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Simultaneous determination of Cr(III), Fe(III), Cu(II) and Pb(II) as UV-absorbing EDTA complexes by capillary zone electrophoresis

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Abstract

Capillary zone electrophoresis (CZE) with on-column UV detection was used to separate and determine Cr(III), Fe(III), Cu(II) and Pb(II) complexes with EDTA. Distribution species–pH diagrams showed that, under the experimental conditions chosen (pH 5.5), $[\text{Me-EDTA}]^-$ and $[\text{Me-EDTA}]^{2-}$ species for trivalent and divalent metals, respectively, were present. By adding a cationic surfactant, such as TTAB (tetradecyltrimethylammonium bromide), to the background electrolyte, an improvement in the peak shapes and shorter migration times were achieved. The chelating complexes showed the following order of mobility in electropherograms: $[\text{EDTA}]^{2-} > [\text{Cu-EDTA}]^{2-} > [\text{Pb-EDTA}]^{2-} > [\text{Cr-EDTA}]^- > [\text{Fe-EDTA}]^-$. At 225 nm under a negative applied voltage of 30 kV, using a capillary of 30.5 cm effective length, in 0.1 M acetate buffer and 0.1 mM TTAB as carrier solution, the complexes were determined within 6 min, but the resolution of the Cu(II) and Pb(II) chelates was poor. However, by using a capillary of 60 cm effective length, simultaneous separation of these chelates the EDTA was achieved. Factorial design was used to investigate the effects of chromium, excess of EDTA and boiling time of the solution on the formation of the $[\text{Cr-EDTA}]^-$ complex. A fitting model was found in which the EDTA concentration was a significant factor. The detection limits of all chelates were in the range 6–27 μM .

1. Introduction

Many methods for the determination of heavy metals have been reported, but often they are tedious and time consuming since they involve preliminary separation steps based on solved

extraction, coprecipitation or ion exchange followed by inductively coupled plasma or atomic absorption spectrometric determination [1,2].

In recent years, capillary zone electrophoresis (CZE) has been shown to be a highly efficient technique for the separation and determination of both organic and inorganic cations and anions [3–7]. The determination and speciation of some metals without using chelating agent have been reported [8,9]. By coupling the electrophoresis

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with metal complex formation, the separation and detection limit of metals have been enhanced. Weston et al. [10] described indirect UV detection for the separation of Group IA, IIA, Mn, Cd, Fe(II), Co, Pb, Ni, Cu, Zn and lanthanide mixtures by CE. In this method, α -hydroxyisobutyric acid was utilized as a complexing agent to aid the separation. On the other hand, Swaile and Sepianak [11] used 8-hydroxyquinoline-5-sulfonate in the mobile phase, so complexes of Ca, Mg and Zn metals were formed within the capillary. In this method, an on-column laser-based fluorescence detection scheme was employed. Neither of the above organic compounds [10,11] forms complexes with Cr(III) [12].

The use of EDTA as a chelating agent in CZE has been reported for the determination of alkaline earth metal ions [13]. EDTA is by far the most widely used chelating agent in analytical chemistry. It forms strong 1 : 1 complexes with many metal ions regardless of the charge of the metal. Several ions of complex nature or high charge react slowly with EDTA. Thus, chromium (III) ions bind water molecules so strongly that these are displaced by EDTA only very slowly, during the course of several days [14].

There are many contradictory reports about the reaction of Cr(III) with EDTA [15–18]. Hamm [19] reported that the reaction rate is independent of the EDTA concentration. Later, it was reported that the reaction could be described as second-order, depending on the EDTA concentration [20]. Various compounds have been reported to have a catalytic effect on this reaction [20,21].

Our aim in this work was to develop a procedure for the simultaneous determination of Cr(III), Fe(III), Cu(II) and Pb(II) by CZE as UV-absorbing EDTA chelates. The experimental conditions of the reaction between chromium and EDTA were investigated by using a factorial experimental design. Based on the distribution species–pH diagrams [22–24], the optimum pH range for the determination of Cr(III), Fe(III), Cu(II) and Pb(II) chelates was found. The

method was applied to the determination of heavy metals in waste waters from tanning processes.

