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Application Note 268

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Determination of Chelating Agents in Drinking Water and Wastewater Samples

INTRODUCTION

Aminopolycarboxylate chelating agents (Figure 1) are used extensively in many domestic products and industrial processes, with the most important applications in cleaning compounds, pulp and paper manufacturing, and agriculture.[1–5] Chelating agents form stable water-soluble complexes with alkali and transition metal ions, thus increasing metal solubility and preventing metal-catalyzed reactions. Therefore, chelating agents prevent metals from interfering with the detergent's ability to remove soils and stains from clothing, from degrading oxidizing and bleaching agents in paper and textile manufacturing, and from precipitating in fertilizers. Chelating agents are also used in soil remediation to remove heavy metal contamination.[6]

Because of their broad application range, chelating agents are typically produced and used in large quantities. In 2004, the global consumption of the most common aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic

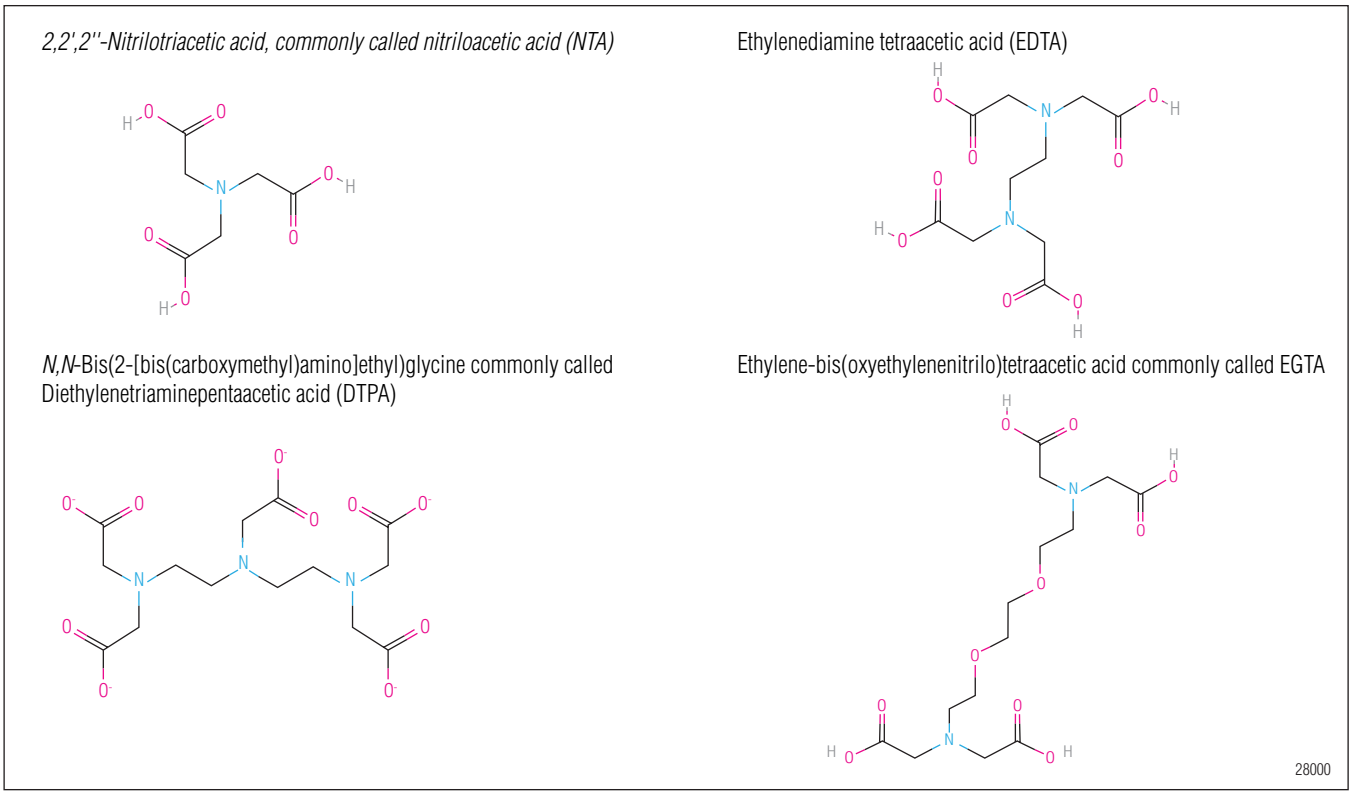

Figure 1. Aminopolycarboxylate chemical structures.

acid (NTA), diethylenetriaminepentaacetic acid (DTPA), and glycol-*bis* (2-aminoethylether)-*N,N,N′,N′*-tetraacetic acid (EGTA)) averaged over 200,000 tons per year.[7] Chelating agents that form low or moderately high stability constants, such as NTA, are readily biodegradable.[5] However, chelating agents that form stronger metal complexes, such as EDTA and DTPA, degrade slowly and therefore are persistent in the environment.[2,3–5,7] Although these chelating agents do not concentrate in the food chain, up to 800 µg/L of EDTA has been found in some U.S. industrial and municipal wastewater treatment plants and up to 12 mg/L in European bodies of water.[2,4,5]

