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# Ion chromatographic separation of selenite and selenate using a polyanionic eluent

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## Abstract

Ion chromatographic separation of selenite and selenate, together with some common inorganic anions ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), was studied using a polyanionic eluent containing perchlorate anion and phosphate buffer. The separated anions were detected by direct UV photometry at low wavelengths near 200 nm. The retention model was proposed for inorganic anions separated on the strongly basic anion-exchanger (HEMA Q-L) with the aid of the perchlorate–phosphate eluent. This model relates the analyte retention to mobile and stationary phase variables. Relationships between the capacity factors and the mobile phase composition (pH, concentrations of perchlorate and phosphate buffer) were measured and compared with the suggested retention model. The perchlorate–phosphate eluent facilitated the effective separation of selenite and selenate in a wide range of pH values.

*Keywords:* Mobile phase composition; Retention models; Selenite; Selenate; Inorganic anions

## 1. Introduction

Selenium is on the one hand an essential nutrient, on the other it may act as a seriously hazardous element; the difference between essential and toxic concentrations is rather narrow. The toxicity and biological activity of selenium, as well as its mobility in the environment, depend on its oxidation state [1–4]. A survey of the occurrence of selenium in the environment and a critical review of the methods of its determination, particularly in water, has been reported [5,6]. With respect to chromatographic techniques (HPLC), selenium has been determined after derivatization to 2,1,3-benzoselenadiazoles [7].

More frequently, however, it has been determined by ion chromatographic (IC) methods. IC allows one to distinguish between oxidation states of selenium and to determine Se(IV) and Se(VI) simultaneously in the form of their oxoanions. Suppressed IC with carbonate/bicarbonate eluents [8–12] as well as nonsuppressed IC [13–15] were used for the determination of Se(IV) and Se(VI) employing conductimetric or, rarely, direct UV photometric detection. Hyphenated techniques, which couple IC separations with sophisticated spectroscopic detection such as plasma atomic emission spectrometry [16–18], are very useful in trace determinations and speciations of selenium.

To minimize the shift of the redox equilibria between oxidation states during chromatographic analysis, the eluent used must be 'inert' (without oxidation/reduction properties) and has to be able to

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work at a suitable pH value (close to that of an original sample). In this work, an eluent containing perchlorate (driving anion) and phosphate buffer was used. In a previous paper, this eluent was applied successfully for the determination of Cr(VI) [19] and is commonly used for the determination of nitrates and nitrites in waters and water extracts [20,21] as well as iodides in various real samples [22].

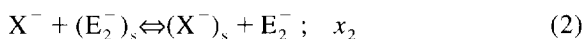
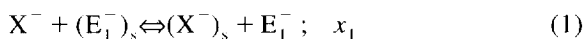
In order to optimise separation conditions, it is desirable to know the relationship between an analyte retention and a mobile phase composition. Simple relationships were derived for the anion separations on anion-exchange columns when only one eluting anion exists in mobile phase [23,24]. On the other hand, more complex retention models should be applied to those systems where more than one eluting species coexist in the mobile phase (polyanionic eluents containing either more kinds of eluting anions or an anion existing in various protonated forms). Many retention models have been developed for various mobile phases; they can be divided into three groups: the dominant equilibrium approach, the competing ion effective charge approach and the dual (multiple) eluent species approach [24]. The most successful and generally applicable models are based on the multiple eluent species approach suggested by Hoover [25] and Jenke and Pagenkopf [26,27]. Hirayama and Kuwamoto [28,29] modified Jenke's method by using the elution system coefficient whereas Yamamoto et al. [30] introduced the concept of an inter-eluent separation factor into Hoover's method. The retention model developed by Mongay et al. [31] relates the capacity factors of analytes to stationary and mobile phase variables using the concept of a global selectivity coefficient. This concept was tested for cases of separations of various inorganic and organic anions with phthalate eluent and an acceptable agreement between predicted and experimental dependences was achieved. This approach was also applied to the separation of metals in the form of their anionic complexes on an anion-exchange column [32] with the aid of oxalate eluent.

