

## Extraction of pertechnetate with tetraphenylphosphonium in the presence of various acids, salts and hydroxides

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Solvent extraction of pertechnetate anions from aqueous solutions of some mineral acids (HCl, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>), (NaCl, NaNO<sub>3</sub>, NaClO<sub>4</sub>, K<sub>2</sub>CrO<sub>4</sub>, NaCO<sub>3</sub>), NaOH and NH<sub>4</sub>OH by tetraphenylphosphonium chloride in chloroform and nitrobenzene was studied. The results are presented in the form of the dependencies of extraction characteristics of TcO<sub>4</sub><sup>-</sup> (distribution ratio, percentage of extraction) on the (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P<sup>+</sup>Cl<sup>-</sup>, H<sup>+</sup> and competitive anion concentrations. The solvent extraction of sub- and super- stoichiometric ratio of TcO<sub>4</sub><sup>-</sup>:(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P<sup>+</sup> was performed. The extraction constant values of ion pairs TcO<sub>4</sub><sup>-</sup>-Cl<sup>-</sup>, TcO<sub>4</sub><sup>-</sup>-NO<sub>3</sub><sup>-</sup>, TcO<sub>4</sub><sup>-</sup>-ClO<sub>4</sub><sup>-</sup> and of individual anions TcO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> were calculated.

### Introduction

Tetraphenylarsonium was used as a reagent in reactions with a number of inorganic and organic anions.<sup>1,9</sup> With large univalent anions it creates only slightly soluble salts, in water however, many of them are well extractable into polar organic solvents in the form of ion associates. Tetraphenylphosphonium as an extraction agent is usually used in hydroxide or chloride forms which are relative well soluble in water. In some cases it is also a suitable reagent for substoichiometric separations of anions by extraction.<sup>8</sup> For quantitative isolation of very small amounts of an element by means of liquid extraction the extraction constant value should be of the order 10<sup>5</sup> or more. If it is necessary to separate one anion from another quantitatively, the ratio of their extraction constant values must be 10<sup>4</sup> at ordinary extraction (with excess of extraction agent) and more than 10<sup>2</sup> to reach the same degree of selectivity when a substoichiometric amount of reagent is used and if the original concentration of the two anions is equal. However, when one of these anions is pertechnetate, it is usually an amine, or component of the system comparable with other anions. On the other hand, the extraction constant, for the TcO<sub>4</sub><sup>-</sup>-(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P<sup>+</sup> ion pair is high, comparing to values for several common anions<sup>5,8,9</sup> and this provides conditions for its effective separation into the organic phase. For example, the distribution ratio for perrhenate, the closest chemical analog of pertechnetate, are the far highest from the large number of anions studied.<sup>5,9</sup> Values 106 and 107 are given for the TcO<sub>4</sub><sup>-</sup> distribution ratio at extraction with Ph<sub>4</sub>As<sup>+</sup> (Ph=C<sub>6</sub>H<sub>5</sub>) and Ph<sub>4</sub>P<sup>+</sup> respectively (10<sup>-4</sup> mol·dm<sup>-3</sup> solutions) from Na<sub>2</sub>CO<sub>3</sub> solution (pH 10) into chloroform.<sup>10</sup> Although ionic radii for Ph<sub>4</sub>As<sup>+</sup> and Ph<sub>4</sub>P<sup>+</sup> differ from each other only by appr. 1% and their ionic volumes in various solvents are very close too<sup>11</sup> it is interesting that the extraction constant for Ph<sub>4</sub>P<sup>+</sup>-ReO<sub>4</sub><sup>-</sup> ion pair (chloroform as organic solvent) is

several times higher<sup>8</sup> than that for Ph<sub>4</sub>As<sup>+</sup>-ReO<sub>4</sub><sup>-</sup> while values of this constant for ionic pairs with perchlorate or permanganate are the same. In contrast, some data about the five times larger value of extraction constant for Ph<sub>4</sub>As<sup>+</sup>-ReO<sub>4</sub><sup>-</sup> ion pair as compared to Ph<sub>4</sub>P<sup>+</sup>-ReO<sub>4</sub><sup>-</sup> are known.<sup>1</sup>

This work is related to a previous one<sup>12</sup> devoted to the extraction of Ph<sub>4</sub>As<sup>+</sup>-ReO<sub>4</sub><sup>-</sup> ion pair and is oriented to a study of Ph<sub>4</sub>P<sup>+</sup>-TcO<sub>4</sub><sup>-</sup> ion pair extraction characteristics using water phases of various compositions and chloroform or nitrobenzene as an organic phase.

### Experimental

Tetraphenylphosphonium chloride contents >98%, (Merck, Germany), sodium chloride Suprapur (Merck, Germany) and other reagents and solvents of analytical grade were used without additional purification. <sup>99</sup>Tc was used either as a stock solution (0.15 mol·dm<sup>-3</sup> TcO<sub>4</sub><sup>-</sup>) or, when necessary, as a standard solution (750 mg <sup>99</sup>Tc per gram of solution) of ammonium pertechnetate (Amersham, England). <sup>99m</sup>Tc as a tracer was added to the initial <sup>99</sup>Tc solutions to simplify measurements of technetium concentration, if necessary. An Amertec II generator (Amersham, England) was used as a <sup>99m</sup>Tc source (available activity 15 GBq). The <sup>99m</sup>TcO<sub>4</sub><sup>-</sup> content was eluted from the generator usually by 5 ml of physiological solution. The extraction was performed in a glass test tube placed in a rotating extractor at 22±1 °C and 1:1 phase volume ratio and took 20 minutes (unless stated otherwise). After finishing the extraction 0.1–2 ml aliquots of both phases were taken for radioactivity measurement and filled up to constant volume with a corresponding non-radioactive phase, if necessary. Samples for <sup>99</sup>Tc β-activity measurements were prepared from both standard and experimental solutions in the same way. A well-type NaI(Tl) scintillation detector in connection with a single-channel amplitude

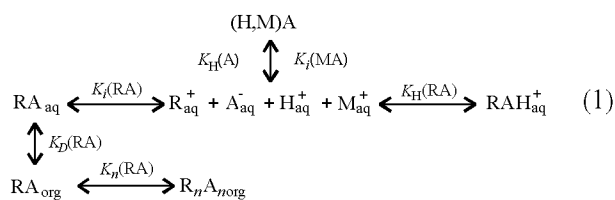
analyser NP420 (MEV, Hungary) was used for measuring of the  $\gamma$ -activity of  $^{99m}\text{Tc}$  samples. To estimate the amount of  $^{99}\text{Tc}$  in solutions when necessary, the  $\beta$ -activity of  $^{99}\text{Tc}$  samples was measured by an NV3101 spectrometric assembly (Tesla, Czech Republic). The activity measurement of the samples was performed with a standard error less than 1%.