In wastewater treatment plants, chelating agents can interfere with metal removal processes, allowing toxic metals to pass through untreated and contaminate the environment.[6,7] Some studies have suggested that >1 mg/L concentrations can interfere with biological processes.[7,8] Therefore, in 2003 the World Health Organization specified a 600 µg/L limit for EDTA in drinking water.[2,9] Based on additional studies, the European Aminocarboxylates Committee established the predicted no effect concentration (PNEC) limit of 2.2 mg/L in the aqueous environment.[3] (PNEC is defined as the predicted concentration that is not expected to cause adverse effects.) Therefore, sensitive analytical methods are needed to monitor surface water, municipal drinking water, and wastewater to meet regulatory compliance in Europe and to address increasing public concerns about the environmental fate of aminopolycarboxylate chelates in the environment.

This study describes the determination of µg/L concentrations of four aminopolycarboxylate chelates, EDTA, NTA, DTPA, and EGTA, in municipal drinking water and wastewater samples. The chelating agents are separated by ion chromatography (IC) on a high-capacity IonPac® AS7 anion-exchange column using methanesulfonic acid to elute the analytes in 16 min followed by pulsed amperometric detection (PAD) with a Pt working electrode. The IonPac AS7 column is designed for separating polyvalent anions and therefore is ideal for this application. Additionally, the column's high capacity minimizes column overload from the high salt matrix in wastewater samples. This method also uses the advantages of PAD to selectively quantify µg/L concentrations of chelating agents without interference from high concentrations of common anions commonly found in environmental samples. The qualification results and effect of the dissolved metals on the chromatography are also discussed. This method provides a selective and sensitive method to directly determine µg/L concentrations of chelating agents and therefore allows monitoring of these persistent contaminants in industrial wastewater samples.

EQUIPMENT

Dionex ICS-3000 or ICS-5000 system including:

SP Single Gradient Pump module with degas option

DC Detector/Chromatography Module (dual-temperature configuration)

AS Autosampler and 10 mL sample tray

ED Electrochemical Detector (P/N 079830)

Electrochemical cell (cell and reference electrode, P/N AAA-061756)

Pt working electrode (P/N 064440 package of six)

Combination pH–Ag/AgCl reference electrode (P/N 061879)

Knitted reaction coil, 125 µL (P/N 053460)

25 µL PEEK™ sample loop (P/N 042857)

Chromeleon® Chromatography Data System (CDS) software

2 L glass eluent bottle, Type GL45 (P/N 045901)

Vial Kit, 10 mL with caps and septa (P/N 055058)

Filter unit for vacuum filtration, 1 L, 0.20 µm nylon (Nalgene® Media-Plus with 90 mm filter, Nalge Nunc International P/N 164-0020) or equivalent nylon filter

Vacuum pump

Sample Preparation:

- Pall Corporation IC Acrodisc®, 25 mm syringe filters, 0.2 µm Supor® (PES) membrane, IC certified (P/N 4583T)
- Filter unit for vacuum filtration, 250 mL, 0.20 µm nylon (Nalgene Media-Plus with 90 mm filter, Nalge Nunc International P/N 153-0020) or equivalent nylon filter
- Hot plate
- pH meter
- 5 mL Disposable syringes
- Sodium hydroxide for pH adjustment

REAGENTS AND STANDARDS

Deionized water, Type 1 reagent-grade, 18.2 MΩ-cm resistivity

Use only ACS reagent-grade chemicals for all reagents and standards

EDTA, disodium dihydrate (disodium ethylenediaminetetraacetate dihydrate, Sigma-Aldrich P/N E4884, FW 372.24)

NTA (nitrilotriacetic acid, Sigma-Aldrich P/N 398144, FW 191.14)

DTPA (diethylenetriaminepentaacetic acid, Sigma-Aldrich P/N 32319, FW 393.35)

EGTA (ethylene glycol tetraacetic acid, Sigma-Aldrich P/N 32319, FW 380.35)

Methanesulfonic acid, >99.5% (Fluka P/N 64280, FW 96.11)

Sodium hydroxide, 50% w/w certified (Fisher Scientific P/N SS254)

pH 7 (yellow) buffer solution (VWR International P/N BDH5046)

pH 4 (red) buffer solution (VWR International P/N BDH5018)

1000 mg/L single element standards used for metal-chelator experiments

- Copper (VWR International P/N JT5713-4)
- Cobalt (VWR International P/N JT5712-4)
- Iron (III) (VWR International P/N JT5764-4)
- Nickel (VWR International P/N JT5770-4)
- Zinc (VWR International P/N JT5791-4)

SAMPLES

Municipal wastewater effluent samples from Cities A and B

Town C surface water

Municipal drinking water from Cities A and B

CONDITIONS

Column:	IonPac AG7 Guard, 2 × 50 mm (P/N 063099) IonPac AS7 Analytical, 2 × 250 mm (P/N 63097)
Eluent:	A: Degassed deionized water B: 200 mM Methanesulfonic acid (MSA)
Gradient:	17.5% B (35 mM MSA) from -5 to 1 min, step to 50% B (100 mM MSA) at 1 min, 50% B from 1 to 12 min, step to 17.5% B at 12 min, 17.5% B from 12 to 16 min
Flow Rate:	0.3 mL/min
Trap Column:	IonPac CTC-1, 9 × 24 mm (P/N 040192)
Temperature:	30 °C
Inj. Volume:	25 µL
Detection:	PAD, Pt disposable WE, waveform (Table 1)
Data Collection Rate:	0.9 Hz
Typical Background:	130–180 nC
Typical Noise:	60–80 pC
Typical pH:	0.9–1.1
Run Time:	16 min