2. Experimental

2.1. Instrumentation

An ISCO (Lincoln, NE, USA) Model 3850 integrated capillary electrophoresis system equipped with high voltage up to 30 kV and reversible polarity was used. Samples were introduced by applying a 3.4-kPa vacuum at the detector end of the capillary. Separations were performed with unmodified fused-silica capillary columns of length 46.5 cm (30.5 cm to the UV detector) and 80 cm (60 cm to the UV detector) with 0.05 mm I.D. A Model 4270 integrator (Spectra-Physics, San José CA, USA) was used to record all data.

A Shimadzu UV-240 UV–Vis recording spectrophotometer was used to record the absorption spectra of metal–EDTA complexes. The pH of solutions was monitored with a Crison Digilab 517 pH meter.

2.2. Reagents and solutions

Stock standard solutions of 1000 mg/l CrCl₃, FeCl₃, Pb(NO₃)₂, CuCl₂, ZnCl₂ and AlCl₃ and EDTA (solid), purchased from Merck, were used to prepare dilute metal–chelate solutions. Stock standard solutions of 0.2 M sodium acetate and acetic acid (Merck), prepared separately, were used to prepare dilute buffer solutions [25]. HPLC-grade TTAB (tetradecyltrimethylammonium bromide), purchased from Scharlau, was used. Super-pure methanol from Romil Chemicals was used as a marker to measure the rate of electroosmotic flow. Purified (18 M Ω) water, obtained using a Millipore Milli-Q water-purification system, was used for all solutions. All solutions were filtered through a 0.45- μ m membrane filter and were degassed by ultrasound.

2.3. Procedure for electrophoresis

The capillary tube was rinsed with deionized water for several hours, then equilibrated with carrier solution for 40 min before the first run. Between each injection the capillary was filled with carrier solution using a syringe purge that flushed the entire capillary in a few seconds. Both ends were dipped into two separate beakers filled with the same carrier solution. The sample solution was introduced into the anodic or cathodic end of the capillary by vacuum injection. Lastly, a high voltage was applied.

2.4. Metal complex preparation

The chelates of Fe(III), Cu(II) and Pb(II) with EDTA were prepared from a mixture of the corresponding metal standard and EDTA solution in 0.05 M acetate–acetic acid and buffer (pH 5.5) at room temperature. An examination of the effects of Cr concentration, excess EDTA concentration and boiling time on the absorbance (A) of [Cr–EDTA] complex formed was carried out by a classical univariate method and by factorial design [26,27]. The fitting model

$$A = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (1)$$

Table 1
The 2^3 factorial experimental design and results of experiments

Expt. No.	x_1	x_2	x_3	H_1	H_2	H_3	H_{mean}	S.D.	H^*
1	-1	-1	-1	3.40	3.20	3.30	3.30	0.10	3.30
2	+1	-1	-1	5.80	5.70	5.80	5.77	0.058	5.76
3	-1	+1	-1	3.35	3.40	3.55	3.43	0.10	3.34
4	+1	+1	-1	6.85	6.90	6.80	6.85	0.05	6.74
5	-1	-1	+1	3.00	3.10	3.00	3.03	0.058	3.02
6	+1	-1	+1	6.00	6.10	6.00	6.03	0.058	6.03
7	-1	+1	+1	3.70	3.40	3.50	3.53	0.15	3.61
8	+1	+1	+1	6.60	6.30	6.20	6.37	0.208	6.46

x_1 , x_2 , x_3 are chromium concentration, EDTA concentration and boiling time, respectively. H (cm) is the experimental peak height and H^* is the calculated value from the fitted model. Experimental conditions: -20 kV, 225 nm, 0.05 M acetate and 0.5 mM TTAB carrier solution (pH 5.5). A fused-silica capillary of 46.5 cm \times 0.05 mm I.D. was used.

allowed us to estimate the effects in which we were interested, and also their possible interactions (b_{12} , b_{13} , b_{23} and b_{123}).