## Results and discussion

In analytical practice generally, tetraphenylarsonium and tetraphenylphosphonium chlorides are regarded as very close in both gravimetric and extractive methods of some anions determination. The presence of other anions than determined can play an important role in both cases, however, while in the first case it is mainly the solubility of particular salts in water in the case of the extractive method an important role is played by the behavior of the reagent itself, by the component to be determined and by other components of the reaction medium in both water and organic phases and in the extraction system as a whole. It is mainly the question of ionic dissociation, molecule association, possible protonisation and extractive participation at various concentration conditions.<sup>1</sup> In one of the first papers in this direction in which tetraphenylphosphonium chloride was used for the extraction of the perrhenate anion, an important role of the chloride anion not only the distribution ratios of rhenium but the reagent itself was pointed out. It is interesting that the distribution ratio of the  $\text{ReO}_4^-$ - $\text{Ph}_4\text{P}^+$  ion pair is higher ( $\sim 800$ ) in the presence of  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  NaCl than that of the  $\text{ReO}_4^-$ - $\text{Ph}_4\text{As}^+$  ( $\sim 500$ ) while in the absence of NaCl the situation is reversed ( $D \sim 1800$  and  $6250$ , respectively), when  $0.05 \text{ mol}\cdot\text{dm}^{-3}$  reagent solution in chloroform as an organic phase is used. As the publications about  $\text{TcO}_4^-$  extraction with tetraphenyl-phosphonium are rare<sup>9,10</sup> and the competitive influence of some anions can be estimated only<sup>5,8</sup> indirectly the  $\text{TcO}_4^-$  extraction in the presence of various anions from acidic (HCl,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ), neutral (NaCl,  $\text{NaNO}_3$ ,  $\text{NaClO}_4$ ,  $\text{K}_2\text{CrO}_4$ ) and basic (NaOH,  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{CO}_3$ ) water solutions with this reagent into chloroform was studied in this paper. Results are given in Figs 1–11 in the form of dependencies of the pertechnetate distribution ratio on concentration values of the competitive anion containing component for four different concentrations of the extraction reagent. It can be seen that, according to their competitive power, the investigated anions can be arranged in the order  $\text{ClO}_4^- \gg \text{NO}_3^- > \text{Cl}^- > \text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ . In all the cases a decrease of pertechnetate distribution ratio can be observed in greater or smaller extent with the decrease of the concentration of the extraction reagent at constant macrocomponent concentration of the competitive anion in the water phase. The changes of

the acidity of the water phase acidity (equal values of HCl and NaCl,  $\text{HNO}_3$  and  $\text{NaNO}_3$ ,  $\text{HClO}_4$  and  $\text{NaClO}_4$  concentrations) have no great influence on the  $D_{\text{Tc}}$  values in the studied systems at equal extraction reagent concentrations. The dependence of pertechnetate distribution ratio values is most expressive for a concentration of the anion with high competitive power ( $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ) in the entire investigated region of reagent concentrations. Such a dependence is weakly expressed for anions with low competitive power ( $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ). It is interesting that NaOH and  $\text{NH}_4\text{OH}$  have different degrees of influence especially at higher concentrations which is probably connected with their different influence to the degree of dissociation of  $\text{Ph}_4\text{POH}$  in the aqueous phase.

Assuming an  $\text{A}^-$  type anion in the presence of an  $\text{R}^+$  cation (where  $\text{R}^+ = \text{Ph}_4\text{P}^+$ ) creates in water phase only one ionic associate type RA extractable into the organic phase. The equilibrium in the extraction system for this pair of ions can be expressed as:



where  $K_{\text{i}}$ ,  $K_{\text{H}}$ ,  $K_{\text{D}}$  and  $K_{\text{n}}$  are the dissociation, protonisation, distribution and association constants for RA and (H, M) A respectively. This scheme includes also the case when the extraction system contains an excess of  $\text{A}^-$  anions (e.g., in the form of salt MA or acid HA) as compared to the tetraphenylphosphonium content. A similar scheme should be considered for any other anion present in the extraction system (e.g.,  $\text{TcO}_4^-$ ) which is competitive to the given  $\text{A}^-$  anion. The extraction equilibrium for  $\text{R}^+$  and  $\text{A}^-$  ion pair is:



and can be characterised quantitatively by a two-phase constant of stability  $K_{\text{A}^-}$  of ionic associate RA:

$$\begin{aligned} K_{\text{A}^-} &= \frac{[\text{RA}]_{\text{org}}}{[\text{R}^+]_{\text{aq}} [\text{A}^-]_{\text{aq}}} = \frac{[\text{RA}]_{\text{org}}}{[\text{RA}]_{\text{aq}} K_{\text{i(RA)}}} = \\ &= \frac{K_{\text{D(RA)}}}{K_{\text{i(RA)}}} \end{aligned} \quad (3)$$

The  $K_{\text{A}^-}$  constant in accordance with Eq. (2) has the meaning of an individual extraction constant for  $\text{A}^-$  anion. If the anion concentration  $[\text{A}^-]_{\text{aq}}$  is equal to the overall analytical concentration of A in the aqueous phase, i.e.,  $[\text{A}^-]_{\text{aq}} = c_{\text{Aaq}}$ , and only the monomeric form RA exist in organic phase then  $[\text{RA}]_{\text{org}} = c_{\text{Aaq}}$ , and

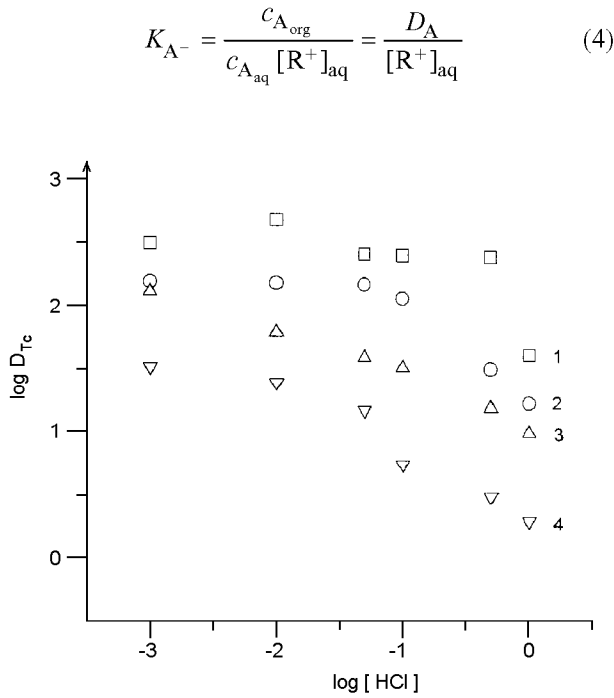


Fig. 1. Relationship between the distribution ratio of technetium and HCl concentration in the aqueous phase. Organic phase: 1 –  $5 \cdot 10^{-3}$  M, 2 –  $1 \cdot 10^{-3}$  M, 3 –  $5 \cdot 10^{-4}$  M, 4 –  $1 \cdot 10^{-4}$  M  $\text{Ph}_4\text{PCL}$  in chloroform

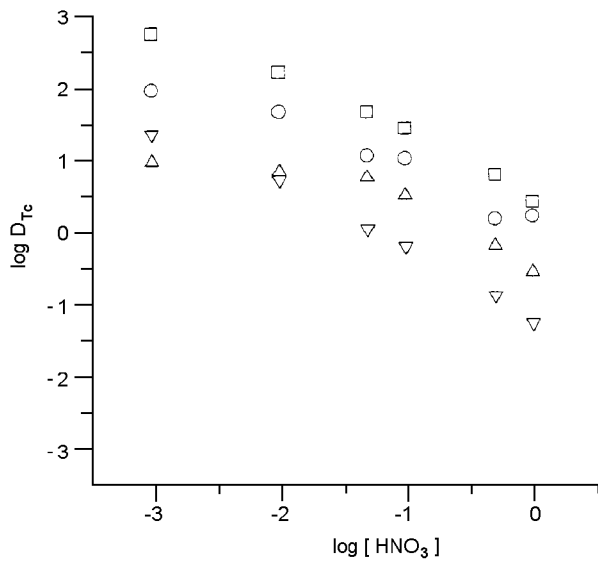


Fig. 2. Relationship between the distribution ratio of technetium and  $\text{HNO}_3$  concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

where  $D_A$  is the component A's distribution ratio. The distribution ratio of the reagent (R) related to A is

$$D_R(A) = \frac{[RA]_{org}}{c_R(A)_{aq}} = \frac{[RA]_{org}}{[RA]_{aq} + [R^+]_{aq} + [RAH^+]_{aq}} \quad (5)$$

