

Separation of chelating agents as copper complexes by capillary zone electrophoresis using quaternary ammonium bromides as additives in *N*-methylformamide

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Abstract

This study presents the use of quaternary ammonium bromides as additives in *N*-methylformamide (NMF) for the separation and quantification of chelating agents as copper complexes by capillary zone electrophoresis (CZE). The new quaternary ammonium bromides were synthesized in our laboratory and used for the first time for CZE applications performed in NMF media. The methods were developed and optimized for determination of six chelating agents (*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid (HEDTA), nitrilotriacetic acid (NTA) and triethylenetetraaminehexaacetic acid (TTHA)) as copper complexes. Among the tested electrolyte additives in NMF media (pH_{app} 10.2) dimethyldioctylammonium bromide (DMDOAB), dimethyldinonylammonium bromide (DMDNAB) and dimethyldidecylammonium bromide (DMDDAB), at a concentration of 20 mmol L⁻¹ improved the separation of the copper complexes. The optimized methods require only 12 min for one analysis, and the detection limits for copper complexes of DMDNAB, the best-performing additive, were $\leq 24 \mu\text{mol L}^{-1}$. Relative standard deviations (R.S.D.) for migration times were ≤ 2.5 , ≤ 2.1 , $\leq 3.1\%$ and for peak areas, ≤ 3.1 , ≤ 3.0 , $\leq 3.2\%$ for DMDOAB, DMDNAB and DMDDAB used as additives, respectively. All three methods were successfully applied to the analysis of natural and wastewater samples. No matrix effects from these samples were observed. The interaction between quaternary ammonium bromides and copper complexes is discussed.

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1. Introduction

Aminopolycarboxylic acids (e.g. ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) and hydroxycarboxylic acids (e.g. *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid (HEDTA)) are widely used in industry, agriculture and soil science. General properties of this kind of chelating agents have already been discussed in several papers [1–7]. Various analysis techniques for detection of carboxylate-based chelating agents have been used [5–14], but methods reported in the literature are mainly focused on EDTA and DTPA. There are only a few papers introducing methods for separation of several industrially and environmentally interesting chelating agents at the same time [5–7,12–14]. The

importance of further method development for large number of complexes simultaneously and the goal of achieving rapid, cheap, more sensitive and easy to perform analysis methods is evident because some of the chelating agents are not easily biodegradable and they enter to the environment via domestic and industrial wastewaters [5,6]. Due to the wide field of applications for chelating agents these substances reach the aquatic environment at considerable concentrations e.g. in Europe the most widely used chelating agent EDTA have been found in surface waters in the range 2–2460 $\mu\text{g L}^{-1}$ [15], DTPA in sewage effluents of paper and pulp mills have been detected in the mg L⁻¹ range and nitrilotriacetic acid (NTA) in municipal wastewater treatment plant influents at the concentrations 54–170 $\mu\text{g L}^{-1}$ [16].

Throughout our CE studies involving chelating agents [5,6,17] we have used Cu(II) to make chelating agents as UV detectable metal complexes. Copper was an obvious choice, because the samples that we have used (also in this study)

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include environmental waters and H^+ , Na^+ , Mg^{2+} and Ca^{2+} are the major ionic components of natural water [18]; at $pH \sim 8$ $Ca(II)EDTA$ and $Mg(II)EDTA$ complexes could be converted to $Cu(II)EDTA$ complex [19]. $Fe(III)EDTA$ is not stable in natural water at $pH > 7$ in the presence of other metal ions [20] and, in order to develop a summation parameter for the total amount of chelating agents, the central ion copper(II) was best suited for the complexation of chelating agents compared to iron(III) and nickel(II) [21].

Our method development started in aqueous media for three conventional chelating agents including literature survey of the methods of other research groups [6]. The benefits of aqueous methods are short analysis time, stability of the system and narrow analyte zones. Aqueous media is usable [5,6] but also some drawbacks are present. Excellent separation of the analytes demanded high concentration of the aqueous phosphate buffer resulting high currents and thus narrower capillaries had to be used [5]. Also detection limits would have been lower [5,6]. Mass spectrometry (MS) combined with CE would offer several benefits (e.g. identification of unknown compounds with m/z -ratio, which is not possible with UV-detection) for determination of chelating agents but our aqueous methods are not suitable for CE/MS technique, because of the unsuitability of phosphate buffer to MS and also due to high amount of water. Nonaqueous media is potential for CE/MS applications.

