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Separation of chromium (III) and chromium (VI) by capillary electrophoresis using 2,6-pyridinedicarboxylic acid as a pre-column complexation agent

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Abstract

A simple method was developed for the simultaneous determination of Cr(III) and Cr(VI) by capillary zone electrophoresis (CZE), where Cr(III) was chelated with ligands to form anionic complexes. Nitrilotriacetic acid, *N*-2-hydroxyethylenediaminetriacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and 2,6-pyridinedicarboxylic acid (PDCA) were investigated as Cr(III) complexing ligands. Of all the ligands studied, 2,6-PDCA with Cr(III) gave the largest UV response and high selectivity for Cr(III). In addition, the condition for pre-column derivatization, including pH, concentration ratio [Cr(III)/2,6-PDCA] and the stability of Cr(III) complexes were also examined. The separation of anionic forms of Cr(III) and Cr(VI) was achieved using co-CZE with UV detection at 185 nm. The electrolyte contained 30 mM phosphate, 0.5 mM tetradecyltrimethylammonium bromide, 0.1 mM 2,6-PDCA and 15% (v/v) acetonitrile at pH 6.4. The detection limits were 2 μ M for Cr(III) and 3 μ M for Cr(VI) and linear plots were obtained in a concentration range of 5–200 μ M. The utility of the method was demonstrated for the determination of Cr(III) and Cr(VI) in contaminated soils. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The speciation of metal with different oxidation states exhibits widely different behaviours in terms of potential toxic effects on environmental and biological system. For chromium, the two most environmental important oxidation states are Cr(VI) and Cr(III). Cr(VI) can be readily reduced to Cr(III) in the biosphere, and both can be taken up by humans and other ecological receptors [1]. Recently,

much of the interest arises from the growing need to identify the chromium speciation responsible for toxic effects on environmental and biological systems [2], e.g., Cr(VI) is highly toxic even in a small concentration, however Cr(III) can be considered as an essential element for human beings in a proper concentration range, and it can be toxic only in very high concentrations. There are many methods used for the determination of chromium speciation. Methods mainly include flow injection analysis (FIA) or liquid chromatography (LC) coupled with different detection techniques [3]. FIA with either off-line or on-line preconcentration is frequently used where the species are detected using electrochemical detection

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(ED) [4], spectrophotometry (UV–Vis) [5,6], chemiluminescence (CL), fluorimetry (FL) [7–9], or atomic absorption spectrometry (AAS) [10–13]. During LC [14], chromium species can be separated by reversed-phase chromatography after the formation of neutral chelates by the addition of a complexing agent to the mobile phase [15,16], ion-pairing [17–19] or ion chromatography [20,21]. It may also be coupled with atomic emission spectrometry (AES), or inductively coupled plasma mass spectrometry (ICP-MS) [15–21]. These methods are all useful techniques and offer high detection sensitivity for chromium in environmental samples. However, they still do not satisfy all requirements for routine analysis because of their complicated process design and the need for expensive instruments in the case of AAS and ICP-MS.

Capillary electrophoresis (CE) is an attractive approach for the separation of metal species [22] due to its high efficiency and separation speed. One of the problems using CE for the separation of cations has a similar mobility, resulting in poor resolution. However, complexation of cations with a ligand to form anionic complexes can be used to modify the mobility of the cation as each cation will complex with the ligand to a different degree determined by the complexes stability [23,24]. In principle, two approaches are used in the CE separation of metals. One is on-line complexation, where a soluble ligand is added to the running electrolyte and weak complexes are rapidly formed. Indirect UV detection is usually employed and carboxylic acids are usually used as the weak ligands [23,24]. Another approach is pre-column complexation, where an excess of strong ligand is added to the sample to form complexes prior to CE analysis [25]. This method allows for direct UV detection of the metal ions after chelating with suitable UV absorbing ligands. Compared to indirect UV detection, the latter approach is more preferable due to increase selectivity and sensitivity [25], and has been used successfully for the analysis of real samples [26–28].

