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## Technetium speciation: non-size effects in size-exclusion chromatography

Arend V. Harms<sup>a,\*</sup>, Johannes T. van Elteren<sup>a</sup>, Henk A. Claessens<sup>b</sup>

<sup>a</sup>Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, Netherlands

<sup>b</sup>Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

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### Abstract

The predominant separation technique used in technetium speciation, e.g., in plant material, is size-exclusion chromatography. However, interactions of technetium compounds with the stationary phase, i.e., non-size effects, have been reported. To evaluate these effects, the interaction of three technetium compounds, the pertechnetate anion ( $\text{TcO}_4^-$ ), the anionic Tc–diethylenetriaminepentaacetate complex (Tc–DTPA), and the cationic  $[\text{Tc}(\text{V})\text{O}_2(1,4,8,11\text{-tetraazacyclotetradecane})]^+$  complex (Tc–cyclam) with three different types of size-exclusion packing material, Sephadex G-25, Zorbax GF-250 and HEMA-SEC BIO 1000 has been studied. The effects of the composition of the mobile phase and the column temperature on the distribution coefficients of the three technetium compounds was measured. It is shown that non-size effects play a dominant role in the separation of these technetium compounds.

**Keywords:** Non-size effects; Mobile phase composition; Column temperature; Distribution coefficients; Technetium

### 1. Introduction

Technetium, with atomic number 43, is the lightest element, that has only radioactive isotopes. From an environmental point of view, the most important isotope is technetium-99, a  $\beta^-$ -emitter with  $E_{\beta,\text{max}} = 292$  keV and a half-life of  $2.13 \cdot 10^5$  years; it is a fission product of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . The main sources of technetium-99 to the environment are the nuclear power generation and associated industry, nuclear weapon testing programs, and to a lesser degree, diagnostic nuclear medicine [1,2]. The high solubility and the mobility in soil of the pertechnetate anion ( $\text{TcO}_4^-$ ), the dominant chemical form of technetium in aerobic environments [3,4], combined

with the large soil-to-plant transfer factor of technetium [3,5], have stimulated research in the radioecology of this element. The available data [6–9] suggest the uptake and metabolism of pertechnetate in plants to, so far unidentified, reduced technetium compounds. Aqueous size-exclusion chromatography, with its mild separation conditions, is predominantly used to separate these, potentially labile, compounds [6–11].

In ideal size-exclusion chromatography, a separation results from the distribution of a solute between the moving mobile phase and the stagnant portion of the mobile phase, retained within the porous structure of the stationary phase. However, apart from these sieving effects, interaction of technetium compounds with the stationary phase (non-size effects) was shown by studies concerning the

\*Corresponding author.

environmental behaviour of technetium-99 or the development of technetium-99m compounds used as imaging agents in diagnostic nuclear medicine [12–18].

For pertechnetate large elution volumes and, consequently, high distribution coefficients (up to 29) were observed on Sephadex material [12]. Interaction of labile technetium complexes with size-exclusion material results in degradation or column adsorption of these complexes [13–18]. For instance, technetium compounds, isolated from spinach plants grown on nutrient solutions that have been spiked with  $\text{NH}_4^{99}\text{TcO}_4$ , were adsorbed to a substantial degree (up to 80%) on several types of columns [6].

Generally, non-size effects in size-exclusion chromatography comprise adsorption, ion-exclusion [19], hydrophobic interaction [20] and ion-exchange [21]. To evaluate the influence of these non-size effects on technetium speciation, we investigated the behaviour of three technetium compounds: the pertechnetate anion ( $\text{TcO}_4^-$ ), the anionic Tc–diethylenetriamine-pentaacetate complex (Tc–DTPA) [22–24] and the cationic  $[\text{Tc}(\text{V})\text{O}_2(1,4,8,11\text{-tetraazacyclotetradecane})]^+$  complex (Tc–cyclam) [22] on three different types of size-exclusion packing material: a soft polydextran gel (Sephadex G-25), a silica-based hydrophilic packing (Zorbax GF-250) and a rigid polymer gel (HEMA-SEC BIO 1000). The influence of the composition of the mobile phase and the column temperature on the selectivity of these chromatographic systems, caused by the non-size effects, has been studied.

