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Determination of chromate ion in chromium plating baths using capillary zone electrophoresis with micellar solution

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Abstract

Chromate anion (CrO_4^{2-}) has been determined by capillary zone electrophoresis with on-column UV detection at 273 nm by using a negative power supply. A fused-silica capillary (53 cm × 0.05 mm I.D.) was employed and a high voltage of 20 kV was applied.

The addition of a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB) in the buffer solution reverses the direction of the electroosmotic flow (EOF) in the capillary, so that EOF augments the mobility of the anion. This results in an exceedingly short analysis time of under 2 min.

From migration time data, the electroosmotic mobility, the electrophoretic mobility of the micelle and apparent electrophoretic mobility of the chromate ion in the micellar solution were determined as a function of the concentration of TTAB.

Linear calibration for chromate ion was established over the concentration range 25–300 pg with a detection limit of 1.2 pg/nl by using a 0.01 *M* carbonate buffer and 5 m*M* TTAB solution (pH 10).

The method was applied to the determination of the chromate anion in a rinse water from chromium plating baths.

1. Introduction

There is a rapidly increasing demand for fast and reliable analytical methods for the determination of chemical forms of elements in environmental samples. The interest in chromium is motivated by the fact that its toxicity depends critically on its oxidation state. It has long been known that Cr(III) and Cr(VI) have very different biological and toxicological properties. Whereas Cr(III) is essential for mammals, Cr (VI) is considered to be a moderate to severe toxic agent [1]. Cr(III) and Cr(VI) enter the environment as a result of effluent discharge from steel works, electroplating, tanning industries, oxidative dyeing, chemical industries and cooling water towers.

In view of the difference between the oxidation states, and in order to follow the reaction pathways in the environment, it is increasingly important to monitor the concentration of the individual chemical species as well as the total concentration of chromium in the environment.

Of the numerous methods developed for chromium speciation, those which physically separate the individual species followed by direct quantification are preferred because they are relatively fast and require only minimal sample

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pretreatment. In this context, methods such as HPLC or flow injection analysis, coupled with photometric or spectrometric detection, have been employed most for the determination of chromium species [2–5] and the use of capillary zone electrophoresis (CZE) is emerging as an alternative technique.

In recent years CZE has been shown to be a highly efficient in the separation of small inorganic and organic cations and anions [6,7]. On the other hand, the use of CZE for the separation of metal species with good resolution has also been shown to be feasible [8–10].

Under a conventional CZE system, anions with an electrophoretic mobility higher than the electroosmotic mobility of the bulk electrolyte escape detection and it is necessary to reverse the polarity of the applied electric field. Therefore, the separation of highly mobile inorganic and organic anions usually requires longer times than the separation of cations and it is not possible to perform both analyses together in a single run. However, it has been shown that the addition of a cationic surfactant to the electrolyte significantly reduces the migration times for anionic species by reducing or reversing the electroosmotic flow (EOF).

Previously, some authors have reported a reversed EOF direction when a long-chain cationic surfactant, such as: cetyltrimethylammonium bromide [11,12], dodecyltrimethylammonium bromide [13] or tetradecyltrimethylammonium bromide (TTAB) [14], was added to the electrolyte. A cationic surfactant with a longer alkyl chain is preferred because the EOF can be suppressed or reversed at lower concentration. In this way, the influence on the constitution of the background electrolyte can be reduced [15].

In our experiments, TTAB was the cationic surfactant chosen; it is electrostatically attracted to the silanol groups on the inner wall of the capillary. It effectively shields these negative charges from the bulk of the electrolyte and creates a net positive wall charge.

In this paper, the determination of chromate anion by CZE with a micellar solution containing TTAB is described. The effect of the cationic surfactant concentration on electroosmotic and electrophoretic mobilities is also studied. The results were applied to the determination of the chromate ion in rinse waters from chromium plating baths.

2. Experimental

2.1. Instrumentation

An integrated capillary electrophoresis system ISCO (Lincoln, NE, USA) Model 3850, equipped with high-voltage power supply (0–30 kV) with a reversible polarity and vacuum injection control was used.

