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Determination of EDTA in used fixing solutions by capillary electrophoresis

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Abstract A capillary electrophoretic method for the determination of EDTA has been developed. EDTA was converted to Ni(II)-EDTA prior to separation, separated from Fe(III)-EDTA, thiosulphate, bromide and polythionates using a fused silica capillary (57 cm × 75 μm I.D.) filled with a borate buffer (50 mmol L^{-1}; pH 8.5; applied voltage, 30 kV) and detected at 214 nm. The separation time is about 6 min. The detection limit achieved is 2×10^{-6} mol L^{-1} for EDTA. This method was applied for the determination of free EDTA in used fixing solutions.

Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used as metal-masking additive in various industrial branches. Like other aminopolycarboxylic acids, its release into the environment may affect the distribution of metals within the aquatic ecosystem and may remobilise heavy metals from sediments. For instance, free EDTA can be present in the fixing solutions used for photography and should be monitored before and during their decomposition by electrolytic oxidation.

A variety of chromatographic methods have been developed for the analysis of EDTA. Gas chromatography involves a preliminary derivatisation step of the carboxylic group by esterification which is complicated and time-consuming [1–3]. Alternatively, EDTA and other aminopolycarboxylic acids may be determined as their negatively charged iron(III) [4–6] or copper(II) [7–9] complexes by ion chromatography or by ion-pair high-performance liquid chromatography (HPLC). However, these HPLC methods are not applicable to fixing solution samples which contain large amounts of UV absorbing ions such as $FeEDTA^-$, thiosulphate, bromide, polythionates.

Therefore, a simple and quick capillary electrophoretic (CE) technique for the determination of EDTA in fixing solutions is developed. It is based on a pre-capillary complexation of free EDTA with Ni(II) ions followed by capillary electrophoretic determination of the negatively charged chelate using direct UV detection at 214 nm.

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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 i.d. and 57 cm long (50 cm to the detector) were used. The solutes were injected in the hydrodynamic mode by overpressure ($3.43 \cdot 10^3$ Pa). System Gold software was used for data acquisition. Detection was performed by direct UV absorbance at 214 nm. All experiments were conducted at 25 °C temperature.

Reagents and procedure

All chemicals used were of analytical-reagent grade. Deionised 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 ions were prepared from $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 7H_2O$ salts (Merck, Darmstadt, Germany). Ethylenediaminetetraacetic acid (EDTA) was obtained from Fluka (Neu-Ulm, Germany).

Electrophoretic buffer solutions were prepared from disodium hydrogenphosphate dihydrate or boric acid by adding a 0.1 mol L^{-1} NaOH solution to adjust to the desired pH.

The capillary was rinsed with 0.1 mol L^{-1} sodium hydroxide and water for 5 min, then equilibrated with carrier electrolyte for 5 min 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.

Results and discussion

Choice of the derivatising agent

The UV absorption of EDTA is relatively low. Therefore, direct UV detection of this species requires pre-capillary or on-capillary complexation of the EDTA into a UV absorbing chelate. Most of the methods are based on the complexation of EDTA with Fe^{3+} or Cu^{2+} ions with subsequent determination by HPLC. However, the use of iron(III) ions in our system is complicated because fixing solutions already contain large amounts of $FeEDTA^-$ chelate. Thus, the derivatisation with Fe^{3+} requires at least two separate runs of the same sample: one before and the other after the addition of an excess of iron ions. Moreover, since the calculation of the amount of free EDTA is based on the differences between two signals, the large amount of $FeEDTA^-$ in relation to free EDTA would cause relatively high deviations. Therefore the metals investigated in this study were Cu^{2+} and Ni^{2+}. These both cations form chelates with EDTA stable enough for the derivatisation (logK = 18.8 and 18.5 for Cu^{2+} and Ni^{2+}, respectively) but less stable than $FeEDTA^-$ (logK = 25.1). Those chelates have strong UV absorption at 214 nm. Preliminary investigations showed that in principle each of the two cations tested is suitable for the derivatisation of EDTA but the addition of Cu^{2+} to real samples results in a precipitation of the uncomplexed excess of copper ions, probably with sulphur species present in the sample. Thus, the use of Cu^{2+} ions additionally requires filtration of the sample solution after complexation. Consequently, Ni^{2+} was selected for all further investigations.