In this paper, the method of Mongay et al. was applied to the complex eluent containing the perchlorate anion together with phosphate anions. Relationships were derived between analyte capacity factors and the mobile phase composition. The

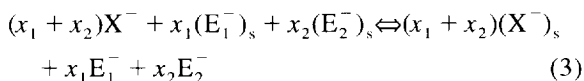
dependences of capacity factors on the mobile phase parameters (perchlorate and phosphate concentrations, the pH value) were measured and interpreted using the suggested retention model. The retention model was applied to the separation of Se(IV) and Se(VI) anions. For comparison, some common inorganic anions were also involved in the study.

## 2. Theory

It is commonly accepted that, if an ion-exchange mechanism governs retention on a column, a dependence between the logarithm of the capacity factor and the logarithm of eluent concentration is a straight line with a slope given by the ratio of charges of an analyte and an eluting ion. However, this dependence holds true only for simple monoanionic eluents, but not for eluents containing more than one eluting anion. This can be demonstrated in the following hypothetical example. Consider a monovalent anion,  $X^-$ , eluted from an anion-exchange column with a mixed eluent containing two eluting anions,  $E_1^-$  and  $E_2^-$  (dianionic eluent). None of the anions participate in side equilibria, such as protonation. The partial ion-exchange reactions are described by the following equations



where the subscript *s* refers to the stationary phase. In the overall process the equilibria described by Eq. (1) and Eq. (2) participate with the contributions  $x_1$  and  $x_2$ , respectively. The global equilibrium on the column can be expressed:



Taking into account that  $x_1 + x_2 = 1$ , the global selectivity coefficient is defined as the equilibrium constant of the global reaction described in Eq. (3):

$$K_{E_1E_2}^X = \frac{[X^-]_s [E_1^-]^{x_1} [E_2^-]^{x_2}}{[X^-] [E_1^-]_s^{x_1} [E_2^-]_s^{x_2}} \quad (4)$$

The capacity factor is given as the ratio of the

amount of an analyte in the stationary phase to that in the mobile phase:

$$k = \frac{w}{V_m} \frac{[X^-]_s}{[X^-]} \quad (5)$$

where  $w$  is the mass of stationary phase and  $V_m$  is the volume of the mobile phase in the column. It holds true for the column capacity:

$$Q = [E_1^-]_s + [E_2^-]_s + [X^-]_s \quad (6)$$

The last term on the right-hand side of Eq. (6) may be neglected under common chromatographic conditions, because the amount of analyte ions is small compared to the amount of eluting ions. In order to solve this set of equations we need one additional equation. In our example, the bond between the eluting anion  $E_2^-$  and the stationary phase is  $a$  times more intense than that between  $E_1^-$  and the stationary phase. As the concentration of each eluting species in the stationary phase is proportional to its concentration in the mobile phase, it can be expressed:

$$\frac{[E_2^-]_s}{[E_1^-]_s} = \frac{a[E_2^-]}{[E_1^-]} \quad (7)$$

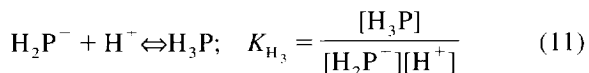
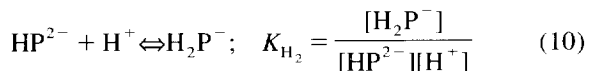
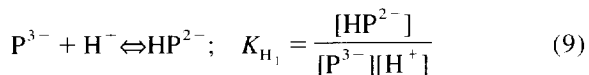
On combining Eq. (4), Eq. (6) and Eq. (7) and substituting in Eq. (5) we obtain:

$$k = \frac{wK_{E_1E_2}^X Q a^{x_2}}{V_m([E_1^-] + a[E_2^-])} \quad (8)$$

Even in this simplified example, the dependence between the capacity factor and the eluent concentration cannot be transformed to a linear log–log form. Only when one of the concentrations  $[E_1^-]$  or  $[E_2^-]$  is negligible do we obtain a common linear dependence  $\log k$  vs.  $\log$  (eluent concentration) with an expected slope ( $-1$  in our example).