A 53 cm × 50 μm I.D. unmodified fused-silica capillary tube with a 33 cm distance from the injection point to the detector cell was employed. Detection was carried out by on-column measurements of UV absorption at 273 nm. All experiments were performed with an applied voltage of 20 kV.

Electropherograms were recorded using a Spectra-Physics (San Jose, CA, USA) SP-4270 integrator.

Samples were introduced hydrodynamically at the cathode (negative polarity) by vacuum for a constant period of time (5–10 s) depending on the desired volume of injection.

A Perkin-Elmer Model 2380 atomic absorption spectrometer was used to determine the total concentration of chromium in rinse water by atomic absorption spectrometry (AAS).

2.2. Reagents and solutions

Buffer solutions were prepared from sodium hydrogencarbonate, disodium tetraborate or disodium hydrogenphosphate dihydrate, from Merck (Darmstadt, Germany) by adding 0.1 *M* NaOH solution to adjust its pH to 10.

HPLC-grade TTAB, obtained from Scharlau, was used without further purification. TTAB solution was added to buffer solution to reverse of the direction of the EOF.

HPLC-grade methanol from Romil Chemicals and analytical-grade anthracene from Merck were used without further purification.

Stock standard solutions of sodium chromate were prepared by dissolution of an accurately weighed amount of the analytical-grade reagent supplied by Merck in a 0.01 *M* solution of the appropriate buffer, followed by dilution as required.

The pH of solutions was adjusted at 10 to obtain only the chromate anion in the solution, in absence of the rest of the chromium complexes, which can be at lower pH.

The acidic rinsewater sample was provided by Inoxcrom (Barcelona, Spain). No sample pretreatment other than dilution in buffer solution was required.

Purified (18 MΩ) water using a Millipore Milli-Q water purification system was used for all solutions.

The buffer and sample solutions were filtered through a 0.45 μm membrane filter from Lida (Kenosha, WI, USA) and were degassed by ultrasonication.

2.3. Procedure

Before sample injection, the capillary was washed with 0.1 *M* NaOH solution for 30 min, followed by rinsing with the buffer solution for 30 min. Between each injection the capillary was filled with the buffer solution using a syringe purge that flushed the entire capillary in a few seconds, and both ends of the tube were dipped into two separate beakers filled with the same buffer solution.

Vacuum injection sample is carried out by placing the inlet of the capillary into a vial of sample (75 μl). After a constant period of time (5–10 s), the inlet of the tube was returned to the beaker and a high voltage (20 kV) was applied.

3. Results and discussion

3.1. Control of electroosmotic flow

In a conventional CZE system, the detector is located near the cathode and the EOF direction is toward the cathode, hence the chromate anion moves toward the anode and is not detected because its electrophoretic mobility is higher than the electroosmotic mobility (μ_{eo}), whose directions are opposed. It might be imagined that this problem could be solved simply by reversing the polarity of the applied electric field. Fig. 1A shows the resulting electropherogram indicating that its peak is badly broadened, probably caused by the great difference in mobility values between the chromate and buffer [16].

However, this problem can be overcome by simultaneously reversing both the polarity of the applied electric field and the intrinsic direction of the EOF. Under these conditions, and in order

