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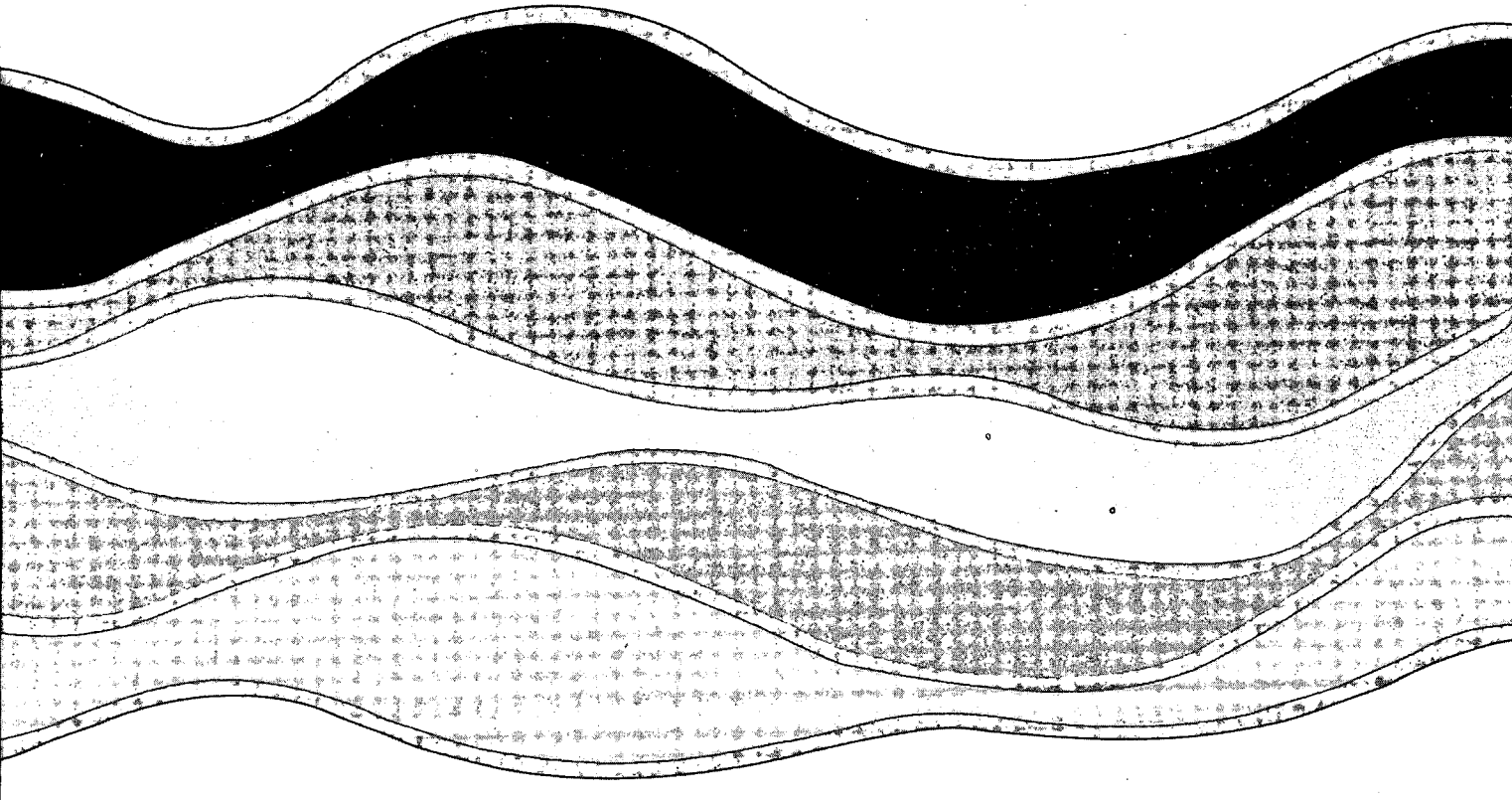

DETERMINATION OF NITRILOTRIACETIC, ETHYLENEDIAMINETETRAACETIC AND DIETHYLENETRIAMINEPENTAACETIC ACIDS IN SEWAGE TREATMENT PLANT AND PAPER MILL EFFLUENTS

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Determination of Nitrilotriacetic, Ethylenediaminetetraacetic and Diethylenetriaminepentaacetic Acids in Sewage Treatment Plant and Paper Mill Effluents

by

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MANAGEMENT PERSPECTIVE

The presence of organic chelating acids such as NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid), and DTPA (diethylenetriaminepentaacetic acid) in sewage treatment plant (STP) and paper mill effluents can be a burden to the aquatic ecosystem. NTA and DTPA are both toxic and suspected carcinogens. Since EDTA and DTPA are not easily removed by waste treatment processes, their discharge to surface water can lead to the mobilization of toxic heavy metals in sediments and to the contamination of drinking water. Using a newly developed method, the above three acids were detected in nearly all STP effluents collected from eight southern Ontario municipalities. As a result of rather heavy use of DTPA by the paper recycling industry, high levels of DTPA were found in the final effluents collected from some of those mills. This work marks the first report for the occurrence of DTPA in effluent samples collected in Canada.

SOMMAIRE À L'INTENTION DE LA DIRECTION

La présence d'acides organiques chélateurs comme le NTA (acide nitrilotriacétique), l'EDTA (acide éthylènediaminetétracétique) et le DTPA (acide diéthylènetriaminepentacétique) dans les effluents des stations d'épuration des eaux usées et des fabriques de pâte à papier peut nuire aux écosystèmes aquatiques. Le NTA et le DTPA sont toxiques et tous deux sont soupçonnés d'être cancérigènes. Étant donné que l'EDTA et le DTPA sont difficilement éliminés par les procédés de traitement des eaux usées, leur rejet dans les eaux superficielles peut provoquer une mobilisation des métaux lourds toxiques présents dans les sédiments et la contamination de l'eau de boisson. À l'aide d'une nouvelle méthode, nous avons détecté ces trois acides dans presque tous les échantillons d'effluents de stations d'épuration prélevés dans huit municipalités du sud de l'Ontario. L'industrie de recyclage du papier faisant une assez grande utilisation du DTPA, des concentrations élevées de cet acide ont été mesurées dans l'effluent terminal de certaines de ces usines. Nos travaux sont les premiers à faire état de la présence de DTPA dans les échantillons d'effluents recueillis au Canada.