### 2.1. Retention model for the perchlorate–phosphate eluent

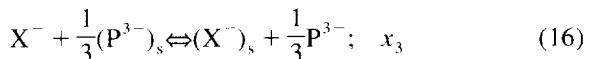
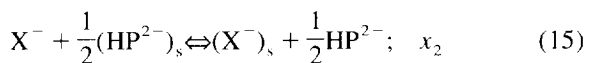
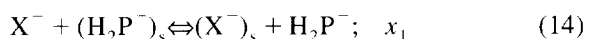
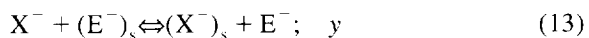
In this polyanionic eluent, perchlorate anion (henceforth denoted  $E^-$ ) coexists together with various protonated forms of the phosphate anion (denoted  $H_{3-i}P^{i-}$ ). The protonation is described by the following equations



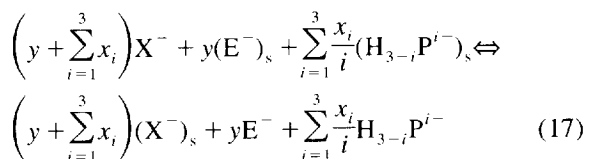
where  $K_{H_1} \dots K_{H_3}$  are the protonation constants. The total phosphate concentration,  $c_p$ , is given by the sum

$$c_p = \sum_{i=0}^3 [H_{3-i}P^{i-}] \quad (12)$$

The following ion-exchange reactions occur in the system (for monovalent sample anion,  $X^-$ )



The global equilibrium is given:



where  $y$  and  $x_i$  express the contributions of the respective partial reactions to the retention process. The condition  $y = \sum x_i = 1$  is always satisfied. Then the global selectivity coefficient is given:

$$K_{E,P}^X = \frac{[X^-]_s [E^-]_s^y \prod_{i=1}^3 [H_{3-i}P^{i-}]_s^{\frac{x_i}{i}}}{[X^-] [E^-]_s^y \prod_{i=1}^3 [H_{3-i}P^{i-}]_s^{\frac{x_i}{i}}} \quad (18)$$

Eq. (5) holds true for the capacity factor again, whereas the column capacity is equal to:

$$Q = [E^-]_s + \sum_{i=1}^3 i [H_{3-i}P^{i-}]_s \quad (19)$$

Using an analogous approach to Mongay et al. and

the above example, we adopted the following assumptions: (1) the bond between the perchlorate anion and the stationary phase is  $a$  times more intense than that between the monovalent phosphate anion ( $\text{H}_2\text{P}^-$ ) and the stationary phase; (2) the intensity of the bond between the eluting phosphate anion and the stationary phase is proportional to the charge of the anion. Then we can write:

$$\frac{[\text{E}^-]_s}{[\text{H}_2\text{P}^-]_s} = \frac{a[\text{E}^-]}{[\text{H}_2\text{P}^-]} \quad (20)$$

$$\frac{[\text{H}_{3-i}\text{P}^{i-}]_s}{[\text{H}_2\text{P}^-]_s} = \frac{i[\text{H}_{3-i}\text{P}^{i-}]}{[\text{H}_2\text{P}^-]} \quad (21)$$