Pre-column complexation CE methods have recently been reported for the separation of Cr(III) and Cr(VI) [25]. Normally Cr(III) and Cr(VI) cannot be separated by CE. The reason is that their charge is opposite and charge values are different. However, when Cr(III) is complexed with a suitable ligand, to

form an anionic complex, it is possible to simultaneously determinate oxidation states in one run. Aminopolycarboxylic acids, including ethylenediaminetetraacetic acid (EDTA), 1,2-cyclohexanediaminetetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA), have been used as ligands to convert Cr(III) into negatively charged complexes and successfully used to the determination of chromium in real samples [29–34]. Oleski et al. described that the determination of Cr(II) and Cr(III) by CE–ICP-MS using 8-hydroxyquinone-5-sulfonic acid as a complexing reagent [33], and Mei et al. reported that the use of CE–ICP-AES for the determination of these species [34]. Recently, Himeno et al. [35] have reported the use of Mo(VI) reacted with Cr(III) to form water-soluble $[\text{CrMo}_6\text{O}_{24}\text{H}]^{3-}$, followed by CE separation with direct UV detection. Previously, 2,6-pyridinedicarboxylic acid (2,6-PDCA) had been used as the electrolyte for CE separation of metals such as Ni(II), Cu(II) and Fe(II) and organic anions [36,37], and mobile phase in ion chromatography for indirect UV detection of inorganic anions, cations, and carboxylic acids in ion chromatography [38,39]. These results suggested that 2,6-PDCA offered a high selectivity and UV responsive ligand for metal ions. In this paper, we report the separation of Cr(III) and Cr(VI) by CE with direct UV detection in a single run based on Cr(III) complexation with 2,6-PDCA. In order to evaluate the proposed method, 2,6-PDCA was also compared to other ligands commonly used in CE analysis. The proposed method was applied to the determination of aqueous chromium speciation in a long-term tannery contaminated soil.

2. Experimental

2.1. Chemicals

All reagents (analytical grade) were obtained from Sigma–Aldrich (Sydney, Australia) and dissolved in Milli-Q water without further purification. Standard solutions of the $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared daily from a 10 mM stock solution in Milli-Q water and diluted to the required concentrations before use. Electrolyte required for CE was

prepared by dissolution of an appropriate amount of NaH_2PO_4 in Milli-Q water, where contained appropriate amounts of tetradecyltrimethylammonium bromide (TTAB) and organic solvent. All electrolytes were filtered through a Millipore 0.45- μm membrane filter and degassed in an ultrasonic bath prior to use. Electrolyte pH was adjusted with 0.1 M NaOH or 0.1 M H_3PO_4 solution.

2.2. Sample preparation

An excess of ligand, 4 mM ligand (1.0 ml), was added to a tube containing 1 mM $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 ml) and heated on a water bath for 5 min at 80°C. Heating is required because of Cr(III) kinetics inert. A 0.5-ml volume of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mM) solution was transferred to a test tube and excess 1.0 ml ligand (4 mM) added [30]. After cooling to room temperature, the mixture was subjected to CE analysis. Soil solution was obtained by exchanging the contaminated soil with water in a 1:5 ratio (soil: deionised) for 2 h in an end over end shaker, centrifuging at 3200 g for 15 min and filtering through 0.45- μm Schleicher and Schuell syringe filters. Total Cr and soluble Cr(VI) in the soil solution was analysed in the same day.

2.3. Instrumentation

All CE experiments were performed using a Quanta 4000 instrument (Waters, Milford, MA, USA). The system was controlled by Millennium (Waters) software. Separation was carried out on fused-silica capillaries of 80 cm (effective length 75.5 cm) \times 50 μm I.D. The UV detector was set at 185 or 214 nm. Total Cr was determined using AAS (GBC, Model 906, Australia). Cr(VI) was analysed by ion chromatography using standard method 7199 [40]

2.4. Electrophoretic procedures

Prior to use, a capillary was pretreated with the following cycles: 0.1 M NaOH for 20 min, 0.01 M NaOH for 20 min, deionised water for 30 min and 30 mM phosphate buffer for 30 min. The capillary was pre-conditioned with phosphate buffer for 2 min for each run. Samples were injected in the hydrostatic

mode for 30 s. The capillary was held at 25°C, and the applied constant voltage was -20 kV. Identification of each of the solutes was based on the migration time and was verified by spiking samples with known standards. 0.05% (v/v) benzyl alcohol was used as a neutral marker for the determination of the electrophoretic mobility. The electroosmotic mobility and the electrophoretic mobility of the solute and marker were calculated using equations described previously.

