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Determination of diethylenetriaminepentaacetic acid in pulp mill effluent by ion-interaction reversed-phase liquid chromatography

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Abstract

A method for analysing diethylenetriaminepentaacetic acid (DTPA) in pulp and paper mill effluent using ion-interaction reversed-phase liquid chromatography is presented. The analysis is based on formation of the iron(III) complex of DTPA and its separation on a C_{18} column using 4 mM octylamine in a water–acetonitrile mobile phase. A photodiode array detector is used in the analysis to enable peak purity of the Fe–DTPA peak to be compared between samples and standards. DTPA concentrations ranging from <1 to 200 mg l^{-1} may be measured using the technique. Elimination of the FeCl_3 reagent in the sample-preparation stage enabled the measurement of DTPA complexed to iron(III). This feature has been used to demonstrate that a significant proportion of the DTPA present in effluent is present in the iron form. The method has been applied to the analysis of DTPA in pulp and paper mill effluent at concentrations ranging from 1 to 20 mg l^{-1} . Recoveries of DTPA spiked into two sets of samples at levels of 2 and 4 mg l^{-1} averaged 102% with standard deviations of 12 and 16%, respectively. The use of the method to measure DTPA at various locations in the process has indicated that there was a major reduction in the DTPA concentration in pulp and paper mill effluent across the pulping and effluent treatment processes.

1. Introduction

Chelating agents are widely used in industrial processes and in detergents. Their use in the paper industry is primarily in association with hydrogen peroxide bleaching of pulp. One of the most efficient and widely used chelating agents is diethylenetriaminepentaacetic acid (DTPA) as it forms stable chelates with metals such as iron, manganese and copper, which are in pulp at concentrations of up to 100 mg kg^{-1} . In the

absence of a chelating agent, these metals effect catalytic decomposition of hydrogen peroxide, thus reducing its efficiency and causing excessive usage of hydrogen peroxide to achieve a given level of brightness in the paper. Assuming no removal by chemical or biological means, DTPA concentrations in paper mill effluent could be as high as 100 mg l^{-1} . Chelating agents such as DTPA, nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) have the potential to mobilise heavy metals from sediments [1,2], and to inhibit their removal by precipitation in effluent treatment processes [3]. While

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these chelating agents are supposedly stable, there is evidence that in combination with iron(III), DTPA, NTA and EDTA may be photo degraded in sunlight [4].

Several methods are available for measuring the chelating agents NTA and EDTA in effluents by HPLC [5–7], GC [8,9] and polarography [10]. Methods published specifically for DTPA [11–14] include one where ion-interaction chromatography was used with Fe–DTPA formed in situ in the HPLC column [13].

This paper describes the formation of metal–DTPA complexes with the metal ions iron(III) and bismuth for determining DTPA in pulp and paper effluent using ion-interaction reversed-phase HPLC coupled with photodiode array UV detection for both qualitative and quantitative analysis. The metal–DTPA complex is formed prior to injection onto the HPLC so that, in the case of iron, exclusion of the metal reagent enables Fe–DTPA naturally present in the sample to be estimated. The method is applied to the analysis of effluents at various stages of the pulping and effluent treatment processes and show that DTPA is removed by either chemical, photochemical or biochemical degradation mechanisms.

2. Experimental

Water from a Waters Milli-Q apparatus was used to prepare all aqueous solutions. Analytical-reagent grade chemicals were used to prepare 0.1 M FeCl₃/0.1 M HCl and 0.1 M Bi(NO₃)₃/0.8 M HNO₃. A 50 mM octylamine (Aldrich) solution in acetonitrile (HPLC grade) was passed through an acetonitrile-rinsed C₁₈ solid-phase extraction column (Analytichem Bondelut, part No. 607406). A 4 mM ion-interaction reagent (IIR) solution was prepared by diluting 160 ml of the 50 mM octylamine stock solution to 2 l with Milli-Q water. The IIR solution pH was then adjusted to 6 with 2 M H₂SO₄. The IIR solution made in this manner contained 8% CH₃CN. This solution was then filtered through a 0.2- μ m nylon membrane filter and subjected to ultrasound for 10 min. A phosphate buffer was

prepared by dissolving 65 g Na₃PO₄ in 1 l of water and adjusting to pH 8 with phosphoric acid.