On combining Eq. (18), Eq. (19), Eq. (20) and Eq. (21) and expressing the terms  $\text{H}_{3-i}\text{P}^{i-}$  with the aid of the protonation constants and the total phosphate concentration we obtain

$$k = \frac{C_1}{\left\{ a[\text{E}^-] + \frac{c_p(9 + 4K_{\text{H}_1}[\text{H}^+] + K_{\text{H}_1}K_{\text{H}_2}[\text{H}^+]^2)}{1 + K_{\text{H}_1}[\text{H}^+] + K_{\text{H}_1}K_{\text{H}_2}[\text{H}^+]^2 + K_{\text{H}_1}K_{\text{H}_2}K_{\text{H}_3}[\text{H}^+]^3} \right\}^{y + \sum \frac{x_i}{i}}} \quad (22)$$

where

$$C_1 = \frac{w}{V_m} K_{\text{E,P}}^x a^y 2^{\frac{x_2}{2}} 3^{\frac{x_3}{3}} Q^{y + \sum \frac{x_i}{i}} \quad (23)$$

For low pH values (high concentrations of  $[\text{H}^+]$ ) the second term in the brace in the denominator of Eq. (22) may be neglected and Eq. (22) is simplified to the logarithmic form

$$\log k = \log C_1 - \left( y + \sum \frac{x_i}{i} \right) \log a - \left( y + \sum \frac{x_i}{i} \right) \log [\text{E}^-] \quad (24)$$

which expresses a linear dependence between the logarithm of the capacity factor and the logarithm of the eluent concentration. As noted by Mongay et al. [31], because  $y + \sum \frac{x_i}{i} < 1$ , the slope of the linear dependence is smaller (in an absolute value) than that predicted for simple monoanionic eluents. This explains some discrepancies observed in previously published papers [28].

In a similar way, as shown above, the relations for the divalent sample anion,  $\text{X}^{2-}$ , can be derived:

$$k = \frac{C_2}{\left\{ a[\text{E}^-] + \frac{c_p(9 + 4K_{\text{H}_1}[\text{H}^+] + K_{\text{H}_1}K_{\text{H}_2}[\text{H}^+]^2)}{1 + K_{\text{H}_2}[\text{H}^+] + K_{\text{H}_1}K_{\text{H}_2}[\text{H}^+]^2 + K_{\text{H}_1}K_{\text{H}_2}K_{\text{H}_3}[\text{H}^+]^3} \right\}^{2\left(y + \sum \frac{x_i}{i}\right)}} \quad (25)$$

For low pH values:

$$\log k = \log C_2 - 2\left(y + \sum \frac{x_i}{i}\right) \log a - 2\left(y + \sum \frac{x_i}{i}\right) \log [\text{E}^-] \quad (26)$$

### 3. Experimental

The liquid chromatograph consisted of an HPP 5001 high-pressure pump, an LCI 30 injection valve with 20- $\mu\text{l}$  sampling loop, a TZ 4261 chart recorder (all from Laboratorní přístroje, Prague, Czech Republic) and an LCD 2040 UV-Vis spectrophotometric detector (ECOM, Prague, Czech Republic) operated typically at a wavelength of 200 nm, if not stated otherwise. Separations were carried out on a glass column 150 $\times$ 3 mm packed with Separon HEMA Q-L, 10  $\mu\text{m}$  sorbent (polymeric anion-exchange material based on a matrix of the hydroxyethyl methacrylate copolymer with a low specific ion-exchange capacity).

The following stock solutions were prepared: 1 mol/l  $\text{NaClO}_4$ , 0.4 mol/l  $\text{KH}_2\text{PO}_4$  and 0.1 mol/l  $\text{H}_3\text{PO}_4$ . Mobile phases were prepared by mixing the stock solutions in required ratios and adjusting to desired pH with diluted NaOH. Stock solutions of the tested anions were prepared from their sodium salts at concentrations of 100 mg/l ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), 200 mg/l Se(IV) and 1000 mg/l Se(VI) and diluted with mobile phase before measurements. All chemicals were of analytical-reagent grade (Lachema, Brno, Czech Republic) and solutions were prepared in redistilled water.

The mobile phases were deaerated in an ultrasonic bath before measurements. The mobile phase flow-rate was 0.3 ml/min. Measurements were carried out at laboratory temperature ( $22 \pm 2^\circ\text{C}$ ).

