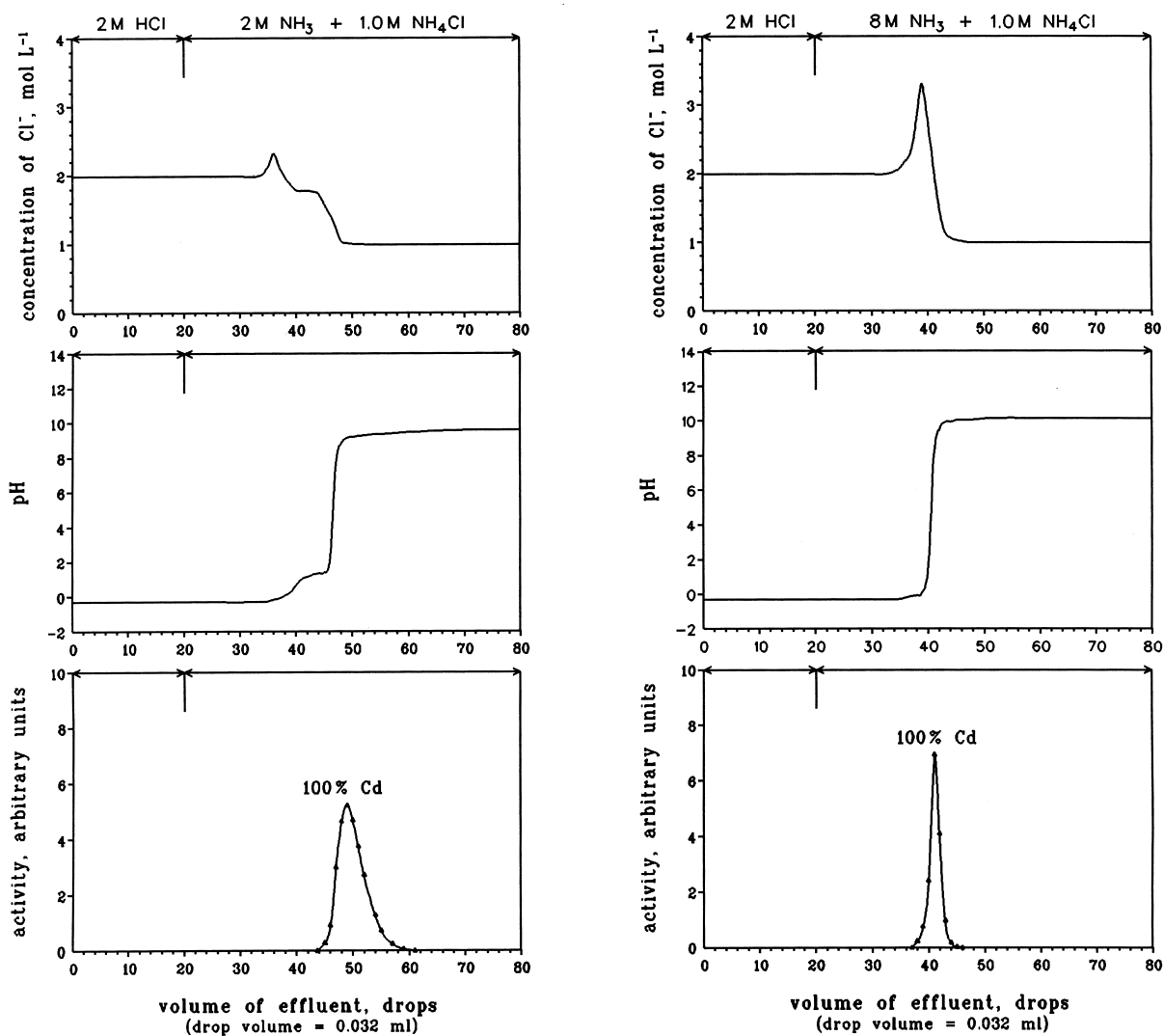Thus, Chelex 100, commonly regarded as cationic

Fig. 4. Elution behaviour of cadmium (retained as chloride complexes on Retardion 11A8) with ammonia solutions, and accompanying profiles of chloride ions concentration and pH in the effluent. Column: 8.5 cm×0.0707 cm²; Retardion 11A8 (23–46 μm); temperature 25°C; flow-rate: 1.1 cm min⁻¹.

chelating ion exchanger is de facto an amphoteric ion exchanger and analogously, as it was in case of Retardion 11A8, the ion exchange function of the resin is affected by acidity and composition of the mobile phase.

Many papers are devoted mainly to applications of Chelex 100 for the preconcentration of trace elements as a group (e.g. transition metals, heavy metals, rare earth elements) [12–16]. The process is

accomplished in an effective and convenient way using small column, on which trace elements can be retained from very large volumes (e.g. natural waters, sea waters etc.) [12,13,17–19] where the cation-exchange (chelating) function of the resin is employed.