3. Results and discussion

3.1. Effects of EDTA and boiling time on the formation of [Cr–EDTA]⁻ complex

Three factors were taken into account, each at two levels: chromium concentration (x_1), EDTA concentration (x_2) and boiling time (x_3). The concentration levels were 0.38 and 0.77 mM for Cr(III) and 1.07 and 5.37 mM for EDTA. The boiling time of the solution was 10 and 20 min. The heights of the peaks (H) obtained by CZE were the responses studied. Samples were analysed in triplicate. The experimental design and the results obtained are shown in Table 1. Calculations were made using Statgrafics Software Version 5.0, which yields the following expression:

$$H = 48.89 + 14.66x_1 + 2.56x_2 + 0.988x_1x_2 - 1.388x_1x_2x_3 \quad (2)$$

It was verified that this function was adequate [26]. The third factor b_3 , and also the interactions b_{13} (Cr and t) and b_{23} (EDTA and t),

proved insignificant. On replacing the coded variables with real variables, the fitted model was

$$H = 23.58 + 35.62[\text{Cr}] - 5.87[\text{E}] - 1.23t + 12.29[\text{Cr}][\text{E}] + 0.38[\text{E}]t + 2.13[\text{Cr}]t - 0.66[\text{Cr}][\text{E}]t \quad (3)$$

where $[\text{E}]$ = EDTA concentration, $[\text{Cr}]$ = chromium concentration and t = boiling time.

From the factorial experiment investigation, we concluded that the excess EDTA for low concentrations of Cr(III) has a significant effect on promoting the attainment of equilibrium. It

seems that this complex will dissociate into chromium cation and EDTA at low excess concentrations of EDTA. Boiling for 10 min was sufficient for completion of the reaction. Good agreement between the experimental design conclusions and the univariate method was obtained. For an EDTA to metal molar ratio of 5 and higher and with boiling for 5–10 min the chelate was formed quantitatively. It was also

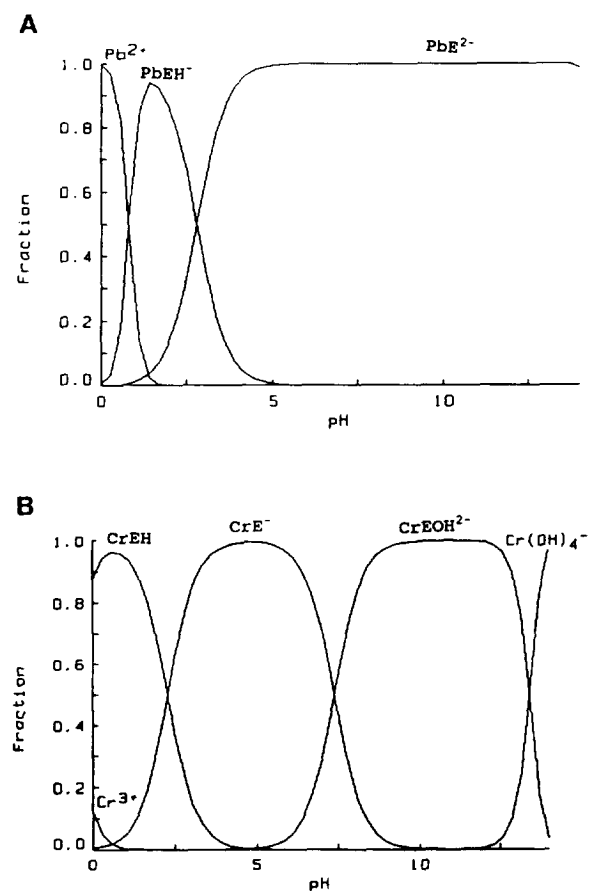


Fig. 1. Distribution species-pH diagrams. Total metal concentration, 20 $\mu\text{g}/\text{ml}$. (B) For Cr-EDTA complex; similar diagrams were obtained for Fe-EDTA and Al-EDTA. (A) For Pb-EDTA; similar diagrams were obtained for Cu-EDTA and Zn-EDTA. E = EDTA.