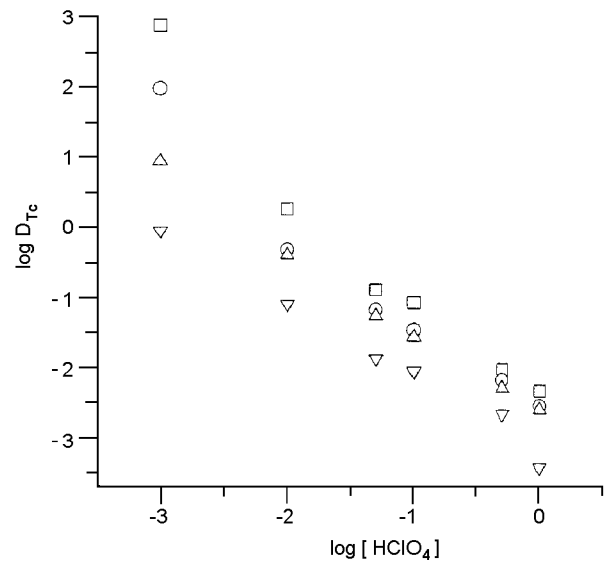


Fig. 3. Relationship between the distribution ratio of technetium and  $\text{HClO}_4$  concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

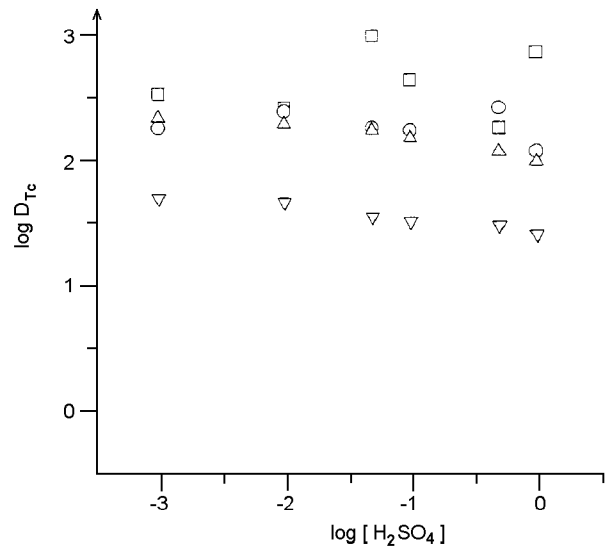


Fig. 4. Relationship between the distribution ratio of technetium and  $\text{H}_2\text{SO}_4$  concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

and the concentration  $[R^+]_{aq}$  in the Eq. (4) at  $V_{aq} = V_{org}$  has a value of:

$$[R^+]_{aq} = \frac{c_R^0}{(D_R(A)+1) \frac{[A^-]_{aq}}{K_i(RA)} + 1 + \frac{K_H(RA)}{K_i(RA)} [A^-]_{aq} [H^+]_{aq}} \quad (6)$$

where  $c_R^0$  is the initial concentration of the reagent in the organic (or aqueous) phase.

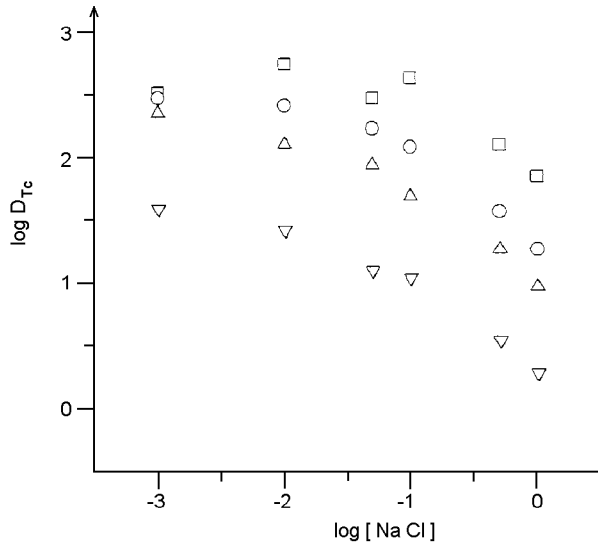


Fig. 5. Relationship between the distribution ratio of technetium and NaCl concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

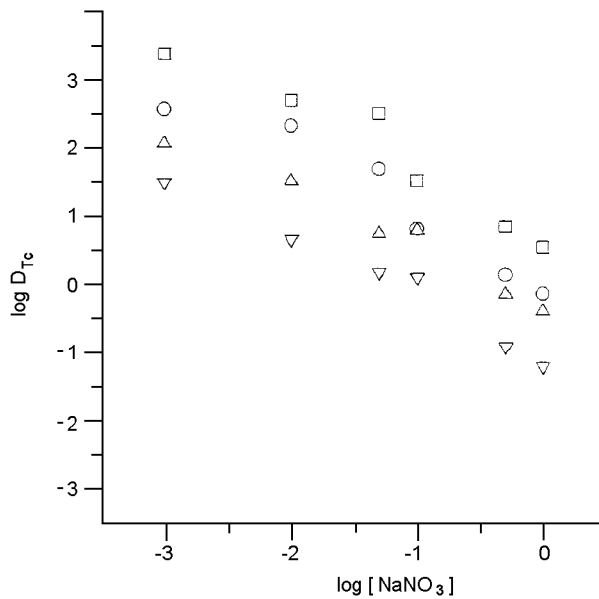


Fig. 6. Relationship between the distribution ratio of technetium and NaNO<sub>3</sub> concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

If the A<sup>-</sup> and TcO<sub>4</sub><sup>-</sup> anions are present in the extraction system at the same time, the equilibrium state

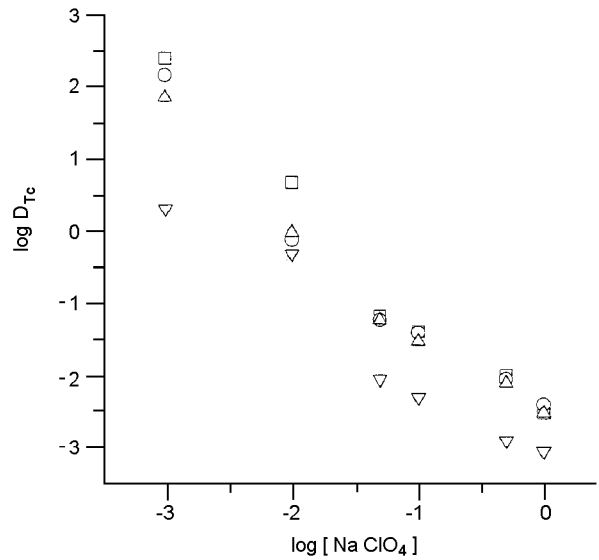


Fig. 7. Relationship between the distribution ratio of technetium and NaClO<sub>4</sub> concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

