

# Determination of novel complexing agents in pulp and paper mill effluents and in lake water by liquid chromatography

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Received 3 March 2005; received in revised form 21 July 2005; accepted 25 July 2005

Available online 22 August 2005

## Abstract

A simple and sensitive high performance liquid chromatographic (HPLC) method with UV detection was developed for the determination of new diethanolamine derivative complexing agents. The quantitation of three complexing agents was accomplished as their Cu(II) complexes and their separation on a reversed phase C<sub>18</sub> column using 0.01 M tetrabutyl ammoniumhydroxide and methanol as isocratic mobile phase. The limit of detection (LOD) ranges from 0.1 to 2.0 mg/l and the method has a wide linear range, from LOD to 150 mg/l. The method was successfully applied for the analysis of lake water and wastewater effluent from pulp and paper mill spiked with studied complexing agents.

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**Keywords:** Diethanolamine derivatives; HPLC; EDTA; DTPA

## 1. Introduction

The pulp and paper industry utilizes complexing agents, which have the ability to form stable and water-soluble complexes with many metal ions. Transition metals, mainly manganese, iron and copper, are a serious problem in pulp bleaching. At high concentrations, these metals catalyze the decomposition of oxygen based bleaching agents increasing the consumption of the bleaching chemical. The environmental fate of complexing agents, namely ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA), has been under debate. Being a remarkable source of nitrogen and having low biodegradability [1–3] EDTA and DTPA effluents from pulp and paper mills may

cause environmental problems such as mobilization of heavy metals in the natural waters [4].

Therefore, more environmentally friendly complexing agents have been searched for pulp bleaching applications. A series of new alternative low-nitrogen complexing agents *N*-bis[2(carboxymethoxy)ethyl]glycine (BCA3), isomeric mixtures of *N*-bis[2(1,2-dicarboxyethoxy)ethyl]glycine (BCA5) and *N*-bis[2(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) have been designed for pulp and paper industry [5]. The molecular structures of new compounds are presented in Fig. 1. The performance of BCA5 and BCA6 was shown to be comparable to performance of EDTA and DTPA in bleaching sequences of totally chlorine free (TCF) pulp [6]. In the presence of strong oxidants, e.g. per acetic acid (PAA), BCA5 and BCA6 can sequester Fe and Mn from the pulp quite efficiently. A significant advantage of novel complexing agents is that their Mn complexes seem to be inert in the PAA solution while Mn–EDTA and Mn–DTPA complexes were proven to decompose per acetic acid [7].

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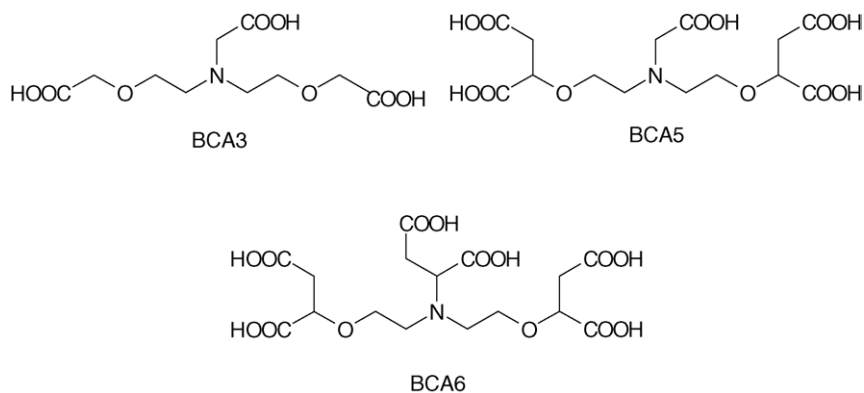


Fig. 1. The molecular structures of BCA3, BCA5 and BCA6.

In this paper, a simple and accurate HPLC assay method is introduced for the quantitative determination of new complexing agents. This paper presents for the first time an analytical procedure for the determination of these compounds.

