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Comparison of chromium speciation by CZE and ion exchange followed by AAS

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Abstract The hydrogen chromate anion ($HCrO_4^-$), which is the predominant species in acidic solutions and solutions with low chromium concentration, was determined by capillary zone electrophoresis (CZE) using UV detection on-column at 200 nm. A fused-silica capillary (55 cm × 50 μm i.d.) was employed with a high negative voltage of 20 kV. Total chromium was determined after reduction by H_2O_2 and its complexation by EDTA. The use of H_2O_2 as reducing agent is advantageous, as it does not increase the conductivity of the solution. Detection limits achieved (for 200 s injection time) were 30 and 8 μg/L for Cr(VI) and Cr(III), respectively. The CZE results obtained for Cr(III) and Cr(VI) were compared with those obtained by ion exchange with subsequent AAS.

Introduction

Chromium exists in the environment mainly as Cr(III) and Cr(VI) species. Whereas, Cr(III) is essential for maintenance of normal physiological functions, Cr(VI) is toxic, mutagenic and more soluble [1–3]. Therefore, the separation of Cr(III) and Cr(VI) and determination of its species has received considerable attention and a variety of approaches has been applied in recent years based on selective pre-concentration of species with subsequent colorimetric, AAS, HPLC, or voltammetric detection [4–20].

Recently, Timerbaev et al. used CZE for the simultaneous speciation of Cr(III) and Cr(VI) in acidic medium, after chelation of Cr(III) with 1,2-cyclo-hexane-diaminetetraacetate at 70 °C, resulting in detection limits of 10 and 50 μg/L for Cr(VI) and Cr(III), respectively [21]. Cr(III) has also been determined by CZE after its complexation with cyanide [22] or EDTA [23]. The advantages of CZE for the detection of metal ions are low cost and time saving [24–27]. In a previous work, we attempted simultaneous determination of Cr(VI) and Cr(III) at pH 3–4 by converting (by boiling) Cr(III) into the negatively charged complex $CrEDTA^-$ [23]. It was observed that Cr(VI) was partly reduced.

In the present work CZE was applied to the determination of Cr(VI), as $HCrO_4^-$, with subsequent detection at 200 nm in acid medium. The determination of CrO_4^{-2} by CZE in alkaline medium (pH 10) and at about 270 nm has been previously reported [28, 29]. Cr(VI) was reduced with H_2O_2 and a significant improvement of the detection limit for $CrEDTA^-$ at 200 nm was observed [21, 23]. The method was applied to samples from chromium plating baths. The results obtained by CZE were compared with those obtained by AAS after previous separation on an ion exchanger.

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Experimental

Apparatus and chemicals. An integrated capillary electrophoretic system, ISCO Model 3850 (Lincoln, NE, USA), equipped with high-voltage up to 30 kV, reversible polarity and hydrodynamic injection technique (by vacuum: 3.4 KPa) was applied. The separation capillary was an unmodified fused silica capillary column 55 cm long (35.5 cm to UV-detector) × 50 μm i.d. (Polymicro Technologies Inc. Phoenix, AZ. USA). The measurements were performed at 200 nm and all sample data were recorded using an integrator SP-Model 4270 (Spectra-Physics, San José, CA, USA).

The pH and specific conductivity of solutions were checked with a Crison-Digilab 517 pH-meter and a Crison 525 conductimeter, respectively. AAS was performed in a Pye Unicam SP-9 equipment.

Stock standard solution prepared from potassium chromate (Merck) were diluted appropriately in sodium acetate buffer (pH 3.8) as running solution. Super pure reagent methanol from Romil Chemicals was used as a marker to measure the rate of electroosmotic flow. Cr(VI) reduction was carried out with hydrogen peroxide from Foret AS. The anion and cation exchange resin used were Dowex 1-X8 and Dowex 50W-X8, respectively. The rest of reagents applied were supplied by Merck ("pro analysi" quality).