A Varian 5060 HPLC system fitted with a Rheodyne 7126 injection valve (100- μ l loop) and a Varian 9060 Polychrom photodiode array detector were used in this study. Two HPLC columns were used in this study, a 25 cm \times 4 mm Econosil 10 μ m C₁₈ column (Alltech) and a 25 cm \times 4 mm Alltima 5 μ m C₁₈ column, to each of which was fitted a Waters C₁₈ precolumn. Samples were injected using a Varian 8050 autosampler and chromatographic data were processed with a Varian Star data system. The absorbance at 258 nm was used to detect the Fe–DTPA complex while Bi–DTPA was detected at 278 nm. The separations were performed isocratically at 2 ml min⁻¹ using IIR solution and acetonitrile in proportions which caused the metal–DTPA solute to elute at about 4–6 min (usually 89% IIR solution and 11% CH₃CN).

The pH of either the DTPA standard (1–20 mg l⁻¹ as the free acid) or an effluent sample was adjusted to 7. The metal–DTPA complexes were formed by adding either 2 ml of 0.1 M FeCl₃ or 0.2 ml of 0.1 M Bi(NO₃)₃ to 10 ml of sample. After standing for 15 min the solution was buffered to pH 7 by the addition of 2 ml of phosphate buffer to remove excess metal ions. The samples were then filtered through a 0.45- μ m filter using an Alltech syringe filter device into an amber glass vial.

3. Results and discussion

3.1. Analytical method development

The newsprint mill at Albury in New South Wales (Australia) discharges its tertiary treated effluent into the River Murray. Environmental regulations require that the mill meet specific environmental licence limits in order to discharge effluent. The environmental licence regulation regarding DTPA required that it be measured as the total of free and chelated DTPA. It was therefore necessary to convert any metal–

DTPA complex to one where the conditional stability constant would be greater than that for any of the metals present in the effluent. Investigation of the effect of pH on conditional stability constants for iron and bismuth complexes of DTPA compared to those for other metals present in the paper mill effluent (Cu, Mn and Zn), clearly showed (Fig. 1) that formation of both bismuth and iron DTPA complexes is preferred over copper, zinc and manganese at $\text{pH} < 6.5$, while at $\text{pH} > 8$ the divalent metals have higher conditional stability constants. Alkaline earth cations such as magnesium and calcium, which form a significant proportion of the total cation content of the effluent being considered, have quite small stability constants relative to the heavy metals, and therefore do not compete in the chelation process. Formation of the appropriate complex (either iron or bismuth) was therefore thermodynamically favoured by keeping the pH at or below 7 in the sample preparation stage and by addition of an excess of the respective cation.

The chromatography of both iron(III)- and bismuth-DTPA complexes was quite similar with respect to retention and the effects of eluent strength and eluent pH upon retention. Using a

mobile phase composition of about 89% IIR solution and 11% acetonitrile, Fe-DTPA eluted at $k' = 3.0$ ($N = 2220$) on the Alltech Econosil column, while Bi-DTPA eluted at $k' = 2.6$ ($N = 4040$). Fe-DTPA eluted on the Alltima column at $k' = 4.6$ with a much narrower peak width ($N = 14\,400$) than the Econosil column so the Alltima column was chosen as the preferred column for analysis of DTPA as the iron(III) complex. Fig. 2 shows chromatograms of 10 mg l^{-1} standards of the Fe-DTPA and Bi-DTPA complexes on the Alltima column.

The influence of eluent octylamine concentration on chromatographic performance was found to be significant. Increasing the octylamine concentration from 1 to 6 mM caused the retention time of both metal-DTPA complexes to increase in a linear fashion. This is consistent with the generally accepted mechanisms of ion-interaction chromatography [16]. The peak width at half height of the Fe-DTPA complex did not change significantly with the increased retention thus giving a marked improvement in column plate count with increase in IIR concentration.

The detection limit achieved by this technique was 0.2 mg l^{-1} when injecting a $200\text{-}\mu\text{l}$ sample and where iron was chosen as the complexing