## 2. Experimental

### 2.1. Chemicals

The complexing agents, BCA3, BCA5 and BCA6 were obtained from Kemira Oyj, Espoo, Finland and they were of technical grade. The purity of the complexing agents were determined by  $^{13}\text{C}$  NMR, contents are presented in Table 1. Due to the molecular asymmetry and due to a non-selective preparation method, BCA5 contains three conformational isomers, SS-, SR-, and RR-BCA5. Similarly, the samples of BCA6 consist of a mixture of six conformational isomers, SSS-, SSR-, SRR-, RRR-, SRS- and RSR-BCA6. The standard solutions of the complexing agents proved to be stable for several months. Tetrabutyl ammoniumhydroxide 40% water solution in  $\text{H}_2\text{O}$  was obtained from Sigma and HPLC-

grade methanol from Lab-Scan.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in NaOH-solution was used for complexation, and 85% *o*-phosphoric acid for pH adjustment of the mobile phase. Deionised water (Milli-Q-water) was utilized for preparing standard solutions and mobile phases. Lake water used in recovery analysis was obtained from Lake Kallavesi, Kuopio, Finland. Pulp and paper mill effluent leaving wastewater treatment was from StoraEnso mills, Varkaus, Finland.

### 2.2. Apparatus

The HPLC apparatus consists of a Hewlett-Packard Series 1050 liquid chromatographic pump, a Hewlett-Packard 4010 Series II UV-detection system and a Hewlett-Packard 1100 series sample injector. An analytical HPLC column Kromasil 10C<sub>18</sub> (4.6 mm × 250 mm) was used.

### 2.3. Sample preparation

The samples were first filtrated through 0.45  $\mu\text{m}$  cellulose membrane filters (Millipore). All BCA compounds were analysed as their copper complexes. The solution of 0.005 M  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 0.005 M NaOH was used to convert the different BCA species into their Cu(II) complexes. This was done by diluting the samples with 0.005 M  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in proportion 6:1. The pH of the samples was around 7. Cu(II) complexes were allowed to form for at least 30 min in the dark and they were stored in the dark until injection in order to prevent photochemical degradation of chelating agents.

### 2.4. Chromatography conditions

As isocratic mobile phase a mixture of tetrabutyl ammoniumhydroxide and methanol was used. A 0.01 M tetrabutyl ammoniumhydroxide solution was prepared in distilled water and the pH of the solution was adjusted to 7.2 when analysing BCA5 and BCA6, and for BCA3 analyses to 7.0 by using 85% *o*-phosphoric acid. Tetrabutyl ammoniumhydroxide and methanol were mixed together in proportion 1:1 for BCA5 and BCA6 analyses and in proportion 3:2 for BCA3 analyses.

Table 1  
Contents of new complexing agents

	Percent
BCA3	62.9
Glycolic acid	9.9
Oxalic acid	8.5
<i>N</i> -Bis(2-hydroxyethyl)glycine	18.7
BCA5	82.1
Oxybis(butanedioic acid)	5.6
Maleic acid	11.5
Malic acid	0.8
BCA6	89.5
"Monoalkylated product": <i>N</i> -[2-(1,2-dicarboxyethoxy)ethyl]- <i>N</i> -(2-hydroxyethyl)aspartic acid	2.9
<i>N</i> -Bis[2-(1,2-dicarboxyethoxy)ethyl]amine	5.1
Sodium fumarate	1.0
Diethanolamine	1.5

Samples were analysed under the following conditions: the flow rate was maintained at 1 ml/min, injection volume 25  $\mu$ l, and detection wavelength  $260 \pm 5$  nm, and column temperature 36 °C. HP ChemStation software was used for chromatogram integration and calculations of the concentrations from peak areas.