Procedures for CZE and ion exchange separation. The sample solution was adjusted to pH 3.8 with acetate buffer and Cr(VI) was measured by CZE at 200 nm, using acetate buffer 0.5 M (pH 3.8)

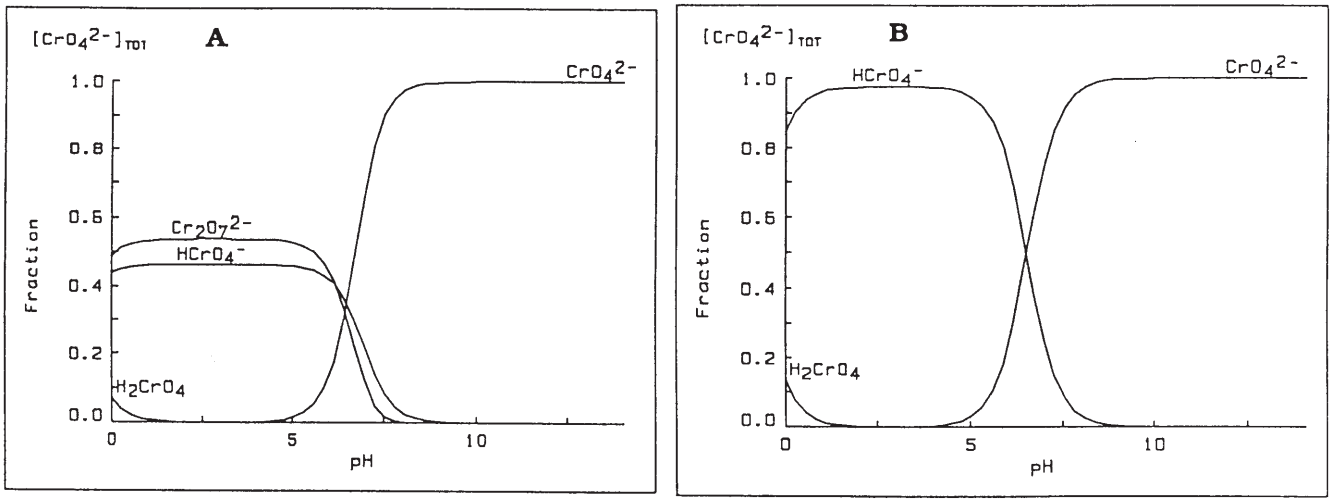

Fig. 1 Species distribution-pH diagrams. (**A**) 2000 µg/mL Cr(VI), (**B**) 20 µg/mL Cr(VI)

as carrier solution. Total Cr was determined after 3–5 min boiling of a sample aliquot with 3–4 mL concentrated H_2O_2 in presence of an excess of EDTA. After the reduction of Cr(VI) to Cr(III) and complexation of Cr(III) to $CrEDTA^-$ the total amount of Cr was measured by CZE [23]. Cr(III) was calculated by difference. The reduction step using H_2O_2 is advantageous as it does not increase the conductivity of the sample solution, allowing the application of stacking effect. All solutions were filtered through a 0.45 µm filter and were degassed by ultrasound.

Ion exchange was carried out as described in [10, 13] with some modifications. The columns (0.8 cm i.d. × 20 cm) were packed with anion or cation exchange resin (about 1.5 g).

The anion exchange separation of Cr(VI) at pH 1–2 (HCl) by an in-situ reduction using solutions such as ascorbic acid, oxalic acid, Fe(II) and hydroxylamine yielded only in recoveries between 75–89%. This low recovery may be due to reduction of Cr(VI) at low pH values. The recovery could be improved using one of the following procedures:

1- The solution containing Cr(III) and Cr(VI) was adjusted to pH 3.8 with an acetate buffer and passed through a cation exchange column at 2 mL min^{-1}. The column was rinsed with two aliquots of 5 mL diluted acetate buffer and twice with 5 mL of Milli-Q water. Chromium (VI) was determined in the combined eluate and washing solution. The desorption of Cr(III) was performed with 4 M HCl.

2- Cr(III) was determined in the combined eluate and washing solution of the sample after passing through an anion exchange resin column. After separation of Cr(III), the resin was transferred to a 50 mL glass beaker. The desorption of Cr(VI) from the cation exchange resin was done by reduction of chromate ions using 10 mL concentrated H_2O_2 solution in acidic medium (0.5 M H_2SO_4). The mixture was boiled for 3–5 min, filtered and transferred quantitatively to a 25 mL flask.

AAS determination of separated Cr species was performed in a N_2O–C_2H_2 flame.

Results and discussion

Determination of Cr(VI) by CZE

As previously reported [28], the separation of Cr(VI) can be efficiently performed in alkaline medium (pH 10), in which only one species prevail. In acidic solution, at high Cr(VI) concentration two chromium species are present, $HCrO_4^-$ and $Cr_2O_7^{2-}$ (Fig. 1A), whilst, at low chromium concentration (< 20 µg/mL, Fig. 1B), Cr(VI) prevails mainly as $HCrO_4^-$, which absorbs in UV range [30, 31].