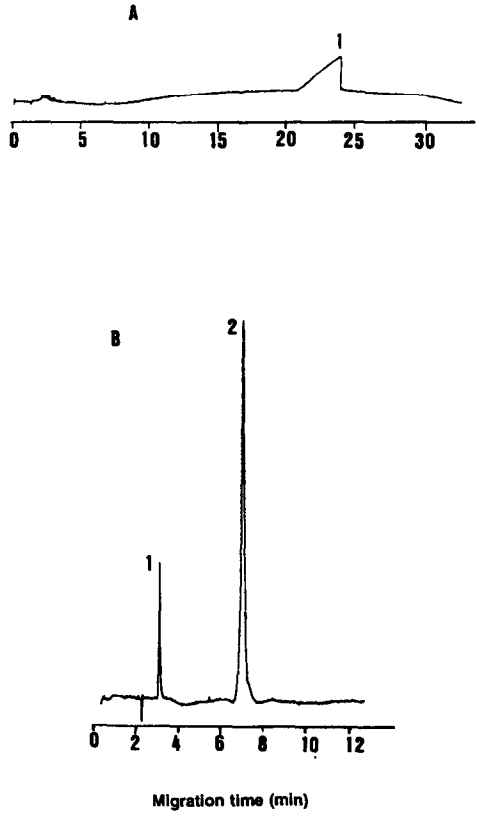

Fig. 1. Electropherograms of standard chromate solutions. Detection wavelength: 273 nm; fused-silica capillary (53 cm × 50 μm I.D.); negative power supply; 0.01 *M* borate buffer (pH 10); applied voltage: 20 kV. (A) No TTAB, 320 pg CrO_4^{2-}; (B) 20 m*M* of TTAB, 64 pg CrO_4^{2-}. Peaks: 1 = CrO_4^{2-}; 2 = anthracene.

Table 1
Effect of TTAB concentration on electroosmotic mobility and electrophoretic mobility of the micelle, using different buffer solutions at a constant concentration of 0.01 *M* at pH 10

TTAB (m*M*)	Phosphate				Carbonate				Borate			
	t_0	μ_{eo}	t_m	$\mu_{ep(m)}$	t_0	μ_{eo}	t_m	$\mu_{ep(m)}$	t_0	μ_{eo}	t_m	$\mu_{ep(m)}$
0	2.1	6.9			2.1	6.9			2.2	6.6		
0.5	9.5	−1.5	9.5	0	3.3	−4.4	3.3	0	3.4	−4.3	3.4	0
1.0	4.9	−3.0	4.9	0	3.3	−4.4	3.3	0	3.4	−5.2	2.8	0
5.0	3.6	−4.0	9.0	2.4	2.8	−5.2	7.9	3.4	2.8	−6.3	8.0	4.5
10.0	3.6	−4.0	8.3	2.2	2.8	−5.2	6.9	3.1	2.3	−6.3	8.0	4.5
20.0	2.9	−5.0	5.2	2.2	2.9	−5.0	7.4	3.0	2.3	−6.6	7.3	4.6
90.0	2.8	−5.2	6.1	2.8								

Applied voltage 20 kV. Negative power supply. t_0 and t_m in min; μ_{eo} and $\mu_{ep(m)}$ in 10^{-4} cm^2 V^{-1} s^{-1}.

to reduce the migration time of chromate ion, the cationic surfactant TTAB was added to the buffer solution. Table 1 shows the results obtained when different TTAB concentrations are added to the different buffer solutions. Reversed EOF (the negative sign of μ_{eo} means that the migration is toward the anode) was observed at less than the critical micelle concentration (CMC) of TTAB (its value is 3.4 m*M* [17]). As Table 1 shows, for the three buffers the EOF direction is reversed at 0.5 m*M* of TTAB.

3.2. Measurement of electroosmotic and micelle mobilities

The electroosmotic mobility is readily determined by measuring the migration time of methanol (t_0) and can be obtained from the equation [18]

$$\mu_{eo} = LL_D/Vt_0 \quad (1)$$

where L is the capillary length, L_D is the length of capillary to the detector cell and V is the applied voltage.

Methanol has been used to mark t_0 because is not associated with the micelles. Methanol is not detected by absorption of UV light but absorbs here due to the slight change of the refractive index [19].

The micelle mobility (μ_m) is determined by measuring the migration time of a fully solubilized solute, which is completely distributed in the micellar interior and moves with the same velocity of ionic micelles for time t_m. Anthracene has been used to mark t_m [20].

The micelle and electroosmotic mobilities are related by the relation:

$$\mu_m = \mu_{eo} - \mu_{ep(m)} \quad (2)$$

where $\mu_{ep(m)}$ is the electrophoretic mobility of the micelle.

By taking into account the sign of the migration direction, we can calculate $\mu_{ep(m)}$ from

$$\mu_{ep(m)} = [LL_D(1/t_m - 1/t_0)]/V \quad (3)$$

It should be noted that the directions of EOF and electrophoretic migration of micelles are opposite (Fig. 2).