3. Results and discussion

3.1. Choice of complexing ligand for Cr(III)

In order to achieve high UV response and selectivity, complexing ligands should satisfy several requirements including (1) the ligand should only form a single distinct complexing with Cr(III) under derivatization conditions; (2) the complex remains stable during electrophoresis, and (3) the complex has large UV absorptivity [25,41,42]. In this work, EDTA, *N*-2-hydroxyethylethylenediaminetriacetic acid (HEDTA), DTPA, nitrolotriacetic acid (NTA) and 2,6-PDCA were used as ligands for chelation with Cr(III). The complexes formed were separated using an electrolyte containing 30 mM phosphate, 0.5 mM TTAB at pH 6.0 as shown in Fig. 1a–e. For all five ligands, the Cr(III) complexes were detected longer with excess free ligand. The free ligand peak appeared before the Cr(III) anionic complex peaks because their charge/mass ratio was greater than that of the Cr(III) complexes. However, two or more peaks and a small UV response were observed using EDTA, HEDTA and DTPA. This can be attributed to the formation of different Cr(III) anionic complexes under the derivation conditions [22]. In contrast, only one complex peak was observed using either 2,6-PDCA or NTA as a complexing ligand. However, a larger UV response for the Cr(III) complex was obtained using 2,6-PDCA due to the complex absorptivity ($43\,680\text{ M}^{-1}\text{ cm}^{-1}$, 192 nm) [36]. However, in this study, there was less UV response for all five ligand complexes at 214 nm. This is not unexpected, since the carboxylate group of the ligand has stronger absorbency below 210 nm [29,30,32]. For example, Cr(III) chelated with 2,6-PDCA at 185

