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Separation of metal complexes of ethylenediaminetetraacetic acid in environmental water samples by ion chromatography with UV and potentiometric detection

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ABSTRACT

An ion chromatographic method is described for the analysis of several metal complexes of ethylenediaminetetraacetic acid (EDTA) in water samples. Separations are achieved on C_{18} bonded silica, typically using a mobile phase comprising 1% (w/v) cetrimide–1.2 m*M* phosphate buffer (pH 7)–25% (v/v) acetonitrile–15% (v/v) methanol, as well as on a polymer-based anion exchanger using 2 m*M* phosphate buffer (pH 7) as eluent. Direct UV detection at 250 nm is employed for EDTA complexes of Fe(III), Cu(II), Pb(II) and Ni(II), whilst UV detection at 250 nm after post-column reaction with copper ions is utilized for EDTA complexes of Zn(II), Cd(II), Co(II), Pb(II), Ni(II) and Cu(II). Detection limits are in the range 1.5–4.0 ng for direct UV detection and 30–50 ng for post-column reaction detection. Indirect potentiometric detection after post-column reaction with copper ions is utilized with metallic copper as the indicator electrode, giving detection limits in the range 1.0–1.5 μg. These separations are applied to the determination of metal–EDTA complexes in river water at the ppb[b] level and to remobilization studies of metal ions in sediment.

INTRODUCTION

Aminopolycarboxylic acids are widely used in industrial processes and in particular as substitutes for phosphates in detergents. After release to the environment these chelating agents may affect the distribution of metals within aquatic ecosystems. Reliable analytical methods for monitoring metal complexes of aminocarboxylic acids in natural water are still lacking. In this paper the use of ion chromatography is investigated for the analysis of metal complexes of ethylenediaminetetraacetic acid (EDTA), which is one of the most widely used aminopolycarboxylic acids.

Some information on the ion chromatographic behaviour of several metal–EDTA complexes is already available. On the one hand, total EDTA has been determined by formation of the copper complex [1,2] or the iron complex [3–5] before

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separation using ion-interaction chromatography; on the other hand, various metal ions have been separated by *in situ* formation of metal–EDTA complexes using a mobile phase which contains EDTA [6–11]. From this literature it can be concluded that both anion-exchange chromatography and ion-interaction chromatography should be adequate for the determination of metal–EDTA complexes in water samples.

For the analysis of environmental water samples a detection mode with a certain degree of selectivity is necessary in order to avoid extensive sample cleanup. In this work we have employed UV detection at 250 nm, including a post-column reaction for those metal–EDTA complexes which do not give a direct UV response at this wavelength. Furthermore, we have also investigated the application of a potentiometric detector with a copper electrode, since this has already proved useful for the analysis of free aminocarboxylic acids [12].

EXPERIMENTAL

The ion-chromatographic instrumentation consisted of a Millipore Waters (Milford, MA, USA) M510 pump, a Rheodyne (Berkeley, CA, USA) 7010 injection valve with a 120-μl loop, a Waters M484 UV absorbance detector and finally a Waters NRC-1094 mixing device for post-column mixing of the reagent delivered by a Waters M45 pump. The cell of a Waters 464 electrochemical detector equipped with a metallic copper working electrode and a Ag/AgCl (3 *M* KCl) reference electrode was used for potentiometric detection. This cell was connected to a Beckman (Fullerton, CA, USA) Φ34 pH meter. Chromatograms were recorded using a homemade analog-to-digital converter, interfaced with an Apple IIe computer.

Stock solutions of EDTA complexes were prepared by mixing equimolar solutions of EDTA and the metal ion. These solutions were diluted as required. Ion-interaction chromatography of the Fe(III)–EDTA complex was performed on a metal-free Waters Deltapak C_{18} column (250 × 4 mm I.D.). The mobile phase consisted of a 10-m*M* tetrabutylammonium chloride solution in 10 m*M* sodium acetate containing 10% acetonitrile and adjusted to pH 4.5 using acetic acid. Ion-interaction chromatography of all the other metal–EDTA complexes investigated in this study was carried out on a stainless-steel Waters μBondapak C_{18} column (250 × 4 mm I.D.). The mobile phase was prepared by dissolving 10 g of cetyltrimethylammoniumbromide (cetrimide) in 600 ml of 2 m*M* phosphate buffer pH 7 and diluting to 1000 ml with a mixture of methanol and acetonitrile of varying ratio. A Waters IC Pak A (50 × 4.6 mm I.D.) column was used for ion-exchange chromatography with 2 m*M* phosphate buffer pH 7 as the mobile phase.