Very few attempts were done to exploit the amphoteric character of Chelex 100 for practical separations. Radiochemical isolation of mercury
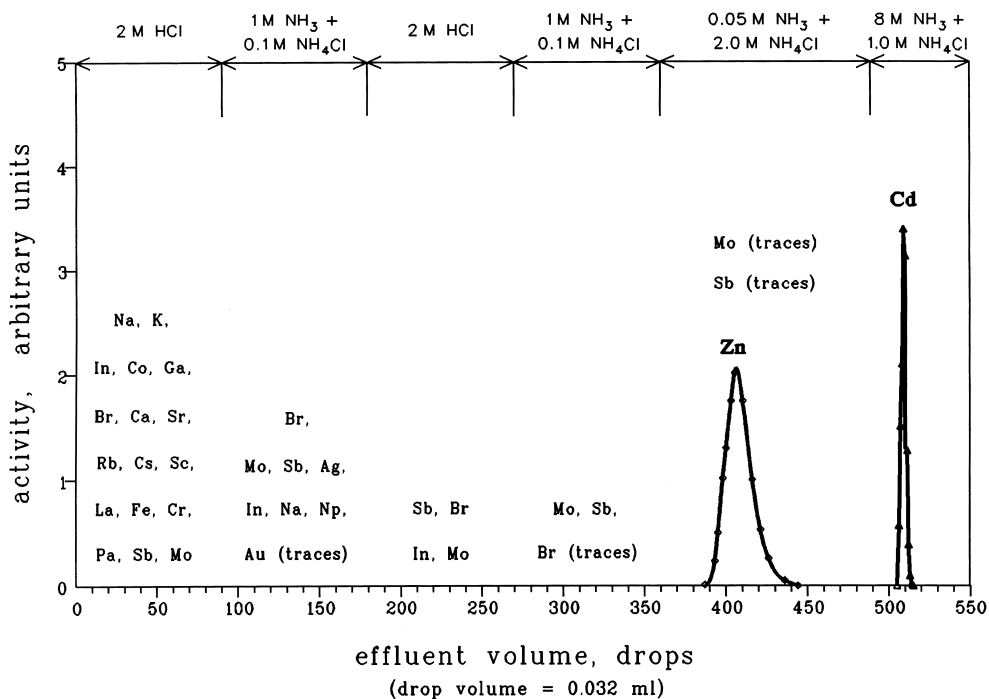
Fig. 5. Separation of cadmium from other elements by stepwise elution using Retardion 11A8. Column: 12.0 cm×0.0707 cm^2; Retardion 11A8 (23–46 μm); temperature 25°C; flow-rate: 1.0–1.3 cm min^{-1}.

using the anion-exchange function of Chelex 100 was been reported [30] in an NAA procedure for the determination of this metal in biological materials.

It seemed interesting to investigate using Chelex 100 not only for preconcentration purposes, but also for separation of individual elements from each other. It was presumed that the amphoteric character of the resin should be in some cases useful in raising the selectivity of ion exchange separations.

The ion exchange behaviour of 13 elements was investigated by batch equilibration in three systems: Chelex 100—HCl solutions, Chelex 100—acetate or phosphate buffer solutions of pH from slightly acidic to slightly basic and Chelex 100—NH$_3$ solutions at constant NH$_4$Cl concentration (0.1 mol l^{-1}). The dependencies of mass distribution coefficient (λ) vs. C_{HCl} pH and C_{NH_3} are presented in Fig. 6.

In very dilute HCl solutions (approx. 0.01 mol l^{-1}) a number of the investigated elements are still strongly held by iminodiacetic groups c.f. Fig. 6a. In the range 0.01–0.1 mol l^{-1} HCl these groups