Table 1. Waveform[10]

Time (sec)	Potential vs Ag/AgCl (V)	Gain Region[a]	Integration	Ramp[a]
0.00	+ 0.30	Off	Off	Ramp
0.31	+ 0.30	Off	Off	Ramp
0.32	+ 1.15	Off	Off	Ramp
0.64	+ 1.15	On	On (Start)	Ramp
0.66	+ 1.15	On	Off (End)	Ramp
0.67	- 0.30	Off	Off	Ramp
1.06	- 0.30	Off	Off	Ramp
1.07	+ 0.30	Off	Off	Ramp

[a] The gain and ramp are instrument settings for the ICS-3000 (and ICS-5000) electrochemical detector.

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent A (Degassed Deionized Water)

When preparing eluents, use high quality, Type 1, 18.2 MΩ-cm resistivity deionized water that contains as little dissolved gas as possible, which can cause increased noise in electrochemical detection. To prepare 2 L of Eluent A, degas 2 L of deionized water by using vacuum filtration and ultrasonic agitation with applied vacuum for 10 to 20 min. Connect the eluent bottle to the Eluent A line, place the eluent bottle under ~4 to 5 psi of nitrogen or another inert gas, and prime the pump. Also, prepare 1 L of degassed Type 1 water weekly for the AS Autosampler flush solution.

Eluent B (200 mM MSA)

To prepare 2 L of eluent, degas 2 L of deionized water by using vacuum filtration and ultrasonic agitation with applied vacuum for 10 to 20 min, add 1974 ± 0.1 g of the degassed deionized water into a 2 L glass GL45 eluent bottle placed on a top loader balance, and add 38.4 ± 0.1 g (26 mL) of MSA. Connect the eluent bottle to Eluent B line, place the eluent bottle under ~4 to 5 psi of nitrogen or another inert gas, mix the eluent thoroughly, and prime the pump with the new eluent.

Stock Standard Solutions

To prepare 500 mg/L of individual EDTA and NTA stock solutions, transfer 64.1 ± 0.1 mg of the disodium EDTA dihydrate and 50 ± 0.1 mg of the NTA anhydrous reagent, respectively, into separate 100 mL Class A volumetric flasks. Add deionized water to the 100 mL mark. Mix the standard solutions thoroughly by inversion until the reagents are fully dissolved. EGTA and DTPA are slightly soluble in water, and therefore require additional mixing. To prepare the EGTA and DTPA stock solutions, add 50 mg of reagent plus 75 mL of deionized water and a stir bar into separate 100 mL Class A volumetric flasks. Stir for at least 3 h with a magnetic stirrer until the reagents are fully dissolved. Remove the magnetic stir bar, rinse the stir bar into the volumetric flask, and dilute to the 100 mL mark with deionized water. Mix the solutions thoroughly by inversion.

Intermediate and Working Standard Solutions

To prepare combined 10 mg/L EDTA, 20 mg/L NTA and DTPA, and 40 mg/L EGTA intermediate standards, pipet 400 µL of 500 mg/L EDTA, 800 µL of 500 mg/L NTA and DTPA, and 1600 µL of 500 mg/L EGTA stock standards into a 20 mL glass scintillation vial. Add deionized water to 20.000 g total weight and mix thoroughly. To prepare the five working standards, pipet 100, 200, 400, 1000, and 2000 µL of the combined intermediate standards into individual 20 mL glass scintillation vials placed on an analytical balance. Add deionized water to 20.000 g total weight and mix thoroughly. The first working standard, containing 50 µg/L EDTA, 100 µg/L NTA and DTPA, and 200 µg/L EGTA, was used to determine the limit of quantification (LOQ) and diluted 1:1 with water to determine the limit of detection (LOD). Prepare the working standards daily, the intermediate standard weekly, and the stock standard monthly. Store at 5 °C.

Sample Preparation

All surface, municipal, and wastewater effluent samples were filtered prior to analysis to remove particulates using an individual 250 mL Nalgene 0.2 µm filter flask. Syringe filters (Pall Corporation Acrodisc) were used during the initial evaluations and are also suitable. Additionally, the wastewater effluent samples were also degassed with ultrasonic agitation and applied vacuum for 30 min and diluted 1:10 to reduce the matrix effects. All samples were spiked with 200 µg/L EDTA, DTPA, and NTA, and 400 µg/L EGTA from the 100 mg/L stock solutions for accuracy determinations.

Metal-Chelate Solutions

To prepare the metal-chelate solutions, first make a 0.5 mg/L EDTA, NTA, and 1 mg/L DTPA, EGTA mixed standard solution by pipetting 20 µL each of the 500 mg/L EDTA and NTA, and 40 µL each of the 500 mg/L DTPA and EGTA stock solutions into a 20 mL scintillation vial. Add deionized water to a total weight of 20.000 g. Add 25 and 250 µL aliquots of the 1000 mg/L metal standard (Fe^{+3}, Cu^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}) to separate 5 mL aliquots of the mixed standard and then mix the solutions thoroughly.