The post-column reagent was a solution of 0.1 m*M* copper sulphate solution in 0.3 *M* acetic acid. The flow-rates of the mobile phase and of the post-column reagent were 0.9 ml/min each.

River water samples from Lane Cove River, Sydney, were passed through a Millipore (Bedford, MA, USA) 0.45-μm Millex filter and then through a Waters C_{18} SepPak cartridge before injection.

RESULTS AND DISCUSSION

Separation of EDTA complexes

During this study we restricted ourselves to the determination of EDTA complexes of Fe^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+}. Because of its versatility we employed ion-interaction chromatography on C_{18} bonded silica with tetraalkylammonium salts as ion-interaction reagents. Mobile phases in the neutral pH range were considered to be advantageous for our purposes because mobile phases of low or high pH could lead to severe disturbances of the equilibria between metal ions and EDTA in the samples during the chromatographic separation.

All the above-mentioned metal–EDTA complexes gave well-shaped peaks in eluents of pH 7, except the Fe(III)–EDTA complex. For this complex, it was necessary to use a mobile phase of pH 4.5 in order to obtain satisfactory peak shape. Unfortunately, at any pH below 5 severe problems were encountered when using stainless-steel columns for the analysis of Fe(III)–EDTA in the presence of an excess of free EDTA. Fe(III) released from the stainless-steel frits of the column tended to react with free EDTA leading to erroneously high results for Fe(III)–EDTA. These interferences could be overcome by employing a metal-free column (Waters Deltapack C_{18}), which was used for all further analytical work on Fe(III)–EDTA.

Optimization experiments for separation of all other metal–EDTA complexes at pH 7 revealed that sufficient selectivity of the mobile phase could be achieved only by using very hydrophobic ion-interaction reagents (such as cetrimide), together with relatively high amounts of organic modifier in the mobile phase. Acetonitrile, methanol and tetrahydrofuran were tested as organic modifiers. The selectivity of mobile phases containing methanol or tetrahydrofuran was practically the same so that only methanol and acetonitrile were used as organic modifiers for further experiments.

UV detection of EDTA complexes

UV detection at 250 nm was found adequate for the determination of Fe(III)–EDTA in the river water samples examined. In cases where the detection selectivity is insufficient at this wavelength, higher wavelengths in the range between 280 and 300 nm can be utilized without severe loss of sensitivity. The detection limit (measured with standards for a signal-to-noise ratio of 3) was about 1.5 ng Fe(III)–EDTA injected. Linear response was observed up to at least 200 ng injected ($r = 0.9998$, $n = 7$). A typical chromatogram of a spiked river water sample is shown in Fig. 1.

Direct UV detection at 250 nm is also possible for Cu–EDTA, Pb–EDTA and Ni–EDTA, although the sensitivity for Ni–EDTA is only about a tenth of that for Cu–EDTA or Pb–EDTA. A mobile phase with only acetonitrile as organic modifier (40%, v/v) was used for this separation, giving capacity factor, k', values of 2.3, 3.0 and 4.3 for Pb–EDTA, Ni–EDTA and Cu–EDTA, respectively. Detection limits (measured with standards for signal-to-noise ratios of 3) were about 4 ng injected for Pb–EDTA and Cu–EDTA and about 40 ng for Ni–EDTA. Linear response was obtained over at least two orders of magnitude ($r > 0.9995, n = 7$). A series of experiments was carried out to illustrate the applicability of this chromatographic separation to remobilization studies of heavy metals in river water. A 100-ml sample of river water was spiked with 2 ppm of free EDTA and left in contact with 50 g sediment for a certain time. A typical