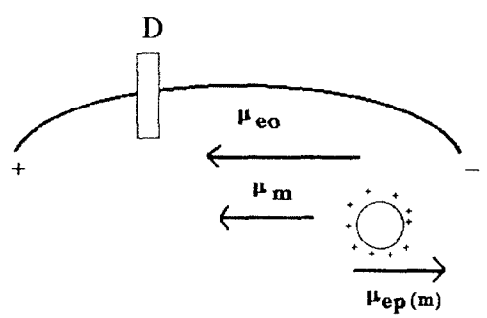

Fig. 2. Schematic illustration of mechanism with TTAB micelle in the buffer solution. Negative power supply. D = Detector; circle shows the cationic micelle.

In a series of experiments, the influence of the TTAB concentration in the buffer was investigated. As can be seen in Table 1, the electroosmotic mobility obtained is always lower than in absence of cationic surfactant, but it slightly increases as the TTAB concentration increases. On the other hand, the micelles begin to form in the solution at a TTAB concentration between 1.0 and 5.0 m*M*. This value is in accordance with the CMC value of TTAB (3.4 m*M*). Moreover, when the micelles are formed no appreciable change in the magnitude of the $\mu_{ep(m)}$ is noted.

Table 1 also shows that μ_{eo} is greater than $\mu_{ep(m)}$. This means that the micelles are transported toward the anode but exhibit a slower net mobility than the bulk aqueous phase.

3.3. Measurement of electrophoretic mobilities

In the absence of cationic surfactant, and taking into account the electropherogram of Fig. 1A, the electrophoretic mobility of the chromate anion in the buffer solution, $\mu_{ep}(CrO_4^{2-})$, can be calculated as the sum of the observed mobility of the anion and the electroosmotic mobility (Fig. 3A). By taking into account the sign of the migration direction, $\mu_{ep}(CrO_4^{2-})$ may be calculated from the following equation

$$\mu_{ep}(CrO_4^{2-}) = (LL_D(1/t_R + 1/t_0))/V \quad (4)$$

where t_R is the migration time of chromate anion.

It should be noted that the direction of electrophoretic mobility of the anion is the reverse of that of EOF.

Table 2 shows for the three buffers that $\mu_{ep}(CrO_4^{2-})$ is greater than μ_{eo} (Table 1). For this reason the chromate ion escapes detection with a positive-polarity power supply.

When the cationic surfactant is added (Fig. 3B) the difference between the observed mobility of chromate ion and the electroosmotic mobility can be considered to be the apparent electrophoretic mobility of the chromate in the micellar solution ($\mu^*_{ep}(CrO_4^{2-})$) and can be calculated from the equation

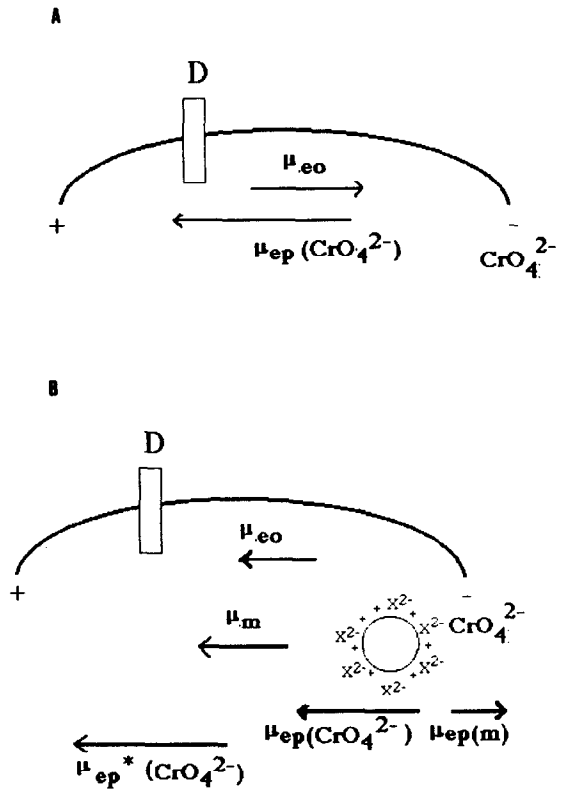

Fig. 3. Schematic illustration of mechanism. Negative power supply. (A) Chromate anion in the capillary without TTAB in the buffer solution; (B) chromate anion and TTAB micelle in the capillary. $X^{2-} = CrO_4^{2-}$.

$$\mu^*_{ep}(CrO_4^{2-}) = [LL_D(1/t_R - 1/t_0)]/V \quad (5)$$

In this case the electrophoretic and electroosmotic mobilities are in the same direction: toward the anode.

