

Determination of Dissolved and Adsorbed EDTA Species in Water and Sediments by HPLC

Bernd Nowack,* Franz Günter Kari, Sabine U. Hilger, and Laura Sigg

Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), CH-8600 Dübendorf, Switzerland

This paper describes a method for determining EDTA species in various environmental samples at low molar concentrations by high-performance liquid chromatography (HPLC). Distinction between Fe^{III}EDTA and all the other species can be made. NiEDTA can be detected semiquantitatively. The fraction of EDTA adsorbed to suspended particles or to sediments can be determined after desorption with phosphate. After complexation with Fe(III), the EDTA is detected by reversed-phase ion-pair liquid chromatography as the Fe^{III}EDTA complex at a wavelength of 258 nm. The behavior of a variety of metal–EDTA complexes during analysis was checked. Determination of different EDTA species (Fe^{III}EDTA, NiEDTA, and adsorbed EDTA) is possible in river water, groundwater, and effluents from wastewater treatment plants. Fe^{III}EDTA was found to be the main species, at 30–70%; NiEDTA was <10% in most of the samples. Adsorbed EDTA was detected in suspended particles from rivers and wastewater treatment plants and in sediment cores from a lake. The method is suitable for a variety of different samples with different concentration ranges.

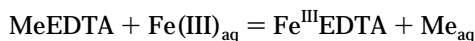
The synthetic complexing agent ethylenediaminetetraacetic acid (EDTA) is widely used in industrial, pharmaceutical, and agricultural applications. Due to its low biodegradability,^{1,2} it is present in sewage effluents,^{3–5} fresh water,^{5–7} and groundwaters.⁸ EDTA forms very stable complexes with heavy metals and has therefore often been suspected to remobilize adsorbed or precipitated heavy metals from river sediments or aquifers.⁹

The determination of the concentrations and especially the speciation of EDTA is important for understanding its environmental fate. However, there exist hardly any studies focusing on the speciation in natural waters^{6,10} or the adsorption of EDTA onto natural particles. Adsorption and sedimentation could play a role in the elimination of EDTA in lakes.¹¹

A gas chromatographic method is available for the determination of EDTA.^{5,12} This method needs a long pretreatment procedure and is therefore not suitable for bigger field evaluations. Of the methods developed for EDTA analysis, only the HPLC methods have a low enough detection limit.^{8,13,14} The method described here is based on the HPLC method of Kari⁵ and Zobrist and Schönenberger.¹⁵ The method was developed for laboratory systems for concentrations down to 10^{–8} M. In this method, 1 mL of sample is evaporated and dissolved in a formate buffer at pH 3.3, which is the optimal pH for complexation with Fe(III). Because some metal–EDTA species react slowly with iron(III), the solution is heated to 90 °C for 0.5 h. The Fe^{III}EDTA complex is then detected after separation with a UV detector at a wavelength of 258 nm.

This method was adapted to the analysis of very low concentrations in natural waters (down to 2 × 10^{–9} M). A preconcentration step is therefore needed. Because the method of Kari⁵ and Zobrist and Schönenberger¹⁵ already includes an evaporation step, the same procedure was used. In waters with high calcium and magnesium concentrations (up to 5 × 10^{–3} M), these ions may influence the determination due to matrix effects. We have investigated the effect of the removal of Ca and Mg by a cation-exchange column, which allows an easy preconcentration.

In the HPLC methods described,^{8,12,16} calibration was done with free EDTA. Exchange reactions with the free ligand were found to be fast. In natural waters, EDTA exists mainly in the form of CaEDTA or ZnEDTA¹⁰ and probably NiEDTA. These species have slow exchange kinetics.¹⁰ Therefore, a method for the determination of EDTA in natural waters has to be tested by standard addition with species other than uncomplexed EDTA. A heating step which accelerates formation of the Fe(III) complex is used by Kari⁵ and Zobrist and Schönenberger.¹⁵ Methods without this step^{8,13} may underestimate the amount of EDTA species that have slow exchange kinetics. We have checked the influence of heating on the complexation reaction



for some important metal–EDTA species.

Calculations showed that NiEDTA might play an important role in the speciation of EDTA in natural waters. For a Glatt water

