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Short communication

Capillary electrophoretic determination of inorganic selenium species

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Abstract

The performance of pyromellitic electrolyte for capillary zone electrophoresis of inorganic selenium species in the presence of selected common anions with indirect UV detection was investigated. The separation was achieved with pyromellitic electrolyte at pH 8.8 and hexamethonium hydroxide as the electroosmotic flow modifier. Obtained detection limits of 0.17 μg ml^{-1} for Se(VI) and 0.29 μg ml^{-1} for Se(IV) were improved by a factor of 5–7 in comparison with chromate electrolyte, which has been mainly employed for selenium analysis. Good resolution for nitrate–Se(VI) peaks were obtained.

Keywords: Water analysis; Selenium anions

1. Introduction

In recent years, capillary electrophoresis (CE) has increasingly been used for chemical speciation purposes [1–3]. At the present stage of development, capillary electrophoresis represents a valuable alternative or complementary technique to HPLC due to short analysis time, low sample consumption, high separation efficiency, and relatively low operating cost. As there are no interactions between the analytes and a stationary phase, the equilibrium between different species of a given sample is undisturbed.

In selenium speciation analysis, the coupling of CE with ICP–MS detection is good choice due to its good sensitivity and selectivity [4–6]. However, the design of a suitable interface is necessary because of the very small quantities of injected sample and low flow-rate through the capillary. Commercial CE systems offer only UV-absorbance detection because of its on-line compatibility with fused-silica capillaries. The application of indirect UV detection requires the presence of a chromophoric compound in the separation buffer providing a background signal. The absorbing species in the electrolyte also act as a carrier, therefore, selection of a suitable absorbing ion must include not only consideration of high sensitivity but also of separation efficiency. Chromate electrolyte has been mainly employed for selenium speciation analysis due to its high electrophoretic mobility [7–10]. Other methods include the derivatisation of the analytes before the electrophoretic procedures. Nitrilotriacetic acid, added to a sample mixture as a derivatisation agent to form UV-adsorbing chelates, was used for the simulta-

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neous determination of lead, mercury and selenium by CE [11].

This paper reports the study of the performance of pyromellitic buffer for capillary electrophoresis of inorganic selenium anions in the presence of chlorides, nitrates and sulfates with indirect UV detection. The parameters of the electrolyte buffer system, including the pH value and organic modifier, were investigated to give reasonable selectivity and sensitivity. The aim was to improve the resolution, especially between nitrate and Se(VI) peaks, which is unsatisfactory with chromate electrolyte [8–10].

2. Experiments

Experiments were performed with a Beckman P/ACE MDQ capillary electrophoresis instrument. Separations were carried out using fused-silica capillaries of 60 cm (50 cm effective length)×75 μm I.D. from Supelco (Bellefonte, PA, USA). Hydrodynamic injection mode was applied for 10 s. Indirect detection was performed at 254 nm.

The capillary was treated with 1 mol l^{-1} NaOH, 0.1 mol l^{-1} NaOH and then with Milli-Q water (each for 5 min), followed by the carrier electrolyte for 15 min. Before each electrophoretic run, the capillary was conditioning with the running electrolyte for 2 min. At the end of the experiments, the capillary was rinsed for 15 min with deionised water.

Carrier electrolyte was prepared using 1,2,4,5,-benzenetetracarboxylic acid (pyromellitic acid, PMA) from Sigma (St. Louis, MO, USA). As an electroosmotic flow modifier, hexamethonium hydroxide (HMOH) was used. It was prepared by passing a solution of corresponding bromide salt (Sigma) through a column filled with the anion-exchange resin Amberlite IRA-410. The pH was adjusted with sodium hydroxide and triethanolamine (Sigma). Dimethylsulfoxide (5% DMSO) was used as a marker for the electroosmotic flow.

Stock solutions (1000 mg l^{-1}) of Se(IV) and Se(VI) were prepared from selenous acid (Riedel–de Häen, Hanover, Germany) and ammonium selenate (Merck, Darmstadt, Germany). Chloride, nitrate and sulfate stock solutions were obtained from their sodium salts (POCh, Poland). Working solutions were prepared daily by appropriate dilution.