The metal-chelate solutions were analyzed before and after treatments used to remove the metal from the chelating agent. All of the selected metal-chelate solutions were evaluated with Treatment 1, described below. The copper- and iron-chelate solutions were evaluated with all four treatments.

- *Treatment 1:* Withdraw 4 mL of solution with a 5 mL disposable syringe. Pass the solution through an OnGuard® M cation trap cartridge. Discard the first mL passing through cartridge and collect the remainder of sample after it passes through the cartridge. The OnGuard M cation trap cartridge is designed to remove divalent transition and alkali metals.
- *Treatment 2:* Adjust the sample to pH 11 with a dilute sodium hydroxide solution. Filter the solution with a Pall IC syringe filter.
- *Treatment 3:* Adjust the sample to pH 11 and heat the solution to 50 °C for 30 min. Cool to room temperature, adjust the volume to the starting volume, and then filter the solution with a Pall IC syringe filter.
- *Treatment 4*: Prepare the solution with Treatment 3 followed by Treatment 1.

PRECAUTIONS

Any solution treated with base must be filtered to remove particulates prior to injection. Acid eluents, such as the MSA used in this application, must only be stored in glass eluent bottles to reduce contamination introduced from the polymeric bottles.

SYSTEM PREPARATION AND CONFIGURATION

Preparing the System

To prepare the system, remove any previous metal contaminated components and conduct routine maintenance on the AS autosampler and the pumps. If the AS autosampler has not been maintained recently or has been exposed to high concentrations (mg/L) of metals, it may be necessary to install and calibrate a new AS injection port transfer line and install and align a new AS needle assembly.

Configuring the System

To configure the system, install the ED and the IonPac CTC-1 (9 × 24 mm) trap column after the pump and install ~61 cm yellow PEEK (0.076 mm i.d./0.003 in i.d.) tubing to the trap column outlet. The trap column removes any residual dissolved metals in the eluent. Install the free end of the yellow PEEK tubing, the 25 µL sample loop, and heat exchanger on the injection valve. Flush with 100 mM MSA eluent for 1 h at 1.0 mL/min to waste. Then install the IonPac AG7 guard and AS7 analytical column using red PEEK (0.127 mm i.d./0.005 in i.d.) tubing, which is temporarily directed to waste and flushed with deionized water for 10 min at 0.3 mL/min followed by 100 MSA eluent at the same flow rate overnight. Refer to the product manuals for more information.[11,12]

Assembling the Electrochemical Cell

To assemble the electrochemical cell, follow the instructions in AN 188, calibrate (from pH 7 to pH 4) and install the reference electrode and a Pt disposable working electrode.[13] Connect one free end of the 125 µL knitted reaction coil to the outlet of the analytical column and the other end to the cell inlet. Connect a small section (~4 to 6 in) of red PEEK tubing in the cell outlet as a backpressure loop. As a precaution, wait until after the pump is delivering eluent to the cell and the pH <2 before turning on the ED cell and loading the waveform. Equilibrate the system with the cell at least an hour to obtain a stable baseline and peak response. The working electrodes exhibited the minimum lifetime (two weeks) or greater, based on the peak response of >80% relative to the initial peak response of a newly installed and stabilized electrode.

Monitoring pH

Monitoring pH during sample analyses provides details on reference electrode drift and noise, and confirms proper eluent preparation. To monitor and record the pH, insert *Log* commands in the Chromeleon program by opening the instrument method, selecting *Script Editor*, highlighting a row, right click, insert a new time, enter the command *Log* and enter the value *pH*.

RESULTS AND DISCUSSION

To determine aminopolycarboxylate chelates, the IonPac AS7 (2 × 250 mm) was selected because it is a high-capacity anion-exchange column designed for the separation of polyvalent anions. The strong acid eluent partially protonates the analytes, thus reducing the effective charge, and allowing elution of the analytes from the column.[14–16] The IonPac AS7 column was previously used with PAD to separate the target chelating agents using 100 mM MSA eluent. The selectivity for these chelators was NTA < EDTA < DTPA < EGTA.[17] However, NTA and EDTA peaks were weakly retained and could co-elute with other less retained sample components. To improve this method, the eluent conditions from 25 to 150 mM MSA were evaluated to increase the resolution of EDTA and NTA from the void volume, while eluting DTPA and EGTA from the column within a reasonable time to improve sample throughput. This was accomplished by setting the initial eluent condition at 35 mM MSA for 1 min to elute EDTA and NTA and then stepping the concentration to 100 mM to elute EGTA and DTPA within 16 min. These conditions reverse the selectivity between NTA and EDTA, which indicates that NTA is very responsive to changes in eluent strength.