- (1) Tiedje, J. M. *Appl. Microbiol.* **1975**, *30*, 814–817.
- (2) Bolton, H. J.; Li, S. W.; Workman, D. J.; Girvin, D. C. *J. Environ. Qual.* **1993**, *22*, 125–132.
- (3) Alder, A. C.; Siegrist, H.; Gujer, W.; Giger, W. *Water Res.* **1990**, *24*, 733–742.
- (4) Kari, F. G.; Giger, W. *Water Res.* **1995**, *30*, 122–134.
- (5) Kari, F. G. Dissertation, ETH No. 10698, Dübendorf, Switzerland, 1994.
- (6) Kari, F. G.; Giger, W. *Environ. Sci. Technol.* **1995**, *29*, 2814–2827.
- (7) Giger, W.; Schaffner, C.; Kari, F. G.; Ponusz, H.; Reichert, P.; Wanner, O. *EAWAG-News* **1991**, *32*, 27–31.
- (8) Bergers, P. J. M.; de Groot, A. C. *Water Res.* **1994**, *28*, 639–642.
- (9) Bourg, A. C. M.; Crouzet, C.; Bertin, C. In *Transport and Reactive Processes in Aquifers*; Dracos, Th.; Staufer, F., Eds.; A. A. Balkema: Rotterdam, 1994.
- (10) Xue, H. B.; Sigg, L.; Kari, F. G. *Environ. Sci. Technol.* **1995**, *29*, 59–68.
- (11) Ulrich, M. Dissertation, ETH No. 9632, Dübendorf, Switzerland, 1991.

- (12) Schürch, S.; Dübendorfer, G. *Mitt. Geb. Lebensmittelunters Hyg.* **1989**, *80*, 324–334.
- (13) Sillanpää, M.; Kokkonen, R.; Sihvonen, M.-L. *Anal. Chim. Acta* **1995**, *303*, 187–192.
- (14) Ye, L.; Lucy, C. A. *Anal. Chem.* **1995**, *67*, 2534–2538.
- (15) Zobrist, J.; Schönenberger, R. Unpublished results, EAWAG, Dübendorf, Switzerland, 1993.
- (16) Chinnick, C. C. T. *Analyst* **1981**, *106*, 1203–1207.

sample containing 1.93×10^{-8} M photostable EDTA (all EDTA species except Fe^{III} EDTA) and typical total dissolved concentrations of metals (Zn, 1.26×10^{-7} M; Cu, 7.2×10^{-8} M; Ni, 3.95×10^{-8} M; Ca, 1.88×10^{-3} M; natural ligands for Cu and Zn as determined by Xue and Sigg¹⁷), the equilibrium speciation was calculated with the speciation program MICROQL.¹⁸ Under these conditions, 99.5% of the EDTA should be present as NiEDTA, and the remaining EDTA species as ZnEDTA and CaEDTA. To check this calculation and see whether NiEDTA is as important as predicted, the analytical quantification of NiEDTA is needed.

Metal–EDTA complexes were shown to be adsorbed on oxide surfaces depending on the pH and the complexed metal.^{19,20} Under natural conditions, iron oxides are assumed to be the major adsorbents for metal–EDTA complexes.^{21,22} Nowack and Sigg²⁰ have shown that phosphate can compete with metal–EDTA species for adsorption sites on iron oxides. Metal–EDTA species adsorbed at the goethite surface ($\alpha\text{-FeOOH}$) could be desorbed totally by using a 0.002 M phosphate solution as well at low pH as at high pH.

However, there is no study focusing on measurement of adsorbed EDTA in natural samples. In this work, it was tested whether phosphate can be used to desorb EDTA species from natural particles. Both suspended particles from rivers and effluents from sewage treatment plants and lake sediments were measured.

EXPERIMENTAL SECTION

Apparatus. The liquid chromatography was performed with a Jasco PU-980 HPLC pump. The autosampler was equipped with a sample loop of 200 μL . A Lichrocart RP-18 column (E. Merck, Darmstadt), length 250 mm, diameter 4 mm, and a Lichrocart 4-4 precolumn was used. The eluent was degassed with a Henggeler DG-4 degasser. Detection was with a UV detector (Jasco UV 970) at a wavelength of 258 nm. Gynksoft software was used for integration.

Reagents and Chemicals. All water was obtained from a Barnstead nanopure apparatus (NPW water). The mobile phase (0.02 M formate buffer, pH 3.3) was prepared by dissolving tetrabutylammonium bromide (TBA-Br, 0.001 M), sodium formate (0.005 M), formic acid (0.015 M), and acetonitrile (8%) in nanopure water. A formate buffer was prepared by dissolving sodium formate (0.005 M) and formic acid (0.015 M) in water. TBA-Br solution (0.05 M) was prepared by dissolving TBA-Br in formate buffer. A $\text{Fe}(\text{III})$ solution (0.001 M) was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.01 M HNO_3 in water. Phosphate solution (0.1 M) was obtained by dissolving $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ in 100 mL of NPW.

