Talanta 83 (2011) 1595–1600

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Capillary zone electrophoresis for U(VI) and short chain carboxylic acid sorption studies on silica and rutile

Vladimir Sladkov[a,b,*], Yujia Zhao[a,b], Florence Mercier-Bion[a,b]

[a] CNRS, Institut de Physique Nucléaire (IPN), UMR 8608, Orsay F-91406, France
[b] Univ Paris-Sud, Orsay F-91405, France

ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form
15 November 2010
Accepted 22 November 2010
Available online 1 December 2010

Keywords:
Capillary zone electrophoresis
Carboxylic acids
Uranium
Silica
Rutile
Sorption

ABSTRACT

Capillary zone electrophoresis was used to study the uranyl and short chain carboxylic acid sorption on silica and rutile. The separation and the simultaneous determination (in a single run) of a number of short chain carboxylic acids (oxalic, formic, acetic and propionic) and U(VI) with direct UV detection is developed for the analysis of solutions after the sorption experiments. The reverse polarity mode is used (the injection is performed at the negative end). The matrix effect of Si(IV) (possible silica dissolution product) and perchlorate (added for constant ionic strength in sorption experiments) on the separation of U(VI) and organic acids is investigated. The influence of methanol addition in carrier electrolyte on the separation selectivity of given analytes is also studied. Under the chosen conditions (carbonate buffer (ionic strength of 0.1 M), pH 9.8, 0.15 mM of tetradecyltrimethylammonium bromide, 25% (v/v) of methanol) the calibration curves are plotted. They are linear in two ranges of concentration from $\sim 1 \times 10^{-5}$ to $\sim 1 \times 10^{-3}$ M for oxalate, acetate, propionate, U(VI) and $\sim 1 \times 10^{-4}$ to $\sim 1 \times 10^{-3}$ for formate. The accuracy of the procedure is checked by the "added-found" method in simulation solutions. The relative standard deviations of the concentrations found are within the range of 1–10% and the recovery is in the range of 90–115%. This method is applied for the analysis of aqueous samples issued from sorption experiments on silica and rutile. The obtained results indicate that the given organic acids decrease uranium sorption both on silica and rutile. These experiments demonstrate that short chain carboxylic acids can influence the mobility and the chemistry of U(VI) in the environment.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The uranium migration in the environmental systems is an important concern [1,2]. The knowledge of the transport of radionuclides through the environment is crucial not only for fundamental geochemistry but also for assessing the risk posed by long-term storage of nuclear waste [2] or proliferation of uranium contamination after widespread use of depleted uranium in some world regions [1].

The sorption of uranium species (usually present as U(VI)) on minerals can modify their migration in the environment. The sorption of U(VI) in batch experiments was a subject of many investigations on different matrices: TiO_2 [3], Al_2O_3 [4], silica [2,4], goethite [5,6] and natural clays (smectites [7], metakaolin [8], sepiolite [9], montmorillonite [4]).

The interest for metal sorption in the presence of organic matter has grown in recent years. In a number of papers, special attention is paid to the influence of natural organic matter (NOM) on uranium sorption in soil and plant matrices [10] and onto hematite [11]. The effect of acetic and oxalic acids on U(VI) sorption was studied onto α-alumina [12] and the influence of citric, malonic and succinic acids on U(VI) sorption was investigated on suspended silica [13].

The short chain carboxylic acids present a special interest as they may be released in the environment through the decay of plant matter, animal residue and microbial tissues. They can also be used as simple models of more complicated natural organic matter.

In batch experiments of the sorption study of U(VI) in presence of organic acids, generally radioactivity measurement methods were used for the determination of analytes of interest. For U(VI) measurements a liquid scintillation method with ^{233}U [2,11,13,14] or ^{232}U [12] as tracers was used. For the organic acid determination, ^{14}C spiked solutions (acetic, oxalic acids) were used in [12], for the determination of humic acids, the total organic carbon analyzer was also used in [11]. One of the main disadvantages is that the methods used do not allow the simultaneous determination of U(VI) and organic acids. The preparation and purification of spiked isotopes is also required. Moreover, radiochemical measurements

* Corresponding author at: Institut de Physique Nucleaire, UMR CNRS 8608, 15 rue G.Clemenceau, 91406 Orsay, France. Tel.: +33 0169156406; fax: +33 0169156470.
E-mail address: sladkov@ipno.in2p3.fr (V. Sladkov).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.11.055

demand special requirements for the safety and the management of radioactive waste. Thus the use of this method needs several time and reagent consumption steps. This significantly increases the cost of analysis.

A reliable and simple method can be useful for the simultaneous determination of organic species, which are presented as anions, and of U(VI) species, which are present in cationic forms in supernatant after a solid separation.

The application of capillary zone electrophoresis (CZE) for this type of sample can be fruitful. The attractive feature of CZE for the sample analysis of this type is a possibility to determine the cations and anions simultaneously in a single run. Time and reagent consuming separated determination of U(VI) and organic acid anions can thus be avoided. One of the approaches used for this purpose consists in the transformation of cations (or anions) into negatively (or positively) charged complexes [15–19]. In this case they migrate in the same direction as anions (or cations). CZE is already applied for U(VI) separation from lanthanide [20], transition metal [21], rare-earth ions [22,23] and for the separation of organic acids [24,25]. Another attractive feature of CZE is that it enables the determination of ionic solutes in complex matrices of industrial, environmental, food and biological samples [19,24–33] with minimal (dilution, filtration) pre-treatment steps.