The analytes were detected by PAD using a Pt working electrode and a three-potential Pt waveform optimized at 100 mM MSA.[10]

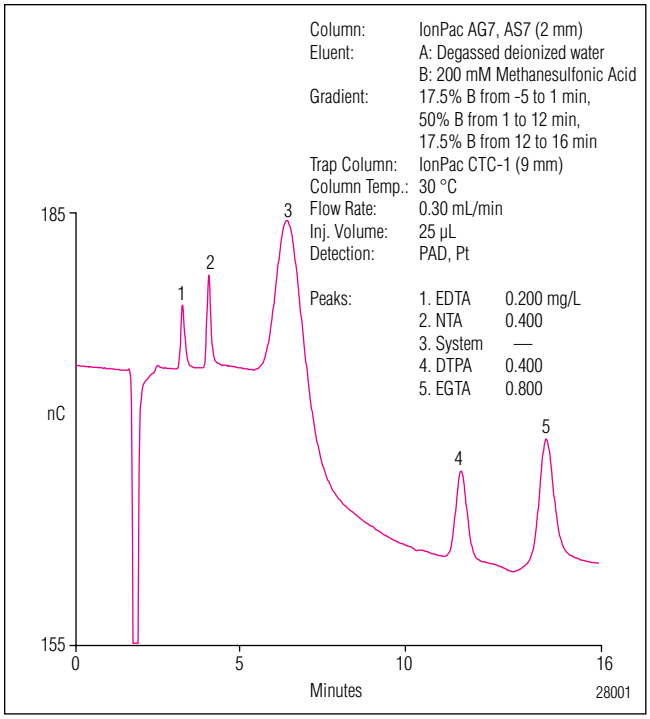

Figure 2. Mixed aminocarboxylate chelate standard separated and detected by anion-exchange chromatography with pulsed amperometric detection.

Figure 2 shows the separation of 200 µg/L EDTA, 400 µg/L NTA and DTPA, and 800 µg/L EGTA standards in deionized water. The peaks show good peak symmetry (A_s <1.2) except for NTA and EGTA (A_s = 1.4), efficiencies >4000 plates, and peak responses well above the baseline. The large peak at approximately 5 min is a baseline disturbance from the eluent step change at 1 min. The CTC-1 (9 × 24 mm) trap column adds a 5 min void time and therefore the change in baseline from the eluent step change occurs around 6 min in the chromatogram. The eluent concentration is reduced to the initial conditions at 12 min and held through the injection of the next sample, which produces an approximately 9 min total equilibration.

Table 2. LOD, LOQ, and Linearity Results

	Linear Range (µg/L)	Coefficient of Determination (r^2)	LOD (µg/L)	LOQ (µg/L)
EDTA	50–1000	0.9991	15	50
NTA	100–2000	0.9992	20	67
DTPA	100–2000	0.9992	30	100
EGTA	200–4000	0.9993	63	210

n = 7

LOD and LOQ are defined as 3× and 10× S/N.

Limit of Detection, Limit of Quantification, Linear Range, and Precision

To qualify the method, the estimated limit of detection (LOD), limit of quantification (LOQ), linear range, and precision were determined. The LOD and LOQ were determined by measuring the peak-to-peak noise in 1 min increments from 20 to 60 min in four replicate runs without a sample injection and found that the noise averaged 65 ± 12 pC. The estimated LODs and LOQs were calculated based on the peak response of the standards at 3× and 10× the signal-to-noise (S/N) (Table 2). The estimated LODs ranged from 15 to 63 µg/L and the LOQs ranged from 50 to 210 µg/L. To determine the method linearity, five combined calibration standards from 50 to 1000 µg/L EDTA, 100 to 2000 µg/L NTA and DTPA, and 200 to 4000 µg/L EGTA were injected in four replicates, which produced coefficients of determination (r^2) >0.999. The retention time precisions, based on seven replicate injections of 0.50 mg/L EDTA, 1.0 mg/L NTA and DTPA, and 2.0 mg/L EGTA combined standards, had RSDs of <0.3. NTA, EDTA, DTPA, and EGTA had peak area precisions of 2.35, 2.17, 3.37, and 2.48 RSDs, respectively.

Chelating Agents in Surface Water, Municipal Drinking Water, and Wastewater Samples

This method was applied to five municipal water samples that included surface water, drinking water, and wastewater effluent from two municipalities. All samples were filtered to remove particulates prior to analysis. Trace EGTA concentrations (0.13 to 0.18 mg/L) were detected in all samples. However, trace concentrations of EDTA (≤50 µg/L) were only detected in the wastewater samples. DTPA and NTA were not detected in any of the samples investigated in this study.

To determine the accuracy of the method, the samples were spiked with 0.200 mg/L EDTA, NTA, and DTPA, and 0.400 mg/L EGTA. Figure 3 Chromatogram B shows the chromatography of the unspiked surface water sample with only EGTA detected. Figure 3 Chromatogram C shows the same sample spiked with known concentrations of chelating agents. A water blank (Figure 3 Chromatogram A) is shown for comparison. As shown, EDTA was well resolved from a small baseline dip and from NTA. DTPA and EGTA eluted well after the baseline disturbance at ~7 min and a larger dip at 10 min.