ABSTRACT

A method for the determination of nitrilotriacetic (NTA), ethylenediaminetetraacetic (EDTA), and diethylenetriaminepentaacetic (DTPA) acids in sewage treatment plant (STP) and paper mill effluents has been developed. The chelating acids were extracted by solid phase extraction cartridges packed with strong anion-exchange resins and were eluted by a small volume of 16 M formic acid. After conversion into their 1-propyl esters, the acids were quantified by gas chromatography using a nitrogen-phosphorus selective detector and confirmed by GC/MS with a Mass Selective Detector. At a pH of 3.5, the recovery of these acids varied from 83 to 104% in water and STP effluent samples fortified to levels from 1 to 1000 μg/L. Based on a concentration factor of 100, the detection limit for these acids was 0.5 μg/L. All three acids were found in STP effluents, although the concentrations were relatively low for EDTA (<100 μg/L) and DTPA (<15 μg/L) in most samples. In contrast, much higher concentrations (>1000 μg/L) of NTA were observed for nearly all primary STP effluents. A large variation in the levels of these acids was observed in the paper recycling mill effluents collected. Although their concentrations were mostly <150 μg/L, the levels of DTPA were very high (>2500 μg/L) in the effluents obtained from two mills that use this chelating agent to remove metal ions. DTPA was not detected and the concentrations for NTA and EDTA were <11 μg/L in the effluents collected from the non-recycling paper mills.

RÉSUMÉ

Nous avons mis au point une méthode permettant de doser la présence des acides nitrilotriacétique (NTA), éthylènediaminetétracétique (EDTA) et diéthylènetriaminepentacétique (DTPA) dans les effluents des stations d'épuration des eaux usées et des fabriques de pâte à papier. Les acides chélateurs ont été extraits à l'aide de cartouches d'extraction en phase solide remplies de résines échangeuses d'anions très actives, puis ils ont été élués par un faible volume d'acide formique 16 M. Après conversion en leurs esters 1-propyliques, les acides ont été dosés par chromatographie en phase gazeuse à l'aide d'un détecteur sélectif azote-phosphore, puis les mesures ont été confirmées par CG/SM et un discriminateur de masse. À un pH de 3,5, la récupération des acides allait de 83 à 104 % dans les échantillons d'eau et d'effluents de stations d'épuration fortifiés à des concentrations de 1 à 1 000 μg/L. Avec un facteur de concentration de 100, la limite de détection de ces acides était de 0,5 μg/L. Les trois acides étaient présents dans les effluents, mais les concentrations observées étaient relativement faibles pour l'EDTA (<100 μg/L) et le DTPA (<15 μg/L) dans la plupart des échantillons. Par contre, on a observé des concentrations beaucoup plus fortes de NTA (>1 000 μg/L) dans presque tous les effluents primaires des stations d'épuration des eaux usées. On a observé une grande variation des concentrations de ces acides dans les échantillons d'effluents d'usines de recyclage du papier. Même si les concentrations étaient la plupart du temps inférieures à 150 μg/L, celles de DTPA étaient très élevées (>2 500 μg/L) dans les effluents de deux usines qui emploient cet agent chélateur pour éliminer les ions métalliques. On n'a pas détecté la présence de DPTA et les concentrations de NTA et d'EDTA étaient inférieures à 11 μg/L dans les échantillons d'effluents des usines qui ne recyclaient pas le papier.

INTRODUCTION

The presence of large amounts of reactive phosphate in lake water in the 1960's has led to the rapid eutrophication of the Great Lakes. Phosphate-based detergents in domestic sewage were identified as a major source of this nutrient. As a remedial measure, the environmental protection agencies of Canada and the United States introduced measures to reduce the input of phosphorus from domestic sewage by limiting the phosphate content in laundry detergents. Nitrilotriacetic acid (NTA) has become a preferred, albeit controversial, substitute for the triphosphate as a detergent builder in Canada since it has a low eutrophication potential and good chelating properties [1,2]. However, because of the concerns on possible health effects, NTA was withdrawn in 1970 from consumer products in the United States. A more recent decision by USEPA permitted the reintroduction of NTA in those states where phosphate-based detergents were banned.

Ethylenediaminetetraacetic acid (EDTA) and its salts have been used by the food industries to promote color retention in dried and canned food. They are also employed in detergents and cleansers, used as metal-complexing agents in pulp bleaching and for a variety of industrial applications such as electroplating and photographic processing.

The sodium salt of diethylenetriaminepentaacetic acid (DTPA) is the active ingredient in Versenex 80, a chelating agent manufactured by the Dow Chemical Company. Recently, this agent has been used extensively by the paper recycling industries in Canada where hydrogen peroxide is used to brighten the de-inked pulp [3]. Metal ions of iron, copper, manganese, etc., in waste paper and mill water catalyze the decomposition of hydrogen peroxide to molecular oxygen which does not contribute to the bleaching action. Chelating agents are used as scavengers of these ions so that the wasteful decomposition of hydrogen peroxide can be prevented in the de-inking process. The cost, complexing ability as well as its oxidative stability under basic conditions make DTPA the chelating agent of choice in those processes. Typically, a 0.2% (w/w) charge of DTPA on oven dried fibre is required to provide optimal brightness of the pulp [3].

The occurrence of chelating acids in the environment can pose a threat to the health of the aquatic ecosystem. For example, EDTA and DTPA can lead to the mobilization of toxic heavy metals in sediments by the formation of soluble complexes. DTPA is toxic to algae and bacteria at low mg/L levels [4]. There was an allegation that NTA could enhance the embryotoxic and teratogenic effects of heavy metals such as cadmium and mercury. NTA and its degradation product, iminodiacetic acid, are suspected carcinogens [5]. NTA at mg/L levels in the primary effluents of sewage treatment plants (STP) and at μg/L levels in drinking water has been found [1,2].