## 2. Experimental

### 2.1. Chemicals

All chemicals were of analytical grade, and were obtained from Aldrich or Sigma (Sigma-Aldrich Chemicals, Bornem, Belgium). Millipore (Milford, MA, USA) Milli-Q Plus water was used for all solution preparations. Technetium-99 was obtained as ammonium or potassium pertechnetate from Amersham (Amersham, Buckinghamshire, UK). The synthesis of Tc–DTPA and Tc–cyclam, described

elsewhere [25], is a modification of the procedure by Volkert et al. [22].

### 2.2. Equipment

The used HPLC-apparatus included: a Bio-Rad (Hercules, CA, USA) Series 5000T System equipped with a Model 2700 solvent delivery system and titanium pump heads, a Rheodyne 7125T titanium injector (sample loop 20  $\mu\text{l}$ ), a Bio-Rad HRLC System Interface, an IBM compatible 286 PC with Microsoft (Redmond, WA, USA) Windows 3.1 based Series 800 HRLC System v. 2.30 software and a Model 2100 fraction collector. A Shimadzu (Kyoto, Japan) Model SPD-10AV variable (190–900 nm) UV–Vis detector, with an inert PCTFE flow cell, was used to measure the absorbance at 245 nm. To control the temperature of the column, an Eppendorf CH-430 column heater and an Eppendorf TC-50 temperature controller (Alltech, Deerfield, IL, USA) were used. All tubing, frits and fittings were made of titanium or PEEK (polyether ether ketone). The mobile phase was degassed with helium, and filtered through a 0.22  $\mu\text{m}$  Millex-GV filter (Millipore), prior to use. The extinction coefficient  $\epsilon$  of pertechnetate at 245 nm, was determined to be  $6.2 \cdot 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

An Alltech (Deerfield, IL, USA) MF-Plus (Metal-Free) HEMA-SEC BIO 1000 size-exclusion column was used (250 mm  $\times$  4.6 mm I.D.; total volume  $V_c$ : 4.15 ml; particle size: 10  $\mu\text{m}$ ; exclusion limit  $M_r$ :  $1.2 \cdot 10^6$ – $1.8 \cdot 10^6$ ). The packing material is a macroporous hydrophilic copolymer of 2-hydroxyethyl-methacrylate and ethylene dimethacrylate. Blue Dextran 2000 (Sigma) was used to determine the interstitial volume,  $V_0$ , (i.e., 1.6 ml) of the column. The specifications of the manufacturer listed an internal pore volume,  $V_i$ , of 1.1 ml. A MF-Plus Guard column (Alltech) was used as pre-column (10 mm  $\times$  4.6 mm I.D.).

A Rockland (Newport, DE, USA) Zorbax Bio Series GF-250 size-exclusion column was used (250 mm  $\times$  9.4 mm I.D.; total volume  $V_c$ : 17.3 ml; particle size: 5  $\mu\text{m}$ ; pore size: 150  $\text{\AA}$ ; exclusion limit  $M_r$ :  $0.4 \cdot 10^6$ ). The zirconium stabilised packing material has been made hydrophilic by covalently binding an organosilane reagent to the silica support. Blue Dextran 2000 (Sigma) was used to determine the

interstitial volume,  $V_0$ , (i.e., 5.9 ml) of the column. The specifications of the manufacturer listed an internal pore volume,  $V_i$ , of 6.3 ml. A Zorbax Diol guard column (Rockland) was used as pre-column (12.5 mm×4 mm I.D.).