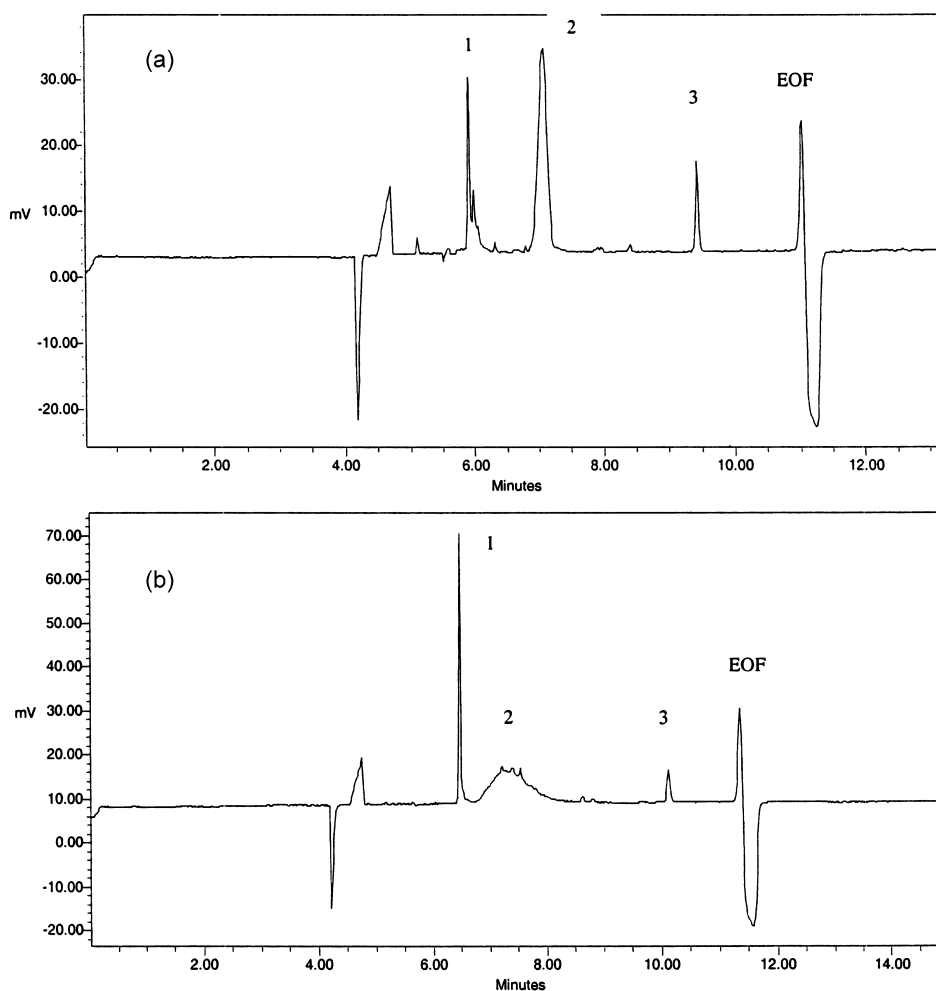


Fig. 1. Electropherograms of Cr(III) complexed with various ligands. (a) EDTA, (b) HEDTA, (c) DTPA, (d) NTA, (e) 2,6-PDCA. 1, Free ligand; 2, Cr(III) complex (I); 3, Cr(III) complex (II). 0.25 mM for Cr(III). Conditions: capillary, fused-silica capillary 80 cm (effective length 75.5 cm) \times 50 μ m; electrolyte, 25 mM sodium phosphate, 0.25 mM TTAB, 15% (v/v) acetonitrile at pH 6.40; applied potential, -20 kV; hydrostatic injection, 30 s, UV detection at 185 nm. Capillary temperature, 25°C.

nm had a peak area six-times greater than that obtained at 214 nm. The selectivity of the ligand for common metal ions [Ca(II), Mg(II), Mn(II), Zn(II), Co(II), Cd(II), Ni(II), Cu(II), Pb(II), Fe(III)] was also tested. This indicated that EDTA, HEDTA and DTPA chelated with most of the tested metal ions, while NTA and 2,6-PDCA showed a higher selectivity for Cr(III). Although 2,6-PDCA complexes with Ni(II), Cu(II) and Pb(II) forming $(M[L]_2)^{2-}$ [43], these complexes have significantly different mobilities to $[Cr(L)_2]^{1-}$ due to the lower charge and therefore does not interfere with the determination of

Cr(III). Thus, 2,6-PDCA was the more suitable ligand for Cr(III) determination because it satisfied above the requirements most readily.

3.2. Pre-column derivatization conditions

Work on 2,6-PDCA as an eluent in ion chromatography [44,45] has shown that eluent pH and ligand concentration play important roles in the formation of anionic complexes. Similarly, the conversion of Cr(III) to an anionic Cr(III) complex is highly