Retention times of analytes were determined as an average from at least triplicate injections and capacity factors were calculated by the usual method. The column dead volume (time) was assessed from

disturbances on the chromatograms brought about by the injection of sample or redistilled water (water dip).

#### 4. Results and discussion

The mobile phase used in this work contains perchlorate anions and phosphate buffer, hence the analyte retention and separation can potentially be affected by the change of the perchlorate concentration, the concentration of phosphate buffer and/or by the change of its pH. An effect of the phosphate concentration was investigated using the mobile phases containing varied concentrations of phosphate buffer whereas the perchlorate concentration (0.01 mol/l) as well as the pH value ( $6.5 \pm 0.05$ ) were kept constant. As can be seen from Fig. 1, the analyte retentions are affected very little by the phosphate buffer concentration. The monovalent phosphate anion, which has a low eluting capability compared with perchlorate, predominates in the mobile phase at the given pH. Significant reduction of analyte retention with the phosphate concentration was observed only for selenate. It is evident that changes in the phosphate buffer concentration will be ineffective for the optimization of separations.

In a similar way an effect of the perchlorate

concentration was studied; concentrations of perchlorate were varied within the range 0.001–0.02 mol/l, whereas the phosphate concentration (0.02 mol/l) and the pH value ( $6.5 \pm 0.05$ ) were kept constant. Because the contribution of the phosphate anions to the eluting process is small, we can use the simplified equations [Eq. (24) and Eq. (26)] to express the relationships between the analyte capacity factors and the eluent composition. The experimentally assessed dependences in Fig. 2 comply with the derived relationships. The slopes of the experimental dependences of  $\log(\text{capacity factor})$  vs.  $\log(\text{perchlorate concentration})$  are listed in Table 1. As predicted from the developed retention model, the slopes are less than 1 for monovalent analyte anions and less than 2 for divalent anions. Under the given conditions, selenate is present as a doubly charged anion  $\text{SeO}_4^{2-}$ , while selenite behaves as a monovalent anion (its effective charge is  $-1.02$  [33]).

Dependences of the analyte retention on the mobile phase pH were measured at constant concentrations of perchlorate (0.01 mol/l) as well as phosphate buffer (0.02 mol/l) as seen in Fig. 3a. In general, at low pH values phosphate is present as a monovalent anion which does not contribute to the retention process, and therefore the analyte retention is independent of the pH. At higher pH values, a divalent phosphate anion appears to have higher

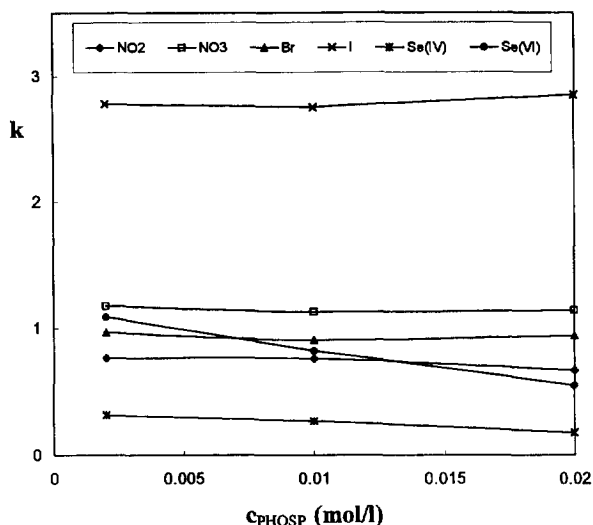


Fig. 1. Dependences of the capacity factors on the phosphate buffer concentration. Mobile phases contain 0.01 mol/l  $\text{NaClO}_4$  and phosphate buffer, pH adjusted at  $6.5 \pm 0.05$ .