The aim of the present work is to study the possibility of the adaptation of CZE for the simultaneous determination of a number of short chain carboxylic acid anions (oxalate, formate, acetate, propionate) and U(VI) ions directly in the solution after sorption experiments. The main concern is the optimisation of the separation conditions and the study of the matrix effect on the separation. The method is validated on standard mixture solutions and applied to the determination of U(VI) and the short chain carboxylic acids in the solution after the sorption on oxides: silica and rutile. Silica is chosen as one of the most abundant natural compound. Titanium oxide is chosen as it is often used as a good model for oxides, due to its stability and low solubility in a wide pH range allowing the study of sorption of uranyl ions in the domain where they are highly soluble. Moreover it has well known structure [3]. The obtained data are used for studies of sorption behaviour of U(VI) in the presence of organic acids in aqueous solutions, and their mutual influence.

2. Experimental

2.1. Chemicals and solutions

All chemicals used were of analytical reagent grade. Formic, acetic, propionic, oxalic acids, sodium orthosilicate and methanol were provided by Sigma–Aldrich. Sodium perchlorate hydrate (99.99%) ($NaClO_4 \times xH_2O$, where $x = 0.9829$) were provided by Sigma–Aldrich. The stock of $UO_2(ClO_4)_2$ solution (0.1 M in 0.63 M $HClO_4$) was obtained by dissolving $UO_2(NO_3)_2 \times 6H_2O$ (>99% FLUKA puriss) in 12 M $HClO_4$ (MERCK Suprapur) and by evaporating the resulting solution to almost dryness on a sand bath. The residue was dissolved in concentrated $HClO_4$ and evaporated again. This last operation was repeated three times. Uranyl acetate was purchased from Fluka. The carbonate buffers were prepared from sodium hydrocarbonate (Fluka) and sodium hydroxide solution (Merck). Tetradecyltrimethylammonium bromide (TTAB) was purchased from Fluka. Silica (SiO_2) (particle size of 380 mesh) and rutile (TiO_2) (particle size of 325 mesh) were supplied by Merck and CERAC, respectively. All solutions were prepared with deionised water (Millipore direct Q, $R = 18.3\ M\Omega$).

2.2. Apparatus and software

Capillary electrophoresis measurements. P/ACE system MDQ capillary electrophoresis instrument (Beckman Coulter, France) was used. The system comprises a 0–30 kV high-voltage built in power supply, equipped with a diode array detector. A capillary (75 μm I.D., 375 O.D.), made from fused silica, was obtained from Beckman Instruments. It had a total length (L) of 31.2 cm and an effective separation length (l) of 21 cm. The capillary was housed in an interchangeable cartridge with circulating liquid coolant. The temperature was maintained at 25 °C. Data acquisition and processing were carried out with the Karat 32 software (Beckman Coulter, France).

pH measurements. A pH-meter GLP-21 (Crison Instruments, France) and a combination electrode were used for pH measurements after calibration against NIST standards (4.01 and 7.00, Crison Instruments). An aliquot of solution was used for each measurement.

EXCEL® and ORIGIN® software programs were used for the calculation and the graphical data treatment.

For the speciation diagram construction the MEDUSA software (KTH Royal Institute of Technology, Chemistry Department) was used. For the buffer concentration calculations the PHOEBUS software program (Analis, Namur, Belgium) was used.

2.3. Capillary electrophoresis procedure

The capillary was conditioned prior to use by successive washes with 1 M, 0.1 M sodium hydroxide, deionised water and the buffer solution under study. It was rinsed 3 min with the buffer between two runs and kept filled with deionised water overnight.

Reverse polarity mode was applied (the injection is performed at the negative end). The potential applied was 10 kV. The injection was done by a pressure of 0.5 psi. The injection time was 3 s. Carbonate buffer with TTAB (0.15 mM) addition to reverse the electroosmotic flow (EOF) was used. The ionic strength (I) of the buffer electrolyte was fixed at 0.1 M.

In this paper direct UV detection was used. U(VI) was detected at 230 nm and carboxylic acids at 190 nm.

Electrophoretic mobility determination. The electrophoretic mobility μ_{ep} ($cm^2\ s^{-1}\ V^{-1}$) was calculated by using the following expression:

$$\mu_{ep} = \frac{Ll(1/t - 1/t_{eof})}{V} \quad (1)$$

where L (cm) is the total capillary length, l (cm) is the length between the capillary inlet and the detection window, V is applied voltage in V, t (s) is the migration time of the studied species, t_{eof} (s) is the migration time of methanol (0.3%, v/v), used as a neutral marker for EOF determination. The migration time of the water peak was used for methanol-aqueous background electrolyte (BGE).

Electroosmotic flow measurements. The electrophoretic flow was calculated by using the following expression:

$$\mu_{eof} = \frac{Ll}{t_{eof}V}$$

In our conditions (carbonate buffer with $I = 0.1$ M, pH 9.8, 0.15 mM TTAB) the EOF mobility value was $(2.11 \pm 0.05) \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$ ($n = 5$, $P = 0.90$). The value of RSD for electroosmotic flow value over five consecutive injections did not exceed 2.5%.