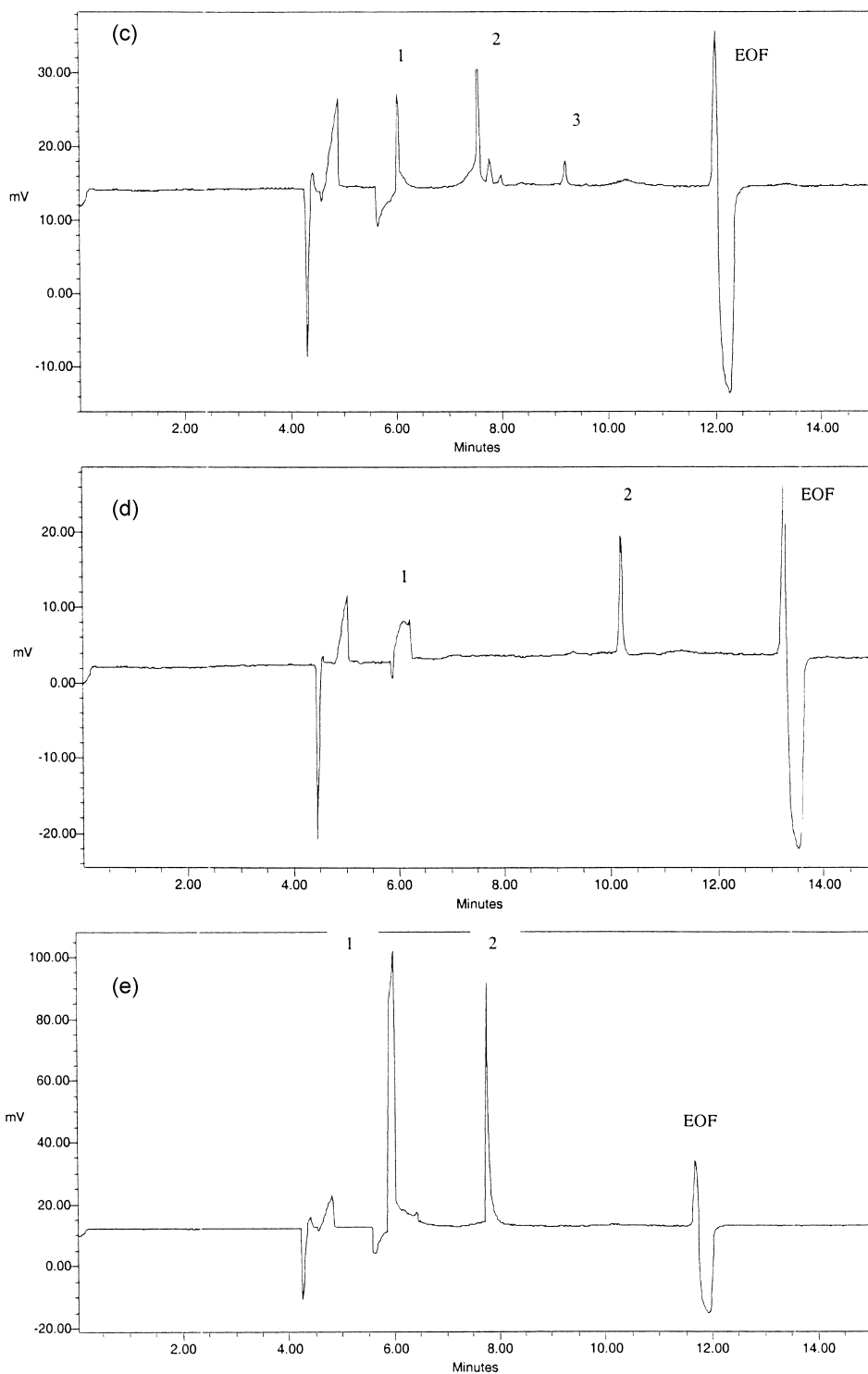


Fig. 1. (continued)

dependent upon on pH and the concentration as shown by the following equations [43]:



Since the $\text{p}K_{\text{a}}$ values for 2,6-PDCA are $\text{p}K_{\text{a}1}$ 2.16, and $\text{p}K_{\text{a}2}$ 6.92, the pH was tested in the range 2.5–7.5. The formation of $[\text{Cr}(\text{PDCA})_2]^{-}$ was determined by co-CZE at 185 nm. Fig. 2 shows that the formation of $[\text{Cr}(\text{PDCA})_2]^{-}$ significantly depends on the solution pH. Peak area was increased as the pH was increased from 2.5 to 3.5. This can be attributed to an increase in the concentration of PDCA^{2-} , leading to formation of $[\text{Cr}(\text{PDCA})_2]^{-}$ via Eq. (1). In contrast, peak area decreased when solution increased above 4.0. A higher solution pH leads to the hydrolysis of the Cr(III) and to the formation of the precipitate described via Eq. (3). Therefore, the optimum solution pH of 3.5 was used in all subsequent experiments.

From Eq. (1), it can be seen that concentration ratio (Cr(III)/2,6-PDCA) during derivatization affected the formation of $[\text{Cr}(\text{PDCA})_2]^{-}$. The affect of the concentration ratio is shown in Fig. 3. In general, peak area increased as the concentration ratio increased, peak area increased linearly up to a con-

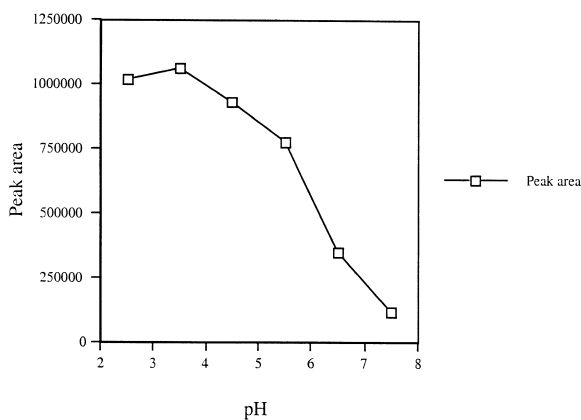


Fig. 2. Effect of pH on the chelating reaction between Cr(III) and 2,6-PDCA. 2,6-PDCA: 1.0 mM; Cr(III): 0.25 mM. Separation conditions as in Fig. 1.