Fig. 1B shows a good symmetrical peak obtained under these conditions, and the migration time of the chromate is much less than in absence of TTAB.

Apparent electrophoretic mobilities of the chromate, $\mu^*_{ep}(CrO_4^{2-})$, as function of TTAB concentration are shown in Table 2. It can be seen that the addition of TTAB reduces considerably the migration time of the chromate anion (t_R) for the three buffers, which allows the chromate ion to be determined in under 2 min.

When micelles are formed, the anion is electrostatically adsorbed on the surface of the

Table 2
Effect of TTAB concentration on migration time and electrophoretic mobilities of chromate

TTAB (m*M*)	Phosphate			Carbonate			Borate		
	t_R	μ^*_{ep}	μ_{ep}	t_R	μ^*_{ep}	μ_{ep}	t_R	μ^*_{ep}	μ_{ep}
0	19		−7.7	22		−7.6	24		−7.2
0.5	1.6	7.6		1.2	7.7		1.3	6.9	
1.0	1.5	6.7		1.2	7.7		1.3	6.0	
5.0	1.9	3.6		1.7	3.4		1.7	2.3	
10.0	2.3	2.3		2.3	1.1		2.4	−0.2	
20.0	2.4	1.1		2.9	0.0		3.1	−1.9	
90.0	2.8	0.0							

Conditions as in Table 1. t_R in min; μ^*_{ep} and μ_{ep} in 10^{-4} cm^2 V^{-1} s^{-1}.

cationic micelle, reducing the migration velocity of the anion. This can be observed in Table 2, where $\mu^*_{ep}(CrO_4^{2-})$ decreases when the TTAB concentration increases. When the TTAB concentration reaches certain values (90 m*M* for phosphate, 20 m*M* for carbonate and slightly higher than 10 m*M* for borate buffer), $\mu^*_{ep}(CrO_4^{2-})$ is zero.

Table 2 also shows that, for carbonate and phosphate buffers, the observed mobility of the chromate is greater than electroosmotic mobility. However, for borate buffer (10 m*M* and 20 m*M* of TTAB) the inverse phenomenon is observed, so $\mu^*_{ep}(CrO_4^{2-}) > 0$.

3.4. Choice of experimental conditions

By comparing of the results with the different buffers, it seems that μ_{eo} and $\mu_{ep(m)}$ values follow the order: borate > carbonate > phosphate, which is the inverse of that found for $\mu^*_{ep}(CrO_4^{2-})$.

The different behaviour observed for the tree buffers can be understood in terms of the electrostatic adsorption of the corresponding anion of the buffer on the surface of the micelle, which competes for the chromate anion.

Borate, a Lewis acid [21], is found in mild alkaline solutions as a mixture of $B(OH)_4^-$ and $B(OH)_3$. At pH 10, the predominant form is $B(OH)_4^-$, while the carbonate anion is in transition between 50% HCO_3^- and 50% CO_3^{2-} and the phosphate is in the solution as HPO_4^{2-}. When the borate anion is in the solution, since it is a Lewis acid, it forms a polar bond with the hydroxide ions, acquiring a greater mobility than the other buffers. This fact means that the electroosmotic mobility will be greater than for carbonate and phosphate (Table 1), and as a consequence the absorption of chromate anion on the micelle is favoured over that of borate. This fact is reflected in a lower apparent electrophoretic mobility of the chromate in the micellar solution, $\mu^*_{ep}(CrO_4^{2-})$, than in the other buffers (Table 2).

