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Journal of Chromatography A, 1085 (2005) 240–246
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of synthetic chelating agents in surface and waste water by ion chromatography–mass spectrometry

Thomas P. Knepper [a,*], Andreas Werner [a], German Bogenschütz [b]

[a] *Europa University for Applied Sciences Fresenius, Limburger Strasse 2, D-65510 Idstein, Germany*
[b] *Deutsche METROHM GmbH & Co. KG, Filderstadt, Germany*

Received 26 October 2004; received in revised form 31 May 2005; accepted 6 June 2005

Abstract

Coupling of ion chromatography with electrospray mass spectrometry (IC–MS) is a simple, sensitive and quick method for the determination of polar organic traces in water samples without derivatization. Analysis of the chelating agents ethylenediamino tetraacetate (EDTA) and diethylenetriamino pentaacetate (DTPA) in aqueous samples was done by IC–MS on an anion exchange column after simple sample preparation steps. Quantification down to a concentration level of 1 $\mu g\,L^{-1}$ even in wastewater influents and effluents was achieved utilizing ^{13}C marked internal standards and measuring the individual $[M-H^+]^-$ and stable $[M-4H^+ + Fe^{3+}]^-$ cluster ions. The method was validated against certified, but more time consuming routine methods. Applying this method a series of several European water samples were analyzed for EDTA and DTPA indicating their nature as polar persistent pollutants.

Keywords: Chelating agents; Polar organic micropollutants; Ion chromatography–mass spectrometry; IC–MS; analysis; EDTA; DTPA; Aquatic environment

1. Introduction

Synthetic chelating agents, e.g. the investigated ethylenediamino tetraacetate (EDTA) and diethylenetriamino pentaacetate (DTPA) (Fig. 1) are utilized in many industrial applications, e.g. in the textile, photo, and pulp and paper industries as well as in galvanic enterprises [1]. Even if the toxicity of the investigated synthetic complexing agents is low, they still can be classified as environmentally relevant, since they are microbial poorly degradable and exhibit an excellent water solubility. Thus, their removal during drinking water treatment utilizing filtration and biodegradation steps tends to be low or non existent [1–8].

EDTA is present in the $\mu g\,L^{-1}$-range in almost all anthropogenically influenced surface waters in, e.g. Germany [1,2]. Concentration data regarding DTPA are quite scarce [1,9,10]. Reported values of these compounds in surface waters are mostly in the range of the detection limit (LOD) between 1 and 2 $\mu g\,L^{-1}$, whereas maximum concentrations can easily reach values of several 10th of $\mu g\,L^{-1}$. DTPA-concentrations detected in the effluents of paper and pulp mills are in the $mg\,L^{-1}$ range.

The validated and certified analysis of EDTA and DTPA is recommended to be done after enrichment on either anion exchange material or vaporization and derivatization to the tetra-isopropyl- or tetrabutyl-ester. After gas chromatographic (GC) separation either nitrogen–phosphorous detection (NPD) or mass spectrometric (MS) detection can be performed [11]. Problems are often encountered in both the enrichment step and the derivatization part which is quite often incomplete. The determination of EDTA–Fe complexes by high-performance liquid chromatography (HPLC) with UV detection is inadequate for the analysis of low concentrations as it lacks the necessary sensitivity [12].

It was proposed that the development of a sensitive method to analyze the polar and ionic organic acids without derivatization may simplify the existing methods and allow the determination in complex matrices including a high salt content. The most selective and sensitive method for such

* Corresponding author. Tel.: +49 6126 935264; fax: +49 6126 935210.
E-mail address: Knepper@fh-fresenius.de (T.P. Knepper).

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doi:10.1016/j.chroma.2005.06.045

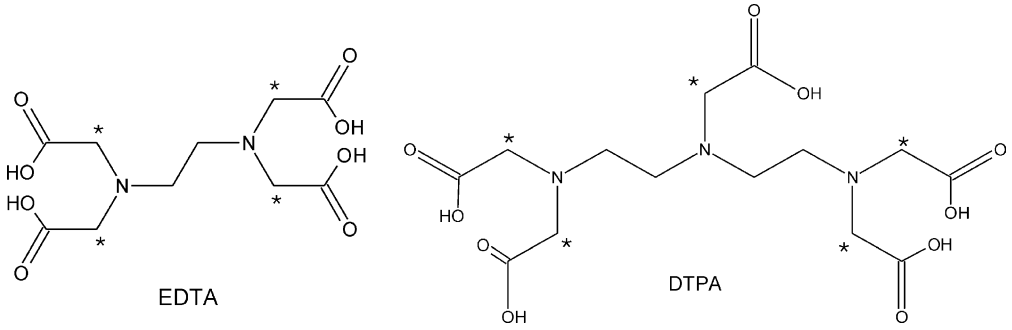

Fig. 1. Chemical structures of the investigated chelating agents. (*) Position of ^{13}C in the ^{13}C-labelled standards.

