Speciation of metals in different oxidation states by capillary electrophoresis using pre-capillary complexation with complexones

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Ethylenediaminetetraacetic (EDTA), cyclohexane-1,2-diaminetetraacetic (CDTA) and diethylenetriaminepentaacetic (DTPA) acids were investigated and compared as complexing agents for the speciation of chromium(VI/III), vanadium(V/IV) and iron(III/II) ions by capillary electrophoresis. The chromium(III) was selectively chelated with DTPA in order to impart a negative charge and similar mobility to both the chromium(III) and chromium(VI) species. The best complexing agent for the determination of vanadium species was found to be EDTA. The addition of an excess of EDTA, CDTA or DTPA to the solution containing both iron species causes the rapid and complete oxidation of iron(II) into iron(III) by ambient oxygen. Therefore for the simultaneous determination of both iron species two different complexing agents were used: *o*-phenanthroline for Fe^{2+} and CDTA for Fe^{3+}. Detection was carried out by direct UV absorption depending on the properties of the formed complexes. For all species studied the calibration graphs were linear over at least two orders of magnitude of concentration. The detection limits were in the range from 1×10^{-6} mol l^{-1} for Fe^{II} to 8×10^{-6} mol l^{-1} for Cr^{VI}. Application of the method to the speciation of metal ions in real samples is also demonstrated.

Keywords: *Capillary electrophoresis; speciation; chromium(VI/III); vanadium(V/IV); iron(III/II); complex formation; aminopolycarboxylic acids*

Metal speciation is important in a variety of environmental, biological, geological and medical applications. The chemical and physical properties of a metal species depend very much on its oxidation state, hence an accurate determination of each species is important to evaluate the potential risk of some metals.

Various methods for the speciation of metals with different oxidation states have been introduced in recent years. High-performance liquid chromatography (HPLC) in its various forms is undoubtedly the premier technique for metal speciation.[1,2] HPLC is especially potent for speciation studies when coupled to element-specific detection systems based on inductively coupled plasma atomic absorption, atomic emission or mass spectrometry.[3–7]. However, for routine analysis a simple conventional detection based on UV/VIS detection is more favourable. In this technique, the procedure often involves the converting of one or both metal species into stable derivatives prior to analysis using selective complexation.[8–13] In this context, three significant advantages for complexation can be identified: (i) more sensitive direct spectrophotometric detection can be performed; (ii) using complexation, positively charged species can be converted into the complexes having the same charge as negatively charged ions; this offers the possibility to determine all species in a single run; (iii) the preservation of the original oxidation states is often possible by choosing suitable complexing agents.

An alternative method proposed in this paper is capillary electrophoresis (CE). Despite relatively worse migration time and peak area reproducibility and lower detection sensitivity with respect to HPLC, capillary electrophoresis offers certain advantages such as the ability to separate the complex mixtures of ions quickly and efficiently, low operating costs, ease of operation and automation, *etc*. The application of CE to the separation of metal chelates has been growing rapidly since 1990.[14–35] A number of complexing reagents have already been examined for the pre-capillary or on-capillary conversion of metal ions into stable negatively charged chelates. Various polyaminocarboxylic acids such as ethylenediaminetetraacetic acid (EDTA),[19–28] cyclohexane-1,2-diaminetetraacetic acid (CDTA)[29–33] and others[21,34,35] are most frequently used for this purpose. However, the application of these complexing reagents for the simultaneous determination of metal ions in different oxidation states has been reported only in a few studies.[25,31,33]

This paper focuses on speciation of metal ions in different oxidation states [Cr^{VI}/Cr^{III}; V^{V}/V^{IV}; Fe^{III}/Fe^{II}] by CE with particular emphasis on the role of complexation. Complexing reagents examined for this purpose were common polyaminocarboxylic acids with well known complexing properties.

Experimental

Instrumentation

Separations were performed on a P/ACE 2100 apparatus (Beckman Instruments Inc., Fullerton, CA, USA) equipped with a UV detector with wavelength filters (200, 214, 230 and 254 nm). Fused silica capillaries (Polymicro Technology, Phoenix, AZ, USA) of 75 μm id were used. The solutes were injected in the hydrodynamic mode by overpressure (3.43×10^3 Pa). System Gold software was used for data acquisition. All experiments were conducted at 25 °C using a liquid thermostated capillary cartridge.