DTPA, also a suspected carcinogen, is one of the most widely used chelating agents in Europe and, in contrast with NTA, it resists degradation in the sewage treatment system [6]. There is presently no restriction on its use in Canada and the United States. Recently in Germany, the occurrence of DTPA at low μg/L levels in river water has been reported [7]. To date, no data regarding the occurrence, persistence, degradation and environmental fate of DTPA in Canada are available.

Several analytical methods have been described for the determination of NTA in water and effluent samples [8-11]. Most of them were based on an anion-exchange resin column preconcentration step, followed by alkylation of the acids and gas chromatographic detection of the esters with a nitrogen selective detector. Application of these methods was later extended to the determination of EDTA [12] and DTPA [7]. Using solid phase extraction cartridges packed with strong anion-exchange resins, we have developed a rapid and quantitative method for the simultaneous determination of NTA, EDTA and DTPA in effluent samples. A brief survey of the levels of these acids in some Canadian STP and paper mill effluents is also presented.

EXPERIMENTAL

Chemicals

NTA (99%) and EDTA (99.6%) were 'Baker Analyzed' reagents. DTPA (97%), formic acid (96%) and acetyl chloride were obtained from Aldrich. 1-Propanol was a product of Caledon. Formic acid was redistilled before use. 16 M formic acid was prepared by diluting 736.5 g of formic acid to 1 L with water. Didecylmethylamine (>90%), obtained from Fluka, was used as an internal standard in gas chromatography. Hexane, dichloromethane and isooctane were distilled-in-glass grade solvents available from Burdick and Jackson. Anhydrous sodium sulfate (BDH) was heated to 500°C overnight, cooled and stored in glass bottles before use.

Stock solutions of NTA, EDTA and DTPA at 1000 μg/mL were prepared by dissolving 100 mg of each acid in 2 mL of 1 M NaOH and dilution to 100 mL with deionized water. Mixtures of the three acids at 100 and 10 μg/mL were prepared by mixing 1 mL each of the stock solutions and dilution to 10 and 100 mL, respectively, with water.

Effluent samples

Grab samples of the primary and final STP effluents from eight southern Ontario municipalities were collected in 4 L solvent bottles. Grab and 24-hr composite final effluent samples were also collected from selected paper mills in Ontario and Quebec, some of them known to recycle newsprint and other paper products. They were stored at 4°C in the dark and were usually extracted in less than five days after collection. Since the stability of these acids in effluents was unknown, they should be regarded as unstable and be extracted as soon as practical.

Extraction of acids from effluent samples

Prior to extraction, the sample was shaken for 30 s and ca. 110 mL of the effluent was filtered through a 47 mm diammeter Whatman GF/C filter. One hundred mL of this filtered

subsample was acidified to a pH of ca. 3.5 with 50 μL of 16 M formic acid. Strong anion-exchange (SAX) resins with quaternary amine functional groups and chloride counterions were used for the extraction of NTA, EDTA and DTPA in effluents. In this work, the Supelco LC-SAX (500 mg) solid phase extraction (SPE) tubes and the 12-port Visiprep-DL vacuum manifold with disposable Teflon liners were used. The SPE tube was conditioned by eluting the packing with the following solvents: (1) 5 mL of 1 M NaOH, (2) 10 mL of water, (3) 3 mL of 1 M formic acid, and (4) 10 mL of water. During conditioning, the flow rate was adjusted to ca. 3 mL/min by applying a vacuum (12- to 15-in Hg) to the manifold with a vacuum pump. Care was taken not to allow the SPE tube to dry out during conditioning and the subsequent sample adsorption. After the pH was adjusted to ca. 3.5 with the 16 M formic acid, the filtered effluent was passed through the resin tube at a flow rate of ca. 3.5 to 4 mL/min by adjusting the vacuum to just below 20-in Hg. Caution: according to Supelco, a vacuum of 20-in Hg and/or a flow rate of 5 mL/min should not be exceeded. At the end of the extraction, vacuum was applied to the tube for 0.5 min before the acids were eluted with 3 mL of 16 M formic acid. The eluate collected in a 15 mL disposable screw cap test tube was evaporated just to dryness at 80°C.

Derivatization

To the dried extract, 1.8 mL of 1-propanol and 200 μL of acetyl chloride were added. The addition of acetyl chloride must be very slow in order to avoid bumping. The mixture was heated at 100°C for 1 hr. and was then evaporated to ca. 0.2 mL in a 80°C water bath. After it was cooled to room temperature, 2 mL of dichloromethane/hexane mixture (1:3, v/v) and then 5 mL of 0.001 M NaOH were added. The test tube was vigorously shaken for 1 min to facilitate the partitioning of the esters into the organic layer. After phases separated, the upper layer was passed through a 5 cm column of anhydrous sodium sulfate prepared in a disposable Pasteur pipet and the extract was collected in a 15 mL graduated tube. The extraction was repeated twice with two 2 mL aliquots of the dichloromethane/hexane mixture. The combined organic extract was evaporated by a gentle stream of nitrogen in a 40°C water bath in the presence of 1 mL of isooctane as a keeper. After addition of 20 μL of a 400 ng/μL solution of didecylmethylamine in isooctane as an internal standard, the final volume was adjusted to 1.0 mL. Dilution of the final extract, if required, was made in 1% 1-propanol in isooctane (v/v).

Chromatographic analysis and mass spectral confirmation

Final analysis of sample extracts was carried out with a Hewlett-Packard (HP) 5890 Series II Plus gas chromatograph equipped with a nitrogen-phosphorus selective detector (NPD), cool on-column injector, and a HP7673 autosampler. Instrument control, data acquisition and report generation were achieved by a personal computer running the HP3365 ChemStation software under the Microsoft Windows environment. A piece of deactivated fused silica, 1 m x 0.53 μm, was joined to the 12 m x 0.2 mm i.d. x 0.33 μm HP-1 analytical column at the injector end with a glass union to facilitate automatic on-column sample injection. The GC oven temperature program was: 70°C initial (kept for 1 min), then increased to 200°C at a rate of 30°C/min and to 290°C at a rate of 10°C/min and the final temperature was kept for 5 min. The injector was set at a temperature 3°C above the oven (oven tracking) and the NPD was set at 300°C. Carrier gas (helium) linear velocity was held constant at 32.5 cm/s by means of an electronic pressure controller. Flow rates for the make-up and detector gases were: helium 25 mL/min, hydrogen 3.2 mL/min, and air 100 mL/min.