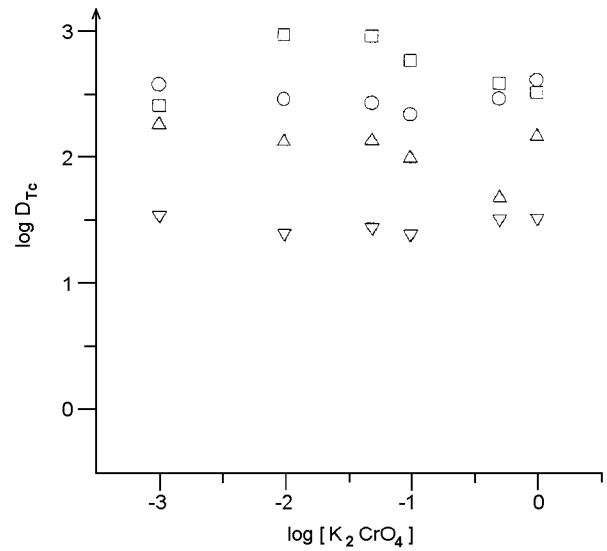


Fig. 8. Relationship between the distribution ratio of technetium and K<sub>2</sub>CrO<sub>4</sub> concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

of the competitive processes of the A<sup>-</sup> and TcO<sub>4</sub><sup>-</sup> anions extraction can be expressed either by  $K_{A^-}$  and  $K_{TcO_4^-}$

values according to Eqs (3) or (4) for two parallel reactions of type (2) or as a consecutive process of anion exchange between water and organic phases according to:



The equilibrium constant of this process (so called extraction exchange constant)  $K_{\text{TcO}_4^- - \text{A}^-}$  can be expressed by:

$$\begin{aligned} K_{\text{TcO}_4^- - \text{A}^-} &= \frac{[\text{RTcO}_4]_{\text{org}} [\text{A}^-]_{\text{aq}}}{[\text{TcO}_4^-]_{\text{aq}} [\text{RA}]_{\text{org}}} = \\ &= \frac{K_D(\text{RTcO}_4) K_i(\text{RA})}{K_D(\text{RA}) K_i(\text{RTcO}_4)} = \frac{K_{\text{TcO}_4^-}}{K_{\text{A}^-}} = \frac{D_{\text{Tc}}}{D_{\text{A}}} \end{aligned} \quad (8)$$

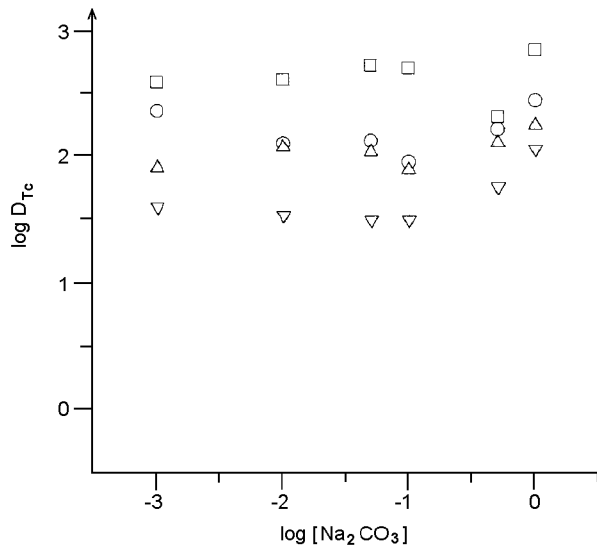


Fig. 9. Relationship between the distribution ratio of technetium and  $\text{Na}_2\text{CO}_3$  concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

where  $D_{\text{Tc}}$  is the pertechnetate distribution ratio whereby fulfilling of equal conditions like in the case of Eq. (4) is assumed. A relation analogic to Eq. (5) is valid for reagent (R) to pertechnetate distribution ratio in which the symbol A has been changed to  $\text{TcO}_4^-$ . An overall reagent  $D_{\text{R}}$  distribution ratio with regard to both anions is:

$$D_{\text{R}} = \frac{[\text{RA}]_{\text{org}} + [\text{RTcO}_4]_{\text{org}}}{[\text{RA}]_{\text{aq}} + [\text{RTcO}_4]_{\text{aq}} + [\text{RAH}^+]_{\text{aq}} + [\text{RTcO}_4\text{H}^+]_{\text{aq}} + [\text{R}^+]_{\text{aq}}} \quad (9)$$

and  $[\text{R}^+]_{\text{aq}}$  can be calculated according to:

$$[\text{R}^+]_{\text{aq}} = \frac{c_{\text{R}}^0}{(D_{\text{R}} + 1) \left( 1 + \frac{[\text{A}^-]_{\text{aq}}}{K_i(\text{RA})} + \frac{[\text{TcO}_4^-]_{\text{aq}}}{K_i(\text{RTcO}_4)} + F \right)} \quad (10)$$

where  $F$  is

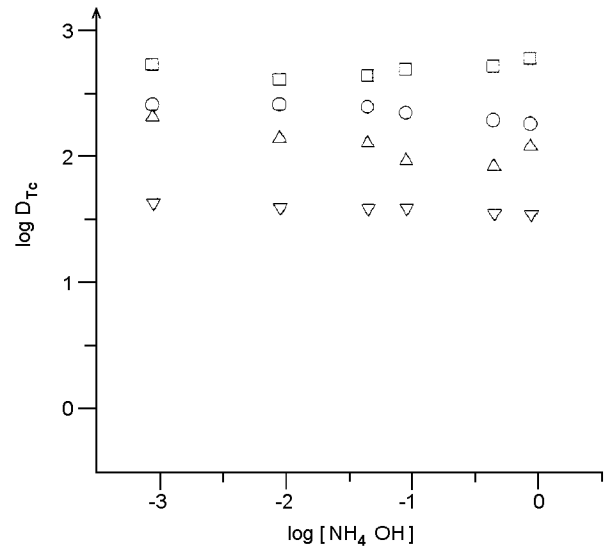


Fig. 10. Relationship between the distribution ratio of technetium and  $\text{NH}_4\text{OH}$  concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

$$F = [\text{H}^+]_{\text{aq}} \left( \frac{K_{\text{H}}(\text{RA})}{K_i(\text{RA})} [\text{A}^-]_{\text{aq}} + \frac{K_{\text{H}}(\text{RTcO}_4)}{K_i(\text{RTcO}_4)} [\text{TcO}_4^-]_{\text{aq}} \right)$$

In a simple case, when  $\text{TcO}_4^-$  is present in the system in trace concentration and Eq. (4) conditions are fulfilled, i.e.,  $c_{\text{Raq}} = [\text{R}^+]_{\text{aq}}$ ,  $c_{\text{Aaq}} = [\text{A}^-]_{\text{aq}}$ ,  $c_{\text{Tcaq}} = [\text{TcO}_4^-]_{\text{aq}}$ , the  $[\text{R}^+]_{\text{aq}}$  can be calculated according to the simplified relation:

$$[\text{R}^+]_{\text{aq}} = \frac{c_{\text{R}}^0}{D_{\text{R}}(\text{A}) + 1} \quad (11)$$

if the distribution ratio  $D_{\text{R}}(\text{A})$  value is known at a given concentration of majority anion  $\text{A}^-$  in the aqueous

phase. However, such data are rare in the literature, the experimental conditions for their determination are defined incompletely<sup>5,9</sup> and the same is valid for values of the individual extraction constants of some anions calculated<sup>8</sup> from such data.