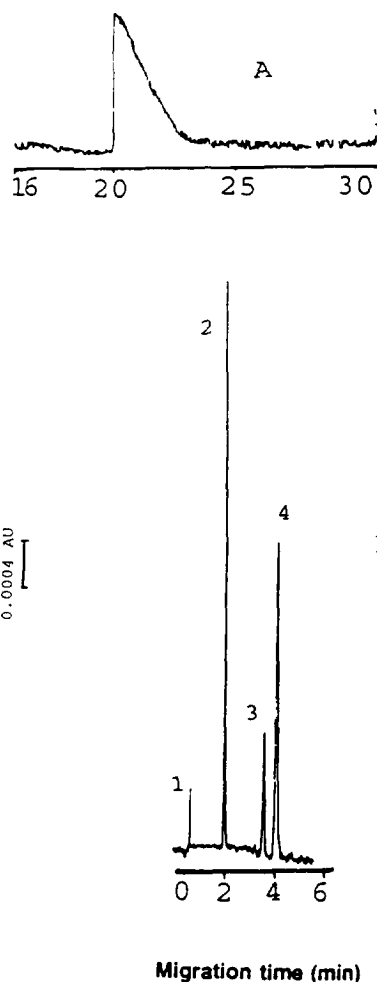


Fig. 2. Electropherogram obtained at 20 kV, negative voltage applied. Detection wavelength, 225 nm; fused-silica capillary (46.5 cm \times 50 μm I.D.); 0.05 M acetate buffer (pH 5.5); sampling time, 2 s (A) No TTAB, 40 $\mu\text{g}/\text{ml}$ Cr(III); (B) 0.5 mM TTAB in carrier solution, 20 $\mu\text{g}/\text{ml}$ of each metal. Peaks: 1 = NO_3^- ; 2 = Cu-EDTA, Pb-EDTA, EDTA; 3 = Cr-EDTA; 4 = Fe-EDTA.

observed that the formation of the $[\text{Cr-EDTA}]^-$ complex at room temperature lasted several days, which has also been reported on the literature [14]. We observed that, after 3 h at 60°C, the peak height on the electropherogram was smaller than that obtained for the solution boiled for 10 min.

3.2. Detection of metal complexes

The distribution species–pH diagrams (Fig. 1) showed that in the pH range 4.0–6.5, the following species were present: $[\text{Cr-EDTA}]^-$, $[\text{Fe-EDTA}]^-$, $[\text{Al-EDTA}]^-$, $[\text{Zn-EDTA}]^{2-}$, $[\text{Cu-EDTA}]^{2-}$ and $[\text{Pb-EDTA}]^{2-}$. This information was in good agreement with the peaks obtained in the electropherograms. The maxima of the absorption spectra of these species were at the wavelengths 225 nm for $[\text{Cr-EDTA}]^-$, 260 nm for $[\text{Fe-EDTA}]^-$ and $[\text{Cu-EDTA}]^{2-}$ (both broad shaped) and 245 nm for $[\text{Pb-EDTA}]^{2-}$, while $[\text{Zn-EDTA}]^{2-}$ and $[\text{Al-EDTA}]^-$ absorb only negligibly in the range 190–215 nm. The molar absorptivities of $[\text{Cr-EDTA}]^-$, $[\text{Cu-EDTA}]^{2-}$, $[\text{Pb-EDTA}]^{2-}$ and $[\text{Fe-EDTA}]^-$ were 2000–4500 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. The highest

value was found for iron. EDTA also absorbed in the aforementioned range, having a maximum at 202 nm. In our experiments, detection was generally carried out at 225 nm, as the complexes studied can be determined simultaneously. Nevertheless, depending on the solute, a suitable wavelength can be chosen in order to achieve the highest sensitivity.