2.4. Sorption procedure

The 0.1 g of silica or rutile powder was placed in polypropylene tubes with 10 ml of aqueous solution with the required pH. The tubes were mechanically shaken at the room temperature for 48 h for hydration of solids. After this operation an aliquot of solution

(2 ml) was replaced by the analyte solution with the required concentration and pH. The solution was equilibrated for 48 h to ensure equilibrium conditions were attained. U(VI) sorption was studied as a function of the equilibration time. It was found that for U(VI) sorption on silica the equilibrium was attained for 4 h. The desorption phenomena were not observed within an equilibration time between 4 and 50 h. For U(VI) sorption on rutile the equilibrium was attained for 10 h. The titanium oxide has high affinity for U(VI) [34], so the desorption phenomena are unlikely to be probable within the equilibration time, used in this study. After equilibration, the tubes were centrifuged at 3500 rpm during 30 min for the separation of the aqueous phase from solid and colloidal silica. In order to establish if centrifugation influences the U(VI) sorption, two samples were examined with silica. They were prepared in the same way, except for the final separation of aqueous phase from solid. For the first sample the separation was performed by a simple decantation during about 1.5 h and for the second, a centrifugation during 30 min was used. No influence of centrifugation on U(VI) sorption was found. The results obtained were the same.

The supernatant was used for the CZE measurements. The sample was diluted (2–10 times) with water, as needed.

The percentage sorption (% sorbed) was defined as:

$$\%\ \text{Sorbed} = \left[\frac{(S_i - S_f)}{S_i}\right] \times 100 \qquad (2)$$

where S_i and S_f are the analytical signals (peak surfaces) of analyte, presented in aqueous phases before and after the sorption.

3. Results and discussion

3.1. Optimisation of electrolyte carrier composition

For the simultaneous determination of the analytes of interest, the carbonate buffer as a background electrolyte is chosen, as U(VI) forms anionic complexes in this medium and the organic acids under study are completely dissociated and also presented as anions (pH of carbonate buffers is in the range of 9.0–11.0). Thus, the simultaneous determination of U(VI) and organic acids may be performed. The ionic strength of 0.1 M was chosen to have quite a large concentration of total carbonate (compared to the analyte concentrations under study) and to respect Ohm's low. At $I = 0.1$ M the total carbonate concentration is about 0.055 mol l^{-1}. We can be sure that at the maximum U(VI) concentration used (1×10^{-3} mol l^{-1}) all U(VI) is present as carbonate complex species. Moreover, due to the U(VI) interaction with carbonate anions, the formation of complexes of U(VI) with organic acid ligands can be avoided as carbonate ions are present in large excess (0.055 mol l^{-1} against 2×10^{-3} mol l^{-1} of maximum organic acid concentration used). Moreover, the constant stability value of predominant U(VI)–carbonate complex formed in this pH range (Fig. 1) is much larger ($\log \beta^{\circ}_3 = 21.60 \pm 0.05$ [35]) than the more stable complex of U(VI) with the present anions (oxalate: $\log \beta^{\circ}_1 = 7.13 \pm 0.16$ [36]). In this case the U(VI) determination can be more precise.

As U(VI) forms several complex species with carbonate at different pH (Fig. 1), the influence of pH on electrophoretic mobility of U(VI) is studied.

3.1.1. pH effect

The effect of pH values of carbonate buffer under study in the range 9.0–11.0 on U(VI) peak shape is presented in Fig. 2. A mobility scale for the abscissa is used in this figure. At pH 9.8, we observe the most suitable peak for the analytical measurements. From the speciation diagram presented in Fig. 1, we can state that at this pH the U(VI) is practically at 100% in the form of carbonate complex species $UO_2(CO_3)_3^{4-}$. The contribution of other species

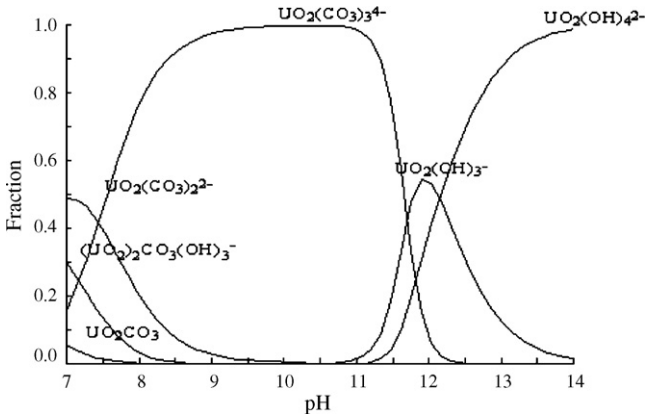

Fig. 1. Speciation diagram of 5×10^{-5} M U(VI) in carbonate solution. C_{tot} (carbonate) = 0.005 M.

($UO_2(CO_3)_2^{2-}$, $UO_2(OH)_3^{-}$, $UO_2(OH)_4^{2-}$) is negligible. The pH in the range from 9.8 to 10.4 can be suitable for U(VI) determination. Thus the carbonate buffer with pH 9.8 is used for further experiments.

3.1.2. Study of methanol effect on separation selectivity

In these conditions the electropherogram of the ions of interest is obtained (Fig. 3, bottom curve). The peaks of U(VI) and formate are not separated. The system peak disturbs also the analytical signal of U(VI). To improve the separation, the addition of organic solvent in BGE is tested.

Hydro-organic electrolytes can be applied for improving the separation selectivity [37–39]. In this case the selectivity can be changed due to the charge and/or solvation property changes with the increase of the organic solvent concentration in aqueous electrolyte.