The situation becomes more simple when the majority anion  $A^-$  is practically not extracted by the tetraphenylphosphonium cation and  $[R^+]_{aq} \cong c_R^0$ . Then Eq. (4) for  $TcO_4^-$  can be expressed as:

$$K_{TcO_4^-} \cong \frac{D_{Tc}}{c_R^0} \quad (12)$$

When the majority anion  $A^-$  is very well extracted by  $R^+$  and  $c_A^0$  is in large excess to  $c_R^0$ , i.e.,  $[RA]_{org} \cong c_R^0$ , Eq. (8) can be expressed as:

$$K_{TcO_4^- - A^-} \cong \frac{D_{Tc} [A^-]_{aq}}{c_R^0} \cong \frac{D_{Tc} c_A^0}{c_R^0} \quad (13)$$

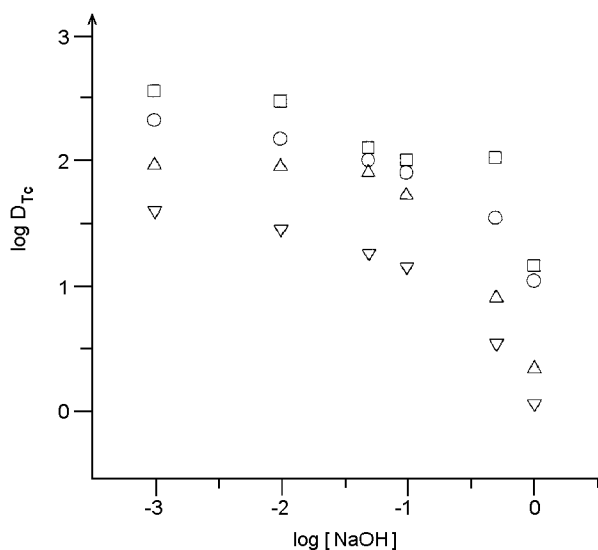


Fig. 11. Relationship between the distribution ratio of technetium and NaOH concentration in the aqueous phase. Organic phase: identical to that in Fig. 1

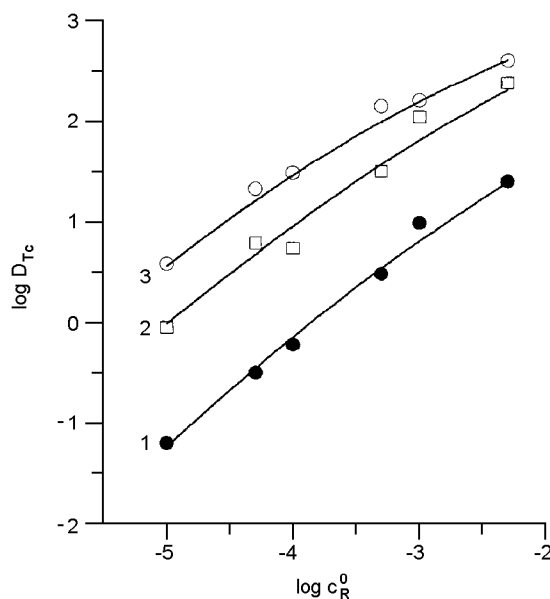


Fig. 12. Logarithmic plots of distribution ratio of technetium vs. initial concentration of  $Ph_4PCL$  in chloroform. Aqueous phase: 1 – 0.1M  $HNO_3$ , 2 – 0.1M  $HCl$ , 3 – 0.1M  $H_2SO_4$

Using Relations (12) and (13), all experimental data given in Figs 1–11 were processed. The systems containing  $NH_4OH$ ,  $H_2SO_4$ ,  $Na_2CO_3$  and  $K_2CrO_4$  like anionic macrocomponents correspond to Relation (12) practically for all extraction reagent concentrations and for all anionic macrocomponent concentrations. The remaining systems (with  $HCl$ ,  $NaCl$ ,  $HNO_3$ ,  $NaNO_3$ ,  $HClO_4$ ,  $NaClO_4$ ,  $NaOH$ ) approach the former ones by calculated  $K_{TcO_4^-}$  values only at a low concentration of the anionic macrocomponent. The  $K_{TcO_4^-}$  value, calculated from Relation (13) for systems containing  $HClO_4$ ,  $NaClO_4$ ,  $HNO_3$  and  $NaNO_3$  as macrocomponents, tends to a constant merely at higher anion  $A^-$  concentrations ( $[c_A^0] \geq 5 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ). For system with  $HCl$  and  $NaCl$ , limited  $K_{TcO_4^- - Cl^-}$  values are reached only at concentrations of  $[c_{Cl^-}^0] \geq 0.5 \text{ mol} \cdot \text{dm}^{-3}$ . Calculated  $K_{TcO_4^-}$  or  $K_{TcO_4^- - A^-}$  values determined in these experiments are given in Table 1. The  $K_{A^-}$  values were calculated as the average  $K_{TcO_4^-}$  ( $2.74 \cdot 10^5$ ) ratio to the  $K_{TcO_4^- - A^-}$  for the corresponding solutions of salts. The above mentioned  $K_{TcO_4^-}$  value is a little lower than the  $K_{ReO_4^-} \cong 4 \cdot 10^5$  value published by TRIBALAT<sup>1</sup> however, our determined  $K_{Cl^-}$  when compared to the same author's value ( $K_{Cl^-} \cong 25$ ) is lower too, so that  $K_{TcO_4^- - A^-}$  and  $K_{ReO_4^- - Cl^-}$  values ( $\sim 1.6 \cdot 10^4$ ) are quite close. The  $K_{NO_3^-}$  given in a previous paper<sup>8</sup> is approximately two times higher than ours and this probably due to different assumptions about reagent distribution in phases and different ways of  $K_{A^-}$  calculation [Eqs (4) and (12), respectively].

The dependence of distribution ratio  $D_{Tc}$  on the initial tetraphenylphosphonium concentration in chloroform is shown in Fig. 12. This dependence at

$\text{TcO}_4^-$  extraction from  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  aqueous solutions of HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  can be approximated practically in the entire region of extraction reagent concentrations by straight lines which slopes very close to 1, i.e., in the extraction process  $\text{TcO}_4^-$  enters the reaction with tetraphenylphosphonium in a molar ratio of 1:1. From the point of the efficiency, view of technetium

extraction aqueous phases can be arranged in the order  $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$  at which  $\text{TcO}_4^-$  is extracted from  $\text{H}_2\text{SO}_4$  medium almost exclusively according to Eq. (2), from  $\text{HNO}_3$  medium prevailingly according to the Eq. (7) and from HCl medium in both ways depending on the phase distribution of the extraction reagent.