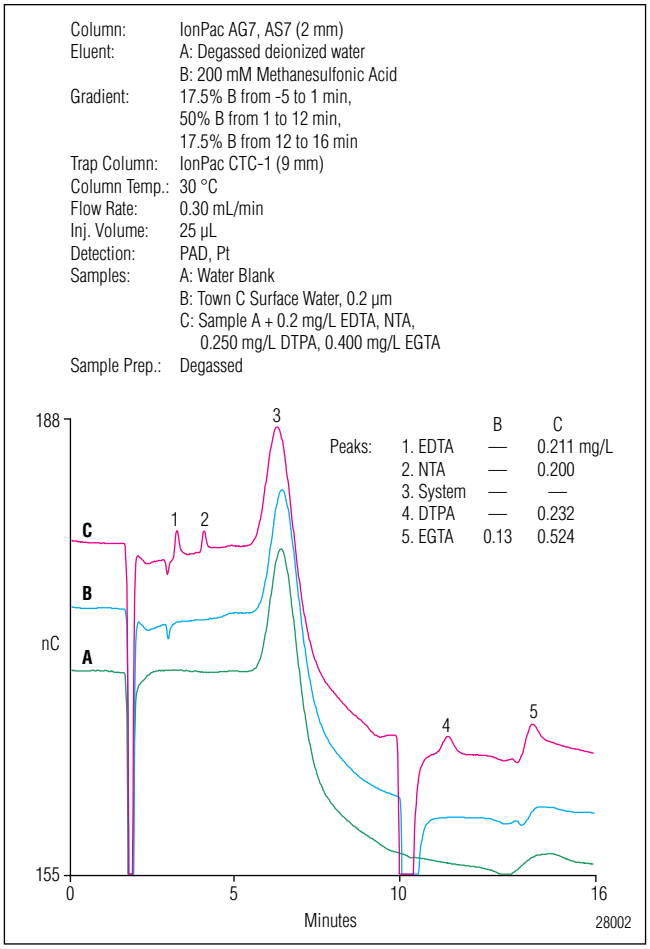

Figure 3. Comparison of Town C surface water B) without and C) with chelates added.

Table 3. Results and Recoveries in Drinking Water and Wastewater Samples						
Sample	**Analyte**	**Amount Found (mg/L)**	**RSD**	**Amount Added (mg/L)**	**RSD**	**Amount Recovered (%)**
Town C Surface Water[a]	EDTA	N.D.	—	0.198 ± 0.008	4.3	107 ± 0.7
	NTA	N.D.	—	0.198 ± 0.012	5.9	108 ± 0.6
	DTPA	N.D.	—	0.232 ± 0.013	5.8	107 ± 0.8
	EGTA	0.13 ± 0.02[c]	3.8	0.565 ± 0.030	5.2	110 ± 2.1
City A Drinking Water[a]	EDTA	N.D.	—	0.198 ± 0.008	4.3	103 ± 0.5
	NTA	N.D.	—	0.198 ± 0.012	5.9	106 ± 0.8
	DTPA	N.D.	—	0.232 ± 0.013	5.8	112 ± 0.9
	EGTA	0.18 ± 0.02[c]	4.6	0.565 ± 0.030	5.2	89.0 ± 3.2
City B Drinking Water[a]	EDTA	N.D.	—	0.198 ± 0.008	4.3	109 ± 1.8
	NTA	N.D.	—	0.198 ± 0.012	5.9	114 ± 0.7
	DTPA	N.D.	—	0.232 ± 0.013	5.8	89.5± 0.6
	EGTA	0.18 ± 0.02[c]	4.6	0.565 ± 0.030	5.2	109 ± 3.2
1:10 Dilution of City A Wastewater Effluent[b]	EDTA	0.054 ± 0.010	18	0.198 ± 0.008	4.3	95.2 ± 0.3
	NTA	N.D.	—	0.198 ± 0.012	5.9	95.1 ± 1.1
	DTPA	N.D.	—	0.232 ± 0.013	5.8	95.5 ± 1.0
	EGTA	0.18 ± 0.02	14	0.565 ± 0.030	5.2	101 ± 6.2
1:10 Dilution of City B Wastewater Effluent[b]	EDTA	0.024 ± 0.009	3.7	0.198 ± 0.008	4.3	101 ± 0.7
	NTA	N.D.	—	0.198 ± 0.012	5.9	107 ± 0.8
	DTPA	N.D.	—	0.232 ± 0.013	5.8	96.0 ± 2.8
	EGTA	0.14 ± 0.02[c]	4.5	0.565 ± 0.030	5.2	124 ± 8.8

n = 5

[a] Samples were filtered with 0.2 µm filter prior to determination

[b] Samples were filtered, degassed for 30 min with ultrasonic agitation and applied vacuum, and diluted 1:10 prior to determination

[c] Calculated value below calibration range

N.D.: Not Detected

The recovery of the chelating agents spiked in the sample ranged from 107 to 110% (Table 3). The municipal drinking water samples had similar chromatography and a slightly larger range of recoveries, compared to the surface water sample (89 to 112%). The initial evaluation of the municipal wastewater effluent samples showed a large baseline disturbance prior to the elution of EDTA, possibly from organic acids and carbonate, which may interfere with the accurate quantification of EDTA. To minimize the matrix effects of the wastewater, the samples were degassed with an applied vacuum and ultrasonic agitation, then diluted 1:10. Using these additional steps, detection of 0.024 and 0.054 mg/L EDTA was achieved in 1:10 dilution of degassed City A and City B wastewater effluent samples, and 95 and 101% recoveries, respectively.