Standard Preparation. A stock Fe^{III} EDTA solution (0.01 M) was prepared by dissolving $\text{NaFeEDTA} \cdot 2\text{H}_2\text{O}$ salt in water. The solution was stored in a aluminum-covered bottle in the refrigerator. A stock EDTA solution (0.01 M) was prepared by dissolving $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ in NPW. Metal–EDTA solutions (0.01 M) were prepared by dissolving the metal nitrate and $\text{Na}_2\text{H}_2\text{EDTA} \cdot$

$2\text{H}_2\text{O}$ in water and boiling for 1 h to be sure that the complex was formed. This time is sufficient even for formation of Cr^{III} EDTA.²³ ZnEDTA was prepared by dissolving $\text{ZnNa}_2\text{EDTA} \cdot 4\text{H}_2\text{O}$ in water. Co^{III} EDTA was prepared according to Huang and Lin:²⁴ $\text{Co}^{\text{III}}\text{Cl}_2$ and EDTA were dissolved in water (100 mL), and a 1 mL aliquot of 30% H_2O_2 was added three times over 24 h.

Sample Treatment for Dissolved EDTA. Samples were collected in opaque PE bottles to avoid photolysis of the Fe^{III} EDTA. The bottles were stored at 4 °C. The water was filtered through 0.2 μm cellulose nitrate filters (Sartorius). If the expected concentration was higher than 4×10^{-8} M, 1–1.5 mL of the sample was pipetted into autosampler vials and evaporated to dryness in an oven at 90 °C. If the expected concentration was lower, the filtrate was passed through a cation exchange column (1 cm length, 0.5 cm diameter, filled with Baker sulfonic acid extraction column material, SPE 7090). The columns were made as described by Johnson²⁵ for the analysis of chromium. The eluate was directly collected in glass vials. Depending on the expected concentration, 2–6 mL was collected. The net weight was determined, and the sample was evaporated to dryness in an oven at 90 °C. Formate buffer (1 mL) and $\text{Fe}(\text{III})$ solution (20 μL) was added. The sample was left for 3 h in a water bath at 90 °C. After the sample was cooled, 40 μL of the TBA-Br solution was added, and the sample was pipetted into autosampler vials. To avoid photolysis of the Fe^{III} EDTA, the samples were stored in the dark between steps.

The columns were regenerated by passing 3 mL of methanol, 2 mL of HNO_3 (5 M), and 4 mL of 1 M NH_4NO_3 (in 0.1 M HNO_3). The column was then washed twice with 6 mL of NPW.

Sample Treatment for Adsorbed EDTA in Water. Depending on the particle concentration, 500–2000 mL of the sample was filtered through 0.2 μm cellulose nitrate filters (Sartorius). The dry net weight of the particles on the filter was determined. Next, 4 mL of a 2×10^{-3} M phosphate solution was added to the filter. After 15 min, the solution was removed by a syringe and filtered through a 0.45 μm filter. The net weight of the remaining phosphate solution was measured. The subsequent treatment was the same as for dissolved EDTA. The method gives an overall preconcentration factor of $f = f_1 f_2$, where f_1 is the volume of water filtered per 4 mL and f_2 is the volume of phosphate solution after desorption. This factor is in the range between 200 and 1500 for surface waters with particle concentrations between 0.5 and 10 mg/L.

Sample Treatment for Adsorbed EDTA in Sediments. The sediment was dried either in an oven at 90 °C or by freeze-drying. An appropriate amount of sediment (0.1–0.5 g) was treated with 20 mL of 0.002 M phosphate solution in a ultrasonic bath for 10 min. The suspension was filtered through 0.2 μm filters (Sartorius) and analyzed for EDTA as described above.

Sample Treatment for Distinction Between Fe^{III} EDTA, NiEDTA, and Other Species. The photolabile species Fe^{III} EDTA was determined by irradiation of the sample in a merry-go-round apparatus with a mercury lamp for 10 min ($\lambda \geq 313$ nm, 852 W m^{-2} for $313 \leq \lambda \leq 436$ nm). The difference between total and photostable EDTA is supposed to be only Fe^{III} EDTA.⁴

(17) Xue, H. B.; Sigg, L. *Limnol. Oceanogr.* **1993**, *38* (6), 1200–1213.

(18) Müller, B. *MaquQL*, V 1.2, A Program to calculate chemical Speciation and Adsorption; EAWAG, Dübendorf, Switzerland, 1993.

(19) Bowers, A. R.; Huang, C. P. *J. Colloid Interface Sci.* **1986**, *110*, 575–590.

(20) Nowack, B.; Sigg, L. *J. Colloid Interface Sci.*, in press.

(21) Jardine, P. M.; Jacobs, G. K.; O'Dell, J. D. *Soil Sci. Soc. Am. J.* **1993**, *57*, 954–962.

(22) Szecsody, J. E.; Zachara, J. M.; Bruckhart, P. L. *Environ. Sci. Technol.* **1994**, *28*, 1706–1716.

(23) Schwarzenbach, G.; Flaschka, H. *Die Komplextometrische Titration*; Enke-Verlag: Stuttgart, 1965.

(24) Huang, C. P.; Lin, Y. T. In *Adsorption from Aqueous Solutions*; Tewari, P. H., Ed.; Plenum Press: New York, 1981.