Single-use Pharmacia (Roosendaal, The Netherlands) PD-10 columns, filled with Sephadex G-25 Medium grade material (particle size range (wet): 90–260  $\mu\text{m}$ ; exclusion limit  $M_r$ :  $5 \cdot 10^3$ ), were used. Twenty 1 ml-fractions were collected. Blue Dextran 2000 (Sigma) was used to determine the interstitial volume,  $V_0$ , (i.e., 3.1 ml) of the column. The specifications of the manufacturer listed an internal pore volume,  $V_i$ , of 6.0 ml.

Technetium-99 was determined with a Packard (Meriden, CT, USA) 2750 TR/LL liquid scintillation analyser, using Ultima Gold XR (Packard) as liquid scintillation cocktail. The duration of the counting period was adjusted to bring the uncertainty of the count rate (95% confidence level) below 2%.

### 2.3. Methods

Retention characteristics in size-exclusion chromatography can be represented by the distribution coefficient  $K_d = (V_e - V_0)/V_i$ , where  $V_e$ ,  $V_0$  and  $V_i$  refer to the elution volume of the solute, the column interstitial volume (mainly the liquid volume between the packing particles) and the internal pore volume, respectively. This distribution coefficient  $K_d$  can be represented as the product of  $K_{\text{SEC}}$ , the size-exclusion distribution coefficient, and  $K_{\text{LC}}$ , the distribution coefficient arising from solute-surface interactions.  $K_{\text{SEC}}$  is constrained to values between 0 and 1, representing the extremes of complete exclusion and permeability of the pore volume by the solute.

## 3. Results

### 3.1. HEMA

For the polymer-based HEMA material the distribution coefficient,  $K_d$ , of pertechnetate is strongly dependent on the sodium chloride concentration of the mobile phase and the column temperature (Fig. 1a). The use of pure water as a mobile phase, results

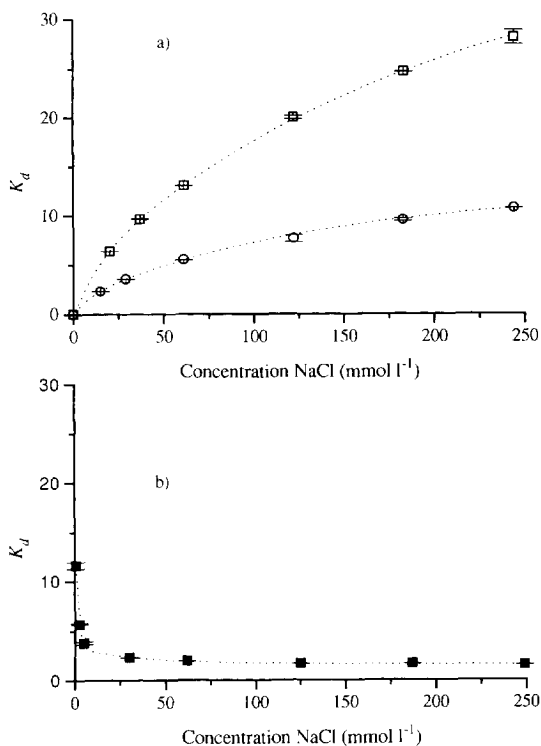


Fig. 1. The distribution coefficient (with standard error),  $K_d$ , of pertechnetate as a function of the sodium chloride concentration of the mobile phase and the column temperature. Mobile phase: water containing several concentrations NaCl; detection: 245 nm absorbance and  $^{99}\text{Tc}$  activity; flow:  $1 \text{ ml min}^{-1}$ . (a) Column: HEMA; ( $\square$ ) column temperature:  $30^\circ\text{C}$ ; ( $\circ$ ) column temperature:  $60^\circ\text{C}$ . (b) Column: Zorbax; column temperature:  $30^\circ\text{C}$ .