For the confirmation of compound identity, a HP5972 Mass Selective Detector (MSD) interfaced to a HP5890 Series II gas chromatograph was used. Sample injection was made, in the splitless mode, by a HP7673 autosampler onto a 30 m x 0.25 mm i.d. x 0.25 μm HP-5-MS column. The temperature program was identical to the one used for NPD work. Injection port and detector interface temperatures were 250°C and 280°C, respectively. A constant carrier (helium) linear velocity of 38.4 cm/s was used. The electron energy and electron multiplier voltage were 70 eV and 2400 V, respectively. Confirmation of the acids was carried out in full scan mode and data were acquired from m/z 40 to 605 at a rate of 1.3 scans/s.

Calibration standards and quantification

Three mL of 16 M formic acid were mixed with a known amount of the acids (e.g. 100 μg each) and the solution was evaporated to dryness in a 80°C water bath. The acids were derivatized as described above for the sample extracts. Dilutions of the products were made with 1% 1-propanol in isooctane (v/v) to prepare calibration standards of 25, 2.5 and 0.25 μg/mL. In all cases, the internal standard was kept at a constant concentration of 8 μg/mL.

From an injection of a derivatized standard, the NPD response factor of the propyl ester of an acid, RF_a, was determined by the following equation,

$$RF_a = W_a/W_{is} * A_{is}/A_a$$

where W_a and W_{is} are the amounts (ng) of the acid and the internal standard, respectively, injected and A_a and A_{is} are the corresponding peak areas. The concentration of an acid in a sample was calculated by the equation:

$$C_a = RF_a * C_{is} * A_a/A_{is} * V_{ext}/V_{sam}$$

where C_a is the concentration (μg/L) of the acid in the sample, C_{is} is the concentration (μg/L) of the internal standard in the final extract, V_{ext} is the volume (mL) of the final extract, and V_{sam} is the volume (mL) of the original effluent sample.

RESULTS AND DISCUSSION

Preparation of standard solutions and derivatization

NTA, EDTA, and DTPA in free acid form are only slightly soluble in water or the common polar organic solvents. However, these acids are easily soluble in NaOH solutions as their sodium salts are very soluble in water. Stock solutions of these acids were prepared by first dissolving 100 mg each of these acids in a small amount (1 or 2 mL) of 1 M NaOH and then they were further diluted with water.

Several alkyl esters of NTA, EDTA, and DTPA have previously been reported for these acids. Methyl [12], 1-propyl [7,9], and 1-butyl [11] esters have been successfully applied to the determination of NTA. While methyl [12] and 1-propyl esters [7] have been used for EDTA, only the propyl ester has been reported for DTPA [7]. In this work, we have briefly compared the formation of the methyl, 1- and 2- propyl, as well as the 1-butyl esters of these acids. Although all these alkyl esters could be prepared by reacting the acids with the appropriate alcohol in the presence of acetyl chloride at 85 or 100°C in this work, the methyl and 2-propyl esters were deemed less suitable for quantitative work because of their lower NPD responses and stability in comparison to the 1-propyl esters. Despite good NPD sensitivity for all three 1-butyl

esters, they were also not investigated further as we were not able to detect the DTPA derivative, presumably due to its very high molecular weight (673), by the MSD.

There are a few precautionary steps that have to be taken in order to obtain the highest yield and reproducible results for the 1-propyl derivatives. To derivatize a calibration mixture, it is imperative to mix 3 mL of 16 M formic acid to an aliquot of the NTA, EDTA and DTPA mixture before it was evaporated to dryness. In the presence of formic acid, an oily residue soluble in 1-propanol was left after evaporation. If formic acid was not added, a white precipitate, i.e. sodium salts of the acids, partially soluble in 1-propanol was formed. In the latter case, biased high results for the effluents would be obtained since the yields of all ester standards were reduced, especially for DTPA. After derivatization, the addition of a strong base such as 1 M NaOH to the propanoic mixture as described in one procedure [7] should be avoided. Otherwise, losses of the products could occur due to a base catalyzed hydrolysis of the esters. Instead, the volume of the reaction mixture was reduced to ca. 200 μL, an organic solvent was added before a diluted base, i.e. 0.001 M NaOH, was introduced to remove the excess acetyl chloride. Since 1-propanol is soluble in both water and organic solvents, this evaporation would help the partitioning of the esters into the organic phase. The completeness of the 1-propylation reaction at different periods of time was studied. Since there were only minor differences in reaction yields between the 0.5, 1, 2, and 3 h reactions, an one-hour reaction time was then used for the rest of this work.

Chromatographic and mass spectral properties of the derivatives

Due to the low volatility of the 1-propyl esters, a short 12 m OV-1 column was chosen for the NPD work. This column provided fast (less than 16 min) elution times yet excellent separation of the three esters as well as the internal standard. On-column injection was used in the final analysis of the acid esters with NPD since this injection technique offered more precise quantification results (3.5% vs. 6.5% relative standard deviation) for DTPA than splitless injection. By the elimination of discrimination in the injection port and syringe needle, higher detector response for the DTPA and, to a smaller extent, EDTA derivatives was also obtained with on-column injection. In this case, the mean response factors for the 1-propyl esters of NTA,

EDTA, and DTPA were 0.71, 0.40, and 0.59. With splitless injection, the mean response factors for DTPA and EDTA 1-propyl esters increased by 38% and 8%, respectively. To avoid changes in the response factor for the DTPA derivative due to adsorption in the chromatographic system, including on-column injection, concentrated sample extracts or standards should be diluted in 1% 1-propanol in isooctane instead of pure isooctane. In order to maintain good peak shape, however, the fused silica pre-column was either cleaned or replaced after ca. 100 sample injections. While 100 pg of the esters could be detected, the NPD response was linear over a range from 250 pg to 25 ng injected. Instead of stearonitrile which was used by other workers, didecylmethylamine was employed as an internal standard for NPD analysis. These two compounds have similar chromatographic properties and can be used interchangeably.