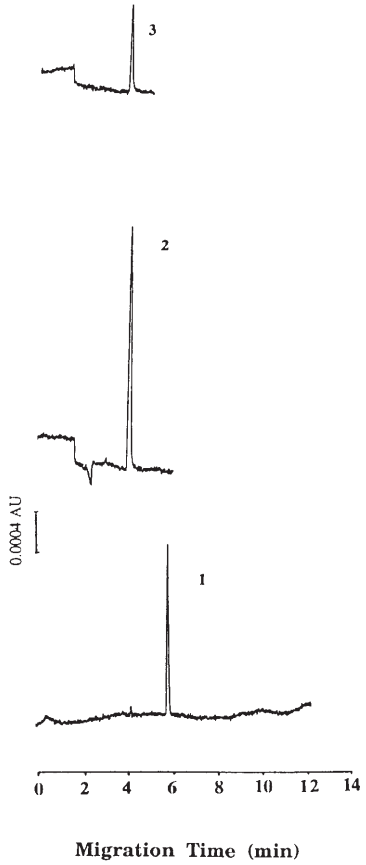

Fig. 2 Electropherograms of Cr(VI): peaks: (*1*) 1 µg/mL Cr(VI) prepared in 5% electrolyte. Carrier solution 0.001 M HCl/0.05 M NaCl. Applied voltage –15 kV, 200 nm, 100 s (*2*) 2 µg/mL Cr(VI) prepared in 4% carrier solution. Carrier solution 0.5 M acetate buffer (pH 3.8). Applied voltage –20 kV, 200 nm, 100 s (*3*) 265 nm, the other conditions as peak 2

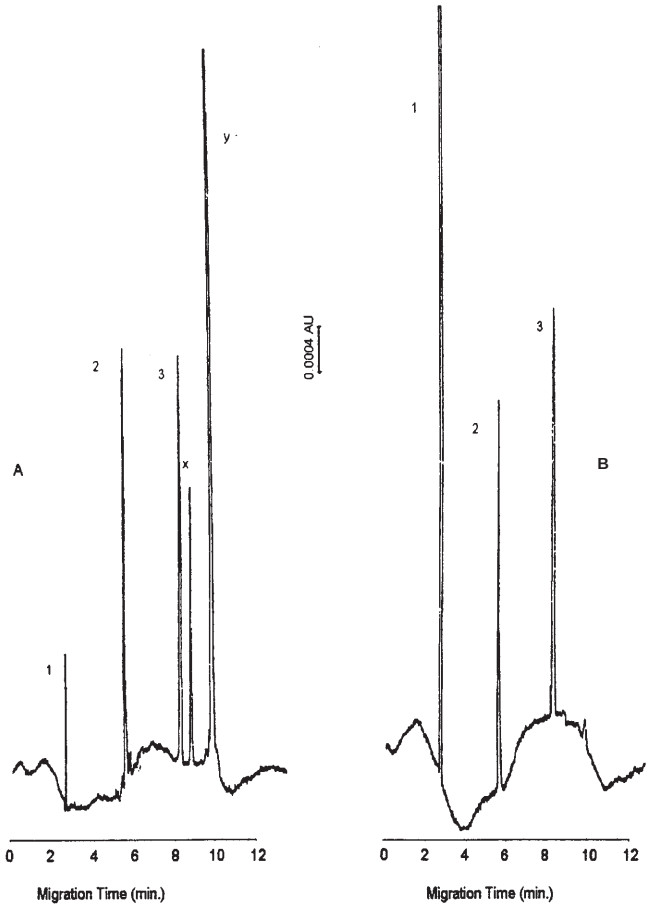

Fig. 3 Electropherogram of 0.8 μg/mL chromium in 4% carrier solution. (**A**) reduction of Cr(VI) by H_2O_2 and its complexation by EDTA, peaks: *1*-NO_3^-, *2*-$EDTA^{2-}$, *3*-$CrEDTA^-$, *x*-unknown and *y*-unknown. (**B**) $Cr(NO)_3$ complexed with EDTA, peaks: *1*-NO_3^-, *2*-$EDTA^{2-}$, *3*-$CrEDTA^-$. Carrier solution 0.5 M acetate buffer (pH 3.8). Applied voltage –20 kV, 200 nm, 100 s

For Cr(VI) determination we employed 0.5 M acetate buffer at pH 3.8 as running solution. Such concentration of the running solution approached better to the conductivity conditions for sample stacking [32]. Satisfactory results were obtained with a mixture consisting of 0.001 M HCl and 0.05 M NaCl, (Fig. 2, electropherogram 1) as supporting electrolyte, which has the advantage of being fully UV transparent at 200 nm, but we preferred controlled buffered solution, pH 3.8, to avoid any Cr(III) hydrolysis process (solubility product of $Cr(OH)_3$ is in the order of 10^{-30}) and any risk of Cr(VI) reduction.