in exclusion of pertechnetate from the column pores and, consequently, in a negligible distribution coefficient. Increasing the sodium chloride concentration of the mobile phase results in significantly higher distribution coefficients. It can be seen that elevation of the temperature results in lower distribution coefficients. The temperature dependence of the distribution coefficient of pertechnetate was studied between 25 and  $85^\circ\text{C}$ , in steps of  $10^\circ\text{C}$ , using a mobile phase of  $250 \text{ mmol l}^{-1}$  NaCl. A van't Hoff plot was constructed (Fig. 2), showing a linear relationship between the logarithm of the distribution coefficient and the reciprocal of the column temperature. The slope of the line,  $(-\Delta H^\circ/R)$ , gives for the standard enthalpy of the retention process,  $\Delta H^\circ$ , a value of  $-29 \text{ kJ mol}^{-1}$ , showing the exothermic

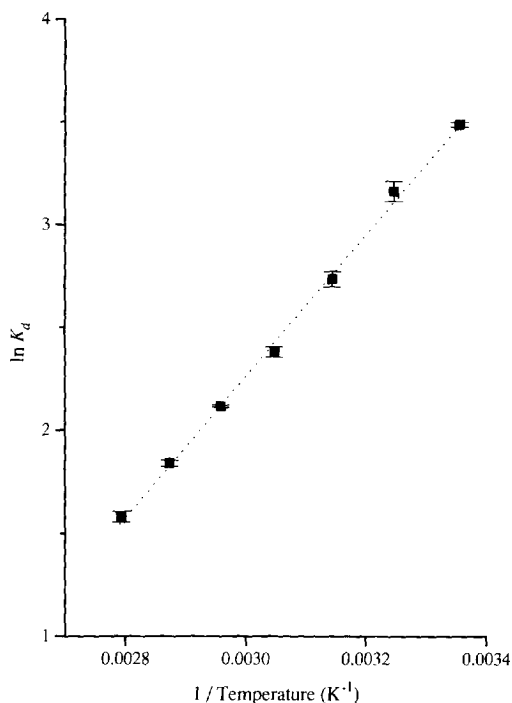


Fig. 2. Van't Hoff plot (the distribution coefficient (with standard error),  $K_d$ , of pertechnetate as a function of the inverse of the column temperature). Column: HEMA; mobile phase: water containing  $250 \text{ mmol l}^{-1}$  NaCl; detection: 245 nm absorbance and  $^{99}\text{Tc}$  activity; flow:  $1 \text{ ml min}^{-1}$ . Slope  $\pm$  S.D.:  $3.44 \cdot 10^3 \pm 30$ ; intercept  $\pm$  S.D.:  $-8.1 \pm 0.1$ ; correlation coefficient: 0.9988;  $n=14$ .

nature of the interaction between pertechnetate and the stationary phase.

The effect of the sodium chloride concentration of the mobile phase on the distribution coefficient at  $60^\circ\text{C}$  of pertechnetate, Tc-DTPA, and Tc-cyclam is shown in Fig. 3. As can be seen from this figure, no separation was obtained between pertechnetate and Tc-cyclam at a NaCl concentration of  $8 \text{ mmol l}^{-1}$ . For optimum selectivity, the NaCl concentration should be  $5 \text{ mmol l}^{-1}$  or exceeding  $12 \text{ mmol l}^{-1}$ . Separation at these NaCl concentrations is feasible, as illustrated in Fig. 4. Quantitative recovery ( $>98\%$ ) was observed for all technetium compounds.

### 3.2. Sephadex

On Sephadex columns similar trends in the distribution coefficient dependence as for the HEMA