In this paper the methanol effect on separation of U(VI), oxalate, formate, acetate and propionate is studied. The methanol addition modifies the pH scale and the acid pKs. For example, pK of the acetic acid is changed from 4.76 in aqueous solution to 5.19 in organic–water mixture with 20% (v/v) of methanol [40]. Since we work with BGE with pH 9.8 and the methanol concentration used does not exceed 25% (v/v), this modification of pK does not influence the degree of dissociation of the acids studied in our conditions. We can state that acids studied stay completely dissociated with methanol addition. Moreover the addition of methanol of 20–25% (v/v) only slightly modifies the pH scale to more ele-

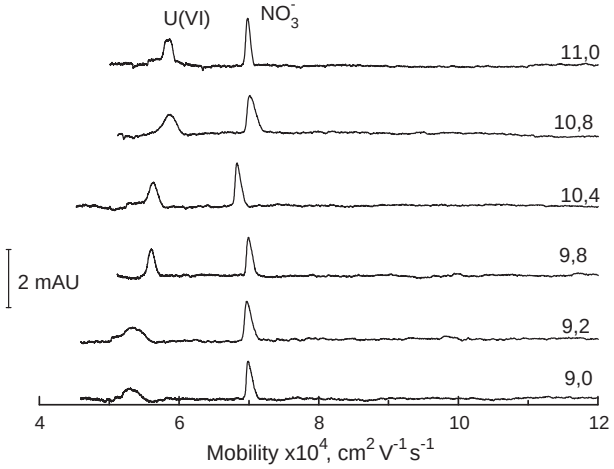

Fig. 2. Electropherograms of solutions, containing 1×10^{-4} M U(VI) and 1×10^{-3} M nitrate, with BGE at different pH values. BGE: carbonate buffer ($I = 0.1$ mol l^{-1}), 0.15 mM TTAB. Detection wave: 230 nm.

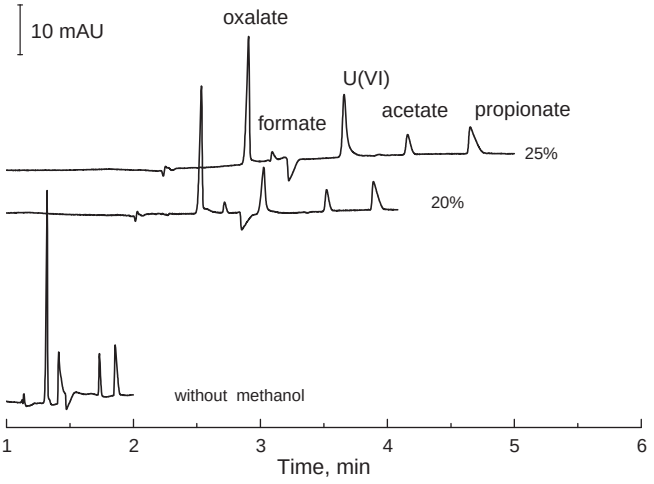

Fig. 3. Electropherograms of solutions, containing 5×10^{-4} M oxalate, 3×10^{-4} M U(VI), 1×10^{-3} M formate, 6×10^{-4} M acetate and 1×10^{-3} M propionate, with BGE, containing different methanol concentrations (v/v). BGE: carbonate buffer (I = 0.1 M), pH 9.8, 0.15 mM TTAB. Applied voltage: 10 kV. Direct UV detection: 190 nm.

vated values [40]. Thus, as the acids are completely dissociated, we can use the term of actual mobility, the mobility of a fully charged ion in a solution of finite ionic strength [41]. The results of actual mobility changes (at I = 0.1 M) for given ions with an increasing of methanol concentration up to 25% (v/v) in BGE, are presented in Fig. 4. As can be seen the mobilities are decreased with an increase in methanol concentration in the BGE. The difference between the actual mobilities of formate and U(VI) is increased, thus the separation selectivity between formate and U(VI) is improved with an increase in methanol concentration in the BGE.

Electrophoretic mobility is given by

$$\mu_{ep} = \frac{q}{6\pi\eta r} \quad (3)$$

where q is the charge of the ionised solute, η the BGE viscosity and r the solute radius. With an increase of the methanol concentration in aqueous BGE (up to 40–50% (v/v)), the viscosity is increased [42]. Thus the mobility is decreased (exp. (3)). It should also be mentioned, that with an increase of methanol concentration, the solvation of ion and solvated radius change too. These changes are not the same for the small organic acid anions and the large high charged anion, as $UO_2(CO_3)_3^{4-}$. Due to this fact, the separation between U(VI) and the formate becomes possible with the increasing methanol concentration in BGE. In Fig. 3, the electropherograms of studied mixture with aqueous BGE and several methanol–water BGEs are presented. From this figure, a good separation between formate and U(VI) is observed with 20% (v/v) methanol in BGE, but the system peak may disturb the analytical signal of U(VI). The use of 25% (v/v) methanol in BGE improves the separation of the given ions.