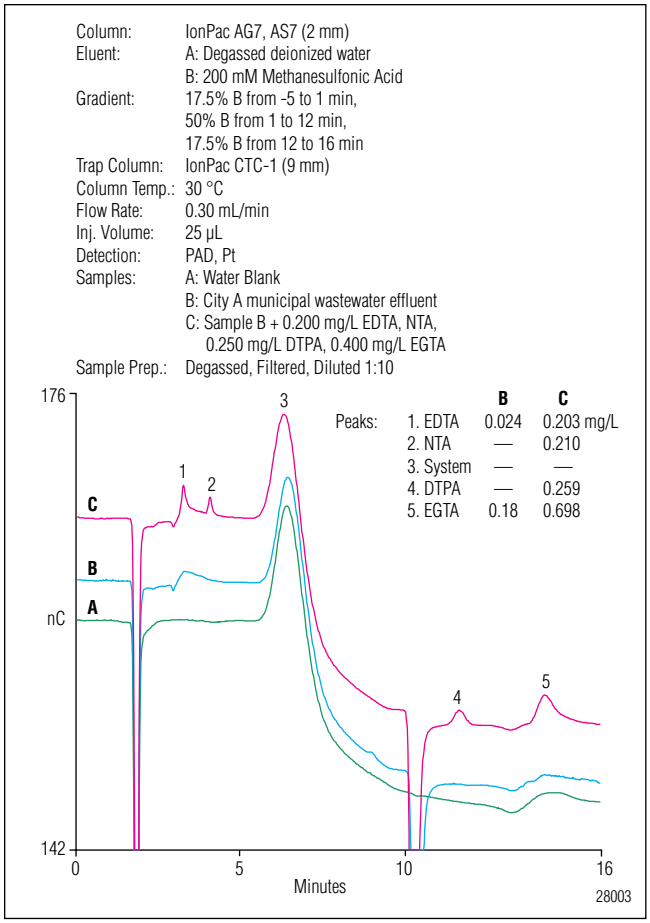

Figure 4. Comparison of 1:10 dilution of City A municipal wastewater effluent B) without and C) with chelates added.

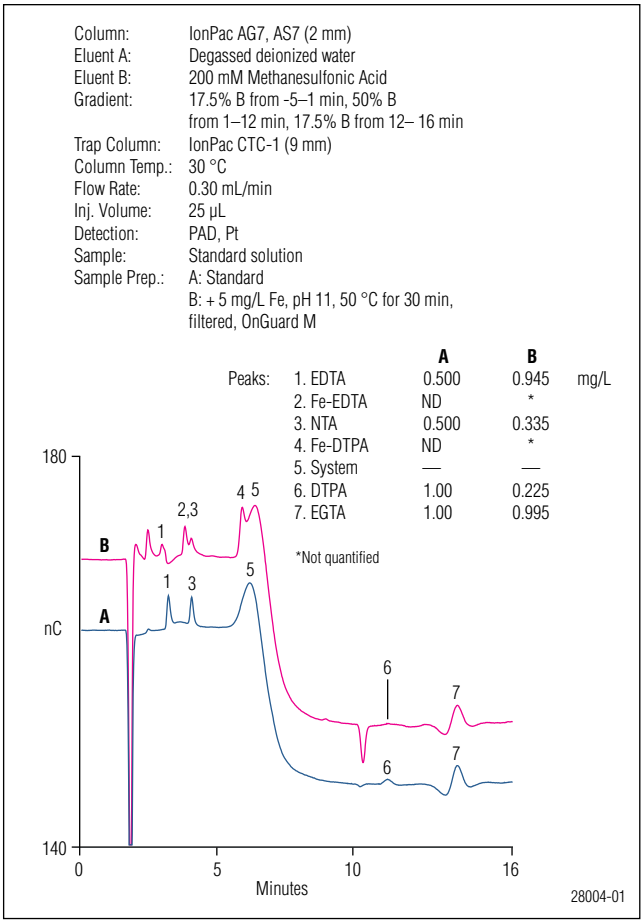

Figure 5. Effect of iron on chelating agents.

Figure 4 compares a water blank and City A municipal wastewater sample with and without 0.200 mg/L of EDTA, NTA, DTPA, and 0.400 mg/L EGTA added. After degassing and diluting the wastewater samples, the negative peak eluting near the EDTA peak was minimized, resulting in improved recovery of EDTA. While these additional sample treatments improved EDTA detection, the sensitivity for all analytes in the municipal wastewater samples was reduced by the dilution factor.