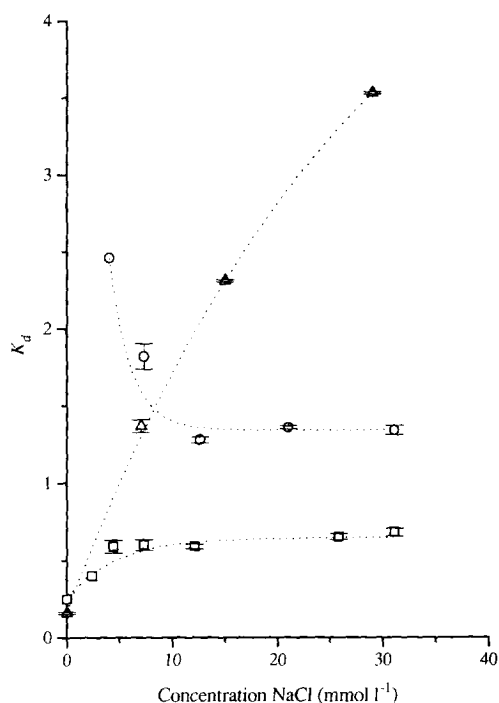


Fig. 3. The distribution coefficients (with standard error),  $K_d$ , of pertechnetate, Tc-DTPA and Tc-cyclam as function of the sodium chloride concentration of the mobile phase. Column: HEMA; column temperature:  $60^\circ\text{C}$ ; detection: 245 nm absorbance and  $^{99}\text{Tc}$  activity; flow:  $1 \text{ ml min}^{-1}$ .  $\Delta$  pertechnetate;  $\square$  Tc-DTPA;  $\circ$  Tc-cyclam.

column are observed (Table 1), although to a lesser extent. The distribution coefficients of pertechnetate and Tc-cyclam are dependent on the sodium chloride concentration of the mobile phase, while for Tc-DTPA only a small influence of the composition of the mobile phase on the distribution coefficient is observed.

### 3.3. Zorbax

The use of water as a mobile phase results in the adsorption of pertechnetate on the silica-based Zorbax column. Addition of sodium chloride to the mobile phase results in a decrease of the distribution coefficient (Fig. 1b). Other compositions of the mobile phase result in comparable distribution coefficients for pertechnetate:  $K_d=2.1$  for  $50 \text{ mmol l}^{-1}$  N-[2-hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid] (HEPES) buffer (pH 7.0;  $30^\circ\text{C}$ ),  $K_d=1.5$  for 50