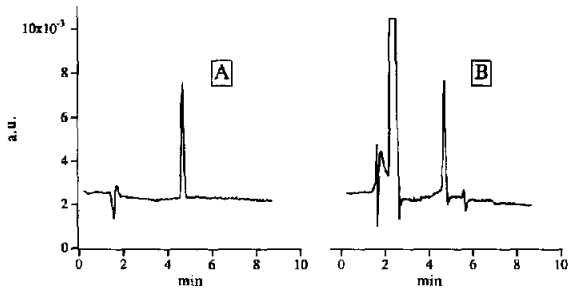

Fig. 1. Chromatograms for the determination of Fe(III)–EDTA in river water. (A) Standard containing 130 ppb Fe(III)–EDTA; (B) river water sample spiked with 130 ppb Fe(III)–EDTA. UV detection at 250 nm.

chromatogram obtained using this method is given in Fig. 2, which shows that Pb–EDTA and Cu–EDTA were detectable at ppb levels.

Zn–EDTA, Cd–EDTA and Co–EDTA show a major UV absorption only at rather low wavelengths but can be detected at 250 nm after conversion to the Cu–EDTA in a post-column reaction using 0.1 m*M* copper sulphate in 0.3 *M* acetic acid as reagent. Under these conditions Pb–EDTA is also converted to Cu–EDTA, whereas Ni–EDTA could not be converted, probably due to slow kinetics. A complete separation of Zn–EDTA, Cd–EDTA, Co–EDTA, Pb–EDTA, Ni–EDTA and Cu–EDTA in a single run could not be achieved, but the methanol/acetonitrile ratio of the organic modifier can be optimized to meet the requirements of specific separation problems. A typical mobile phase containing 25% (v/v) acetonitrile and 15% (v/v) methanol resulted in k' values of 3.3, 3.4, 4.3, 4.4, 5.2 and 6.0 for Pb–EDTA, Cd–EDTA, Co–EDTA, Zn–EDTA, Ni–EDTA and Cu–EDTA, respectively. The limits of detection for metal–EDTA complexes after post-column conversion to Cu–EDTA were between 30 and 50 ng injected. Linearity of response was checked up to 5 μg injected and in all cases the correlation coefficient was better than 0.9995 (n = 7). Fig. 3 shows a chromatogram of a river sample spiked with 1.3 ppm of Cd–EDTA, 1.4 ppm of Zn–EDTA and 11 ppm free EDTA. The peak eluted just prior to Cd–EDTA could be attributed to alkaline earth metal–EDTA complexes, which had been formed in the sample by the excess of free EDTA.

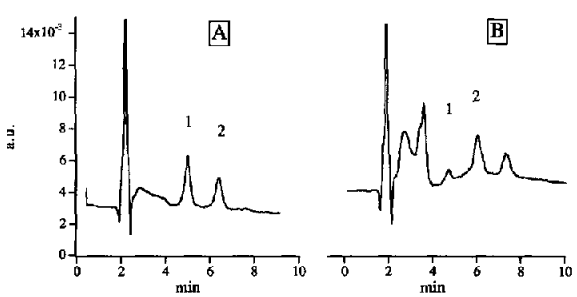

Fig. 2. Chromatograms of (A) standard containing 230 ppb Pb–EDTA and 220 ppb Cu–EDTA; (B) river water, 1 h after spiking the sample in contact with sediment with 2.2 ppm EDTA. Peaks: 1 = Cu–EDTA; 2 = Pb–EDTA. UV detection at 250 nm.

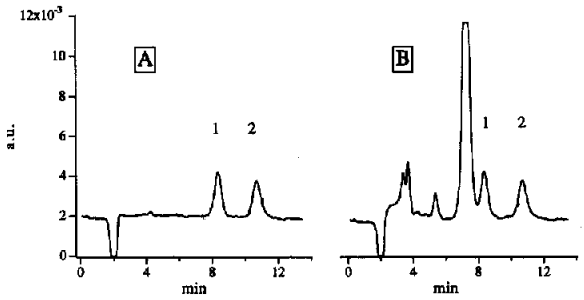

Fig. 3. Chromatograms for the determination of Zn–EDTA and Cd–EDTA in river water. (A) Standard containing 1.3 ppm Cd–EDTA and 1.4 ppm Zn–EDTA; (B) river water spiked with 1.3 ppm Cd–EDTA and 1.4 ppm Zn–EDTA. Peaks: 1 = Cd–EDTA; 2 = Zn–EDTA. UV detection at 250 nm after post-column reaction with copper ions.