Reagents

All chemicals used were of analytical-reagent grade. Deionized water was obtained by passing distilled water through a Waters Milli-Q water-purification system (Millipore, Eschborn, Germany). Stock solutions (0.01 mol l^{-1}) of metal species were prepared from $CrCl_3 \cdot 6H_2O$, $K_2Cr_2O_7$, $VOSO_4$, NH_4VO_3, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (Merck, Darmstadt, Germany). Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), cyclohexane-1,2-diaminetetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA) and 1,10-phenanthroline hydrochloride (phen) were obtained from Fluka (Neu-Ulm, Germany). Stock solutions (5 mmol l^{-1}) of EDTA, CDTA, DTPA and phen were prepared by dissolving the reagents in water.

Tetradecyltrimethylammonium hydroxide (TTAOH) was prepared from tetradecyltrimethylammonium bromide (Merck, Darmstadt, Germany) using anion-exchange resin. Electrophoretic buffer solutions were prepared from disodium hydrogenphosphate dihydrate, boric acid, EDTA, CDTA or DTPA by adding a 0.1 mol l^{-1} NaOH solution to adjust to the desired pH.

Procedures

The capillary was rinsed with 0.1 mol l^{-1} sodium hydroxide and water for 5 min, then equilibrated with carrier electrolyte for 5 or 40 min (without and with the electroosmotic flow modifier, respectively) at the beginning of each day. Between all electrophoretic separations the capillary was rinsed for 2 min with carrier electrolyte. All electrolyte solutions were filtered through a 0.45 μm membrane filter and degassed by ultrasonication.

A procedure for the extraction of orimulsion ash is briefly described as follows: 0.25 g of orimulsion ash was stirred for 24 h at room temperature with 10 ml of 0.1 mmol l^{-1} H_2SO_4, then diluted to 25 ml with 1 mmol l^{-1} EDTA solution (pH 4.0) and filtered through a 0.45 μm membrane filter before use.

The extraction of water-soluble atmospheric aerosols collected on PTFE filters was performed with 10 ml of water by sonication in the ultrasonic bath for 20 min. After extraction the extracts were spiked with appropriate volumes of 5 mmol l^{-1} solutions of phen and (after ≈1 min) CDTA, then filtered and analyzed. In all experiments an appropriate complexing agent was added to give approximately 5×10^{-4} mol l^{-1} concentration in the final sample.

Results and discussion

Speciation of Cr^{III} *and* Cr^{VI}

Chromium provides a typical example because of the fact that different oxidation forms of the same element may show very different chemical properties. Chromium(VI) exists in environmental samples in the form of the highly toxic chromate anion, which exhibits significant UV absorption, whereas less toxic cationic Cr^{3+} has no UV absorbance. In addition, Cr^{3+} forms a very stable anionic complex with a wide number of organic and inorganic ligands.[36] For these reasons, the best approach for the CE determination of both Cr species in a single run is a selective conversion of Cr^{3+} into a UV absorbing negatively charged complex and then CE separation of both anions under optimized conditions. This approach recently was successfully used for speciation of Cr by HPLC[12,13] where EDTA and CDTA were used for selective complexation of Cr^{3+} ions. Both these chelates exhibit relatively strong UV absorption at 214 nm and chromate does not react with complexones.

In this study three complexones, EDTA, CDTA and DTPA, were investigated for the speciation of Cr by CE. Chromium(III) forms with complexones very stable ($\log \beta = 23.4$, 25.6 and 28.3 for EDTA, CDTA and DTPA, respectively) but kinetically inert complexes. At room temperature these reactions require several days to complete the chelation. Therefore all standard solutions and samples containing Cr^{III} were boiled approximately 5 min after addition of a 2–5-fold molar excess of appropriate complexone. Both the chromium species after complexation of Cr^{III} were stable in the pH range 7–9 at least over a period of five days. Electrophoretic behaviour of Cr species was studied at negative polarity in the pH range 7–9 using phosphate carrier electrolyte (20 mmol l^{-1}) containing 0.5 mmol l^{-1} TTAOH as EOF (electroosmotic flow)-modifier. Preliminary investigations showed that the mobility of singly charged Cr^{3+} chelate with EDTA or CDTA differs essentially from that of chromate. The separation of both Cr species after derivatization of Cr^{III} with these complexones requires more than 10 min. In addition, the separation between chromium(III) and iron(III) complexes with both complexones was not complete. These results correspond with those for the Cr^{III}–CDTA chelate investigated by Timerbaev *et al.*[31] Better results were obtained by using DTPA, which forms with Cr^{III} doubly charged and, consequently, a faster migrating anion. In this case, only ≈5 min are required for the separation of both chromate and Cr–$DTPA^{2-}$ anions. Common UV absorbing inorganic anions (Br^-, NO_3^-, NO_2^-, MoO_4^{2-}) and metal ions capable of forming complexes with DTPA (such as Fe^{III}, Cu^{II}, Ni^{II} and others) do not interfere in the determination of Cr species. Fig. 1 illustrates the determination of Cr^{III} and Cr^{VI} in the wastewater from an electroplating plant.