(25) Johnson, C. A. *Anal. Chim. Acta* **1990**, *238*, 273–278.

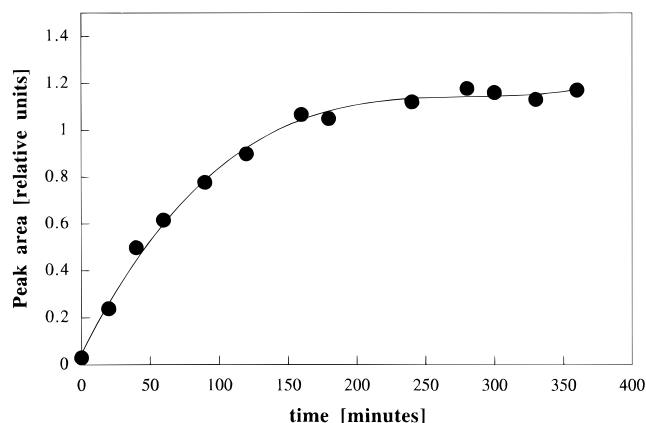


Figure 1. Influence of heating time on formation of Fe^{III} -EDTA from a NiEDTA solution. Addition of 7.15×10^{-7} M NiEDTA to drinking water. The samples were evaporated to dryness and were heated after addition of formate buffer and $\text{Fe}(\text{III})$ at 90°C for different times.

For the determination of NiEDTA, the irradiated sample is measured without addition of $\text{Fe}(\text{III})$ and heating but with evaporation and addition of formate buffer. EDTA or metal-EDTA species flowing through the HPLC column can react with $\text{Fe}(\text{III})$, adsorbed on free SiO_2 groups on the column, forming Fe^{III} -EDTA, which can be detected. NiEDTA does not adsorb at 258 nm. Because NiEDTA reacts only slowly with $\text{Fe}(\text{III})$, it does not form Fe^{III} -EDTA during elution. Because the Fe^{III} -EDTA present in the natural sample is destroyed by the irradiation, all the Fe^{III} -EDTA detected was formed in the column by reaction of the adsorbed $\text{Fe}(\text{III})$ and "fast-reacting" metal-EDTA complexes. The amount of NiEDTA is calculated by the difference of total photostable EDTA and fast-reacting EDTA.

Chromatography. Samples are analyzed under the following conditions: flow rate, 1 mL/min; injection volume, 200 μL ; ambient column temperature; detection at 258 nm; mobile phase, see

Reagents and Chemicals. Time between two injections was 30 min. Calculations of the concentrations are based on peak areas.

Sampling Area. Samples were taken from the River Glatt (Switzerland) and some of its tributaries. The River Glatt originates in Lake Greifen, a eutrophic lake near Zürich. The Glatt Valley is densely populated, and several wastewater treatment plants (WWTPs) discharge their effluents into the River Glatt.

RESULTS AND DISCUSSION

Method. In a first experiment, 7.15×10^{-7} M NiEDTA was added to a sample of drinking water. Aliquots of the sample were heated to 90°C with $\text{Fe}(\text{III})$ for different times. The results are shown in Figure 1. It can be seen that even at this temperature, the NiEDTA reacts only slowly with $\text{Fe}(\text{III})$. NiEDTA cannot be detected at 258 nm, and the peak height corresponds to Fe^{III} -EDTA. Three to four hours is the minimum heating time; otherwise, only part of the fraction of NiEDTA present in water will be determined. Therefore, the HPLC methods published earlier, which do not have such a heating step,^{8,13} may underestimate the total concentration of EDTA, if NiEDTA plays a relevant role in natural waters. We have chosen 3 h as the heating time for the natural samples which contain only low NiEDTA concentrations. At least 95% of the NiEDTA has reacted to Fe^{III} -EDTA after this time.

The influence of addition of $\text{Fe}(\text{III})$ was investigated for 10 different EDTA species. Each species was dissolved in drinking water. One aliquot of each solution was treated as described in the Experimental section, while a second aliquot was analyzed without addition of $\text{Fe}(\text{III})$ and without heating. The results are shown in Figure 2. It can be seen that most of the species react fast with some iron present in the column. This iron is adsorbed on free silica groups that are not occupied by C-18. The species thought to be relevant in natural systems (CaEDTA and ZnEDTA) react especially fast with the iron at the given pH of 3.3. These species are not stable at such low pH values and dissociate fast.