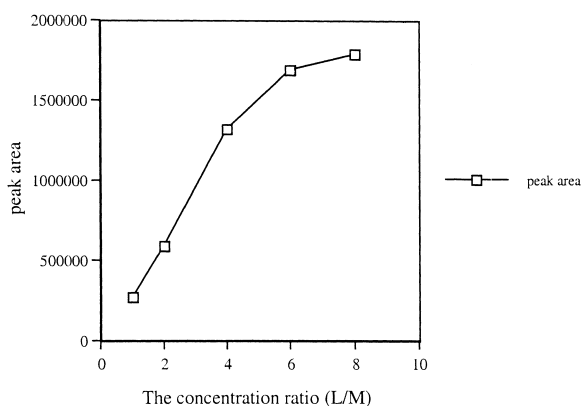


Fig. 3. Effect of the concentration ratio (L/M) on the derivatization. Solution pH: 3.5. Conditions as in Fig. 1.

centration ratio of 4. However, when ratio was above 6, the peak area was almost constant. At all concentration ratio only a single complex peak was observed. Similar results have been observed previously [38,39]. A higher concentration ratio favours the forward chelating reaction because of the increasing of the concentration of 2,6-PDCA. Therefore, the best concentration ratio for obtaining maximum sensitivity was 6 [Cr(III)/2,6-PDCA].

The stability of $[\text{Cr}(\text{PDCA})_2]^{-}$ was determined by repeated injections of solution derivatized at the concentration ratio of 6 at pH 3.5. The derivatization solution was then stored at room temperature and re-analysed every day. The solution exhibited well a stability for up to 5 days (the response obtained from the sample at fifth day is 96.5% of that at on the first day) at room temperature with no degradation being detected by CE. This indicates 2,6-PDCA was suitable for pre-column derivatization of Cr(III) with high selectivity.

3.3. Simultaneous separation of Cr(III) and Cr(VI)

As shown in Eqs. (1)–(3), there is a dynamic equilibrium between Cr(III), 2,6-PCDA and $[\text{Cr}(\text{PDCA})_2]^{-}$. The equilibrium shifts during electrophoresis due to the dissociation of $[\text{Cr}(\text{PDCA})_2]^{-}$. This problem can be overcome by the addition of small amounts of ligand to the running electrolyte [25,29–32]. In addition, the selectivity for the separation of metal anionic complexes can be controlled by the addition of organic solvent [25]. Thus, an

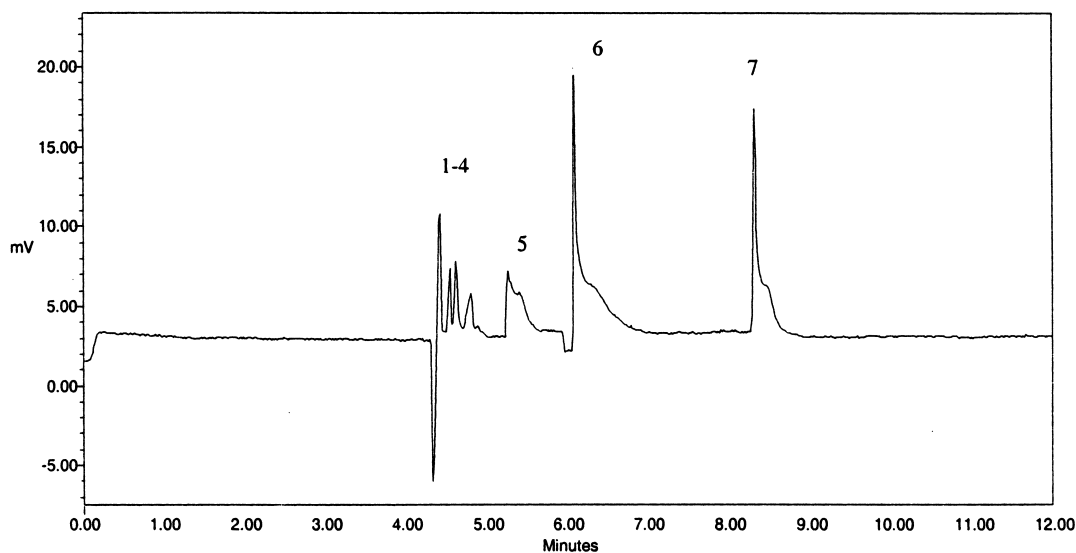


Fig. 4. Separation of Cr(III) and Cr(VI) under optimum CE conditions. 1, Cl^- (0.25 mM); 2, NO_2^- (0.25 mM); 3, NO_3^- (0.25 mM); 4, SO_4^{2-} (0.25 mM); 5, Cr(VI) (0.1 mM); 6, 2,6-PCD (0.25 mM); 7, Cr(III) complex (0.05 mM). Conditions: electrolyte: 30 mM sodium phosphate+0.5 mM TTAB+0.1 mM 2,6-PDCA+15.0% (v/v) acetonitrile at pH 6.40. Other conditions as in Fig. 1.