3. Results and discussion

Pyromellitic acid (PMA) as the carrier anion was chosen due to its higher molar absorptivity (7062 l mol^{-1} cm^{-1}) than chromate electrolyte (3180 l mol^{-1} cm^{-1}), so an increase in sensitivity could be achieved with indirect UV detection. Hexamethonium hydroxide (HMOH) was used in order to decrease or reverse the direction of the electroosmotic flow. The hydroxy form of the modifier allows to work at high pH without increasing the ionic strength, which would result in a high background current. The combination of both negative applied potential and HMOH added to the electrolyte

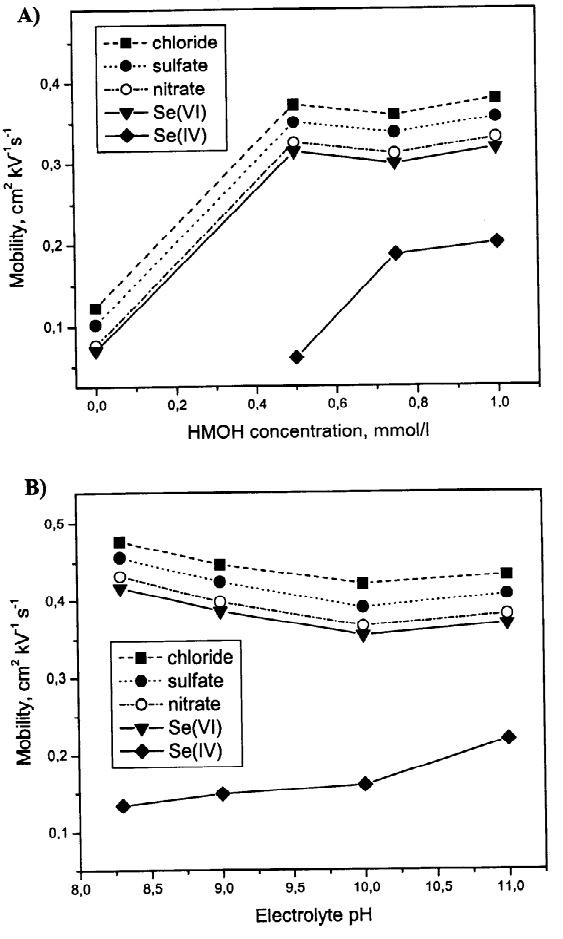

Fig. 1. The apparent mobility of investigated anions as a function of (A) HMOH concentration at pH 10 and (B) electrolyte pH with 0.75 mmol l^{-1} HMOH.

solution have appeared to be convenient to obtain sufficient separation for several anions [12–14].

The effect of HMOH concentration as well as electrolyte pH on mobilities of investigated anions was evaluated at constant potential (−30 kV) by injecting 10 μg ml^{-1} of Se(IV) and Se(VI) in the presence of nitrate, chloride and sulfate (10 mg l^{-1} each). Generally, the apparent mobility increased with increasing concentration of HMOH to reach a plateau at 0.5 mmol l^{-1} (Fig. 1A). Only for Se(IV) a further increase in modifier concentration resulted in evident shortening of its migration time and thus, an increase of the mobility of this selenium species was observed. A neutral species (DMSO) exhibits a constant migration time over hexamethonium concentration range of 0.75–1.0 mmol l^{-1}, which indicates the small contribution of the EOF to the migration time of charged compounds. Our results suggest that the direction of the EOF was not changed using HMOH in the interval of concentrations studied, although it was significantly reduced. This may be due to low adsorption onto the capillary wall. The addition of another modifier—TTAOH (tetradecyltrimethylammonium hydroxide)—to the background electrolyte (at pH 10.2) led to minimising the time of analysis, however, its solution is unstable which is probably associated with the tendency to form insoluble pairs with some electrolyte components [15].