Speciation of V^{IV} *and* V^{V}

The determination of vanadium(IV) and vanadium(V) species in a single run by CE without a derivatization procedure is also complicated because V^{IV} in solution predominantly exists in the cationic vanadyl (VO^{2+}) form, whereas V^V exists in the form of vanadate or polyvanadate anions. Only under acidic conditions (pH < 3) vanadate also exists as a VO_2^+ cation. This property of V^V species was used by Thornton and Fritz.[37] They separated VO^{2+} and VO_2^+ cations at pH 2.3 by CE with aqueous HCl or $HClO_4$ as the electrolyte using direct UV detection at 185 nm. However, the application of such systems to the speciation of vanadium in real samples could be complicated because most of inorganic and organic ions also absorb at this wavelength. In the commonly used wavelengths range, *i.e.*, above 200 nm only vanadate ions show significant absorption. Thus, the speciation of V^{IV} and V^V by CE after selective complexation of vanadyl ion or both vanadium species seems to be more favourable.

Electrophoretic behaviour of vanadium complexes with EDTA, CDTA and DTPA was investigated at negative polarity under the following conditions: (i) in the pH range between 4 and 6 using acetate carrier electrolyte (50 mmol l^{-1}) without any pretreatment of capillary and (ii) in the pH range between 8 and 10 using borate carrier electrolyte (50 mmol l^{-1}) with 0.5 mmol l^{-1} TTAOH as EOF-modifier. However, under both these conditions less stable V^V chelates with all three chelating agents were partially or completely decomposed in the capillary during the separation process. This resulted in very broadened and a poorly shaped peak of vanadate anion (using CDTA) or two peaks (using EDTA and DTPA), where one of those corresponds to the vanadate and the other to the V^V chelate.

In our previous work[35] for the CZE separation of common metal ions we have used an aqueous solution of complexone as a carrier electrolyte. This approach improves the separation efficiencies of metal complexes because of two following reasons. Firstly, the dissociation of less stable metal complexes is suppressed. Secondly, the better resolution and peak shape were obtained because the mobility of the chelate anions is similar to the mobility of the complexone anion in the electrolyte. In addition, in most cases the pre-capillary derivatization of metal ions is not necessary.

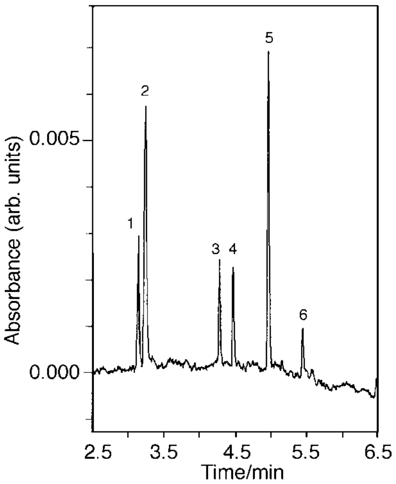

Fig. 1 Speciation of Cr^{III} and Cr^{VI} in waste water from an electroplating plant. Electrolyte, 20 mmol l^{-1} Na_2HPO_4, 0.5 mmol l^{-1} TTAOH, pH 8.0; capillary, 50/57 cm; applied voltage, −15 kV; direct UV detection at 214 nm; injection time, 12 s. Peaks: 1, CrO_4^{2-}; 2, NO_3^-; 3, Ni^{II}; 4, Cr^{III}; 5, Fe^{III}; 6, unknown peak.

Separations of the two vanadium species pre-capillary complexed with EDTA, CDTA or DTPA using 5 mmol l^{-1} solutions of appropriate complexones as carrier electrolyte at pH 4.5 were compared in order to determine the optimum conditions for the analysis. However, using CDTA electrolyte the V^{V}–CDTA chelate was also partially decomposed during the separation process. The best efficiency and shortest separation time are obtained by using EDTA as a carrier electrolyte. Consequently, this complexone was selected for all further investigations.

Analysis of the standard solutions containing V^{IV} and V^{V} species without and with pre-capillary derivatization showed that the reaction between vanadate and EDTA is too slow for the determination of V^{V} ions without pre-capillary derivatization. Thus, the speciation of vanadium requires both electrolyte containing EDTA and pre-capillary complexation of sample before use.