### 3. Results and discussion

#### 3.1. Complexation with Cu(II)

EDTA and DTPA are usually quantified as their trivalent iron complexes, which are most stable in aquatic solutions [8]. Because the Cu(II) complexes of these novel complexing agents proved out to be the most stable ones over a broad pH range in  $\mu$ M solutions, they were analysed as Cu(II) complexes [9,10]. Furthermore, no interference of other metal ions was observed when Cu(II) chelates were applied. BCA3, BCA5 and BCA6 form complexes for example with Fe(III) only in acidic and in mM solution, in  $\mu$ M solution Fe(III) hydroxides are dominating at whole pH range. BCA5 and BCA6 can be analysed simultaneously. Typical chromatograms for BCA3, BCA5 and BCA6 are presented in Fig. 2.

#### 3.2. Determination of UV–vis spectra and wavelength selection

The UV–vis spectra of Cu(II)–BCA3, Cu(II)–BCA5 and Cu(II)–BCA6 were measured at the range 190–600 nm by using HPLC with UV detector and HP Chemstation software. All three complexes have an absorption maximum at wavelength 250 nm, UV–vis spectra of Cu–BCA5 can be seen in Fig. 3. The samples were analysed at wavelength  $260 \pm 5$  nm to avoid interference of other organic compounds present in humic lake water and in the effluents.

#### 3.3. Method validation

The method was validated by determining the quality parameters: linearity, limits of detection (LOD) and quantitation (LOQ), repeatability, reproducibility and recovery in pulp and paper mill effluent and in lake water. Characteristics of the method are presented in Table 2.

The method is linear from the LOD to 150 mg/l, which is larger than the realistic concentration scale of complexing agents in the pulp and paper mill process and waste waters [11]. For peak area measurements linear calibration graphs were obtained with correlation coefficients 0.996–0.999. Repeatability of the method was calculated from differences between five consecutive injections and reproducibility was determined by analysing the same standard solution in five different days, both parameters were studied at concentrations 5 and 25 mg/l. These values demonstrate that the precision of the method is good for BCA3 and BCA5 and adequate

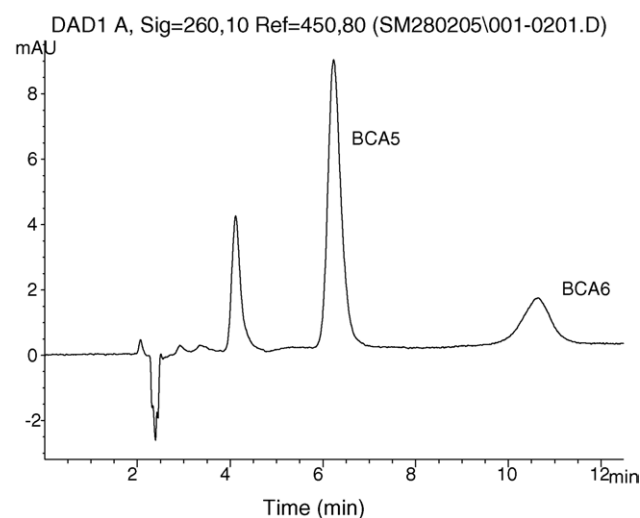
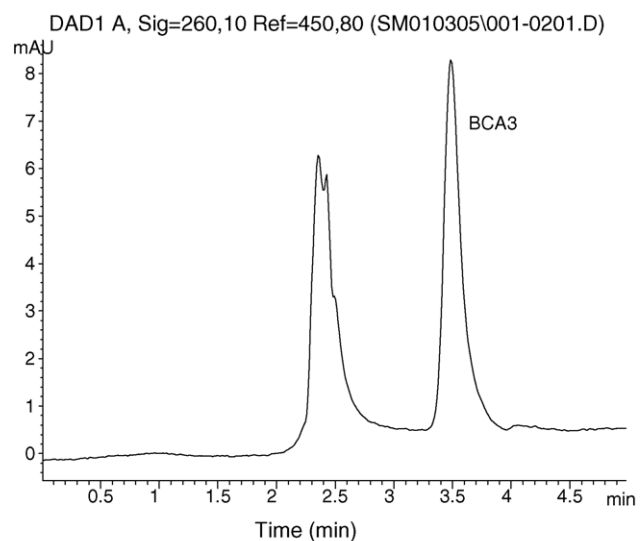


Fig. 2. The chromatograms of BCA3, BCA5 and BCA6 at concentration 10 mg/l. BCA5 and BCA6 were analysed simultaneously. The retention times of BCA3, BCA5 and BCA6 were 3.5, 6.3 and 10.8 min, respectively.