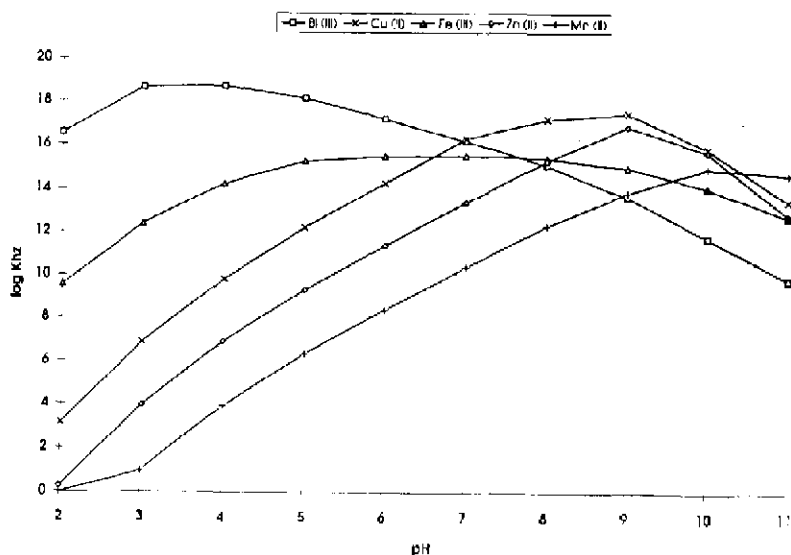


Fig. 1. Conditional stability constants of various metal-DTPA complexes as a function of pH. The curves were calculated from stability constant data supplied by Akzo Chemicals [15].

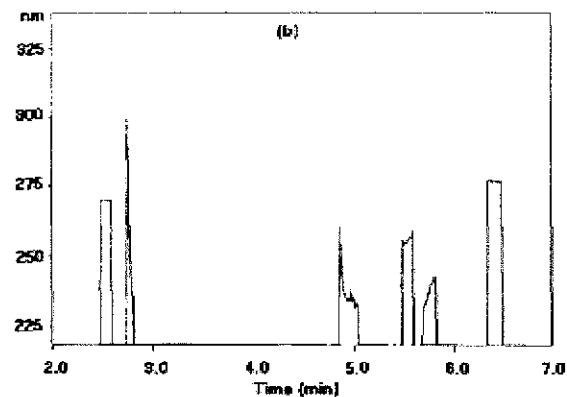
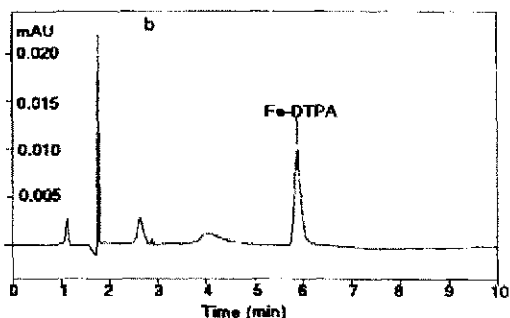
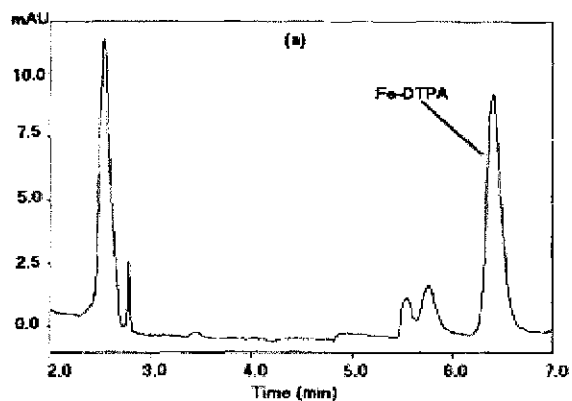
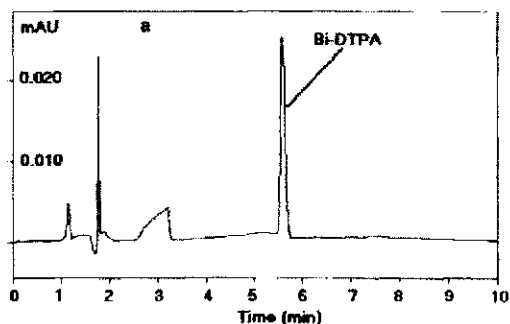


Fig. 2. Chromatogram of metal-DTPA complexes on 25 cm \times 4 mm (5 μ m) Alltech Alltima C_{18} column using 89% 4 mM octylamine (in acetonitrile-water, 8:92) and 11% acetonitrile at 2 ml min^{-1} , 100- μ l injection loop: (a) 10 mg l^{-1} DTPA as Bi-DTPA, detection wavelength 278 nm; (b) 10 mg l^{-1} DTPA as Fe-DTPA, detection wavelength 258 nm.