The stability of both vanadium species after complexation with EDTA was also investigated in the pH range 4–6 and no significant changes in concentrations of V^{IV} and V^{V} over a period of five days were observed.

Most practical samples contain vanadium species at low levels combined with an important ionic matrix. Some inorganic anions such as NO_3^-, NO_2^-, Br^-, CrO_4^{2-}, MoO_4^{2-} also absorb significantly at 214 nm. Moreover, a number of metal cations (such as Fe^{III}, Cu^{II}, Ni^{II} and others) are also capable of forming anionic complexes with EDTA. The increasing concentrations (up to 50 mg l^{-1}) of foreign ions were injected with 1 mg l^{-1} of both vanadium(IV) and vanadium(V) complexes. All ions investigated did not interfere in the determination of vanadium species except molybdate that partially comigrates with VO_2EDTA^{3-} chelate at concentrations of MoO_4^{2-} higher than 5 mg l^{-1}. In order to avoid this interference the effect of the pH of the electrolyte on the migration times of VO_2EDTA^{3-}, $VOEDTA^{2-}$ and MoO_4^{2-} was studied (Fig. 2). As can be seen the dependences of the migration times for $VOEDTA^{2-}$ and MoO_4^{2-} *versus* electrolyte pH are similar, whereas for V^{V}–EDTA chelate at pH < 4.2 the migration time significantly increases. This fact can be explained by the formation of the lesser charged protonated complex VO_2HEDTA^{2-} when acidity was increased. Good separations of vanadium species from foreign ions are observed at pH 4.0. Fig. 3(a) shows the electropherogram of the standard solution of vanadium(IV) and vanadium(V) complexed with EDTA at the optimum conditions. The electropherogram in Fig. 3(b) demonstrates the determination of soluble vanadium species in the aqueous orimulsion ash sample extract.

Speciation of Fe^{II} *and* Fe^{III}

With CE speciation of Fe^{II} and Fe^{III} ions the major problem is the selection of complexing agent suitable for the derivatization of both iron species. Previously reported studies showed the possibility of separating the Fe^{II} and Fe^{III} ions by CE after pre-capillary complexation with EDTA[26] and with CDTA.[32] However, Schäffer *et al.*[25] showed that the addition of an excess of EDTA to the solution containing both iron species causes the rapid and complete oxidation of Fe^{II} into Fe^{III} by ambient oxygen. Such behaviour can be explained by the fact that Fe^{2+} ions form with complexones significantly less stable chelates than Fe^{3+} ($\log \beta = 14.3$ and 25.1 for Fe^{II} and Fe^{III} chelates with EDTA, respectively). Consequently, the addition of the EDTA results in a significant decrease of the redox potential for the Fe^{III}/Fe^{II} pair and therefore shifts the equilibrium toward iron(III). However, many other complexing agents also form with both iron species complexes in which stability differs significantly.[36] Thus, for the simultaneous determination of both ferrous and ferric ions two different complexing agents were selected: *o*-phenanthroline for Fe^{2+} and EDTA for Fe^{3+}. Since both Fe^{II}–phen and Fe^{III}–EDTA have high stability constant values ($\log \beta_3 = 24.3$ for Fe^{II}–phen chelate), the problem of selective stabilization of the +2 oxidation state over the +3 oxidation state (and *vice versa*) causing a reduction of Fe^{3+} or oxidation of Fe^{2+} was eliminated by using these two complexing agents. Recently we have successfully applied such a CE system for the speciation of iron in tap water and groundwater samples.[33] However, instead of EDTA the complexation of iron(III) was performed with CDTA because using this complexone the analysis time was reduced approximately by a factor of two.

The present work demonstrates the applicability of this approach for the speciation of water-soluble iron in atmospheric aerosols. Fig. 4 shows the typical electropherogram of an aqueous extract of atmospheric aerosols collected in the Vilnius region.

Sample analysis

Several parameters related to quantification, including minimum detectable concentration, linearity and reproducibility, were examined under the above optimized conditions. All species studied gave a linear relationship between peak area and concentration over a range of at least two orders of magnitude with correlation coefficients ($n = 5$) ranging from 0.998 to 0.999. The detection limits for a signal-to-noise ratio of 3 and 10 s hydrodynamic injections were in the range from 1×10^{-6} mol l^{-1} for Fe^{II} to 8×10^{-6} mol l^{-1} for Cr^{VI}.