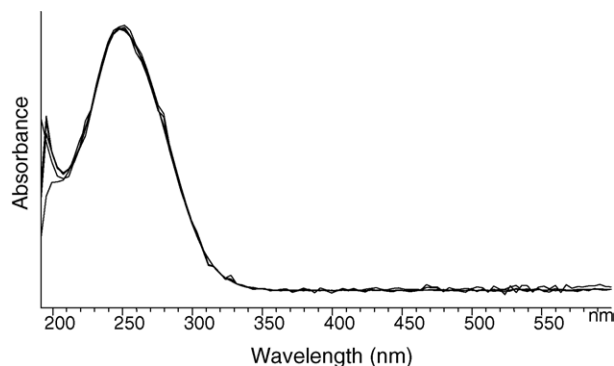


Fig. 3. The UV–vis-spectra of Cu(II)–BCA5 at concentration 40 mg/l.

Table 2  
Characteristics of the method

Specification	BCA3	BCA5	BCA6
Retention time (min)	3.5	6.3	10.8
Linearity, $R^2$	0.999	0.999	0.996
Limit of detection (mg/l)	0.1	0.3	2.0
Limit of quantitation (mg/l)	0.2	1.1	4.0
Repeatability (%)	0.2–0.9	1.0–1.1	1.1–5.5
Reproducibility (%)	0.9–0.9	0.7–2.6	0.7–4.5
Recovery (%), lake water	100–102	100–104	101–102
P&P mill effluent	100–108	100–110	100–104

Linearity is described by linear correlation coefficients ( $R^2$ ) for concentration range LOD–150 mg/l. Limit of detection is based on signal-to-noise ratio 3 and limit of quantitation on ratio 6. Repeatability and reproducibility were studied at concentrations 5 and 25 mg/l ( $n=5$ ) and recoveries at concentrations 5 and 50 mg/l. P&P: pulp and paper.

for BCA6. Limit of detection is based on signal-to-noise ratio 3 and limit of quantitation on ratio 6. The results suggest that the proposed HPLC method is sensitive for the determination of BCA3 and BCA5 and sufficiently sensitive for determination of BCA6.

#### 3.4. Determination in lake water and in pulp and paper mill effluent leaving wastewater treatment

The method described here was applied for the analysis of lake and pulp and paper mill effluent leaving wastewater treatment plant spiked with complexing agents at concentrations 5 and 50 mg/l. Recoveries in lake water were between 100 and 104% and in effluent 100–110%. The matrix effect was more notable in pulp and paper mill effluents than in lake water. Recoveries are showed in Table 2. Also pulp and paper mill waste water going to waste water treatment and bleaching water were tested but disturbing matrix peaks made analysis of complexing agents impossible.

## 4. Conclusions

The determination of the novel diethanolamine derivative complexing agents by the HPLC procedure described in this

paper has proven to be simple, rapid, sensitive and reproducible. After the addition of a Cu(II) solution, and required 30 min complexation time, the sample can be injected directly in the HPLC system and detected by means of a UV detector. Separation of the complexing agents increased in the order  $BCA6 > BCA5 > BCA3$ . The method was demonstrated to be suitable for analysis of studied complexing agents in lake water and in pulp and paper mill effluent leaving wastewater treatment. As expected, no separation of the isomers of BCA5 or BCA6 molecules was obtained in this experiment. However, this method is practical for the determination of the total concentration of these molecules.

## Acknowledgements

The financial support of the National Technology Agency of Finland and the Maj and Tor Nessling Foundation is gratefully acknowledged. The authors wish to thank Mr. Juhani Tarhanen for his skilful help with the HPLC.

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