are protonated and the anion-exchange function starts to be active. Only those metals that form anionic chloride complexes are retained. Hg(II), Ag(I) Au(III) and Pd(II), which form the most stable chloride species, the highest affinity towards Chelex 100 exhibit in 0.01–1 mol l^{-1} HCl solution and with the further increase of C_{HCl}, their mass distribution coefficients distinctly decrease. The reverse situation is observed in case of elements such as Fe(III), Ga(III), Co(II) existing in the form of chloride complexes only in concentrated HCl. Distribution coefficients of these elements at first decrease with the increase of C_{HCl} due to gradual weakening of the bond: metal cation–iminodiacetate group, pass through a minimum and later on increase with further increase of C_{HCl} this time due to anion-exchange function of the Chelex 100. In some cases a maximum appears on $\lambda_{Me} - C_{HCl}$ plots (e.g. Ga(III)). Similar ion-exchange behaviour show metals forming moderately strong chloride complexes e.g. Cd(II), Zn(II). Generally the ion exchange
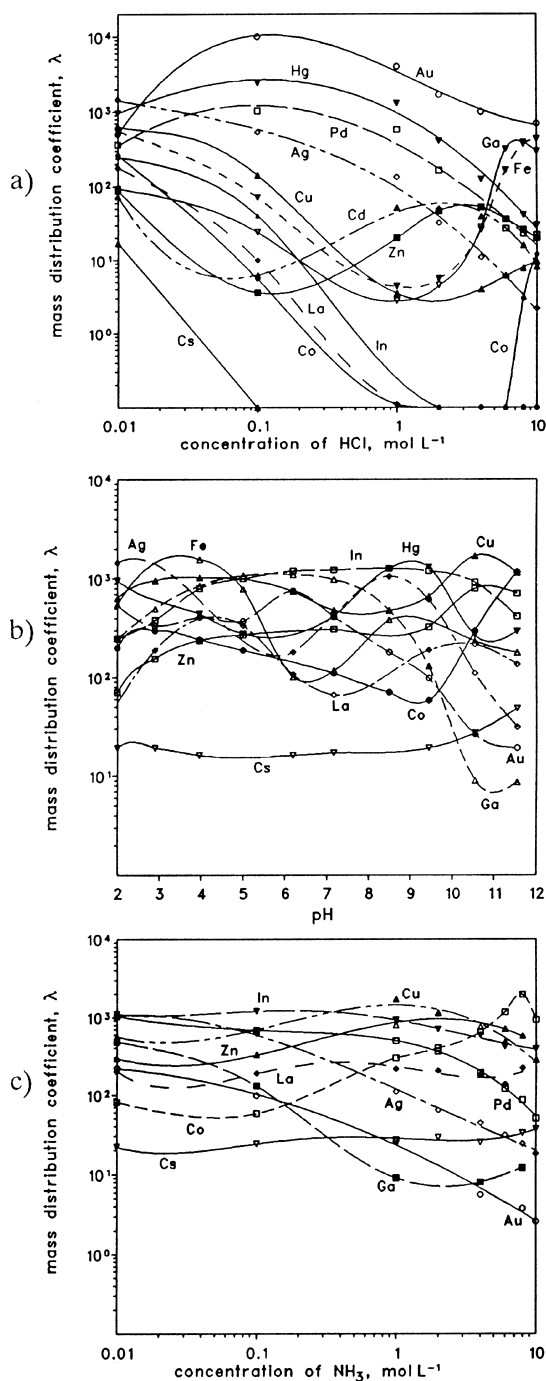
Fig. 6. Mass distribution coefficients of selected elements for Chelex 100 ion exchanger (100–200 mesh) as a function of: (a) C_{HCl}, (b) pH, (c) C_{NH_3} (at constant $C_{NH_4^+}$ equal to 0.1 mol l^{-1}); as determined by batch equilibration. Temperature 25°C.

behaviour of the investigated metals in the concentration range of $C_{HCl} \geq 1$ mol l^{-1} and the shapes of $\lambda_{Me} - C_{HCl}$ plots resemble those observed for weakly and moderately basic ion exchangers [31].

As can be seen from Fig. 6b most of metals, except alkali metals show strong or moderately strong affinity towards Chelex 100 in the broad pH range. Elements, which form the most stable chelates with the functional groups are strongly retained even at low pH values. In basic solutions, metals of amphoteric properties e.g. gallium are weakly bound by the resin due to formation of anionic hydroxy-complexes.

Introducing ammonia into an aqueous phase (c.f. Fig. 6c) brings about substantial changes in the ion-exchange behaviour of metals forming amine complexes e.g. Zn(II), Cu(II), Ag(I), Co(II), Pd(II) due to growing competition between iminodiacetic groups and ammonia molecules for the metal ion. This may be helpful in planning certain separations.

The results of batch equilibration indicate the potential possibility of several interesting separations by ion-exchange chromatography. Only three examples will be explicitly presented here.