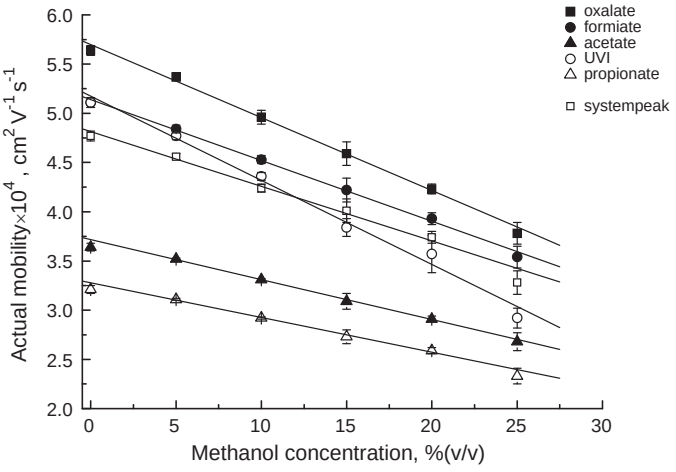

Fig. 4. Effect of the methanol concentration in BGE on the effective mobilities of the analytes studied.

3.2. Study of matrix effects

3.2.1. Perchlorate ions

In several cases, sodium perchlorate ions need to be added in order to maintain constant ionic strength for sorption studies. Thus the influence of the perchlorate ions on a mixture separation is studied. First, BGE without methanol addition is tested. In Fig. 5A the electropherograms of the studied solutions in presence of different perchlorate concentrations are shown. When the perchlorate concentration is 2.5×10^{-3} M, a negative peak appears near the oxalate peak. With an increase in the perchlorate concentration up to 1×10^{-2} M the oxalate peak is disturbed, and its determination becomes impossible (Fig. 5A).

The methanol addition in BGE can help to solve the problem. The effect of the different concentrations of methanol in BGE is studied. The results are presented in Fig. 5B. With 10% (v/v) methanol in BGE the peak of oxalate is less affected by the negative peak. With 25%

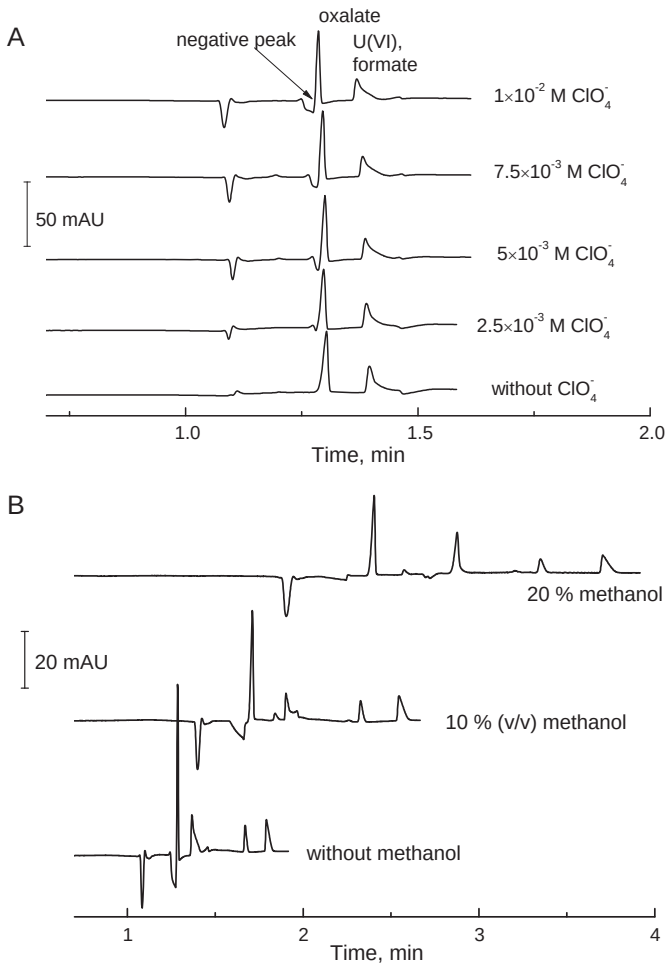

Fig. 5. Electropherograms of solutions, containing of 5×10^{-4} M oxalate, 3×10^{-4} M U(VI), 1×10^{-3} formate, 6×10^{-4} M acetate, 1×10^{-3} M propionate and different perchlorate concentrations (A); the same solutions with 1×10^{-2} M perchlorate at different concentrations of methanol in BGE (B).

Table 1
Parameters of the calibration plots $y = a + bx$ (y denotes the peak surface (AU × s) and x – the concentration (in mol l^{-1})), detection limits and reproducibility of migration times and peak areas. Detection at 190 nm, for U(VI) – at 230 nm.

Analyte	Linearity range, M	$(a \pm \Delta a) \times 10^2$	$b \pm \Delta b$	R^2	n	RSD of standards ($n = 3$), %		DL, M
						Migration time	Area	
U(VI)	1×10^{-5}–1×10^{-3}	0.26 ± 0.17	106 ± 9	0.9986	8	0.96	0.47	1×10^{-6}
Oxalate	1×10^{-5}–5×10^{-3}	0.005 ± 0.07	89 ± 2	0.9997	8	0.81	1.5	5×10^{-6}
Formate	2×10^{-4}–2×10^{-3}	−0.03 ± 0.04	3.1 ± 0.4	0.9958	5	0.85	2.4	1×10^{-4}
Acetate	3×10^{-5}–2×10^{-3}	0.02 ± 0.03	13.3 ± 0.4	0.9990	8	0.98	2.56	5×10^{-5}
Propionate	3×10^{-5}–2×10^{-3}	0.01 ± 0.03	15.1 ± 0.3	0.9995	8	0.99	3.58	6×10^{-5}

n – number of points for calibration curve; R^2 – correlation coefficient; DL – detection limit.