Table 1. Extraction constants of individual anions ( $K_{A^-}$ ) and extraction exchange constants of ion-pairs ( $K_{TcO_4^-A^-}$ )

Chloroform		Nitrobenzene
	$K_{TcO_4^-}$	
( $2.8 \pm 0.1$ ) $\cdot 10^5$ (Figs 1, 4, 5, 8, 9, 10, 11, 17, 19, Eqs (12), (14))		( $4.6 \pm 0.2$ ) $\cdot 10^5$ (Fig. 18, Eq. (14))
( $1.3 \pm 0.2$ ) $\cdot 10^6$ (a) (Fig. 19, Eq. (14), $c_{A^-} = 0$ )		( $2.4 \pm 0.3$ ) $\cdot 10^7$ (b) (Fig. 20, Eq. (14), $c_{A^-} = 0$ )
	$K_{TcO_4^-Cl^-}$	
( $1.8 \pm 0.1$ ) $\cdot 10^4$ (Figs 1, 5, 12, 13, 15, 19, Eqs (13), (16))		( $5.5 \pm 0.3$ ) $\cdot 10^5$ (Figs 14, 15, Eq. (13)) ( $1.8 \pm 0.2$ ) $\cdot 10^6$ (Fig. 20, Eq. (16))
	$K_{Cl^-}$	
73 (Eq. (15), $K_{TcO_4^-}$ (a))		44 (Eq. (15), $K_{TcO_4^-}$ (b))
	$K_{TcO_4^-NO_3^-}$	
( $6.7 \pm 0.5$ ) $\cdot 10^2$ (Figs 2, 6, 13, 15, 19, Eqs (13), (16))		( $4.3 \pm 0.5$ ) $\cdot 10^3$ (Figs 13, 16, 20, Eqs (13), (16))
	$K_{NO_3^-}$	
$2.0 \cdot 10^3$ (Eq. (15), $K_{TcO_4^-}$ (a))		$5.6 \cdot 10^3$ Eq. (15), $K_{TcO_4^-}$ (b))
	$K_{TcO_4^-ClO_4^-}$	
$4.5 \pm 1.1$ (Figs 3, 6, 15, 19, Eqs (13), (16))		$2.7 \pm 0.3$ (Figs 16, 20, Eqs (13), (16))
	$K_{ClO_4^-}$	
$3.0 \cdot 10^5$ (Eq. (15), $K_{TcO_4^-}$ (a))		$8.9 \cdot 10^6$ (Eq. (15), $K_{TcO_4^-}$ (b))

It is known that the nature of organic solvent used has a great influence on the extraction of complexes of ion association type. For this reason we used chloroform and nitrobenzene for comparison which have large difference in their dielectric constants. The  $D_{Tc}$  dependence on the initial concentration of the extraction reagent in chloroform and nitrobenzene is given in Figs 13 and 14, respectively, and they correspond to the  $TcO_4^-$  extraction from  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  NaCl, HCl,  $NaNO_3$  and  $HNO_3$  aqueous solutions. It can be seen that the  $TcO_4^-$  extraction into nitrobenzene is, under otherwise similar conditions, obviously more effective as compared to chloroform, especially at the extraction from chloride medium.  $D_{Tc}$  values for nitrobenzene at higher  $c_R^0$  values approach a constant for  $TcO_4^-$  extraction from NaCl and HCl solutions ( $D_{Tc} > 10^3$ ) as well as from  $NaNO_3$  solution ( $D_{Tc} > 10^2$ ). From the linear parts of dependencies given in Figs 13 and 14,  $K_{TcO_4^-A^-}$  values were calculated (Table 1) using the Relation (13) provided that all the reagent is in organic phase. A remarkable difference between chloroform and nitrobenzene can be observed mainly at the extraction from chloride media when the difference between  $K_{TcO_4^-Cl^-}$  reaches about one half of an order for these solutions.

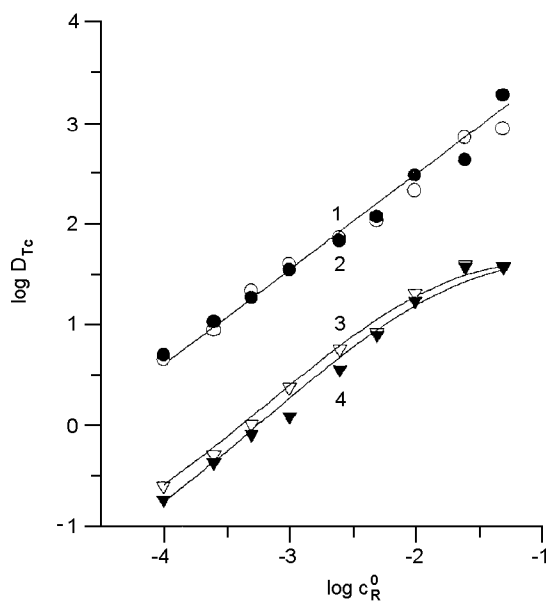


Fig. 13. Logarithmic plots of the distribution ratio of technetium vs. initial concentration of  $Ph_4PCL$  in chloroform. Aqueous phase: 1 – 0.5M NaCl, 2 – 0.5M HCl, 3 – 0.5M  $NaNO_3$ , 4 – 0.5M  $HNO_3$



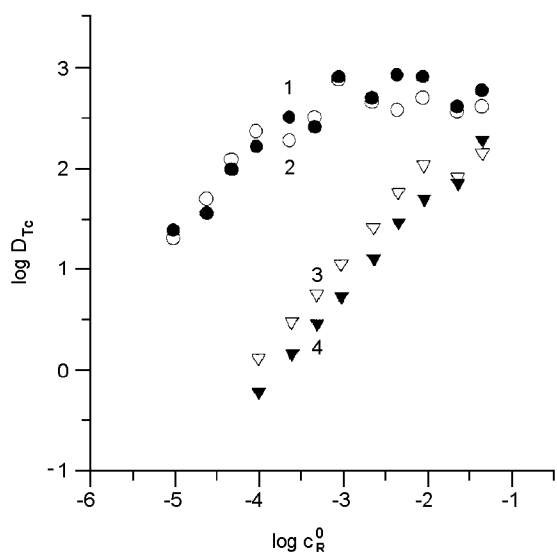


Fig. 14. Logarithmic plots of the distribution ratio of technetium vs. initial concentration of  $\text{Ph}_4\text{PCL}$  in nitrobenzen. Aqueous phase: identical as in Fig. 13

In Figs 15 and 16 dependencies of technetium distribution ratio on hydrogen ion concentration are given at constant ionic strength for  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  aqueous solutions  $(\text{Na}, \text{H})\text{Cl}$ ,  $(\text{Na}, \text{H})\text{NO}_3$  and  $(\text{Na}, \text{H})\text{ClO}_4$  and two different concentrations of the extraction reagent in chloroform (Fig. 15) and nitrobenzene (Fig. 16). The change of technetium extraction is very small or negligible by aqueous phase acidity changes in the investigated range of  $[\text{H}^+]$  values in most cases. Only in the case of  $(\text{Na}, \text{H})\text{NO}_3$ – $0.01 \text{ mol}\cdot\text{dm}^{-3}$   $\text{Ph}_4\text{PCL}$  systems a moderate decrease of technetium extraction with increasing  $[\text{H}^+]$  can be observed. It means that imperfect  $\text{HTcO}_4$  dissociation or extraction reagent protonisation in the aqueous phase does not manifest by technetium extraction. From the point of view of the organic solvents used, the greatest difference in technetium distribution ratio is in the chloride aqueous media while the smallest one is in the perchlorate aqueous media.