The electron-impact mass spectrum for the NTA tripropyl ester exhibited three ions characteristic of the molecule: a weak molecular ion, M^+, at m/z 317, a base peak at m/z 230 corresponding to $[M\text{-}CO_2Pr]^+$ and an ion at m/z 144 corresponding to $[CH_3NCH_2(CH_2CO_2Pr)]^+$. In addition to a weak molecular ion at m/z 460, the EDTA derivative also showed characteristic ions at m/z 373 ($[M\text{-}CO_2Pr]^+$) and 230 ($[M\text{-}CH_2N(CH_2CO_2Pr)_2]^+$, base peak) as well as m/z 144. In contrast, the molecular ion for the 1-propyl ester of DTPA (MW=603) was not observed. Instead, characteristic ions at m/z 516 ($[M\text{-}CO_2Pr]^+$), 373 ($[M\text{-}CH_2\text{-}N(CH_2CO_2Pr)_2]^+$, base peak) and 244 ($[N(CH_2CO_2Pr)_2CH_2CH_2]^+$) as well as m/z 144 were present. Quantification and confirmation of the NTA and EDTA esters at trace levels (detection limit 25 pg/μL) can be achieved in the selected ion monitoring (SIM) mode using the characteristic ions described above. However, presumably because of the low sensitivity of the Mass Selective Detector at high molecular masses, we were unable to detect the DTPA derivative at concentrations below 1 ng/μL in SIM mode.

Preconcentration of effluent samples

Solvent extraction of NTA, EDTA and DTPA cannot be applied to effluent samples since these acids are nearly insoluble in all water immiscible organic solvents. In the past, glass columns packed with strong anion-exchange resins such as the Dowex 1X-2 [9-11] or Bio-Rad AG 1-X2 [7] have been used for the pre-concentration of the polydentate acids. While these

resins produced good recovery for the acids, they were tedious to use because of the need for swelling and packing. Also, with gravity flow, the flow rates of these columns, particularly those with Dowex 1X-2, were slow and thus the time required for the conditioning and sample adsorption could be as long as two to three hours. In our work, we have investigated the use of SPE tubes packed with smaller, 40 μm diameter LC-SAX resins and found that they had a few advantages over the Dowex or Bio-Rad resins (150 to 300 μm). The SPE tubes are already packed and they require much smaller volumes of solvents for conditioning and sample elution. When the latter was complemented by a fast (up to ca. 4 mL/min) flow rate, total sample pre-concentration time (conditioning, adsorption and elution) was typically between 35 and 45 min for 100 mL of effluents. A much smaller volume (3 mL vs. 10 or 40 mL) of 16 M formic acid required for sample elution also translated into a huge saving in time since the evaporation of formic acid before derivatization was a very slow process. Since they are inexpensive, these SPE tubes are disposable and thus there are no possibility for cross contamination in the sample pre-concentration step. Similar to other anion exchangers, the chloride counterions in the LC-SAX resin were replaced by the formate ions, in a two-step procedure, for higher selectivity. The resin was first converted to the hydroxide form by eluting the SPE tube with 1 M NaOH. This was followed by the conversion of the resin to the formate form with 1 M formic acid.

Recovery of NTA, EDTA and DTPA from spiked samples

Other than proper conditioning and avoidance of drying out the SPE tube, sample pH also played an important role for the recovery of these acids. As shown in Table 1, less than 10% of NTA was recovered in spiked tap water, lake water and STP effluent if the sample pH was around 7. Lowering of sample pH to 3.5 and to 3.0 improved the recovery to 89% or above in all types of water. Poor recovery (<5%) was also experienced for EDTA when the sample was neutral although it was >90% if the pH was adjusted to 3.5. However, a further decrease of the pH to 3 or lower resulted in a drop of EDTA recovery to <50%. While low recovery (23 to 27%) was also observed for DTPA in unacidified spiked tap water and lake water samples, quantitative results were obtained at pH 3.5. There was no observable dependence on sample pH for the recovery of DTPA in the two spiked STP effluents. For the highest recovery of all three acids, all samples were then acidified to a pH of 3.5 before extraction.

The recoveries of NTA, EDTA, and DTPA in tap water, lake water, and STP effluent at various levels of fortification were summarized in Table 2. In most cases, over 85% of all acids were recovered. Based on a concentration factor of 100, the detection limit for these acids was 0.5 μg/L.

Determination of the acids in STP and paper mill effluents

The levels of NTA, EDTA, and DTPA in the primary and final effluents collected from eight STPs in southern Ontario were determined by this method (Table 3). In agreement with previous findings [1,2], relatively high concentrations of NTA (from 880 to 6100 μg/L) were found in the primary effluents because of the input from household laundry wastewater. In all but two cases, there was a large (over 30-fold) reduction of the NTA level in the final STP effluent as NTA degraded rapidly under aerobic conditions [1]. In contrast, much lower levels of EDTA (<100 μg/L) and DTPA (<15 μg/L) were found in most primary and final STP effluents. Also, sewage treatment seemed to have minor or no effects on the reduction of their levels. At present, the source of DTPA in municipal sewage effluent is unknown.

Very different concentrations of the chelating acids were detected in the paper recycling mill final effluents (Table 3). The levels of NTA and EDTA varied from <10 to 470 μg/L and from <10 to 1280 μg/L, respectively. High levels of DTPA (>2500 μg/L) were found in two cases while the other effluents had a concentration range from 2 to 164 μg/L. In contrast, DTPA was not detected in the non-recycling paper mill final effluents and the levels of NTA and EDTA were below 11 μg/L. GC/NPD chromatogram of an extract derived from a STP final effluent was shown in Figure 1. The NPD and full scan GC/MS chromatograms of an effluent extract from a paper recycling mill are shown in Figures 2 and 3A, respectively. Despite the complexity of the sample, as indicated in the full scan chromatogram, the NPD chromatogram was simple and free of interference due to the selectivity of the detector. The identities of NTA, EDTA, and DTPA in this sample were confirmed as their mass spectra (Figures 3B, 3C, and 3D, respectively) were nearly identical to the corresponding standards.

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Table 1. Effect of pH on the % recoveries of NTA, EDTA, and DTPA in spiked water samples. Each recovery was an average of two determinations. All effluent results were corrected for blanks.