Effect of Metal Chelation

The effects of metal chelation on the separation of chelating agents has been discussed extensively.[2,4,16] Metal chelates reduce the ionic charge compared to the free chelate due to the binding of the metal, with the exception of NTA, which retains the same ionic charge.[2,4,16] To evaluate the effect of the change in charge distribution on the anionic separation, amounts of 5 and 50 mg/L of iron (III), copper, cobalt, nickel, and zinc were added to individual solutions of the mixed chelate standard (0.5 mg/L EDTA, NTA, 1 mg/L DTPA, EGTA). Some samples were treated with OnGuard M cartridge, which is a cation sample-preparation cartridge designed to remove free metals. The responses and retention times of DTPA, EDTA, and NTA were significantly affected by the presence of iron (Figure 5). The complexed Fe-DTPA eluted 4.5 min earlier at ~6.9 min relative to the uncomplexed DTPA, which eluted at ~11.4 min. In addition, the response of Fe-DTPA increased by ~400%. In contrast to Fe-DPTA, the Fe-EDTA retention time decreased only slightly by 0.5 min and partially co-eluted with NTA, resulting in a 42.5% decrease in peak area response relative to the uncomplexed EDTA. The NTA peak area response was significantly lower (73 to 74%) than the untreated sample. However, no shift in retention time was observed. No changes in responses or retention times were observed for EGTA from the presence of the investigated transition metals.

Previous studies demonstrated that the metal chelates were unstable at a pH <6 and >8.[15] These authors achieved partial success in recovering the chelate after treating the solutions with OnGuard M cartridges. To improve the recoveries of DTPA and EDTA, the effects of treating the solutions by adjusting the pH, heating and filtering the metal precipitates, and treating the complexed chelators with OnGuard M cartridges were evaluated. Metal-chelate sample solutions were diluted 1:10 and 1:100, then prepared by adding aliquots of 1000 mg/L metal standards in an acid matrix to produce a sample solution pH from 1 to 3. In the initial experiments, the iron-chelate test solutions were analyzed without treatment and after treatment with OnGuard M cartridges, but no changes in peak responses and retention times were observed. The metal-chelate sample solutions were also adjusted with dilute sodium hydroxide solution to pH 11 and filtered with a 0.2 µm syringe filter to remove any metal particulates.

Additionally, to improve the metal precipitate formation, aliquots of the iron-chelate solutions were heated at 50 °C for 30 min, then filtered with a 0.2 µm syringe filter. Some aliquots were also treated with OnGuard M cartridges. The best results were found by using Treatment 4, combining pH adjustment, heating, filtering the precipitate, and using an OnGuard M cartridge. As a result of the treatments, another peak appeared at the original EDTA retention time but at 35.7% of the original EDTA peak area (Table 4), along with the Fe-EDTA peak at 3.8 min but at a ~5% lower peak area. The combined peak areas of the two peaks were comparable (93%) to the peak area of EDTA prior to treatment with iron. However, no improvement in the recovery of DTPA was observed. These experiments show that iron binds strongly with DTPA and EDTA, interfering with the separation and quantification of the two chelating agents (Chromatogram C, Figure 5). However, treatment with base, elevated temperature, and OnGuard M cartridges improves the recoveries of EDTA, but the treatment does not completely release the metal from the complex.

Table 4: Recoveries of 0.5 mg/L Chelates in the Presence of Select Metals

Metal	Amount Metal Added (mg/L)	EDTA Recovery (%)	NTA Recovery (%)	DTPA Recovery (%)	EGTA Recovery (%)
Cobalt	5.0	98.7	101	95.6	99.6
	50	95.4	105	84.7	85.3
Copper	5.0	98.7	99.6	98.8	92.6
	50	87.0	95.4	84.8	101
Iron	5.0	~58.5[b]	72.6	--[d]	99.3
	5.0, Treated[a]	35.7[c] ~55.2[b]	83.5	--[d] < LOQ[e]	91.2
	50	~58.9[b]	73.5	--[d]	97.1
Nickel	5.0	90.3	98.8	88.9	92.7
	50	85.9	98.7	93.8	96.4
Zinc	5.0	98.5	97.7	98.9	96.3
	50	93.5	93.1	98.7	103

n = 2

[a] Adjusted to pH 11, heated to 50 °C for 30 min, filtered, and treated with OnGuard M cartridge.

[b] Estimated, based on peak area of Fe-EDTA peak eluting ~0.8 min later than the EDTA peak.

[c] EDTA peak appearing near original retention time.

[d] Fe-DTPA peak eluting near 6 min was not quantified.

[e] DTPA peak detected at original retention time.

CONCLUSION

This experimental study describes a direct, sensitive, and accurate method to determine µg/L concentrations of NTA, EDTA, EGTA, and DTPA in surface water, municipal drinking water, and wastewater samples.

This method takes advantage of the selectivity of the IonPac AS7 column to separate large hydrophobic anionic compounds, such as chelating agents, and the selectivity of PAD to determine low concentrations of these compounds without detecting common anions that are typically present at high concentrations in wastewater samples. Improved recoveries of EDTA in the presence of iron (III) can be achieved by treating the samples with base, elevated temperature, and OnGuard M cartridges. This experimental study determines concentrations of chelating agents needed to assess the contamination levels in water systems and provide adequate safety to the environment.

SUPPLIERS

Sigma-Aldrich, Inc., P.O. Box 951524, Dallas, TX 75395-1524, U.S.A. Tel: 1-800-325-3010. www.sigmaaldrich.com

VWR International, Inc., Goshen Corporate Park West, 1310 Goshen Parkway, West Chester, PA 19380, U.S.A. Tel: 1-800-932-5000. www.vwrsp.com

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