3.3. Modification of electroosmotic flow

Table 2 shows the migration times of the chelates and of methanol for different buffer and TTAB concentrations. The electrophoretic mobilities of $[\text{M-EDTA}]^-$ (trivalent metals) or $[\text{M-EDTA}]^{2-}$ (divalent metals) are higher than and in the opposite direction to those for electroosmotic flow. Without TTAB in the carrier solution, the peak shapes obtained were broad and the migration times were long (Fig. 2A). To control the electroosmotic flow-rate, a cationic surfactant (TTAB) was used, which was found to provide sharp peaks for the organic mixture [28]. From the Table 2, it can be seen that without a modifier the electroosmotic mobility decreases when the buffer concentration increases, as the zeta potential is directly proportional to the

Table 2
Comparison of migration times (min) of metal–EDTA complexes and methanol at different buffer and surfactant concentrations

Buffer (M)	Complex	TTAB (mM)				
		0	0.1	0.2	0.4	0.5
0.025	M–EDTA ^a	7.01	4.35	3.78	3.27	2.84
	Cr–EDTA	46.0	7.82	6.21	4.89	4.03
	Fe–EDTA	>50	9.05	6.99	5.49	4.34
	CH ₃ OH	6.7	19.63		23.0	11.6
0.05	M–EDTA ^a	6.45	4.06	3.73	2.99	2.64
	Cr–EDTA	20.6	6.9	6.04	4.31	3.83
	Fe–EDTA	34.0	8.09	6.86	4.71	4.04
	CH ₃ OH	8.4	32.8		14.9	10.60
0.1	Cu–EDTA ^a	5.68	3.82	3.52	2.77	2.57
	Cr–EDTA	13.08	6.27	5.54	3.89	3.50
	Fe–EDTA	17.09	7.93	6.32	4.26	3.80
	CH ₃ OH	8.50	>35		13.3	9.50

Experimental conditions: –20 kV, except for methanol at TTAB concentrations of 0 and 0.1 mM a positive voltage was applied; sampling time, 2 s; 40 $\mu\text{g}/\text{ml}$ of each metal. Other conditions as in Table 1.

^a M is Cu or Pb.

thickness of the double layer, which decreases in concentrated solutions. For up to 0.1 mM TTAB, the direction of the electroosmotic flow is still towards the cathode, whereas between 0.2 and 0.3 mM the electroosmotic flow-rate is too small as the negative peak of methanol was not obtained even after 40 min. At 0.4 mM TTAB the electroosmotic flow is reversed (towards the anode) as the cationic surfactant is absorbed in the inner wall of the capillary, becoming the dominant factor in determining the interfacial zeta potential. It was verified that at 0.5 mM TTAB the micelles were not formed. Hence TTAB offered an improvement in the peak shape (Fig. 2B) and made the analysis faster.

3.4. Separation of metal complexes

At 0.05 M buffer and 0.5 mM TTAB as the carrier solution, the peaks obtained were sharp, the migration times short and the results reproducible. However, under such conditions the separation of EDTA from $[M-EDTA]^{2-}$ ($M = Pb, Cu$) was not possible, even when a negative voltage of 30 kV was applied. However, at 0.1 M of buffer and 0.1 mM TTAB as the carrier solution, the separation was achieved when the voltage applied was ≥ 23 kV (Fig. 3). We believe that two factors contributed to making the peaks sharper (increasing the resolution) at higher concentrations of carrier solution: (1) the stacking effect and (2) a lower electroosmotic flow-rate. However, under the conditions studied it was not possible to separate $[Cu-EDTA]^{2-}$ and $[Pb-EDTA]^{2-}$ species. The difference in migration times in the best case was 0.06 s. The determination of these species can be achieved by changing the wavelength. At 270 nm only $[Cu-EDTA]^{2-}$ absorbs, while the sum of $[Pb-EDTA]^{2-}$ and $[Cu-EDTA]^{2-}$ can be determined at 245 nm, at which $[Pb-EDTA]^{2-}$ has the highest sensitivity. However, by using a greater capillary length (80 cm), the separation of $[Cu-EDTA]^{2-}$ and $[Pb-EDTA]^{2-}$ was achieved (Fig. 4) and the resolution was 2.32 for both species. The resolutions was calculated as $R_s = \Delta t/w$, where Δt is the difference in migration times