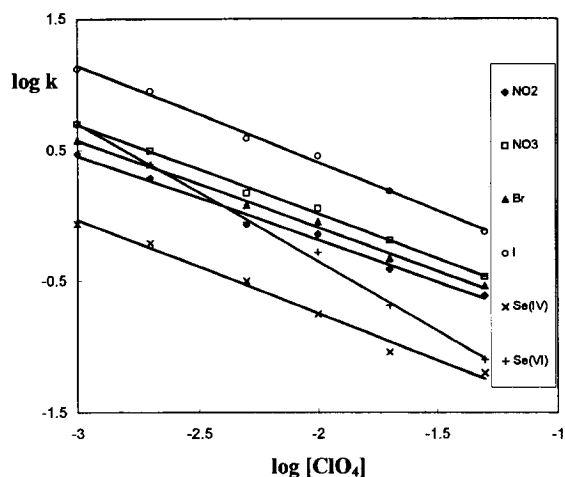


Fig. 2. Dependences of the logarithms of capacity factors on the logarithms of perchlorate concentration. Mobile phases contain 0.02 mol/l phosphate buffer and perchlorate, pH adjusted at  $6.5 \pm 0.05$ .

eluting ability and this causes a decrease in the retention of analytes. Using the derived equations [Eq. (22) and Eq. (25)] we can calculate the dependences of capacity factors on the mobile phase pH; the predicted dependences are shown in Fig. 3b. The protonation constants of phosphoric acid from the literature (34) ( $\log K_{H_1} = 11.54$ ,  $\log K_{H_2} = 7.199$ ,  $\log K_{H_3} = 2.148$ ) were used for calculations, other model parameters were determined from experimental data. The terms  $y + \sum \frac{x_i}{i}$  were determined from the slopes of the linear dependences in Fig. 2 (Table 1) and the constants  $C_1$  ( $C_2$ ) and  $a$  were calculated from the experimentally obtained values of capacity factors measured at a fixed eluent composition. As can be seen from Fig. 3a and Fig. 3b, an agreement

Table 1  
The slopes of the  $\log k$  vs.  $\log(\text{perchlorate concentration})$  dependences

Anion	Slope	Correlation coefficient
$I^-$	-0.737	0.995
$NO_3^-$	-0.681	0.996
$Br^-$	-0.665	0.995
$NO_2^-$	-0.642	0.988
Se(IV)	-0.712	0.989
Se(VI)	-1.053	0.997

between the predicted and measured dependences of  $k$  vs. pH is satisfactory. The divalent selenate anion exhibits a more pronounced dependence of its retention on the mobile phase pH than the monovalent anions. Selenite behaves similarly to monovalent anions over nearly all of the examined pH range. However, a slight increase in its retention at high pH values (observed also by other authors [28]) may be attributed to its dissociation to a divalent state. A more precise retention model for selenite could be elaborated by also taking into account the protonation of analyte anions (protonation constants of selenite:  $\log K_{H_1} = 8.5$ ,  $\log K_{H_2} = 2.75$  [34]), as demonstrated in [31] for various organic anions. However, the derived relationships would be rather complicated and their applications would require a great volume of precise experimental data to establish model parameters.

The relationships derived in this paper as well as the measured dependences allow one to optimize the mutual separation of selenite and selenate. Because these anions exhibit quite different dependences of their retention on the mobile phase composition (selenate behaves as a divalent anion, whereas selenite as a monovalent one), the separation can be readily influenced by a change in the mobile phase variables, most effectively by a change in the perchlorate concentration. The perchlorate-phosphate mobile phase is effective over a wide range of pH. The separation of selenite and selenate improves when the eluent concentration and pH are decreased. On the other hand, when the eluent concentrations are too low, the separated anions form broad and poorly detectable peaks. A satisfactory separation is achieved e.g. with a mobile phase containing 0.02 mol/l phosphate buffer, 0.01 mol/l perchlorate, pH 8.5 (Fig. 4).