(v/v) of the methanol in BGE the oxalate peak is not disturbed at all (Fig. 5B).

3.2.2. Si(IV) ions

Silica can release Si(IV) ions in aqueous solution. The concentration level of Si(IV) released can be at several millimole by litre in aqueous solutions. The effect of Si(IV) on the separation of the studied ions is checked. A small analytical signal of Si(IV) appears only if Si(IV) is presented in the level of concentrations more than 1×10^{-3} M. This peak is situated near the system peak. Thus Si(IV) in this concentration level does not disturb the nearest analytical signals of formate and U(VI).

3.3. Simultaneous determination of U(VI) and short chain carboxylic acid anionic species

3.3.1. Calibration curves

For the calibration curve construction a carbonate buffer (pH 9.8, $I = 0.1$ M) as BGE with a flow modifier TTAB (0.15 mM) is used. As the methanol addition increases the separation selectivity between U(VI) and formate and helps to overcome the matrix effect of perchlorate, the methanol-aqueous BGE (25% (v/v) of methanol) is used. The calibration plot parameters, correlations coefficients, RSD and detection limits (signal to noise ratio of 3) for all analytes studied are summarized in Table 1. The calibration curves are linear in two ranges of concentration from ~1×10^{-5} to 1×10^{-3} M for oxalate, acetate, propionate, U(VI) and ~1×10^{-4} to 1×10^{-3} M for formate. Relative standard deviations (RSD) are less than 1% for migration times and less than 4% – for peak areas. For short-chain organic acids detection at 190 nm is used as these acids lack a chromophore group and they absorb only slightly in the shortwave UV range. For U(VI), the detection at 230 nm is chosen as it is more sensible than at 190 nm. The detection limit is 5×10^{-6} M at 190 nm for U(VI), it is 1×10^{-6} M at 230 nm.

3.3.2. Analysis of simulation solutions

The accuracy of the procedure based on the calibration curve determination is checked by determining the recovery from simulation solutions, containing 1×10^{-2} M perchlorate, 1×10^{-3} M of Si(IV) and ions of interest in the range of concentration from 1×10^{-4} to 2×10^{-3} M.

The results of recovery tests in simulation solutions are listed in Table 2. The results obtained are completely satisfactory for analysis. The recovery is between 90 and 115%. RSD is less than 10%. The deviations from the spiked amounts are in the interval of the instrumental method errors.

3.4. Application for sorption studies on silica and rutile

The developed method is applied for the analysis of real samples issued from the sorption experiments on silica and rutile. The results for the U(VI) sorption on silica and rutile in the absence and in the presence of the organic acids are presented in Fig. 6. Sorption is studied at two pH values: 3 and 5. At pH 3 the sorption of U(VI) on silica in the absence or in the presence of short chain organic acids is insignificant. On the contrary, the U(VI) sorption on rutile is about 25%. There is no influence of organic acids studied on the U(VI) sorption at pH 3. On the contrary at pH 5, short chain organic acids strongly influence sorption both on silica and rutile (Fig. 6B). They drastically decrease the sorption of U(VI) from 70–90% to 15–20%.

The influence of U(VI) on the sorption of formic, acetic and propionic acids at pH 5 on silica is also studied. The results of sorption of acids in the absence and in the presence of U(VI) are presented in Fig. 7. The highest sorption observed is for the formate (about 25%). The presence of 1×10^{-3} M of U(VI) decreases the acid sorption. A significant difference was observed, especially, in the case of the formic acid.

For the interpretation of results obtained it is important to take into account that these acids form the complexes with U(VI) in aqueous solutions [36,43,44]. Certainly, the changes in the speciation of U(VI) in the presence of organic acids in aqueous phase have an impact on sorption behaviour of U(VI). The U(VI) complex species with studied organic acids may have less affinity for solid surfaces investigated in this paper than aqueous U(VI) hydrolysis species.

Table 2
Results of U(VI) and organic acid simultaneous determination in the simulation solutions ($n = 3$; $P = 0.90$).

Species	Amount, M		RSD, %	Rec., %
	Added	Found		
U(VI)	1×10^{-4}	$(1.15 \pm 0.04) \times 10^{-4}$	2.1	115
	4×10^{-4}	$(3.8 \pm 0.2) \times 10^{-4}$	3.3	95
	5×10^{-4}	$(4.6 \pm 0.2) \times 10^{-4}$	2.1	91
	8×10^{-4}	$(7.2 \pm 0.1) \times 10^{-4}$	0.8	90
Oxalate	1×10^{-4}	$(1.15 \pm 0.12) \times 10^{-4}$	6	115
	5×10^{-4}	$(5.0 \pm 0.3) \times 10^{-4}$	4.1	99
	8×10^{-4}	$(7.7 \pm 0.2) \times 10^{-4}$	1.2	97
	1×10^{-3}	$(9.5 \pm 0.2) \times 10^{-4}$	1.3	95
Formate	2×10^{-4}	$(2.2 \pm 0.2) \times 10^{-4}$	4.1	110
	5×10^{-4}	$(4.4 \pm 0.7) \times 10^{-4}$	9.5	88
	8×10^{-4}	$(7.9 \pm 0.7) \times 10^{-4}$	5.3	99
	1×10^{-3}	$(9.5 \pm 0.9) \times 10^{-4}$	5.9	95
Acetate	2×10^{-4}	$(2.2 \pm 0.2) \times 10^{-4}$	5	111
	8×10^{-4}	$(8.0 \pm 0.5) \times 10^{-4}$	4.2	100
	1×10^{-3}	$(9.5 \pm 0.5) \times 10^{-4}$	3.2	95
	1.6×10^{-3}	$(1.45 \pm 0.01) \times 10^{-3}$	0.5	94
Propionate	2×10^{-4}	$(2.2 \pm 0.2) \times 10^{-4}$	6	109
	1×10^{-3}	$(1.06 \pm 0.03) \times 10^{-3}$	1.7	106
	1.4×10^{-3}	$(1.36 \pm 0.09) \times 10^{-3}$	4.2	97
	2×10^{-3}	$(1.90 \pm 0.03) \times 10^{-3}$	0.8	95