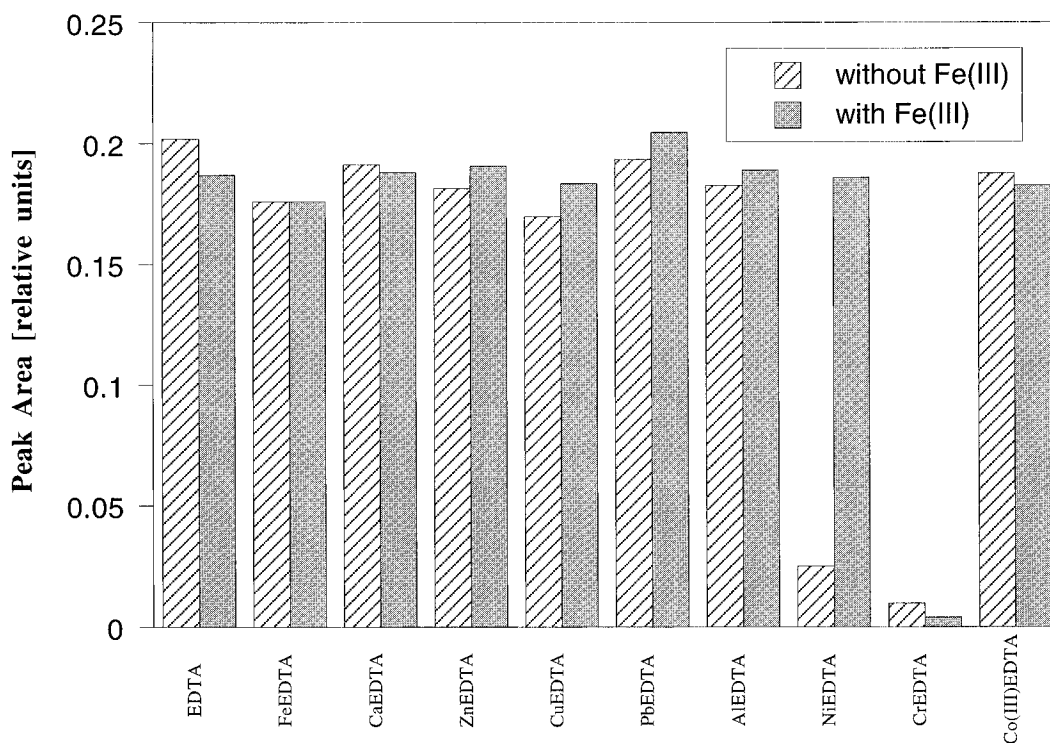


Figure 2. Influence of addition of $\text{Fe}(\text{III})$ to metal-EDTA species on the peak area of Fe^{III} -EDTA. Addition of 2×10^{-7} M metal-EDTA to drinking water. One sample was analyzed without addition of $\text{Fe}(\text{III})$; the other was heated for 3 h after addition of $\text{Fe}(\text{III})$.

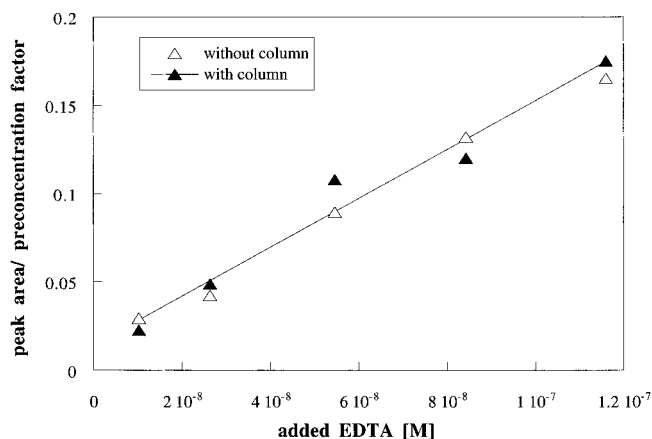


Figure 3. Addition of ZnEDTA to drinking water, measured without and with pretreatment with a cation-exchange column.

The uncomplexed EDTA is then fast-reacting with the iron. Cr^{III} EDTA cannot be detected by HPLC because the complex is too stable, even after 3 h of heating. If Cr^{III} EDTA plays a relevant role in the speciation of EDTA, the methods lead to an underestimation of the total EDTA concentration. Co^{III} EDTA does not react with iron, because its stability constant is much higher, but it also absorbs at 258 nm. NiEDTA is the only species that reacts slowly on the column. Therefore, NiEDTA can be determined semiquantitatively by the difference between the peak areas of direct injection of a sample and the peak areas after addition of Fe(III) and 3 h of heating.

At the low concentrations in rivers, lakes, and groundwaters, a preconcentration step is sometimes needed. In samples with high Ca^{2+} and Mg^{2+} contents (respectively 1.5 and 0.6 mmol/L), not all of the salts can be dissolved after addition of buffer to the evaporated sample, if more than 3 mL was evaporated. No EDTA can be detected in these suspensions. If the sample is passed through a cation-exchange column, the residue can be dissolved, and a preconcentration of up to a factor of 10 is possible. Measurements by ICP-AES showed that calcium and magnesium are removed to >95% by this procedure. Some organic substances that adsorb at 258 nm are also removed. No effect of the cation-exchange column on the calibration curve was found (Figure 3). Calibration curves in distilled water had slopes slightly different from the ones obtained in drinking water. Therefore, it is important to take natural water for calibration instead of distilled water due to the small matrix effects.