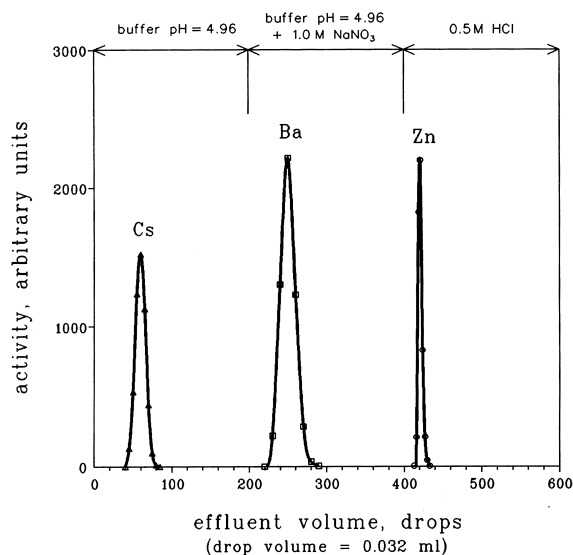The separation of Cs, Ba, and Zn (Fig. 7) is based

Fig. 7. Separation of Cs, Ba and Zn. Column: 6.5 cm×0.0707 cm^2; Chelex 100 (200–400 mesh) [Na$^+$ form]; temperature 25°C; flow-rate: 2.5 cm min^{-1}.

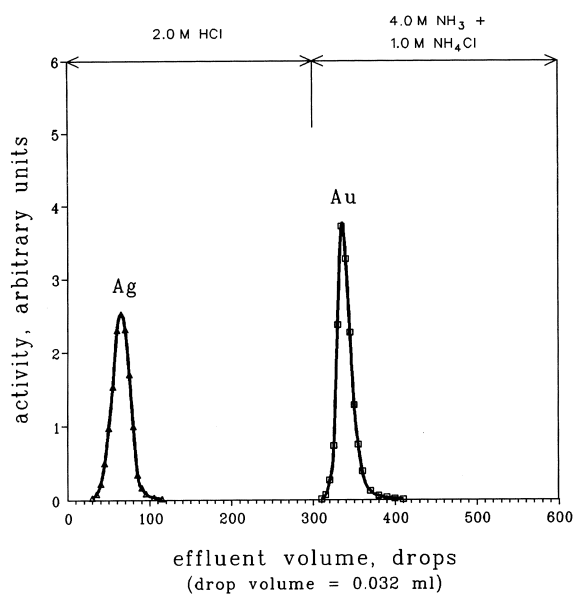Fig. 8. Separation of Ag from Au. Column: 9.7 cm × 0.0707 cm^2; Chelex 100 (200–400 mesh) [Na$^+$ form]; temperature 25°C; flow-rate: 1.4–1.8 cm min^{-1}.

on the difference of stability of chelate complexes formed by these metal ions with iminodiacetic groups.

Separation of Ag and Au (Fig. 8) employs anion-exchange function of the resin where contrary to conventional anion exchangers, gold can be relatively easily recovered from the column. Clean separation of copper and trivalent metal ions (La, Ga, and In) c.f. Fig. 9 illustrate another new separation possibilities with Chelex 100.

4. Conclusions

Amphoteric ion-exchange resins offer new separation possibilities for inorganic ions making it possible to achieve in certain instances more selective isolation of individual elements than monofunctional resins. Further work on theoretical and practical aspects of this approach is in progress.

Acknowledgements
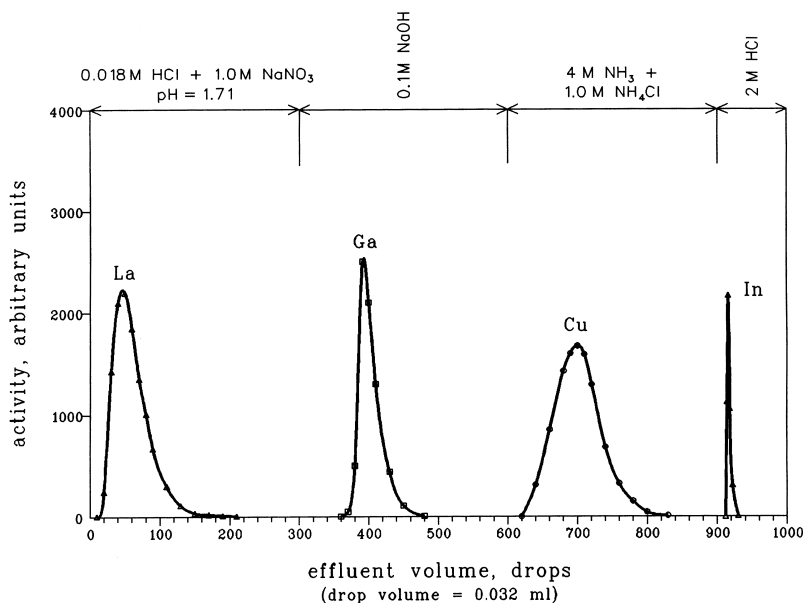
Fig. 9. Separation of La, Ga, Cu and In. Column: 6.5 cm × 0.0707 cm^2; Chelex 100 (200–400 mesh) [Na$^+$ form]; temperature 25°C; flow-rate: 1.5–2.0 cm min^{-1}.

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