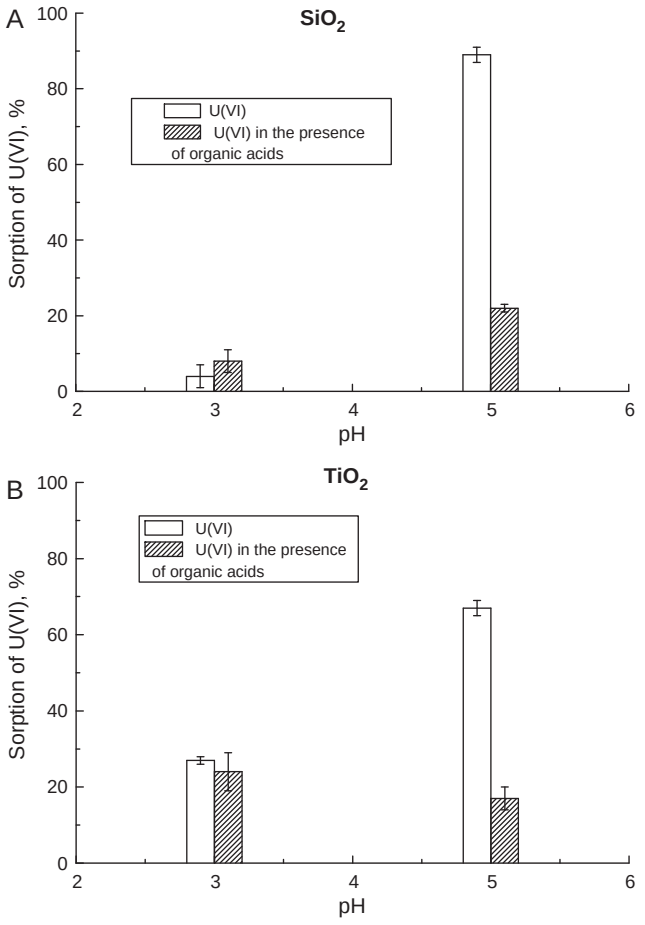

Fig. 6. Results for real sorption samples, obtained for U(VI), studied at pH 3 and pH 5 on silica (A) and rutile (B). Concentrations of analytes in solution before sorption: 1×10^{-3} M oxalate, 1×10^{-4} M U(VI), 1×10^{-3} M formate, 1×10^{-3} M acetate and 1×10^{-3} M propionate.

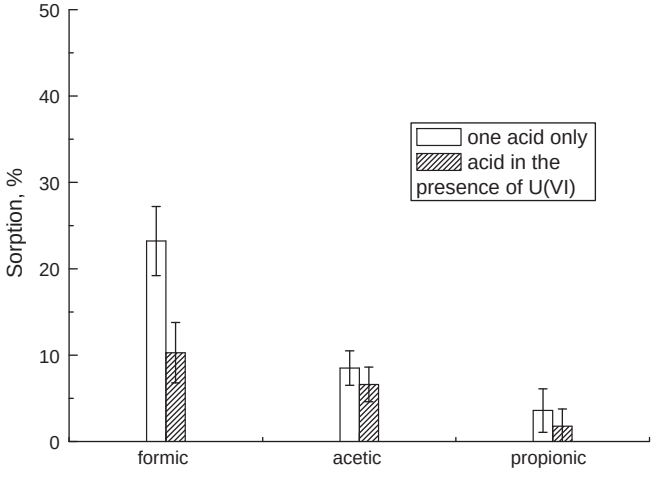

Fig. 7. Results for real sorption samples, obtained for individual organic acid, studied at pH 5 on silica. Concentrations before sorption: 1×10^{-3} M U(VI), 0.1 M formate, 0.1 M acetate and 0.1 M propionate.

4. Conclusions

CZE with direct UV-detection was adapted for the sorption study of uranyl and short chain organic acids on silica and rutile. One of the main advantages of this method is the possibility of a simultaneous determination, in a single run, of the organic acid anions and U(VI) due to the formation of an anionic complex with the carbonate anions of the buffer. The important advantage is also that CZE analysis demands a minimal sample preparation (only dilution). Exhaustive time and reagent consumption sample treatment can thus be avoided. The other advantages of the use of CZE are simplicity, minimal sample volume requirements, and reduced cost of analysis in comparison with radiochemical methods.

The developed simple and reliable method gives one the possibility of studying the sorption processes on solid matrix (silica and rutile). The results obtained are important for the understanding of the influence of sample organic matter on migration behaviour of U(VI) in the environment.