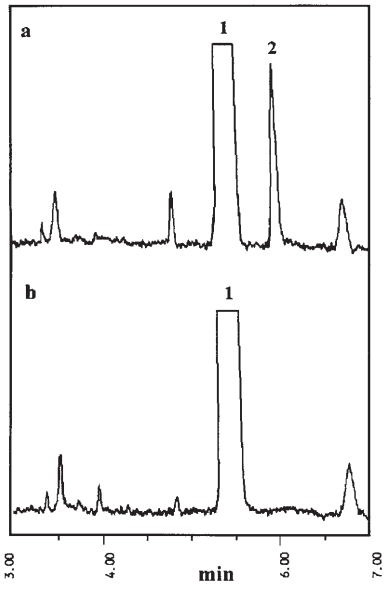

Fig. 1 Electropherograms of fixing solution (1:25 diluted) sample before (*a*) and after (*b*) decomposition by electrolytic oxidation. Electrolyte, 50 mmol L^{-1} borate, pH 8.5; applied voltage, 30 kV; direct UV detection at 214 nm; injection time, 4 s. Peaks: 1 - $FeEDTA^-$; 2 - $NiEDTA^{2-}$

Separation optimisation

EDTA should be determined in a very complex matrix containing large amounts of UV absorbing anions such as Br^-, $S_2O_3^{2-}$, $FeEDTA^-$, polythionates. Metal chelates having relatively low mobilities can be determined in a coelectroosmotic mode (the same direction of electroosmotic and electrophoretic mobility) or in a counterelectroosmotic mode (different directions of electroosmotic and electrophoretic mobility) [10]. The coelectroosmotic mode requires the reversal of the electroosmotic flow normally orientated toward the cathode. Better results were achieved in a counterelectroosmotic mode using 50 mmol L^{-1} borate electrolyte (pH 8.5) with the detection at the cathode. Under these conditions a good resolution between $FeEDTA^-$ and $NiEDTA^{2-}$ in less than 6 min was observed. Moreover, the common simple anions present in the sample do not interfere in the determination of EDTA.

To determine whether an excess of Ni^{2+} ions causes a decomposition of $FeEDTA^-$, various Ni^{2+} standard solutions (up to 10^{-3} mol L^{-1}) were added to standard solutions containing $1 \cdot 10^{-4}$, $5 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$ mol L^{-1} $FeEDTA^-$. No decrease could be observed in the peak areas for $FeEDTA^-$ chelate with increasing Ni^{2+} concentration for all solutions studied. A similar procedure was also performed with 1:25 diluted samples in order to determine an optimal amount of nickel required for a complete complexation of free EDTA. Constant peak areas for $NiEDTA^{2-}$ were observed for all the samples containing higher Ni^{2+} concentrations than $2 \cdot 10^{-4}$ mol L^{-1}. Therefore, $5 \cdot 10^{-4}$ mol L^{-1} Ni^{2+} was added to the samples in the assays.

Sample analysis

Several parameters important for quantitative analysis, including linearity, reproducibility and minimum detectable concentration, were examined under the above optimised conditions.

Table 1 Results of the determination of EDTA in fixing solution samples ($n = 5$)

Sample No	Found EDTA (mmol L^{-1})	Added EDTA (mmol L^{-1})	Found total EDTA (mmol L^{-1})	Recovery (%)
1	5.04	2.50	7.66	102 (2.1)[a]
2	2.71	1.25	4.11	104 (2.8)
3	1.48	0.75	2.18	99 (2.9)
4	–[b]	0.25	0.24	96 (3.4)

[a] values in parentheses are relative standard deviations (%)
[b] not found

The peak area response curve was linear ($r^2 = 0.999$) between $3 \cdot 10^{-6}$ and $5 \cdot 10^{-4}$ mol L^{-1} of EDTA. The detection limit for a signal-to-noise ratio of 3 and hydrodynamic injections of 10 s were approximately $2 \cdot 10^{-6}$ mol L^{-1} for EDTA. However, if required, the limit of detection can be lowered by increasing the sampling time.

The reproducibility was studied by making five consecutive runs with standard solutions containing different concentrations of EDTA. The relative standard deviations of migration times and peak areas were better than 0.8% and 4.5%, respectively.

Finally, the performance of the method was evaluated for several fixing solution samples. The electropherograms for a 1:25 diluted sample containing $5 \cdot 10^{-4}$ mol L^{-1} Ni^{2+} before (*a*) and after (*b*) electrolytic oxidation are shown in Fig. 1. Matrix components do not interfere in the determination. A recovery study was carried out with four samples collected at different times during the decomposition process. The results are given in Table 1. As can be seen, the method proved to be satisfactory for the determination of free EDTA in used fixing solutions. In fact, the system is completely insensitive even to large amounts of Fe-EDTA chelate, bromide, thiosulphate and polythionates, whereas conventional GC and HPLC methods cannot be used for analysis of such samples without additional pretreatment procedures.

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