Calibrations were made in drinking water, adding 5×10^{-9} – 2×10^{-7} M ZnEDTA and preconcentrating by a factor of 3–6. They resulted in linear calibration graphs with correlation coefficients of at least 0.99 ($N > 6$). The curves are linear up to concentrations of 10^{-5} M. Standard additions of PbEDTA to a Glatt water sample gave the same slope as that obtained for the addition of ZnEDTA to drinking water. The correlation coefficient was 0.96 (for $n = 8$). The repeatability for a river water sample ($n = 4$) was $(4.36 \pm 0.26) \times 10^{-8}$ M, and the relative standard deviation was 6%.

Typical chromatograms for a lake water and the effluent of a WWTP are shown in Figure 4. The separation of the EDTA peak is very good for both matrices. Chromatograms from river water or groundwater look similar to that for the lake water, which is shown in Figure 4b. The detection limit, based on a signal-to-noise ratio of 3 and a preconcentration of 2, is 3×10^{-9} M. This method has, therefore, the same detection limit as the HPLC method of ref 8.

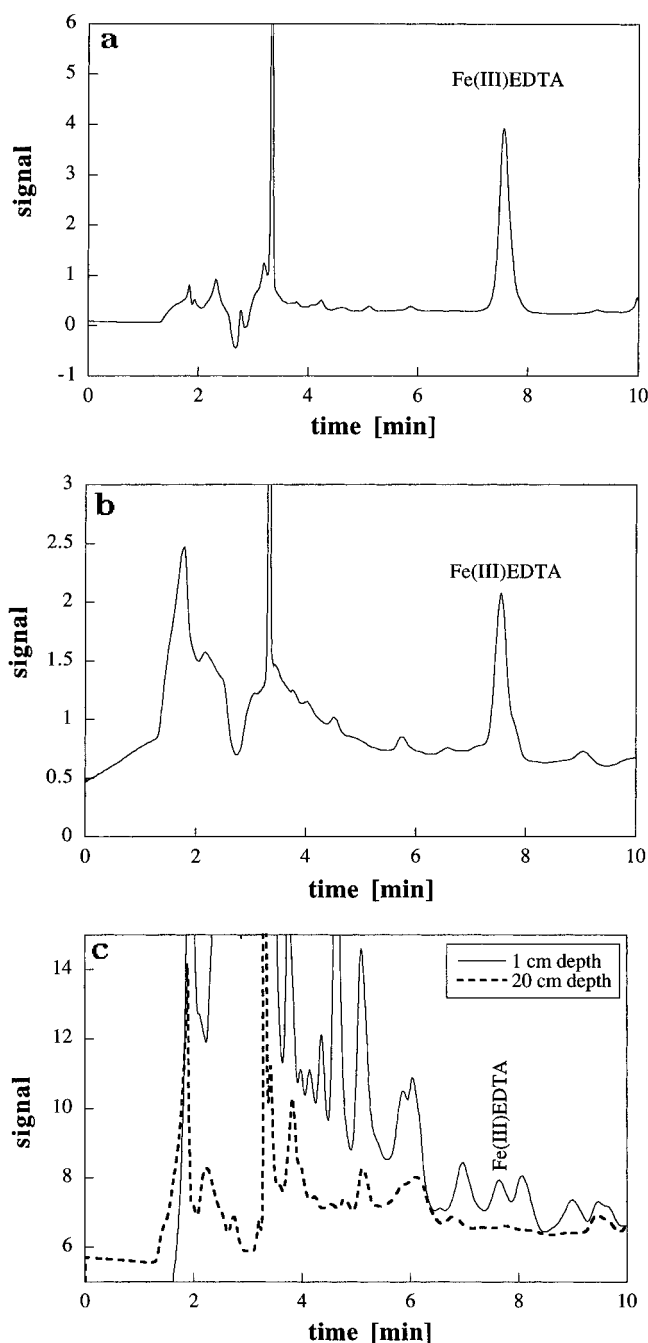


Figure 4. Chromatograms from several samples under the described conditions: (a) effluent of the WWTP Dübendorf, EDTA 7.03×10^{-7} M, no preconcentration. (b) Lake water 1, preconcentration factor 5.5, EDTA 6.77×10^{-8} M. (c) Extract of a sediment core from Lake Greifen at 30 m depth; the two samples are from 1 and 20 cm depth of the core.