Both selenite and selenate can be detected by direct UV photometry, wavelengths below 200 nm are recommended in the literature [35,36]. The limits of detection ( $S/N=3$ ) at 195 nm were 0.8 and 10.4  $\mu\text{g/ml}$  for Se(IV) and Se(VI), respectively, using the chromatographic conditions as in Fig. 4. Sensitivity of the photometric detection decreases dramatically at wavelengths above ca. 205 nm. The limits of detection achieved in our work are comparable with those obtained with the carbonate/bicarbonate eluent [35]; these values, however, are not

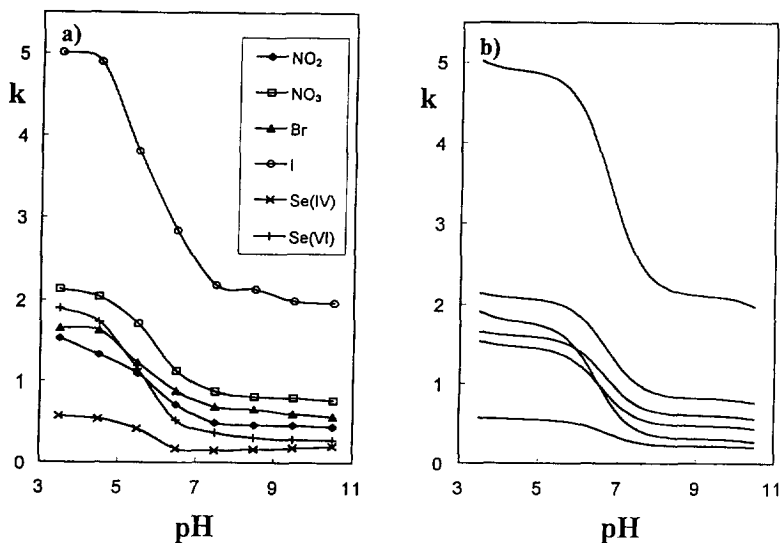


Fig. 3. Experimental (a) and calculated (b) dependences of the capacity factors on pH. Mobile phases contain 0.02 mol/l phosphate buffer and 0.01 mol/l  $\text{NaClO}_4$ . The order of the curves in (b) is the same as in (a).

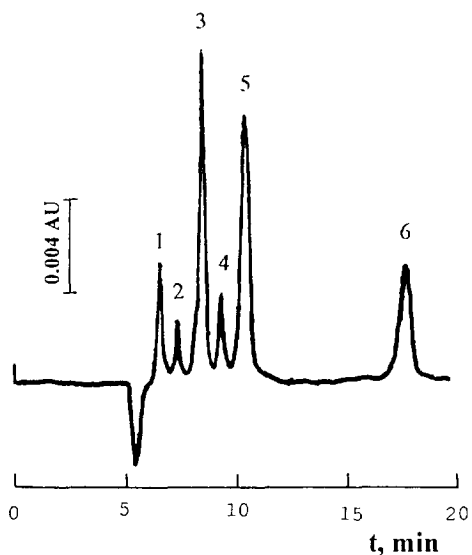


Fig. 4. Separation of the test mixture of anions. Column,  $150 \times 3$  mm, Separon HEMA Q-L; mobile phase, 0.02 mol/l phosphate buffer and 0.01 mol/l  $\text{NaClO}_4$ , pH 8.5. Direct UV detection at 200 nm. Peaks: 1 =  $\text{Se(IV)}$ , 10 mg/l; 2 =  $\text{Se(VI)}$ , 50 mg/l; 3 =  $\text{NO}_2^-$ , 5 mg/l; 4 =  $\text{Br}^-$ , 5 mg/l; 5 =  $\text{NO}_3^-$ , 5 mg/l; 6 =  $\text{I}^-$ , 10 mg/l.

satisfactory for analyses of real, e.g. environmental, samples. Therefore a conjunction of IC with an inductively coupled plasma–atomic emission spectrometry (ICP–AES) is currently being investigated.

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