Water type (conc.)	pH	NTA	EDTA	DTPA
Tap (10 μg/L)	7.5	9	3	23
Tap (10 μg/L)	3.5	89	95	101
Tap (10 μg/L)	3.0	99	92	102
Lake (10 μg/L)	7.2	2	2	27
Lake (10 μg/L)	3.4	95	92	95
STP effluent A (100 μg/L)	7.6	8	4	97
STP effluent A (100 μg/L)	3.5	92	91	101
STP effluent A (100 μg/L)	3.0	103	48	96
STP effluent B (100 μg/L)	3.5	94	97	103
STP effluent B (100 μg/L)	2.6	101	29	92

Table 2. % Recovery (± standard deviation) of NTA, EDTA, and DTPA from various spiked water samples. Number of replication = 4.

Sample type (conc.)	NTA	EDTA	DTPA
Tap water (100 μg/L)	89 ± 2	95 ± 3	101 ± 3
Tap water (10 μg/L)	97 ± 2	90 ± 2	97 ± 4
Lake water (100 μg/L)	95 ± 5	94 ± 5	99 ± 6
Lake water (10 μg/L)	83 ± 7	84 ± 8	95 ± 6
Lake water (1 μg/L)*	94 ± 9	84 ± 8	104 ± 10
STP effluent A (1000 μg/L)	94 ± 5	90 ± 7	93 ± 6
STP effluent A (100 μg/L)*	90 ± 6	89 ± 4	102 ± 4
STP effluent B (100 μg/L)*	92 ± 4	98 ± 4	96 ± 6

* Results corrected for blanks.

Table 3. Concentration ranges (μg/L) of NTA, EDTA, and DTPA in some Canadian STP and paper mill effluents.

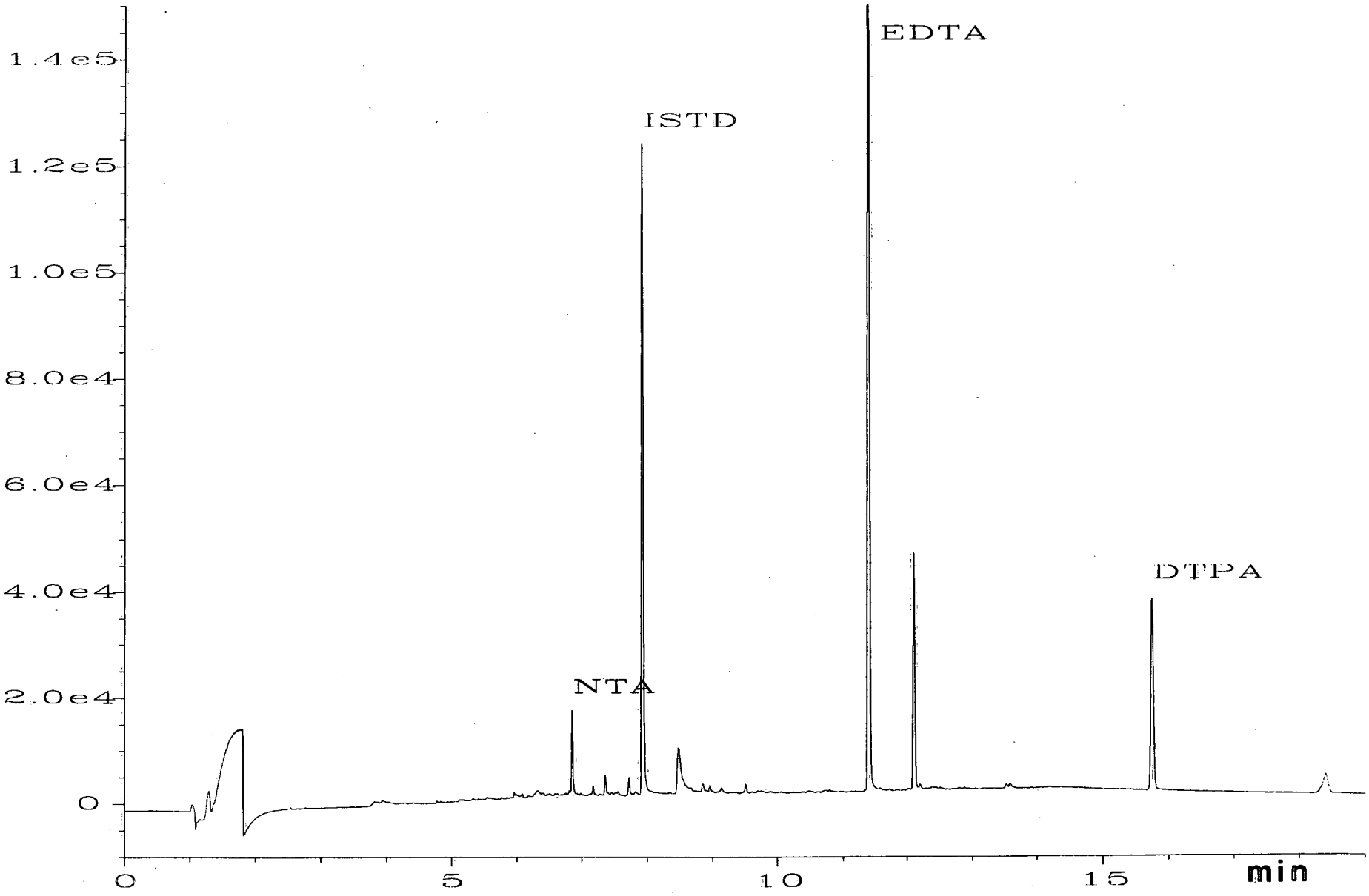
Effluent type	No. of samples	NTA	EDTA	DTPA
STP -- primary	8	878 - 6090	18 - 116	1.0 - 35
STP -- final	8	1.8 - 589	7.7 - 81	0.9 - 22
Paper recycling mills	8	6.0 - 469	1.7 - 1282	2.0 - 2880
Other paper mills	10	<0.5 - 11.1	<0.5 - 11.3	<0.5

LIST OF FIGURES

FIGURE 1. GC/NPD chromatogram of a STP final effluent extract after 1-propylation. Concentrations (μg/L) of the acids in this sample: 6.6 (NTA), 50.9 (EDTA), and 21.6 (DTPA).