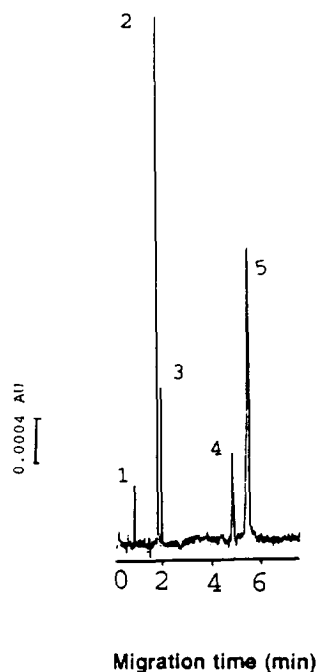


Fig. 3. Electropherogram obtained for a mixture of standard metal solutions in excess of EDTA at -30 kV; 0.1 M acetate and 0.1 mM TTAB in carrier solution; 20 $\mu\text{g}/\text{ml}$ of each metal ion. Other conditions as in Fig. 2. Peaks: 1 = NO_3^- ; 2 = EDTA; 3 = Cu-EDTA, Pb-EDTA; 4 = Cr-EDTA; 5 = Fe-EDTA.

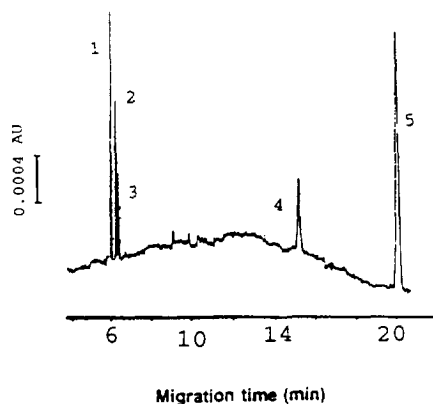


Fig. 4. Electropherogram obtained for a mixture of standard metal solutions in excess of EDTA. Fused-silica capillary (80 cm \times 50 μm I.D.); 40 $\mu\text{g}/\text{ml}$ Cu and Pb, 20 $\mu\text{g}/\text{ml}$ Cr and Fe. Other conditions as in Fig. 3. Peaks: 1 = EDTA; 2 = Cu-EDTA; 3 = Pb-EDTA; 4 = Cr-EDTA; 5 = Fe-EDTA.

between two peaks and w is the width of each peak [29].

3.5. Calibration graphs, detection limit and reproducibility

The calibration graphs obtained for metal complexes at their respective maximum wavelengths were linear up to 60 mg/l, using peak areas (PA) or peak heights (PH), when the sampling time was 2 s. The correlation coefficients were 0.997–0.999 ($n = 6$). The detection limits calculated [30] were 16 μM for Cr, 6.4 μM for Fe, 15 μM for Cu and 27 μM for Pb. At 225 nm the sensitivity of Fe, and Pb determination decreased by 30%, whereas for Cu it decreased by 20%.

The relative standard deviations of peak heights and peak areas for successive injections were found to be less than 6%, and for the migration time it was below 1% ($n = 8$). The mean values obtained for PH, PA and migration times (t_r) with their standard deviations (S.D.) and electrophoretic mobilities (μ_{ep}) are given in Table 3.

In a CZE system, the main factors affecting the separation are the buffer composition, pH and applied voltage. Different voltages in the range 10–30 kV (negative power supply) were applied. The slopes increased with decreasing voltage, but the peaks were broader and the resolution worse. On increasing the voltage, the peaks obtained became sharper and the resolution much better. For all applied voltages, the calibration graphs obtained by regression analy-

sis were linear with correlation coefficients of 0.994–0.999.

The sampling time when a 20 $\mu\text{g/ml}$ [Cr-EDTA]⁻ standard solution was injected was varied from 1 to 65 s. The PH increased linearly over the sampling time from 1 to 10 s ($r = 0.992$), whereas the PA increased from 1 to 65 s ($r = 0.996$). On increasing the injection interval, the peaks became broader and the separation efficiency was poorer, at least for the peaks that have comparable migration times, as is the case with EDTA, Cu and Pb complexes. The sample and carrier solution had similar conductivities (0.05 M buffer concentration of sample and carrier solution), so the stacking effect was not present to improve the peak shapes. On the other hand, it appears that the injected sample volume can be increased when the buffer is 0.1 M and the high voltage applied is around -30 kV. In these cases, two factors with opposite effects affect the sensitivity, and these parameters could be optimized to achieve the optimum conditions.