This HPLC method also works very well for the determination of adsorbed EDTA species. It was possible to desorb EDTA from suspended particles in rivers and from lake sediments using phosphate as the desorption agent. The preconcentration factor is big enough to obtain detectable peaks. The phosphate concentration used has no influence on the analysis of EDTA.

It was confirmed that there is no adsorption of EDTA onto the filters. If a filtered river sample was filtered again and the filter was treated with phosphate, no adsorbed EDTA could be detected. Figure 4c shows a typical chromatogram from a sediment extraction. It was checked by standard addition that the peak corresponds to EDTA. Chromatograms from suspended

Table 1. Concentrations of Dissolved and Adsorbed EDTA in Several Rivers, Lakes, Groundwaters, and Effluents from Waste Water Treatment Plants

sample	EDTA(aq) [M]	EDTA(ads) [M]	EDTA(ads) [mol/g of particles]	adsorption [%]
Chriesbach	1.7×10^{-8}	6.5×10^{-11}	3.6×10^{-8}	0.4
River Glatt	5.3×10^{-9}	6.8×10^{-11}	1.8×10^{-8}	1.3
Lake Greifen, 2.5 m	1.9×10^{-8}	6.8×10^{-10}	2×10^{-7}	3.6
Lake Greifen, 30 m	2.1×10^{-8}	2.7×10^{-10}	1.8×10^{-7}	1.3
WWTP ^a Zürich	6.6×10^{-8}	1.6×10^{-9}	2.6×10^{-7}	2.4
WWTP ^a Dübendorf	7.02×10^{-7}	2.57×10^{-10}	2.9×10^{-7}	0.04

^a WWTP, waste water treatment plant.

Table 2. Speciation of EDTA in Several Samples^a

sample	total EDTA [M]	photostable EDTA [M]	Fe ^{III} EDTA [M]	Fe ^{III} EDTA [%]	NiEDTA [M]	NiEDTA [%]
River Glatt	$(4.37 \pm 0.25) \times 10^{-8}$	$(1.93 \pm 0.27) \times 10^{-8}$	2.44×10^{-8}	56	1.5×10^{-9}	3
groundwater 1	$(6.77 \pm 0.25) \times 10^{-8}$	$(4.61 \pm 0.28) \times 10^{-8}$	2.16×10^{-8}	32	7.7×10^{-9}	11
groundwater 2	$(5.94 \pm 0.25) \times 10^{-8}$	$(3.96 \pm 0.25) \times 10^{-8}$	1.98×10^{-8}	33	nd ^c	nd ^c
groundwater 3	$(1.71 \pm 0.26) \times 10^{-8}$	$(1.20 \pm 0.27) \times 10^{-8}$	5.1×10^{-9}	30	4.2×10^{-9}	24
WWTP ^b Niederglatt	$(7.66 \pm 0.24) \times 10^{-8}$	$(2.88 \pm 0.25) \times 10^{-8}$	4.78×10^{-8}	62	5.5×10^{-9}	7
WWTP ^b Dübendorf	$(2.52 \pm 0.06) \times 10^{-6}$	$(8.95 \pm 0.21) \times 10^{-7}$	1.62×10^{-6}	64	1.18×10^{-7}	5
WWTP ^b Dübendorf	$(7.02 \pm 0.13) \times 10^{-7}$	$(2.32 \pm 0.4) \times 10^{-7}$	4.70×10^{-7}	67	5.3×10^{-8}	8

^a Distinction between photolabile (Fe^{III}EDTA) and photostable EDTA, from which one part is NiEDTA. ^b WWTP, waste water treatment plant. ^c Not detected.

particles look similar. The separation of the EDTA is less good than for the dissolved species, but most of the interfering peaks have a shorter retention time. The comparison of two chromatograms from 1 cm and from 20 cm depth shows no detectable EDTA-peak for the deeper sediment.

To test the recovery in sediments, three samples of a dried lake sediment were spiked with 3.4×10^{-9} – 1.7×10^{-8} mol/g ZnEDTA. ZnEDTA solution was added (0.3–2 mL of 10^{-5} M), and then the sediment was dried again at 90 °C and mixed well. The samples were treated with phosphate as described. The recovery was between 50 and 75%. Standard additions showed that there is no matrix effect. Fresh sediments were spiked with ZnEDTA (4.67×10^{-10} mol/g ZnEDTA) before drying. The recovery was 98% ($n = 2$). The repeatability for a dried lake sediment ($n = 8$) was $(5.36 \pm 0.88) \times 10^{-10}$ mol/g, and the relative standard deviation was 16%. For the low concentration and the complex matrix, this seems to be a reasonable recovery.