At pH 3.8, the electroosmotic flow velocity (v_{eo}) and the analyte migration (v_{el}) were in opposite directions, supporting therefore the stacking efficiency [33]. By applying a negative voltage the hydrogen chromate ion turned up in the electropherograms, thus, demonstrating that electrophoretic mobility (μ_{eph}) was higher than the electroosmotic mobility (μ_{eo}). The values of μ_{eph} and μ_{eo} found were -4.92×10^{-4} cm^2/vs and 1.3×10^{-4} cm^2/vs, respectively [24].

The standard Cr(VI) samples were prepared in 4 to 10% of running solution. The best results obtained were in the

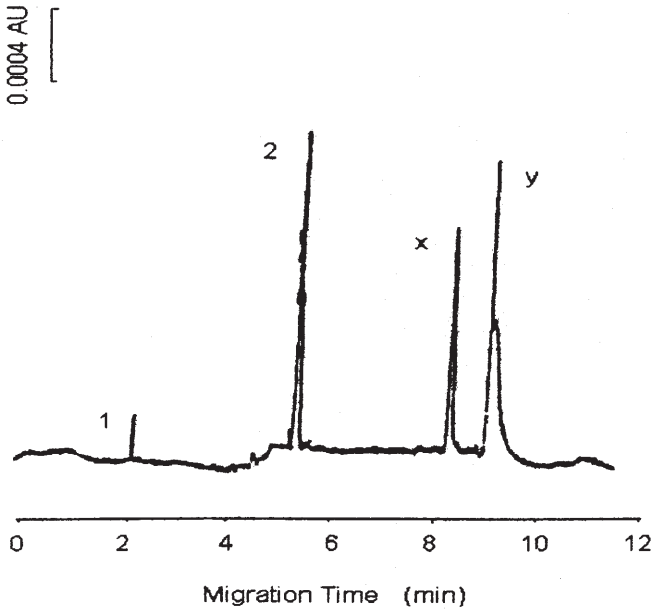

Fig. 4 Electropherograms of: EDTA+ H_2O_2, mixture, peaks *1*-NO_3^-, *2*-$EDTA^{2-}$, *x*-unknown, *y*-unknown. Carrier solution 0.5 M acetate buffer (pH 3.8). Applied voltage –20 kV, 200 nm, 50 s

range of 4 to 5% of running solution using up to 200 s of sampling time. This procedure produced sharp peaks (Fig. 2, electropherogram 2), but at higher sampling time the peaks became broader, therefore decreasing the resolution.

The calibration graph obtained, using peak areas was linear up to 6 μg/mL, but without stacking the linearity was up to 70 μg/mL. The detection limit obtained (according to 3σ rule) was 0.03 μg /mL for Cr(VI) and the relative standard deviation found for peak areas and migration time (n = 8) were 3.8% and 1.5%, respectively, which demonstrate that fluctuation of the baseline for acetate buffer does not influence the precision of the method. Tested concentration was 1 μg/mL of Cr(VI).

Determination of Cr(III) by CZE

Two samples with the same chromium concentration, one prepared from $Cr(NO_3)_3$ stock standard and the other from a Cr(VI) standard solution after its reduction by H_2O_2, were analyzed by CZE to test the quantitative reduction of Cr(VI) to Cr(III). This reaction was followed by heating in the presence of excess of H_2O_2 and chelation of Cr(III) in excess of EDTA at pH 3–4 [23]. It was observed that:

(1) the electropherograms showed the same peak surfaces of $CrEDTA^-$ species for both samples (peaks 3 in Fig. 3 A and 3 B).

(2) No peak of $HCrO_4^-$ was observed after its reduction with H_2O_2, which means that no Cr(VI) was available after its reduction in presence of peroxide (Cr(III) ion produced from the reduction step does not absorb without EDTA addition).

(3) Two unknown peaks, "x" and "y", appeared in the electropherogram when $CrEDTA^-$ was obtained by reduction (Figs. 3 A and 5 B).