The reproducibility was studied by making five consecutive runs of standard solutions at a concentration of 5×10^{-5} mol l^{-1} of each species. The relative standard deviations of migration

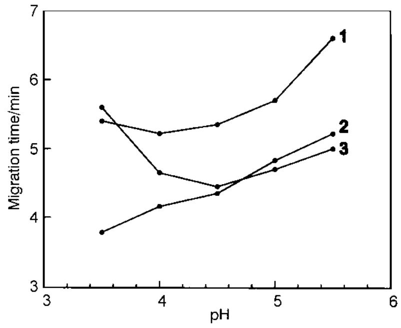

Fig. 2 Effect of electrolyte pH on the migration time of 1, $VOEDTA^{2-}$; 2, molybdate; and 3, VO_2EDTA^{3-} ions. Electrolyte, 5 mmol l^{-1} EDTA; capillary, 50/57 cm; applied voltage, −30 kV; direct UV detection at 214 nm.

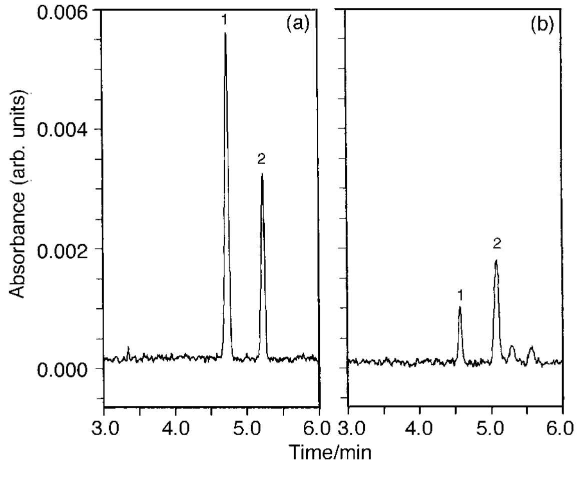

Fig. 3 Electropherograms of (a) standard solution of vanadium species complexed with EDTA and (b) aqueous orimulsion ash sample extract. Electrolyte pH 4.0; injection time, 8 s; other conditions as in Fig. 2. Peaks: 1, V^{V}; 2, V^{IV}.

times and peak areas for all chelates were less than 0.8% and 4.5%, respectively.

In order to evaluate the quantitative performance of the method, several real samples were analyzed by using CE and conventional spectrophotometric methods. For the determination of iron and chromium species and total vanadium the *o*-phenanthroline, diphenylcarbazide and gallic acid methods[38] were used, respectively. The results obtained by both techniques are compared in Table 1. Finally, the recovery tests were performed for the samples spiked with metal species at various concentration levels. The mean recoveries were in the range 94–103% for all analytes studied. These results illustrate that CE offers promise for the speciation of metal ions in real samples.

Conclusions

The results of this work demonstrate that polyaminocarboxylic acids can be successfully used as derivatizing agents for the speciation of metals in two different oxidation states by capillary electrophoresis. Complete complexation of one or both metal species before the separation offers a possibility to determine both ions in a single run with a good detectability using direct UV detection. High efficiencies and short analysis times are some of the advantages of this method in comparison with the conventional spectrophotometric techniques. Work continues in our laboratory towards the adoption of CE to other types of samples of interest.

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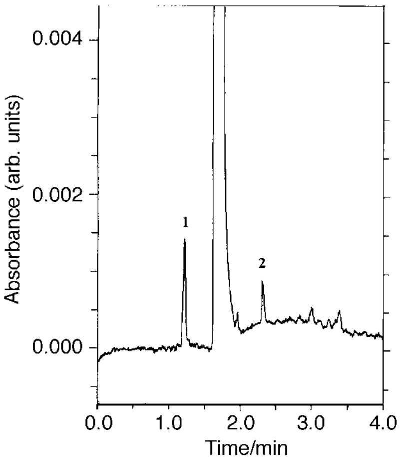

Fig. 4 Speciation of iron in aqueous atmospheric aerosol extract. Electrolyte, 100 mmol l^{-1} borate; capillary, 40/47 cm; applied voltage, 30 kV; direct UV detection at 254 nm; injection time, 12 s. Peaks: 1, Fe^{II}; 2, Fe^{III}.

Table 1 Comparison of CE and conventional spectrophotometric methods for the speciation of metals (n = 5)

		Found/mg l^{-1}	
Sample	Analyte	CE	Spectrophotometry
Wastewater from plating plant	Cr^{III}	0.86	0.94
	Cr^{VI}	1.21	1.12
Aqueous orimulsion ash extract	V^{IV}	0.95	1.36*
	V^{V}	0.36	
Aqueous atmospheric aerosol extract	Fe^{II}	1.40	1.45
	Fe^{III}	0.28	0.26

* Total concentration of vanadium.

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