Nonaqueous capillary electrophoresis (NACE) is rapidly developing analytical technique based on the use of pure organic solvents or mixtures of these as electrolytes. It is well known that most commonly used solvents in CE applications are acetonitrile (ACN) and methanol (MeOH), but nowadays also other solvents like formamide (FA) [22] has been used successfully. The use of *N*-methylformamide (NMF) as background electrolyte (BGE) solvent is rarer. The popularity of MeOH and ACN is due to that they are common in high-performance liquid chromatography (HPLC), they are easy to handle, sufficiently UV-transparent and easily available at high purity and relatively low cost [23]. Properties of organic solvents and basic knowledge about the applications and development of NACE is presented in reviews published during the last six years [24–27].

Usually solvents are used with additives in them, but the first time that NMF was used as an electrolyte without supporting additive was in 1995 by Jansson and Roeraade [28]; this was possible because EOF is present in all organic solvents with high dielectric constants, and NMF has the value of 182.4 [26] (compare methanol 32.7 [26]). Geiser et al. [29] showed that FA and NMF are promising solvents for NACE–ESI–MS for the analysis of β -blockers, and in addition FA and NMF allowed very stable electrophoretic and electrospray currents. Thus the interest to nonaqueous CE methods by exploiting rarely used NMF also for chelating agents rose up.

The suitability of several solvent systems (e.g. FA, NMF, MeOH, etc.) for the separation of highly polar chelating agents was tested in our previous paper [17] and the only usable solvent found for the separation of several copper complexes was NMF at pH_{app} 10.2. NMF can be defined as amphiprotic solvent like FA and water which has ability to both accept and donate a proton [30]. Nucleophilic (ability to bind a proton) and elec-

trophilic (ability to solvate anions) properties of solvent can be described with the solvents donor number (DN) and acceptor number (AN) [30]. NMF has higher DN (205 [30]) than FA (151 [30]) or water (138 [30]), and lower AN (32.1 [30]) than FA (39.8 [30]) or water (54.8 [30]). Thus NMF has comparable high ability to solvate anions like FA or water, but greater basic strength resulting cathodic EOF and net negative charge at the silica surface of the capillary [30]. Both NMF and FA form a chain like hydrogen-bonded structure in the liquid state [31] and thus NMF is suitable solvent for anions with localized charge e.g. our polar copper complexes because they are stabilized by reaction with a hydrogen bond donor [32]. NMF without additives is not ion-free; its autoprotolysis is much more intense (pK_{auto} 10.74) than that of water (pK_{auto} 14.00) and it slowly undergoes hydrolysis, which increases the ionic strength [33]. The suitability of NMF above FA could be explained also by the high ϵ^2/η ratio of NMF (20,000 cP^{-1} at 25 °C) resulting higher efficiency in terms of the number of theoretical plates (for FA the ratio is 3734 cP^{-1} at 25 °C) [29].

In this study NMF was used as solvent and new quaternary ammonium bromides as additives for the simultaneous analysis of CDTA, DTPA, EDTA, HEDTA, NTA and TTHA as copper complexes. Two of the tested quaternary ammonium bromides, dimethyldioctylammonium bromide (DMDOAB) and dimethyldinonylammonium bromide (DMDNAB), are ionic liquids. Compounds generally stated as ionic liquids have melting points $\leq 100^\circ C$ and consist only of ionic species [34,35]. We also prove that the optimized methods can be used in the analysis of natural and wastewater samples without matrix effects. Through this study all chelating agents used are considered as copper complexes, hence this is not mentioned every time they appear in the text.

2. Experimental

2.1. Instrumentation

Electropherograms were obtained on a Hewlett-Packard CE^{3D} G1600 AX apparatus (Hewlett-Packard, Waldbronn, Germany) equipped with a diode array detector (DAD) and an air cooling unit for the capillary. Instrument control and data acquisition were performed with HP^{3D} Chemstation software (Hewlett-Packard, Rev 04.02.). Absorbances at 254 and 280 nm were monitored for the detection of analytes. The uncoated fused silica capillary (Hewlett-Packard, Waldbronn, Germany) was of 75/375 μm i.d./o.d. and total length of 70 cm (61.5 cm to the detector). The capillary cassette temperature was adjusted to 25 °C with air cooling. The operating conditions for a run included a voltage of +30 kV generated by a positive power supply, resulting electric currents from +13 to +28 μA during the optimization procedure. Standards and samples were injected hydrodynamically by overpressure (50 mbar = 5000 Pa) with 3 s injection time. The instrument was placed in air conditioned room (+20 °C).

Apparent pH measurements were done with Orion 720A pH-meter by using Orion Ross combination pH electrode (8103BN), the filling solution of the electrode was 3 M KCl (Orion Cat.

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