FIGURE 2. GC/NPD chromatogram of the propylated extract from a paper recycling mill effluent. Concentrations (μg/L) of the acids in this sample: 61.2 (NTA), 77.4 (EDTA), and 2880 (DTPA).

FIGURE 3. (A) Full scan GC/MS chromatogram of the same extract as in Figure 2. (B), (C), and (D) Mass spectra of the 1-propyl esters for NTA, EDTA, and DTPA, respectively.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DTPA
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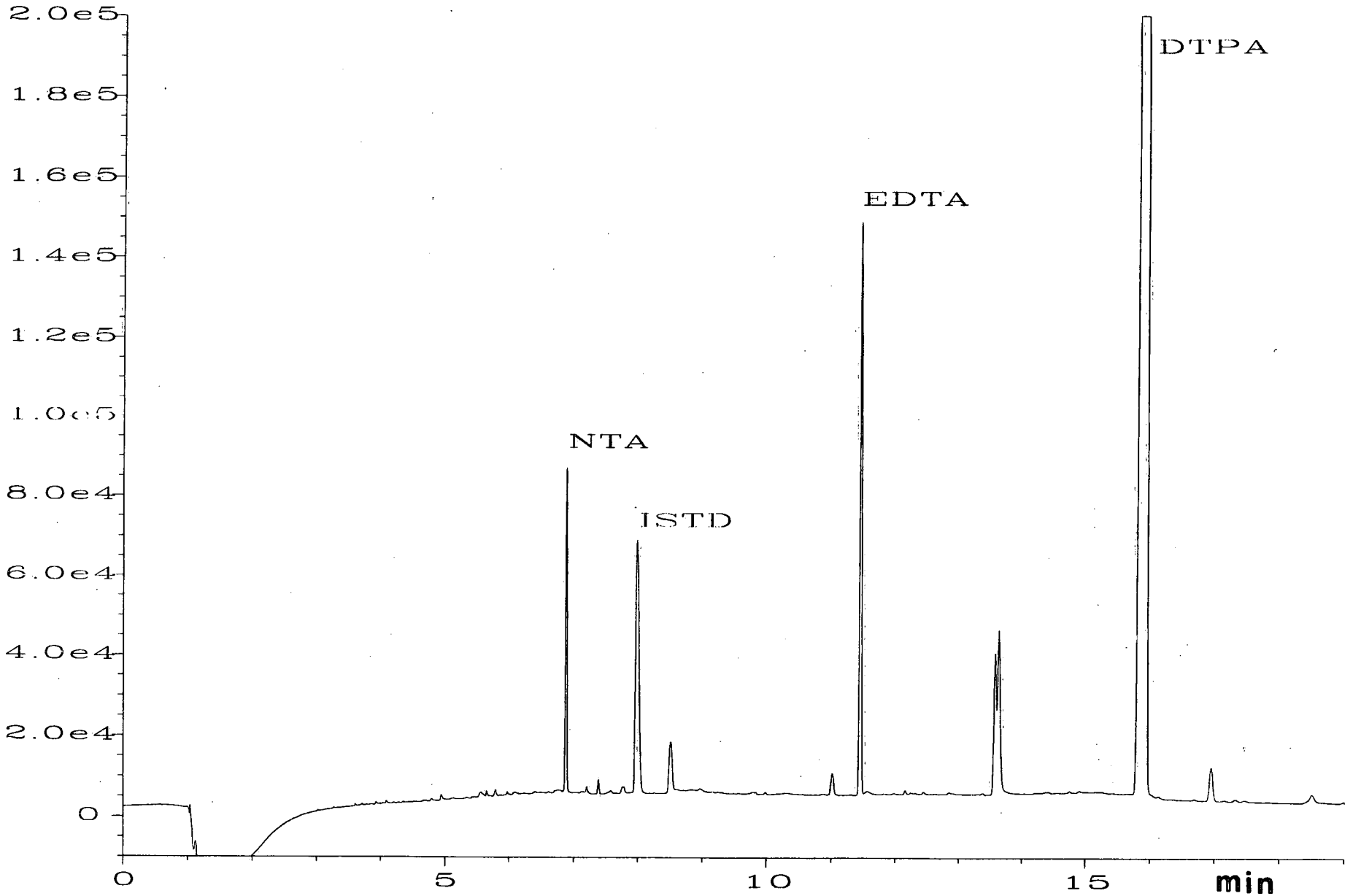
10
15
min