References

[1] I.W. Oliver, M.C. Graham, A.B. Mackenzie, R.M. Ellam, J.G. Farmer, Environ. Sci. Technol. 42 (2008) 9158.
[2] P.N. Pathak, G.R. Choppin, Radiochim. Acta 95 (2007) 507.
[3] G. Lefèvre, J. Kneppers, M. Fédoroff, J. Colloid Interface Sci. 327 (2008) 15.
[4] E.R. Sylwester, E.A. Hudson, P.G. Allen, Geochim. Cosmochim. Acta 64 (2000) 2431.
[5] U. Gabriel, J.P. Gaudet, L. Spadini, L. Charlet, Chem. Geol. 151 (1998) 107.
[6] Z. Guo, Y. Li, W. Wu, Appl. Radiat. Isot. 67 (2009) 996.
[7] C.J. Chisholm-Brause, J.M. Berg, K.M. Little, R.A. Matzner, D.E. Morris, J. Colloid Interface Sci. 277 (2004) 366.
[8] J.R. Memon, K.R. Hallam, M.I. Bhanger, A. El-Turki, G.C. Allen, Anal. Chim. Acta 631 (2009) 69.
[9] R. Donat, J. Chem. Thermodyn. 41 (2009) 829.
[10] A.J. Bednar, V.F. Medina, D.S. Ulmer-Scholle, B.A. Frey, B.L. Johnson, W.N. Brostoff, S.L. Larson, Chemosphere 70 (2007) 237.
[11] J.J. Lenhart, B.D. Honeyman, Geochim. Cosmochim. Acta 63 (1999) 2891.
[12] C. Alliot, P. Vitorge, L. Bion, F. Mercier, New J. Chem. 29 (2005) 1409.
[13] P.N. Pathak, G.R. Choppin, J. Radioanal. Nucl. Chem. 272 (2007) 37.
[14] P.N. Pathak, G.R. Choppin, Radiochim. Acta 95 (2007) 245.
[15] S.-J. Chen, M.-J. Chen, H.-T. Chang, J. Chromatogr. A 1017 (2003) 215.
[16] P. Kubáň, P. Kubáň, V. Kuban, J. Chromatogr. A 836 (1999) 75.
[17] T. Soga, G.A. Ross, J. Chromatogr. A 834 (1999) 65.
[18] O.V. Krokhin, H. Hoshino, O.A. Shpigun, T. Yotsuyanagi, J. Chromatogr. A 776 (1997) 329.
[19] V. Sladkov, B. Fourest, J. Chromatogr. A 1216 (2009) 2605.
[20] M. Macka, P. Nesterenko, P. Andersson, P.R. Haddad, J. Chromatogr. A 803 (1998) 279.
[21] L. Evans III, G.E. Collins, J. Chromatogr. A 911 (2001) 127.
[22] B. Liu, L. Liu, J. Cheng, Talanta 47 (1998) 291.
[23] B. Liu, L. Liu, J. Cheng, Anal. Chim. Acta 358 (1998) 157.
[24] V. Galli, A. García, L. Saavedra, C. Barbas, Electrophoresis 24 (2003) 1951.
[25] C.W. Klampfl, Electrophoresis 28 (2007) 3362.
[26] A.R. Timerbaev, Talanta 52 (2000) 573.
[27] V. Sladkov, B. Fourest, F. David, L. Venault, M. Lecomte, Anal. Bioanal. Chem. 376 (2003) 455.
[28] B. Fourest, V. Sladkov, Radiochim. Acta 93 (2005) 653.
[29] B. Baena, A. Cifuentes, C. Barbas, Electrophoresis 26 (2005) 2622.
[30] N. Bord, G. Cretier, J.L. Rocca, C. Bailly, J.P. Souchez, J. Chromatogr. A 1100 (2005) 223.
[31] K.G. Hopper, H. LeClair, B.R. McCord, Talanta 67 (2005) 304.
[32] I.C. Guimarães, C.C. Rezende, J.A.F. da Silva, D.P. de Jesus, Talanta 78 (2009) 1436.
[33] P. Janoš, Electrophoresis 24 (2003) 1982.
[34] N. Jaffrezic-Renault, H. Poirier-Andrade, D.H. Trang, J. Chromatogr. A 201 (1980) 187.
[35] I. Grenthe, J. Fuger, R. Konings, R. Lemire, A. Muller, C. Nguen-Trung, H. Wanner, Chemical Thermodynamics of Uranium, North-Holland Elsevier Science Publishers B.V., Amsterdam, 1992.
[36] W. Hummel, G. Anderegg, L. Rao, I. Puigdomenech, O. Tochiyama, Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands, Elsevier, Amsterdam, 2005.
[37] C. Huie, Electrophoresis 24 (2003) 1508.
[38] A. Varenne, S. Descroix, Anal. Chim. Acta 628 (2008) 9.
[39] E. Kenndler, Electrophoresis 30 (2009) S101.
[40] J.L. Beckers, M.T. Ackermans, P. Boček, Electrophoresis 24 (2003) 1544.
[41] A. Jouyban, E. Kenndler, Electrophoresis 27 (2006) 992.
[42] J. Thompson, T. Kaiser, J. Jorgenson, J. Chromatogr. A 1134 (2006) 201.
[43] C. Miyake, H.W. Nürnberg, J. Inorg. Nucl. Chem. 29 (1967) 2411.
[44] A. Kirishima, Y. Onishi, N. Sato, O. Tochiyama, J. Chem. Thermodyn. 39 (2007) 1432.