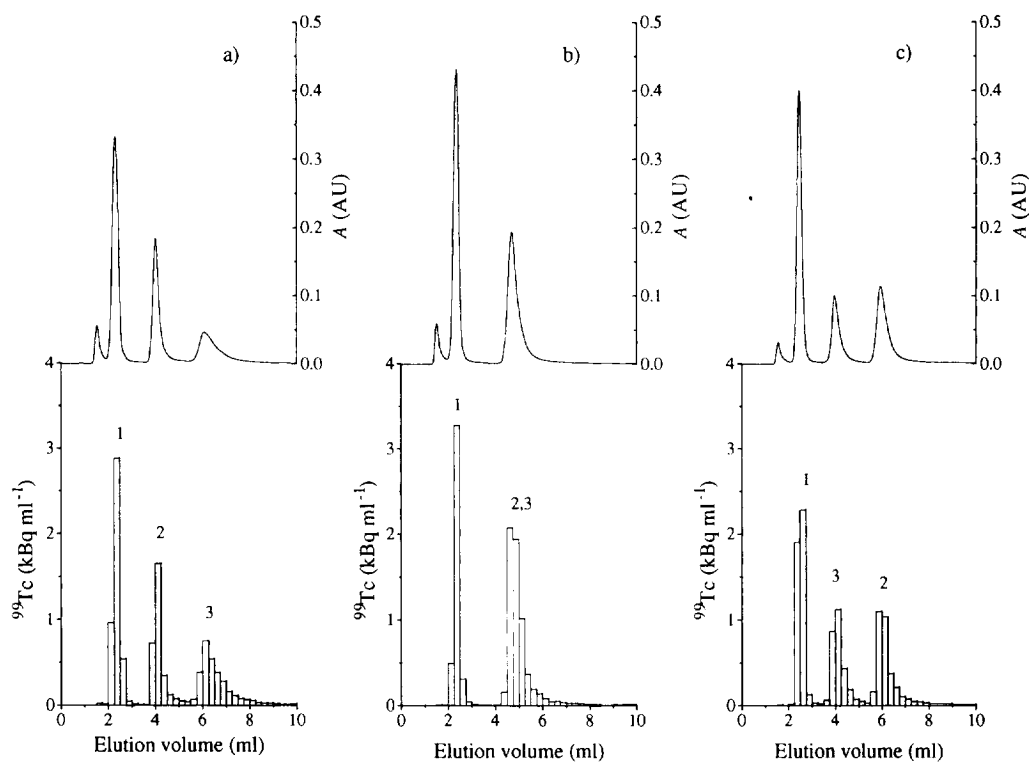


Fig. 4. Separation of Tc–DTPA (1), pertechnetate (2) and Tc–cyclam (3). Column: HEMA; column temperature: 60°C; detection: 245 nm absorbance (top) and  $^{99}\text{Tc}$  activity (bottom); flow: 1 ml min $^{-1}$ . (a) Mobile phase: water containing 5 mmol l $^{-1}$  NaCl. (b) Mobile phase: water containing 8 mmol l $^{-1}$  NaCl. (c) Mobile phase: water containing 13 mmol l $^{-1}$  NaCl.

mmol l $^{-1}$  Na-HEPES buffer and 0.88 mol l $^{-1}$  NaCl (pH 7.0; 60°C), and  $K_d=3.0$  for 0.12 mol l $^{-1}$  NaOAc buffer (pH 4.4; 30°C).

Tc–DTPA and Tc–cyclam are partly and almost completely adsorbed, respectively, on the column using 50 mmol l $^{-1}$  Na-HEPES buffer (pH 7.0; 30°C) as mobile phase. The distribution coefficient for the

Tc–DTPA complex is 1.3. The recovery of Tc–DTPA is between 68 and 90%. An injection of 0.3% (w/w) H $_2$ O $_2$ , to oxidise adsorbed TcO $_2$ , results in an additional recovery of 10 to 15% technetium. Neither the addition of sodium chloride [using 25 mmol l $^{-1}$  Na-HEPES (pH 7.0) buffer and 0.24 mol l $^{-1}$  NaCl as mobile phase], nor the addition of methanol [using 45 mmol l $^{-1}$  Na-HEPES (pH 7.0) and 10% (v/v) MeOH as mobile phase], results in the elution of Tc–cyclam.

Table 1  
Distribution coefficient of pertechnetate, Tc–DTPA and Tc–cyclam as a function of the mobile phase on Sephadex

	TcO $_4^-$	Tc–cyclam	Tc–DTPA
Water	0.6±0.1	1.7±0.03	0.2±0.1
5 mmol l $^{-1}$ NaCl	1.4±0.2	0.8±0.1	0.2±0.1
12 mmol l $^{-1}$ NaCl	1.6±0.1	0.5±0.04	0.3±0.1

The 95% confidence limits of the distribution coefficient,  $K_d$ , of pertechnetate, Tc–DTPA and Tc–cyclam as a function of the sodium chloride concentration of the mobile phase on Sephadex G-25 column at 20°C. Detection:  $\beta^-$  activity ( $^{99}\text{Tc}$ ); injection: 100  $\mu$ l.

#### 4. Discussion and conclusion

As has been pointed out for other charged solutes [26], the observed chromatographic behaviour of the pertechnetate anion, the anionic Tc–DTPA complex, and the cationic Tc–cyclam complex, cannot be fully explained in terms of the sieving effect based on their ionic sizes. Interactions between the technetium

compounds and the stationary phase, i.e., non-size effects, must also be taken into consideration, although their significance is greatly dependent on the properties of the applied solutes and stationary and mobile phases.