Using  $^{99}\text{TcO}_4^-$  ( $^{99\text{m}}\text{TcO}_4^-$ ) with various  $^{99}\text{Tc}$  concentrations and  $\text{Ph}_4\text{PCL}$  solutions with given concentrations of chloroform and nitrobenzene, a pertechnetate extraction titration was accomplished according to Eq. (2). The initial  $^{99}\text{TcO}_4^-$  concentration in the aqueous phase was determined by the  $^{99}\text{Tc}$  volume activity in this phase compared to a standard sample with known  $^{99}\text{Tc}$  content. Tc distribution in phases after extraction was determined by  $^{99\text{m}}\text{Tc}$  activity measurements. Results are given in Figs 17 and 18 for chloroform and nitrobenzene respectively. Each experimental point in Fig. 17 is an average value from two and in Fig. 18 from four independent

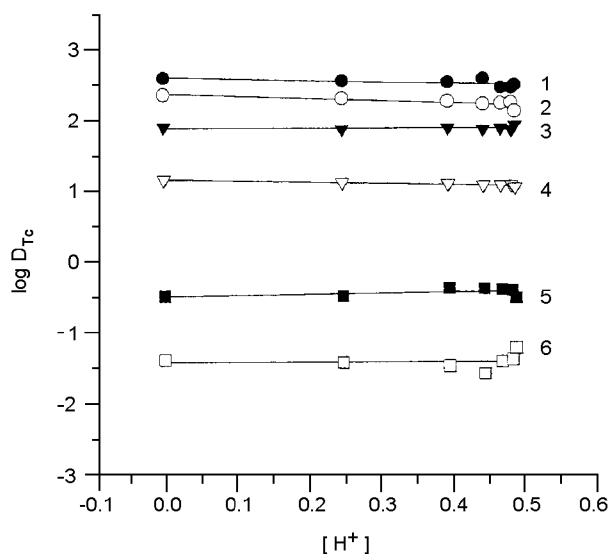


Fig. 15. Influence of hydrogen ion concentration in the aqueous phase on the distribution ratio of technetium at constant ionic strength 0.5: 1,2 –  $\text{NaCl} + \text{HCl}$ ; 3,4 –  $\text{NaNO}_3 + \text{HNO}_3$ ; 5,6 –  $\text{NaClO}_4 + \text{HClO}_4$ . Organic phase: 1,3,5 –  $0.05\text{M}$  and 2,4,6 –  $0.01\text{M}$   $\text{Ph}_4\text{PCL}$  in chloroform

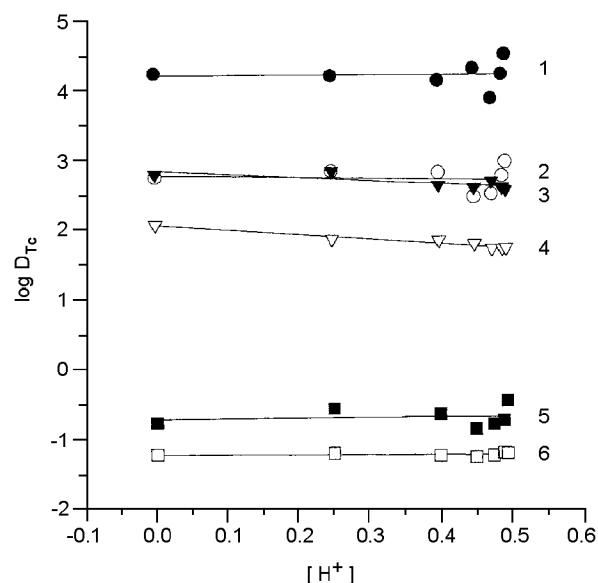


Fig. 16. Influence of hydrogen ion concentration in the aqueous phase on the distribution ratio of technetium at constant ionic strength 0.5: 1,2 –  $\text{NaCl} + \text{HCl}$ ; 3,4 –  $\text{NaNO}_3 + \text{HNO}_3$ ; 5,6 –  $\text{NaClO}_4 + \text{HClO}_4$ . Organic phase: 1,3,5 –  $0.05\text{M}$  and 2,4,6 –  $0.01\text{M}$   $\text{Ph}_4\text{PCL}$  in nitrobenzene

experiments. The mean deviation of the arithmetic average of  $E_{\text{Tc}}$  is less than 1% to the right and less than 0.2% to the left from the equivalence point. It results from the dependencies given that the technetium extraction at substoichiometric ratio  $n_{\text{Ph}_4\text{P}^+}^0 : n_{\text{TcO}_4^-}^0 < 1$

( $n^0$  means overall mole numbers of given component in the system) is virtually quantitative up to the equivalence point. At superequivalent ratio  $n_{\text{Ph}_4\text{P}^+}^0 : n_{\text{TcO}_4^-}^0 > 1$  all tetraphenylphosphonium reacts and the extracted technetium quotient is  $E_{\text{Tc}} = n_{\text{Ph}_4\text{P}^+}^0 : n_{\text{TcO}_4^-}^0$ . This fact was utilized for the preparation of  $\text{Ph}_4\text{PTcO}_4$  solutions with known concentration in chloroform and nitrobenzene without free extraction reagent (the organic phase after extraction was washed twice with deionized water). By contacting such organic phase with deionized water, an equilibrium extraction system was obtained after some time in which  $[\text{TcO}_4^-]_{\text{aq}} = [\text{Ph}_4\text{P}^+]_{\text{aq}}$ . In this case Relation (3) can be expressed in the form

$$K_{\text{TcO}_4^-} = \frac{[\text{Ph}_4\text{PTcO}_4]_{\text{org}}}{[\text{TcO}_4^-]_{\text{aq}} [\text{Ph}_4\text{P}^+]_{\text{aq}}} = \frac{[\text{Ph}_4\text{PTcO}_4]_{\text{org}}}{[\text{TcO}_4^-]_{\text{aq}}^2} = \frac{D_{\text{Tc}}}{c_{\text{Tc}}} \quad (14)$$

where  $c_{\text{Tc}}$  is the technetium concentration in the equilibrium water phase determined according to the comparison of water phase volume activity to a standard sample. Average  $K_{\text{TcO}_4^-}$  value calculated according to Relation (14) from 12 independent experiments for 3 different initial values  $[\text{Ph}_4\text{PTcO}_4]_{\text{org}}^0 \leq 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$  is  $(1.3 \pm 0.2) \cdot 10^6$  in the case of water-chloroform and  $(2.4 \pm 0.3) \cdot 10^7$  in the case of water-nitrobenzene system.  $K_{\text{TcO}_4^-}$  values determined in this way can be regarded as most reliable since the extraction system contains no anions competitive to  $\text{TcO}_4^-$ . Then an individual extraction constant  $K_{\text{A}^-}$  for any other anion  $\text{A}^-$  and given organic solvent can be calculated according to

$$K_{\text{A}^-} = \frac{K_{\text{TcO}_4^-}}{K_{\text{TcO}_4^- - \text{A}^-}} \quad (15)$$

if the value of the exchange extraction constant  $K_{\text{TcO}_4^- - \text{A}^-}$  for the  $\text{TcO}_4^-$  and  $\text{A}^-$  pair of anions is known determined from another type of experiments.