electrolyte, containing 30 mM phosphate, 0.5 mM TTAB, 0.1 mM 2,6-PDCA, and 15% acetonitrile at pH 6.40, was used as the running buffer for the separation of CrO_4^{2-} and $[\text{Cr}(\text{PDCA})_2]^-$, and detected by direct UV at 185 nm. CrO_4^{2-} and $[\text{Cr}(\text{PDCA})_2]^-$ were generally well separated and well defined peaks. Excess of 2,6-PDCA was also detected, appearing prior to $[\text{Cr}(\text{PDCA})_2]^-$ due to the large charge and small size. Some inorganic anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) commonly present in soils were added to the mixture of CrO_4^{2-} and $[\text{Cr}(\text{PDCA})_2]^-$ to determine whether they interfered with CrO_4^{2-} and $[\text{Cr}(\text{PDCA})_2]^-$. Fig. 4 clearly demonstrates that Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , CrO_4^{2-} and $[\text{Cr}(\text{PDCA})_2]^-$ were all well resolved. The migration order was Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , CrO_4^{2-} and $[\text{Cr}(\text{PDCA})_2]^-$. The migration order reflects

differences in both charge and size of the solutes. For example, CrO_4^{2-} is double negatively charged and migrates faster than $[\text{Cr}(\text{PDCA})_2]^-$ which is only single negatively charged.

Calibration plots were obtained by plotting peak area versus concentration. The relationship was linear in the concentration range 5–200 μM . Correlation coefficients (r^2) were in the range 0.9992–0.9999. The detection limits ($S/N=3$) were 2–3 μM and the reproducibility of the migration time (relative standard derivation, $n=5$) from injecting a 100 μM standard mixture was 0.7–2.4%. Analytical characteristics of the test solutes using the proposed method are listed in Table 1.

The proposed method was used to determine Cr(III) and Cr(VI) in extracts of the contaminated soils. A typical electropherogram is presented in Fig.

Table 1
The characteristics for chromium species by the proposed method

Species regression line	Coefficient	Detection limit (μM)	Reproducibility ($n=5$, %)
Cr(III) $y = 10 \cdot 10^5 x - 4.5 \cdot 10^3$	0.999	3	2.0
Cr(VI) $y = 5.63 \cdot 10^5 x - 1.5 \cdot 10^3$	0.998	2	2.4

Conditions as in Fig. 4. Detection limit – signal/noise=3.

5a. The contaminated soil contained only Cr(VI) in detectable concentrations. The peak assessment was verified by spiking the solution with a known concentration of Cr(VI) as shown in Fig. 5b. To confirm the proposed method for the determination of Cr(III), a known concentration of Cr(III) was also added to the soil. The determined concentrations are listed in Table 2, together with the concentration

Table 2

The concentration of Cr(III) and Cr(VI) in contaminated samples determined by the CZE and UV methods

Species	CE (mg/l)	UV (mg/l)	Spiked (mg/l)	Found by CZE (mg/l)	Recovery ($n=3$, %)
Cr(III)	–	–	2	1.96	98.0±3.8
Cr(VI)	0.483	0.486	2	2.48	99.7±2.9

Conditions as in Fig. 4.