Ion exclusion [12], a non-size effect, results in the faster elution of an anionic solute than can be expected from its ionic size. For anions this effect might be observed when a low ionic strength mobile phase is used. This effect is the result of the negative charge of the column material at neutral pH, caused by the presence of a small number of carboxyl or silanol groups. This is demonstrated by the exclusion of pertechnetate on Sephadex and HEMA material, using water as mobile phase, and the distribution coefficient of the anionic Tc–DTPA complex for Sephadex and HEMA material, which turns out to be smaller (i.e., 0.2–0.5) than expected for a solute of its size. The distribution coefficient of Tc–DTPA is only slightly affected by the addition of sodium chloride to the mobile phase. However, the distribution coefficient of Tc–DTPA on silica-based Zorbax material was larger (i.e., 1.3) than expected for a solute of its size.

Hydrophobic interaction [13], another non-size effect that causes more retention than would be expected from the size of a solute, is observed for pertechnetate on Sephadex and HEMA material, when salt has been added to the mobile phase. Borák [27] suggested that hydroxyethyl methacrylate material can be used for the separation of anions. This author claims that differences in the chromatographic behaviour of anions are caused by the degree and type of water arrangement in the vicinity of the anions and the surface. Low-charge density structure-breaking anions, e.g.,  $I^-$  and  $SCN^-$ , are adsorbed on the gel surface, whereas structure-forming anions, e.g.,  $SO_4^{2-}$  and  $F^-$ , are squeezed out of the pores of the gel. The elution sequence of anions corresponds to the lyotropic number (which is derived from the concentration of sodium salts of different anions required to flocculate agar) [28] of the anions, while the adsorption of ions is increased if the mobile phase contains an electrolyte. Pertechnetate, like anions such as  $NO_3^-$ ,  $I^-$ ,  $SCN^-$ ,  $ReO_4^-$  and  $ClO_4^-$ , has a low-charge density, a weak hydration, and, consequently, a high lyotropic number. The dependence of the distribution coefficient of

pertechnetate as a function of the ionic strength of the mobile phase, and the increase of retention with decreasing temperatures on the HEMA material, corresponds to the gel chromatographic behaviour of other anions with a low-charge density [29,30].

A third non-size effect, cation exchange [14], is observed for Tc–cyclam on the Sephadex and HEMA columns when water was used as a mobile phase. Increasing the sodium chloride concentration of the mobile phase, results in a decrease of the distribution coefficients.

The interaction of pertechnetate with Zorbax material, silica particles with a zirconium oxide cladding, covalently bound to a hydrophilic organosilane [31], is contradictory to the other packings. When pure water or low concentration sodium chloride solutions were used as mobile phase, adsorption or high distribution coefficients, respectively, were observed. An increase in the sodium chloride concentration of the mobile phase resulted in a decreasing distribution coefficient (down to 1.5). An explanation for this behaviour might be found in the influence of the zirconium oxide cladding. Hydrous zirconium oxide, like alumina, shows, depending on the pH, both anion (low pH) and cation (high pH) exchange behaviour [32].

Finally, a fourth non-size effect, adsorption, is observed for Tc–cyclam on the silica-based Zorbax column. This result is in accordance with the unsuccessful attempts by Hoffman et al. [33] to develop a separation method for technetium tetraamine complexes on octadecylsilica-bonded column packings. They attributed this behaviour of the complexes to the negatively charged surface of the silica at  $pH > 2$  that strongly interacts with these complexes.

Thus, size-exclusion chromatography provides the chromatographer with several variables (e.g., ionic strength and temperature) to control the retention behaviour of, especially, pertechnetate and the Tc–cyclam complex, thus optimising the separation between technetium compounds. Several non-size effects (i.e., adsorption, ion-exclusion, hydrophobic interaction and cation exchange) play a dominant role in the separation of pertechnetate, the Tc–DTPA complex and the Tc–cyclam complex, using a size-exclusion packing. The HEMA column shows the best separation characteristics for this type of separation, because of the absence of column-adsorption

and, consequently, complete recovery of technetium compounds. We currently use these technetium compounds as internal standards for technetium compounds formed in spinach plants.

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