Solutions with known  $\text{Ph}_4\text{PTcO}_4$  concentration (doped with  $^{99\text{m}}\text{Tc}$ ) in chloroform or nitrobenzene ( $[\text{Ph}_4\text{PTcO}_4]_{\text{org}}^0 \leq 1 \cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) were used as organic phase for a study of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{TcO}_4^-$  anions competition at extraction redistribution with  $\text{Ph}_4\text{P}^+$  cation in systems with exactly defined values of the concentrations of individual components in both phases under equilibrium. Deionized water and  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{NaClO}_4$  solutions with various concentrations were used as aqueous phases. After the extraction equilibrium was reached technetium concentration in both organic and aqueous phases was determined by  $^{99\text{m}}\text{Tc}$  activity measurement. The results of these experiments are

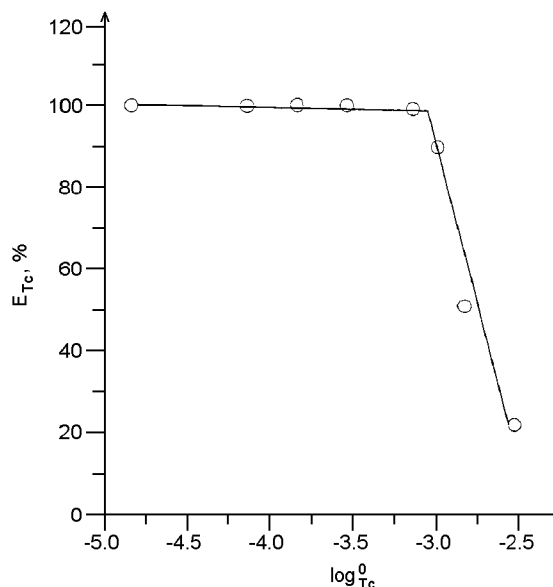


Fig. 17. The percentage of  $\text{TcO}_4^-$  extraction vs. initial concentration of  $\text{TcO}_4^-$  in the aqueous phase at constant initial concentration of  $\text{Ph}_4\text{P}^+$  in chloroform

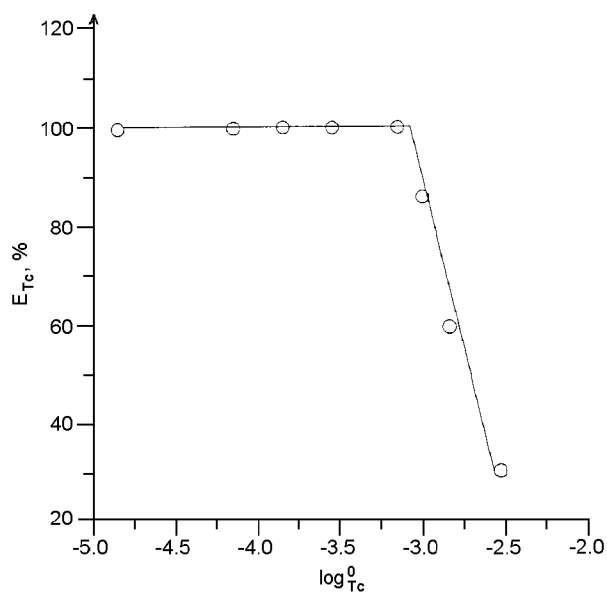


Fig. 18. The percentage of  $\text{TcO}_4^-$  extraction vs. initial concentration of  $\text{TcO}_4^-$  in the aqueous phase at constant initial concentration of  $\text{Ph}_4\text{P}^+$  in nitrobenzene

shown in Figs 19 and 20 in the form  $\log D_{\text{Tc}}$  vs.  $\log c_{\text{Aaq}}^0$  ( $\text{A} = \text{Cl}^-, \text{NO}_3^-, \text{ClO}_4^-$ ).  $\log D_{\text{Tc}}$  at  $c_{\text{Aaq}}^0 = 0$ , it is marked with a dashed line. These data were used for  $K_{\text{TcO}_4^- - \text{Cl}^-}$ ,  $K_{\text{TcO}_4^- - \text{NO}_3^-}$  and  $K_{\text{TcO}_4^- - \text{ClO}_4^-}$  calculations using Relation (8) in the form:

$$K_{\text{TcO}_4^- - \text{A}^-} = \frac{D_{\text{Tc}}}{D_{\text{A}}} = D_{\text{Tc}} \frac{G_{\text{Aaq}}^0}{G_{\text{Tcorg}}^0} - 1 \quad (16)$$

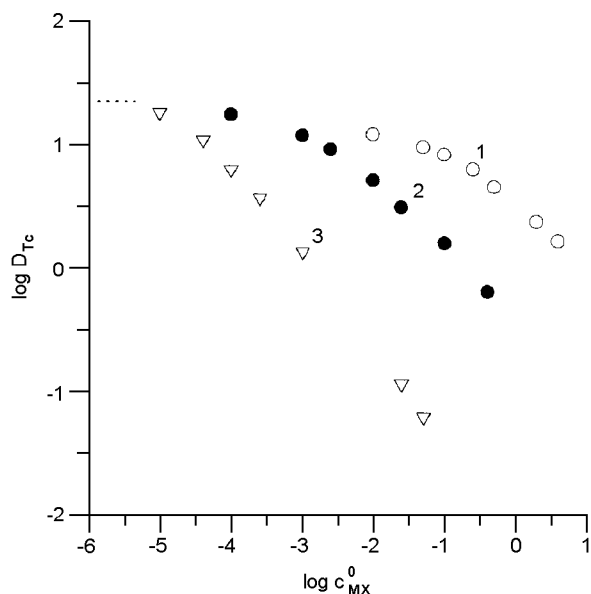


Fig. 19. Logarithmic plots of the distribution ratio of technetium vs. the initial concentration of sodium salt in aqueous phase: 1 – NaCl, 2 – NaNO<sub>3</sub>, 3 – NaClO<sub>4</sub>. Initial organic phase:  $9.91 \cdot 10^{-4}$  M Ph<sub>4</sub>PTcO<sub>4</sub> in chloroform

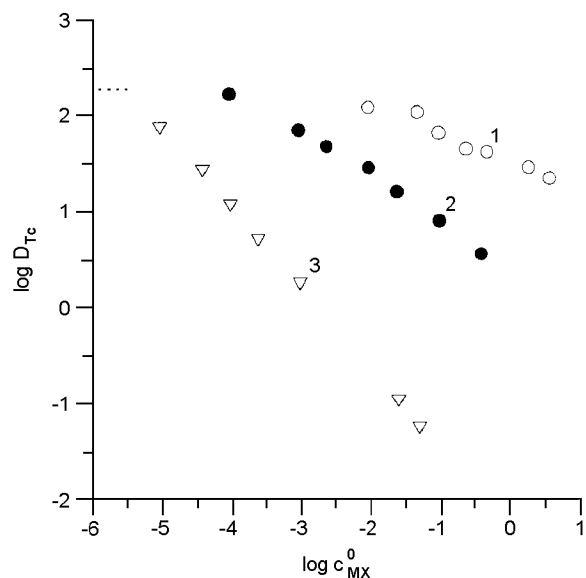


Fig. 20. Logarithmic plots of the distribution ratio of technetium vs. initial concentration of sodium salt in the aqueous phase: 1 – NaCl, 2 – NaNO<sub>3</sub>, 3 – NaClO<sub>4</sub>. Initial organic phase:  $9.98 \cdot 10^{-4}$  M Ph<sub>4</sub>PTcO<sub>4</sub> in nitrobenzene

where  $\Delta c_{\text{Tc org}}$  is the difference between technetium concentrations in the two organic phases, first of which was contacted with deionized water and second one with aqueous solutions of competitive anions with starting concentration  $c_{\text{Aaq}}^0$ . If the drop of technetium concentration in the organic phase after contact with deionized water is negligible as compared to the  $c_{\text{Tc org}}$  then  $K_{\text{TcO}_4^- \text{Cl}^-}$  value can be calculated according to the formula:

$$K_{\text{TcO}_4^- \text{A}^-} = \frac{2c_{\text{Aaq}}^0}{c_{\text{Tc org}}^0} - 1 \quad (17)$$

where  $c_{\text{Aaq}}^0$  is the initial A<sup>-</sup> anion concentration corresponding to the  $D_{\text{Tc}} = 1$  in this case.

\*

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