On the other hand, additional data on the influence of TTAB concentration on the electric current (I) in the capillary for the different buffers are shown in Table 3. Electric current

Table 3
Comparison of current among three buffer solutions at different TTAB concentrations

TTAB (m*M*)	I (μA)		
	Phosphate	Carbonate	Borate
0	14	10	14
0.5	15	11	15
1.0	17	17	20
5.0	20	19	26
10.0	20	20	27
20.0	20	25	31
90.0	37		

Conditions as in Table 1.

increases as the TTAB concentration increases. Moreover, the results indicate that the lowest electric current was for carbonate buffer at the same concentration of surfactant. This fact contributes to minimize the rise in temperature of the liquid in the capillary [22].

From all these reasons, carbonate was chosen as best buffer to determine chromate anion in aqueous solutions. A TTAB concentration value of 5 m*M* was used because the migration time (t_R) of chromate was short enough (1.7 min) and micelles had already been formed. Fig. 4 shows a good symmetrical peak obtained under these conditions.

3.5. Quantification

From the experimental conditions chosen (0.01 *M* carbonate and 5 m*M* TTAB), detection limits were calculated as the amount of sample equivalent to a signal due to the analyte equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal [23]. The detection limit obtained was 1.2 pg of CrO_4^{2-}/nl.

The relative standard deviation (R.S.D) for peak areas and migration times, calculated from injections of 150 pg of standard chromate, was 3.5%.

Peak areas change with the chromate ion concentration, indicating a linear relationship in the range 25 to 300 pg of chromate. The regression equation obtained was $A = -18.0 + 34.4C$, where A is the peak area and C the chromate amount in pg, and the correlation coefficient (r) was 0.997 ($n = 7$). Therefore this method can be employed for the quantitative analysis of the chromate anion.

3.6. Application to rinse waters from chromium plating baths

On the basis of the results obtained for chromate standard solutions, the application of the CZE method to determine chromate anion concentrations in rinsewater samples was attempted.

A sample from chromium plating baths (Inoxcrom) was analyzed. This sample is an acidic (pH 2.6) solution containing Cr(VI) as chromic acid.

After the appropriate dilution (1:10) in 0.01 *M* carbonate buffer solution at pH 10, the pe (= Eh159.16) value of the solution was measured, and was found to be 7.0. Under these experimental conditions of pe and pH and in order to know the predominant species in this aqueous solution, distribution species–pH and pe–pH diagrams for chromium were performed using equilibrium constants given in ref. 24. From the diagrams we can assure that only the chromate anion is present in the solution.

The sample was injected directly into the CZE system and the electropherogram in Fig. 5 was obtained. It can be seen that only one peak was obtained; no other peaks were observed. From the electropherogram, the chromate concentration in the sample was determined.

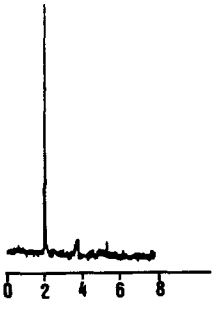

Fig. 4. Electropherogram of standard chromate solution. Micellar solution 5 m*M* TTAB in 0.01 *M* carbonate buffer (pH 10); sample amount 150 pg CrO_4^{2-}, injection volume 5 nl. Other conditions as in Fig. 1.

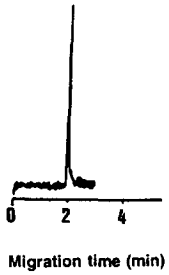

Fig. 5. Electropherogram of commercial sample. Micellar solution 5 m*M* TTAB in 0.01 *M* carbonate buffer (pH 10); dilution (1:10); injection volume 10 nl. Other conditions as in Fig. 1.

The same sample was also analyzed by AAS. The results are 283 and 271 mg of CrO_4^{2-}/l, using CZE and AAS, respectively. Good agreement between the two methods was observed. As AAS gives the total metal concentration, this agreement corroborates that all chromium metal present in the sample is in the form of chromate anion and no other species of this metal are formed under the experimental conditions used.

Finally, we want to point out that the CZE technique, using micellar solution, allows a rapid determination (less than 2 min) of the chromate anion in real samples.

Furthermore, the addition of TTAB to the buffer solution reverses the direction of the EOF and opens up new possibilities for the determination of highly mobile inorganic anions; it may be carried out in a single run with short analysis times in the most diverse matrices and with no sample pretreatment other than a dilution procedure.

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