Potentiometric detection of EDTA complexes

As an alternative to UV detection we investigated the applicability of a potentiometric detector using metallic copper as the indicator electrode [13–15]. The potential of the electrode is governed by the concentration of free copper ions at the electrode surface. This concentration depends on, among other things, the oxygen content and the complexation properties of the eluent. Eluted solutes which form very strong complexes with copper ions will cause a change in the level of copper ions at the electrode surface, thereby producing a decrease in the electrode potential. Therefore, all metal–EDTA complexes with stability constants lower than that for Cu–EDTA should be possible candidates for this detection mode, provided the kinetics of the ligand-exchange reaction between copper ions at the electrode surfacde and the eluted EDTA complexes are suitable. Unfortunately, in our experiments no response could be obtained at the electrode, suggesting that there was insufficient time for the ligand-exchange reaction to occur. As an alternative, we decided to apply the same post-column reagent used above for UV detection to potentiometric detection. In this case, the electrode responds to the changes in the copper concentration of the post-column reagent during elution of metal–EDTA complexes. Co–EDTA, Zn–EDTA, Cd–EDTA and Pb–EDTA could be detected in this way.

When this approach was coupled with the ion-interaction separation used above, the high amount of organic modifier in the mobile phase resulted in extremely high noise levels of the electrode response. Therefore, we combined the potentiometric detection mode with anion-exchange chromatography using a totally aqueous mobile phase. Naturally, this introduced the drawbacks that separation efficiency was poorer and the possibilities of mobile phase optimization more limited than in ion-interaction chromatography. When 2 m*M* phosphate buffer at pH 7 was used as the mobile phase, k' values of 7.6, 8.6, 10.0 and 10.6 were obtained for Cd–EDTA, Pb–EDTA, Co–EDTA and Zn–EDTA, respectively. Detection limits (measured for a signal-to-noise ratio of 3) were between 1.0 and 1.5 μg injected. A typical chromatogram of a river water sample spiked with Zn–EDTA and Cd–EDTA is given in Fig. 4 (potential values given in this figure indicate relative mV changes only and the actual baseline potential was −9.5 mV). The response was non-linear, as could be expected from the Nernst equation and from previous studies with this detector [13–15].

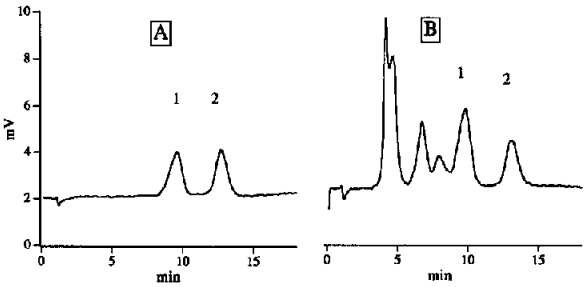

Fig. 4. Chromatograms for the determination of Zn–EDTA and Cd–EDTA in river water with potentiometric detection. (A) Standard containing 109 ppm Cd–EDTA and 98 ppm Zn–EDTA; (B) river water spiked with 128 ppm Cd–EDTA and 88 ppm Zn–EDTA. Peaks: 1 = Cd–EDTA; 2 = Zn–EDTA. Potentiometric detection after post-column reaction with copper ions.

The relatively high detection limits obtained with potentiometric detection indicate that unless appropriate preconcentration techniques are employed, this technique is less suited for environmental samples but may be more advantageous due to its selectivity when difficult matrices, such as waste water, are to be analyzed. In such cases, UV detection is likely to result in complex chromatograms.

An advantage of all the ion chromatographic methods described in this paper is the requirement for simple sample cleanup only, which avoids risks of disturbing the equilibria existing between free and complexed metal ions, leading to quantitative recoveries.

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