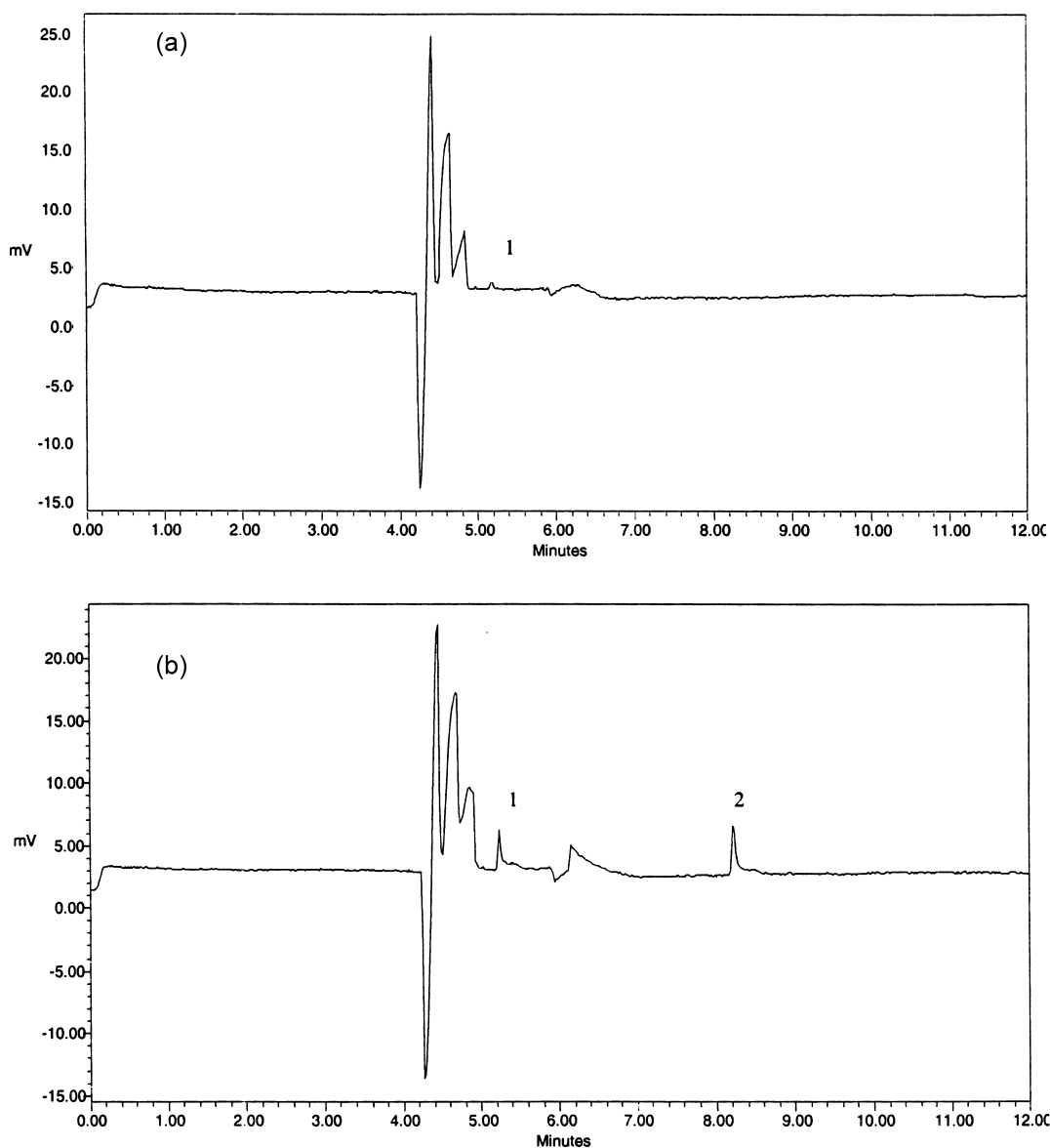


Fig. 5. Contaminated soil extracts analysed by the proposed method. (a) Soil extracts, (b) soil extract spiked known Cr(VI) and Cr(III). 1, Cr(VI); 2, Cr(III). Conditions as in Fig. 4.

determined with spectrophotometry. The results obtained using CE method showed good agreement with results obtained using spectrophotometry.

4. Conclusion

The results of this work demonstrate that 2,6-PDCA can be used as a derivatizing agent for Cr(III) and is therefore a useful ligand for the determining chromium speciation when using CE with direct UV detection. The derivatization conditions, such as solution pH and the concentration ratio (*M/L*) are both important for the formation of a single stable $[\text{Cr}(\text{PDCA})_2]^-$ complex. The proposed method offers high separation efficiency and short analysis time in comparison with conventional spectrophotometric methods. However, the detection limit still does not as yet satisfy that required for real samples. Preconcentration of Cr(III) and Cr(VI) based on solid-phase extraction is being developed to address this problem.

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