In order to examine the unknown peaks "x" and "y" several blanks were tested (H_2O_2; acetate buffer/H_2O_2; acetate buffer/EDTA and EDTA/H_2O_2).

Only EDTA/H_2O_2 displayed the two unknown peaks in the electropherogram (Fig. 4). The unknown species formed did not interfere with chromium determination (this was tested by spiking $CrEDTA^-$ to the EDTA/H_2O_2 blank). The detection limit found for Cr(III)-EDTA at 200 nm for 200 s of injection time was 0.008 µg /mL chromium.

Application

In order to compare CZE and ion exchange-AAS methods for samples from a chromium plating bath from a factory at Barcelona (Spain) were analyzed. Five runs were carried out for each sample in acidic solutions (pH 2.8–3.1). After dilution with acetate buffer solution (the final concentration of the buffer in the sample was about 10 times diluted compared with running solution), Cr(VI) was determined by CZE (Fig. 5 A). Total chromium was determined by CZE after reduction of Cr(VI) by H_2O_2 and its complexation by EDTA (Fig. 5 B). The results obtained for the samples by CZE and those obtained by ion exchange-AAS are given comparatively in Table 1.

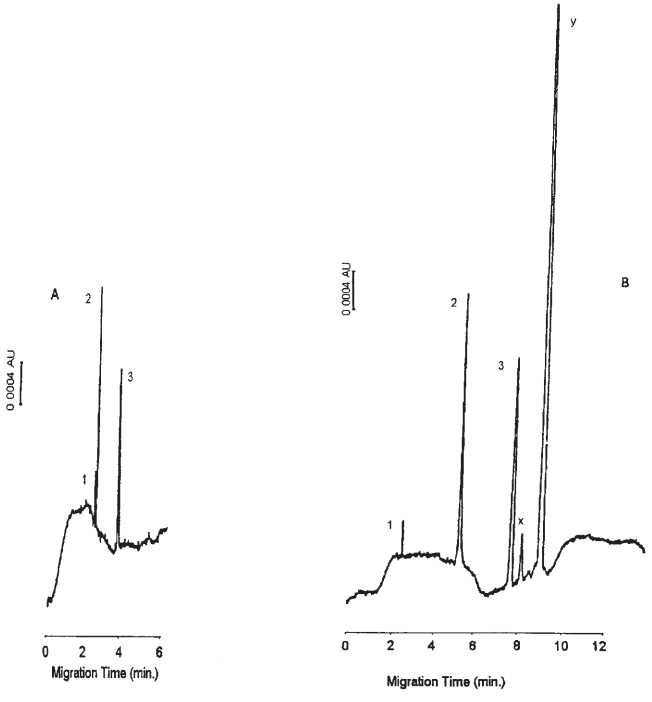

Fig. 5 Electropherogram of a real rinse water sample from chromium plating bath. Carrier solution 0.5 M acetate buffer (pH 3.8). Applied voltage –20 kV, 200 nm, 100 s. (**A**) Peaks: *1*-NO_3^-, *2*-unknown, *3*-Cr(VI). (**B**) Chromium (VI) was reduced by H_2O_2. Peaks: *1*-NO_3^-, *2*-$EDTA^{2-}$, *3*-$CrEDTA^-$, *x*-unknown and *y*-unknown

Table 1 Chromium concentration of chromium plating bath samples obtained by CZE and ion exchange separation (IE-AAS)

Sample No.	Cr(VI) (µg/mL) CZE	Cr(III) (µg/mL) CZE	Cr(VI), (µg/mL) IE-AAS	Cr(III) (µg/mL) IE-AAS	Cr-total (µg/mL) AAS
1	119.0	12.0	114.4	12.6	127.5
2	92.6	9.7	90.1	10.2	104.2
3	145.3	7.8	139.5	8.4	155.4
4	113.4	6.9	108.1	7.6	118.3

Applying t-test for comparing the data of chromium total obtained by both methods no significant differences were found [34]. In contrary, Cr(VI) found by CZE were systematically slightly higher than the respective values found after ion exchange separation. It seems that when applying the ion exchange method some Cr(VI) were reduced to Cr(III) during the absorption process. Thus, t-test applied for values obtained for Cr(VI) using the two methods for three samples showed significant differences. Extending this investigation, no significant difference was found comparing values obtained for total chromium by CZE and AAS (without previous separation) methods. The good agreement between AAS with CZE have been demonstrated earlier [29, 35].

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