Fig. 3. Application of peak purity procedures to an effluent sample. (a) Chromatogram of effluent sample showing Fe-DTPA peak at 6.4 min. DTPA concentration 8.5 mg l^{-1} . Conditions as in Fig. 2. (b) Purity parameter profile across chromatogram.

metal. The greater plate count achieved for Bi-DTPA compared to Fe-DTPA would suggest that bismuth is a more suitable metal for achieving low detection limits. However the recovery rate in effluent samples for DTPA as Bi-DTPA was variable between 50 and 100% and therefore bismuth was considered an unsuitable chelating metal. The calibration curve for Fe-DTPA was linear over the range 2–40 mg l^{-1} , while the standard deviation in peak area associated with injections of standards was 4.6% ($n = 20$).

The ability to qualitatively determine an analyte adds an extra dimension to an analytical method. The use of photodiode array detection enabled this to be achieved in the case of Fe-DTPA. The chromatogram in Fig. 3a is of an

effluent sample containing about 8.5 mg l^{-1} of DTPA, while directly underneath the chromatogram in Fig. 3b is the purity parameter profile for the chromatogram. The purity parameter is a measure of peak purity calculated from the absorbance-weighted mean wavelength for a specified wavelength range. For Fe-DTPA over the wavelength range 220–367 nm, the purity parameter averaged 276.776 ± 0.356 nm over the sample peak compared to a value of 276.933 ± 0.215 nm across a 10 mg l^{-1} standard peak. A level profile across a peak as shown in Fig. 3b is

also a visual indicator of the absence of any interfering compound.

The concept of peak purity was useful in this work to determine which of iron(III) and bismuth was the better metal to use as the chelating metal. It was observed for those samples in which bismuth was used as the chelating metal that the peak purity profile was not as level as for iron and that the peak purity parameter in a sample matrix was significantly different to that in the standard. These factors therefore precluded the use of peak purity as a qualitative tool in the case of Bi–DTPA. Although Bi–DTPA gave a narrower peak than Fe–DTPA, the fact that its peak purity profile was not level in standards and spiked samples, and that recovery of spiked DTPA in some sample matrices was not quantitative, lead to the conclusion that bismuth was less suitable than iron as the chelating metal for this analysis.

In contrast to methods based on ion chromatography in acidic eluents [13,14], our reversed-phase ion-interaction separation at pH 6 enables some speciation studies to be performed. DTPA present in the sample as Fe–DTPA was measured by leaving out the FeCl₃ reagent in the sample preparation stage. Examination of the UV spectrum and peak purity data for the Fe–DTPA peak in unfortified samples showed no

differences to those of samples to which excess Fe³⁺ had been added.

3.2. Application of method to mill effluent samples

DTPA which is already complexed to metals other than the metal added in the sample preparation stage, must be released to form the more thermodynamically stable metal–DTPA chelate in order that total DTPA is measured. While the use of iron(III) as the metal ion was capable of this thermodynamically, it was necessary to ensure that this reaction was kinetically favourable. To demonstrate this, DTPA was added to two effluent samples for which the DTPA concentration had already been measured, after which the samples were left in the dark for 14 days to allow equilibration with metal ions present in the sample. A parallel sample containing no added DTPA was similarly stored. After 14 days, the spiked sample was analysed for DTPA and the unspiked sample was spiked with the same amount of DTPA just prior to addition of the FeCl₃ reagent. As the numbers in Table 1 show, the Fe–DTPA complex formed within the time allowed for in the method. The time that the sample was allowed to stand between addition of the chelating metal and the filtration step was

Table 1
Effect of equilibration time on metal–DTPA formation

| | DTPA concentration (mg l ⁻¹) ^a | |
|--|---|------------------|
| | Untreated effluent | Treated effluent |
| Unspiked DTPA | 20.0 ± 1.2 | 2.1 ± 0.1 |
| Spiked (10 mg l ⁻¹) DTPA (15 min equilibration) | 32.7 ± 0.5 | 13.7 ± 0.5 |
| Spiked (10 mg l ⁻¹) DTPA (after 14 days equilibration) | 31.0 ± 0.1 | 13.2 ± 0.3 |

^aUntreated effluent is taken from a paper mill effluent prior to a biological treatment stage and contains higher amounts of DTPA than treated effluent which has undergone primary, secondary and tertiary treatment. Results are shown as mean ± one standard deviation.

also varied and 15 min was found to be sufficient to allow quantitative formation of the metal-DTPA complex.