an application could be ion chromatography–electrospray ionization mass spectrometry (IC–ESI-MS) with subsequent removal of the salts used as eluent [13]. In the recent literature the application of IC–ESI-MS for the analysis of oxyhalides as well as polar organic pollutants including chelating agents has already been described using a suppressor between IC and MS resulting in a cation exchange of the effluent as well as from the sample against H^+ [13,14].

The usefulness of this new method for the determination of inorganic compounds, such as perchlorate has also been shown [15]. EDTA in concentrations down to 1 μg L^{-1} could also be analyzed by reversed-phase LC–MS, but no data applying this method have been published so far [16].

The aim of our study was not only the development of a reliable quantitative method for very polar organic polyacids, but also the application to samples with a high matrix content and high salt concentrations.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. EDTA, formic acid, sodium hydroxide, sodium carbonate and sodium hydrogen carbonate were obtained from Merck (Darmstadt, Germany), DTPA from Riedel-de Haen (Seelze, Germany). Milli-Q water was used in all experiments. ^{13}C-Labelled standards of EDTA and DTPA (Fig. 1) were obtained from the ESWE Institute (Wiesbaden, Germany) [17]. The SAX material used was obtained from ICT (part no. 9502-0100, mean particle size: 40–70 μm; Bad Homburg, Germany).

2.2. Sample preparation

Water samples (100 ml each) were adjusted to pH 3 by means of 16 M formic acid. After spiking the samples with 5 μg of [^{13}C]EDTA and [^{13}C]DTPA each, enrichment was performed by solid phase extraction. Glass cartridges containing 1 g of SAX anion-exchange material were conditioned with 3 × 2 ml methanol and 3 × 2 ml distilled water. After enrichment the SAX material was rinsed with 3 × 2 ml distilled water and eluted with 6 × 1 ml of 16 M formic acid. The combined eluates were concentrated in a nitrogen stream at 90 °C to dryness and redissolved with 1 ml of LC-Eluent A. After filtration the samples (200 μl) were injected via an autosampler into the IC system.

The ESI-MS system used consisted of a PE series 200 LC pump, a PE series 200 autosampler and a PE Sciex API 150 single quadrupole mass spectrometer equipped with an atmospheric pressure ionization (API) source, via a Turbo ionspray interface. The instrument was run in negative ion mode at an ionization voltage of −3000 V, an orifice voltage of −15 V and a ring voltage of −120 V. The interface temperature was held at 450 °C (the recommended temperature for daily use is 400 °C). As Turbo ion spray and curtain gas in the API source 5.0 purity nitrogen was used at a flow rate of 7 L min^{-1}, and oxygen was used as nebulizing gas, at a flow rate of 1.48 L min^{-1}.

Optimization of the ESI-MS ionisation was performed in order to obtain the most abundant ions for identification and quantification. At the optimum voltage of −32 V for EDTA in addition to the $[M - H^+]^-$-ion (m/z = 291 (295 for ^{13}C); see Figs. 1 and 2) an intense ion corresponding to the Fe^{3+}–EDTA complex $[M - 4H^+ + Fe^{3+}]^-$ (m/z 344 (348 for ^{13}C); see Figs. 1 and 2) was also obtained. This was also found to be the optimum voltage for the $[M - H^+]^-$ ion of DTPA leading to the formation of m/z 392 (397 for ^{13}C); and at a lesser intensity the Fe^{3+}–DTPA complex at m/z 445 (450 for ^{13}C); $[M - 4H^+ - Fe^{3+}]^-$.

2.3. Ion suppression center

The IC 828 Dual Suppressor (METROHM, Herisau, Switzerland) consisted of a suppressor cell, a direct current source and a degassing unit. To assure a flow of 0.3 mL min^{-1} into the ESI-MS interface the IC effluent flow (0.6 mL min^{-1}) was split (1:1) behind the suppressor. An additional conductivity detector (IC Detector 732) was used to follow-up the separation of the inorganic anions, such as chloride, nitrate and sulfate.

2.4. Chromatographic conditions

Separation was performed on a Metrohm Metrosep A Supp5 anion-exchange column (column dimensions