Figure 1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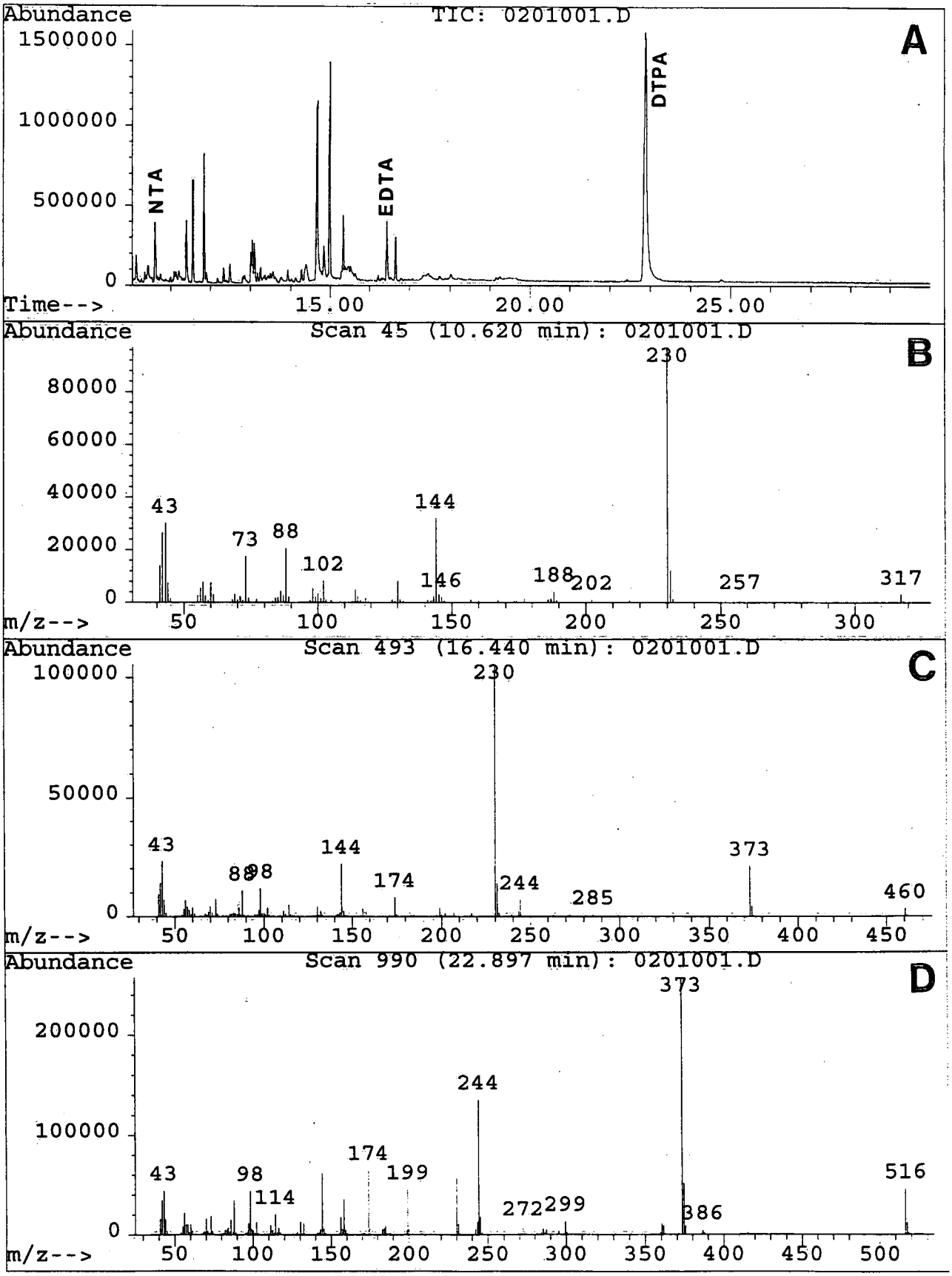
EDTA
DTPA
0
5
10
15
min

Figure 2

Figure 3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25.00
Abundance
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144
146
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98
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272
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386
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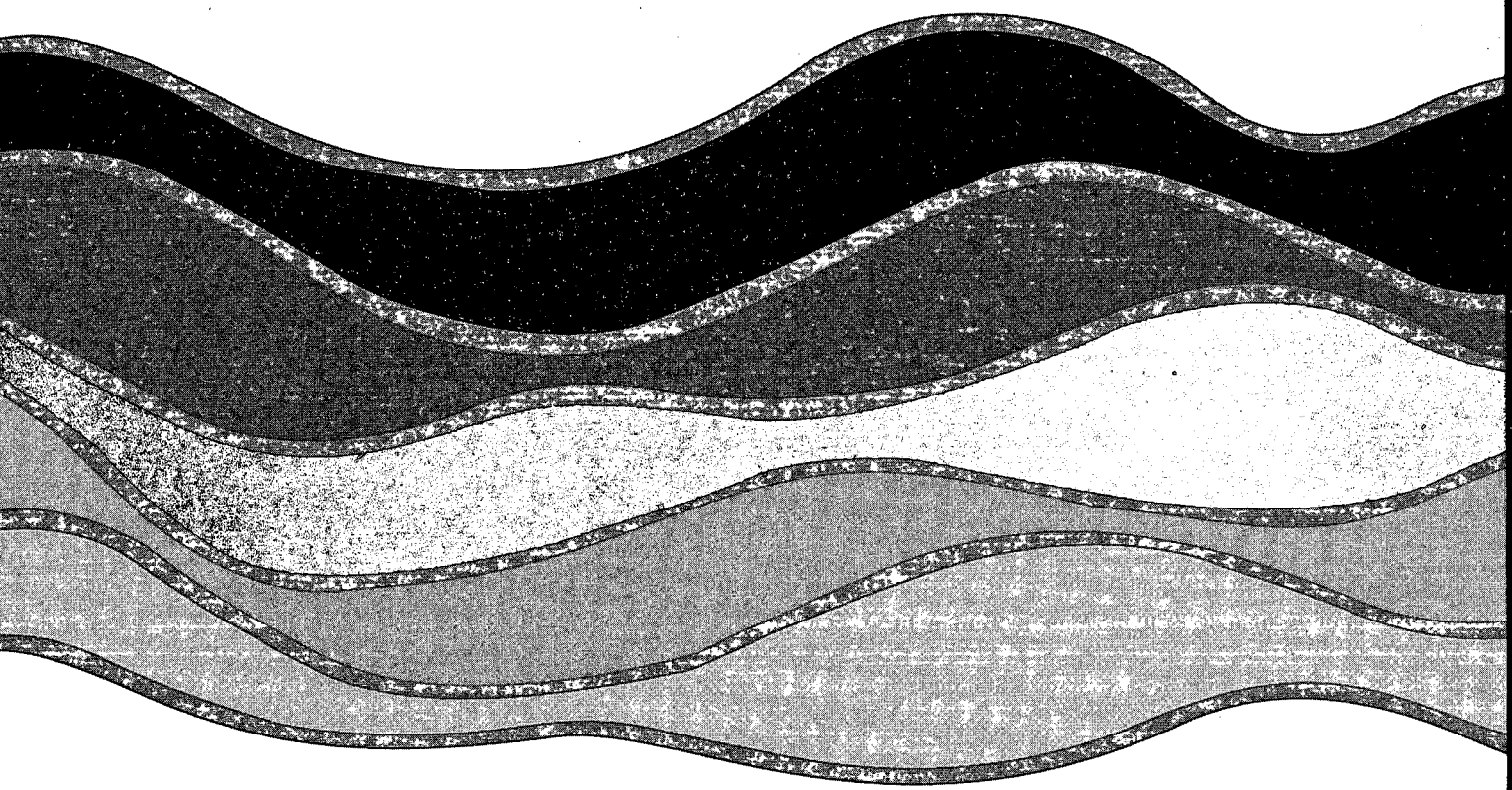

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