The method based on iron(III) as the chelating metal has been applied to the analysis of DTPA in pulp and paper mill effluent over a period of some two years during which time the validity of the method has been assessed by spiking the sample with a known amount of DTPA. Samples from two locations at the mill were routinely analysed twice weekly. One was spiked at the rate of 2 mg l^{-1} while the other was spiked at the rate of 4 mg l^{-1} . The recovery of DTPA from these samples over a four month period was 102% (standard deviation 12%, $n = 32$) and 102% (standard deviation 16%, $n = 32$) respectively.

The technique has also been successfully applied to the analysis of DTPA in effluent from different stages in the pulping process and effluent treatment process, and has been instrumental in determining that DTPA is in fact degraded in these processes. Fig. 4 shows the mass discharge of DTPA at various points across the process calculated from the measured DTPA concentration and average effluent flow-rate. Compared to that used in the pulping process (an average of 217 kg day^{-1}), an average of 86 kg day^{-1} of DTPA is discharged from the pulping process, while an average of 16 kg day^{-1} is

discharged in the final effluent. Clearly, DTPA is degraded in the pulping and effluent treatment process.

Measurement of DTPA as iron-bound DTPA in effluent samples has shown that the iron form of DTPA could account for anything from 2 to 100% of the total DTPA present, with the average being around 50% for the mills final effluent. Iron could therefore exert an important influence on the chemistry of DTPA, so it was necessary to consider a factor that leads to the degradation of DTPA, photooxidation in the presence of iron(III) [4], in sample handling. Samples were protected from exposure to light by collecting them into a light-protected black polyethylene container. Similarly samples prepared for chromatography were also stored in dark glass vials. The large proportion of DTPA normally present as Fe-DTPA also meant that photooxidation could play an important role in the degradation of DTPA in the mills effluent system in those areas where the effluent is exposed to light.

4. Conclusions

The use of ion-interaction reversed-phase liquid chromatography to determine DTPA as the iron(III) complex has enabled DTPA in pulp and

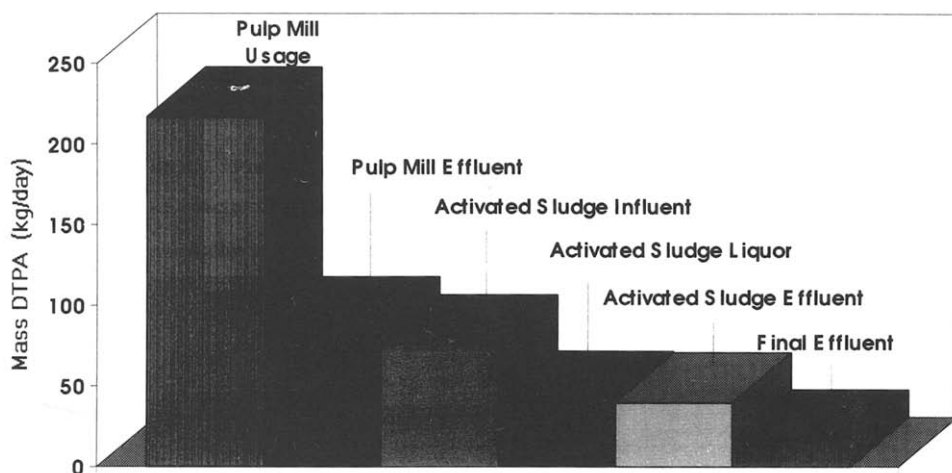


Fig. 4. Average mass daily discharge rates for DTPA at various locations in the mill effluent treatment system compared to daily usage.

paper mill effluent to be determined as both total and iron-bound forms. While bismuth was also found to chelate with DTPA, poor recoveries from some sample matrices and poor reproducibility of peak purity data excluded use of this metal from further investigation. The method has been used routinely to measure DTPA at different stages in the mill's effluent treatment process for over two years with the ability to qualitatively measure the peak purity of the Fe–DTPA peak as it elutes. The data shows that DTPA is significantly reduced in concentration within the mill's process water circuit prior to discharge to the mill's effluent treatment system. Some further reduction in concentration occurred across the biological stage and across the holding lagoon. The ability of the technique to analyse DTPA complexed to iron (Fe–DTPA) shows that the predominant form of DTPA in effluent samples is as Fe–DTPA, and this has implications in the study of degradation routes.

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