The influence of pH was investigated at constant HMOH concentration of 0.75 mmol l^{-1} (Fig. 1B). The apparent mobility decreases slightly for investigated anions when pH is raised from 8.3 to 11.0. Se(IV) is an exception; its mobility appears to be strongly pH dependent. Selenite exists as doubly charged anion over a wide range of pH whereas selenite is essentially deprotonated just at pH ≥10 and an increase in pH results in an increased concentration of its divalent form. These results are in agreement with the model based on acid–base equilibrium developed by McGuffin and Tavares [16] for the prediction of effective electrophoretic mobility. However, a high electrolyte pH leads to increased background noise and affects the peak shape for Se(IV) as well as the reproducibility. The migration time relative standard deviations ($n=5$) at pH 9.0 were 0.9 and 1.7% for Se(VI) and Se(IV), respectively, and 1.9 and 9.8% at pH 11.0. The PMA–HMOH electrolyte system has been buffered with triethanoloamine. This amine at pH ≥8 is available in the free base form and thus not add a counter anion to the electrolyte [13]. Increasing the applied negative potential can significantly shorten the analysis time without the loss in resolution (Fig. 2). Based on the above results, final experimental conditions were selected: 2.25 mmol l^{-1} PMA, 3 mmol l^{-1} TEA, 1 mmol l^{-1} HMOH, 6.5 mmol l^{-1} NaOH, pH 9, applied voltage −30 kV. Under this conditions five investigated anions can be separated in a single run in less than 9 min.

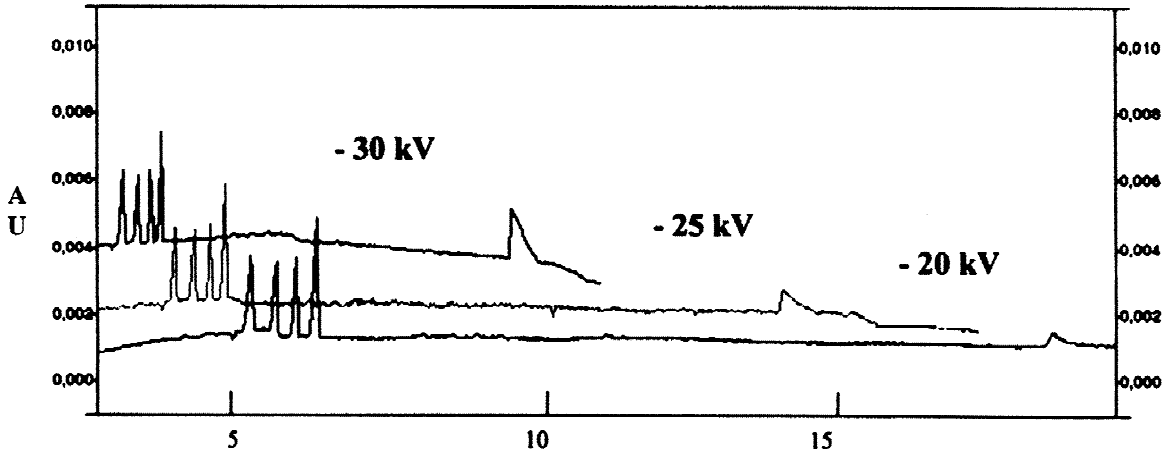

Fig. 2. Electropherograms of investigated anions at different voltages. Electrolyte: 2.25 mmol l^{-1} PMA, 3 mmol l^{-1} TEA, 1 mmol l^{-1}HMOH, pH 9.

The obtained results with PMA for separation of inorganic selenium species in the presence of selected anions electrolyte were compared with the performance of chromate buffer [7–10]. The separation was carried out at a voltage of −30 kV by injection of 5 μg ml^{-1} Se(IV) and Se(VI) together with nitrate, chloride and sulfate ions (10 mg l^{-1} each). The chromate electrolyte yielded the same migration order of investigated anions as that obtained for PMA and all analytes showed shorter migration times. However, at low concentration of CTAB modifier the nitrate peak eluted together with Se(VI). The increase in modifier concentration generates selectivity effect for nitrate–selenate peaks. The best conditions (R_s=0.89) was achieved for 3 mmol l^{-1} CTAB. At this concentration, the solution has only limited solubility. The problems with instability of this electrolyte were reported earlier; the migration times of inorganic anions were found steadily reduced upon ageing of the chromate buffer [17,18]. The analytical conditions proposed by Cassiot et al. [10] prevent determination of Se(VI) in the presence of nitrate because R_s was always well below the quantification level. Other workers obtained sufficient resolution but only with very low concentration of nitrate [8]. In our study the application of pyromellitic electrolyte with HMOH as an electroosmotic modifier (even at its three times lower concentration) gave the resolution for nitrate–Se(VI) peaks R_s=1.32. The comparison of the analytical parameters for determination of Se(IV) and Se(VI) using both electrolytes are presented in Table 1. The reproducibility of the migration timer and corrected area (peak area divided by the migration time) was determined for a concentration level of 10 μg ml^{-1} (n=6). The detection limits (3δ) was much better for pyromellitic electrolyte resulting from the fact that its molar absorptivity is higher than that for chromate. The interferences generated by the presence of carbonate probably cause lower sensitivity for Se(IV). The detection limits of selenium species with