3.6. Application to waste waters from tanning industries

A suitable volume of the unknown sample was transferred into a 100-ml erlenmeyer flask and the pH was adjusted to 5.5 by adding ca. 15 ml of 0.1 M acetate buffer. Then 0.2 g of EDTA was added and the mixture boiled for 10 min. The violet colour of [Cr-EDTA]⁻ formed very rapidly. After allowing the solution to cool it was transferred quantitatively into a 50-ml measuring

Table 3
Results obtained for migration time (t_r), peak heights (PH), peak areas (PA) (mean \pm S.D.) and electrophoretic mobility (μ_{ep}) with successive injections ($n = 8$)

Complex	t_r (min)	PH (cm)	PA	μ_{ep} ($10^{-4} \text{ cm}^2/\text{v} \cdot \text{s}$)
Cu-EDTA ^a	2.64 \pm 0.011	4.8 \pm 0.22	9987 \pm 594	-3.4
Cr-EDTA	3.83 \pm 0.013	4.5 \pm 0.21	9789 \pm 520	-2.0
Fe-EDTA	4.04 \pm 0.014	11.5 \pm 0.43	27178 \pm 1426	-1.8

Experimental conditions: 40 $\mu\text{g/ml}$ of each metal in excess EDTA solution (1 : 5); 0.05 M acetate and 0.5 mM TTAB in carrier solution. Other conditions as in Table 2

^a Under such conditions only one peak was obtained for Pb and Cu chelates.

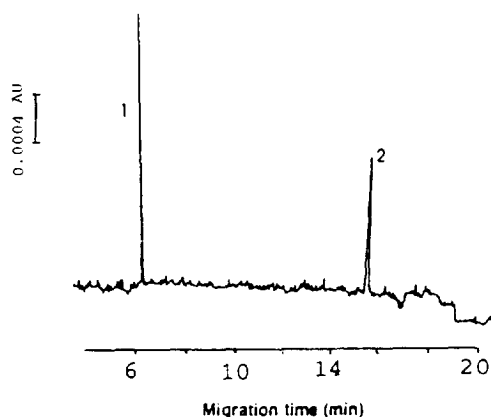


Fig. 5. Electropherogram of a tannery sample obtained at -30 kV; 0.1 M acetate and 0.1 mM TTAB in carrier solution (pH 5.5); Fused-silica capillary (80 cm \times 50 μ m I.D.). Sample preparation: diluted, pH adjusted to 5.5, Me-EDTA formed by boiling for 10 min in excess EDTA, filtered, degassed and injected. Peaks: 1 = EDTA; 2 = Cr-EDTA, 26.14 μ g/ml Cr(III).

flask and diluted to volume with 0.1 M acetate buffer. After homogenization the solution was filtered through a 0.45 - μ m filter, degassed and injected directly into the CZE system. The final concentration of Cr(III) in the prepared solution has to be 3 – 60 μ g/ml. Depending on the particular application, this procedure can be modified.

Waste waters from a tanning process (Colomer y Munmany, Barcelona, Spain) were analysed. After the appropriate dilution and complexation according to the above procedure, only Cr(III) was found (Fig. 5). The chromium content in the sample was 653.5 μ g/ml.

4. Conclusions

The absorptivity curves of $[\text{Cr-EDTA}]^-$, $[\text{Fe-EDTA}]^-$, $[\text{Cu-EDTA}]^{2-}$, $[\text{Pb-EDTA}]^{2-}$ and $[\text{EDTA}]^{2-}$ showed maxima in the wavelength range 200 – 270 nm and in the pH range 5 – 6 , which are suitable for analytical purposes. This work demonstrated that CZE provides fast and highly efficient separations of these cations as UV-absorbing chelates with EDTA. Excellent agreement between data taken from distribution

diagrams and peaks of the electropherograms were observed. The separation was improved by increasing the capillary length and voltage.

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