Analyses. In Table 1, EDTA concentrations are listed from several surface waters and groundwaters, including effluents of some WWTPs. Total dissolved and adsorbed EDTA was determined. In all samples with particulate matter, adsorbed EDTA was detected. These concentrations were higher in the effluents from WWTP. The fraction of adsorbed EDTA was about 1%. As already estimated theoretically by Kari,⁵ the fraction of adsorbed EDTA is very low. However, for determining the fate of EDTA in a lake or in the sea, the removal by settling particles may still be a relevant process. The method may provide analytical background and data for modeling purposes. Ulrich¹¹ has hypothesized the incidence of such an elimination process in lakes.

In Table 2, the speciation of EDTA in several samples is shown. The HPLC method worked very well for all waters from high concentrations in WWTP effluents (up to 2.5×10^{-6} M) with high organic concentrations to groundwaters with very low concentrations of EDTA ($\sim 10^{-8}$ M). The fraction of Fe^{III}EDTA is about 30% for river water and groundwater samples and 60–70% for WWTP samples. This is in the same range determined by earlier

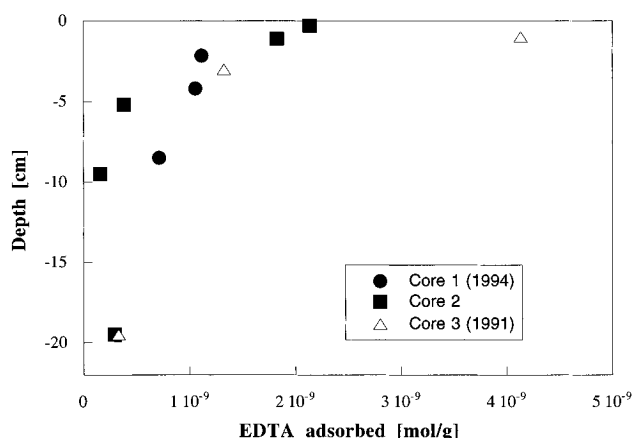


Figure 5. Concentration of adsorbed EDTA in three sediment cores from Lake Greifen at 30 m depth. EDTA was desorbed by phosphate.

investigations in the same area with the gas chromatographic method.^{4–6} The concentration of FeEDTA, however, should be very low (<1%), based on equilibrium calculations for these samples.⁵ The very slow exchange kinetics of FeEDTA are the reason for the nonequilibrium.¹⁰ Analytical determination is, therefore, the only way to obtain the fraction of FeEDTA. Due to its strong adsorption, even at high pH,²⁶ FeEDTA may be a key parameter regarding the elimination of EDTA by adsorption.

The fraction of NiEDTA is between 3 and 25% of total EDTA, being usually below 10%. Calculations based on known stability constants and measured concentrations of metals, EDTA, and some natural ligands for Cu and Zn show that NiEDTA should be the most important species (up to 100% of EDTA should be present as NiEDTA). The determination of NiEDTA, however, gave much lower concentrations. This may be due either to slow coordination kinetics of the exchange of dissolved nickel to the

(26) Nowack, B.; Lützenkirchen, J.; Behra, P.; Sigg, L., submitted to *Environ. Sci. Technol.*

metal-EDTA species in the river water or to the occurrence of specific natural nickel ligands. For an accurate calculation of the EDTA speciation, it is therefore necessary to develop a method for the determination of the organic Ni complexes, similar to that for Zn or Cu.¹⁷

In some sediment cores from Lake Greifen, the adsorbed EDTA was determined (Figure 5). The measured EDTA concentrations in the sediment are in the range 2×10^{-10} – 4×10^{-9} mol/g. If the sediment has a water content of 80% with a concentration of EDTA of 2×10^{-8} M in the pore water (the same concentration as in the overlaying water), this leads to a concentration of 8×10^{-11} mol/g EDTA in the solid phase. The EDTA concentration from the pore water is, therefore, at least 1 order of magnitude lower and does not affect the determination of the adsorbed EDTA. The highest concentrations were found in the

top layer. For all cores, a decline in the concentration was found in deeper layers. Biodegradation of EDTA under anaerobic conditions can be excluded.²⁷ It is probably due to the smaller input concentrations. Sediments in Lake Greifen at 20 cm depth are about 40 years old.²⁸ The occurrence of EDTA in sediments supports the hypothesis of the elimination of EDTA by settling particles in lakes.¹¹

ACKNOWLEDGMENT

This work was supported by the Körber-Stiftung, Hamburg, Germany. The work of Jürg Zobrist and René Schönenberger, who improved the analytical conditions of the HPLC method, is acknowledged.

Received for review July 25, 1995. Accepted November 22, 1995.[⊗]

AC9507505

(27) Bolton, H.; Li, S. W.; Workman, D. J.; Girvin, D. C. *J. Environ. Qual.* **1993**, 22, 125–132.

(28) Wan, G. J.; Santschi, P. H.; Sturm, M.; Farrenkothen, K.; Lück, A.; Werth, E.; Schuler, Ch. *Chem. Geol.* **1987**, 63, 181–196.

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1996.