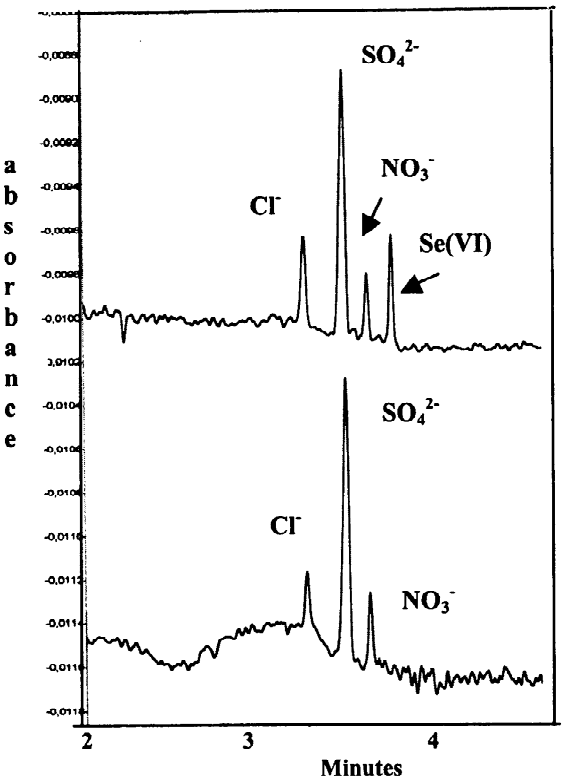

Fig. 3. Electropherogram of commercial mineral water ''Kinga'' spiked with 3 μg ml^{-1} of Se(VI). Conditions as in Table 1 for PMA electrolyte.

Table 1
Comparison of the analytical parameters for the analysis of inorganic selenium species using different electrolytes

Parameter	PMA electrolyte[a]		Chromate electrolyte[b]	
	Se(VI)	Se(IV)	Se(VI)	Se(IV)
Migration time (min)	4.17	9.65	1.91	2.25
RSD (migration time, %)	0.9	1.7	0.9	1.2
Corrected peak area (%)	2.8	4.6	3.2	4.8
Detection limit				
μg l^{-1}	170	290	980	2050
mol l^{-1}	2.2×10^{-6}	3.7×10^{-6}	1.2×10^{-5}	2.6×10^{-5}

[a] 2.25 mmol l^{-1} PMA, 1 mmol l^{-1} HMOH, 1.6 mmol l^{-1} TEA, pH 8.8.
[b] 5 mmol l^{-1} Na_2CrO_4, 3 mmol l^{-1} CTAB, 20 mmol l^{-1} DEA, pH 9.3.

PMA electrolyte and indirect UV detection were improved compared with those obtained previously [8,9]

A preliminary application of the developed method to analysis of natural water samples (tap and mineral waters) was made. The electropherograms of commercial mineral water (Kinga) spiked with both selenium species (3 μg ml^{-1} each) using PMA electrolyte is shown in Fig. 3. It was possible to detect only Se(VI). The results of analysis by CE were in good agreement with the concentration introduced into the sample; the recovery was $92 \pm 6\%$ ($n = 4$). The resolution between Se(IV) and carbonate/hydrocarbonate peaks was not sufficient to allow the quantification of selenite concentration. This was also observed in the work of Gilon and Potin-Gautier [8] as well as by Cassiot et al. [10]. It is noteworthy to mention that Se(VI) was the only Se species in several lake waters [19] and thermal water sample [8].

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