Metal ion interferences in reverse polarity capillary zone electrophoretic analysis of Hanford Defense Waste for ethylenediaminetetraacetic acid (EDTA) and \(n\)-hydroxyethylethylenediaminetriacetic acid (HEDTA)

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Received 24 December 1998; received in revised form 05 May 1999; accepted 25 May 1999

Abstract

Chemical characterization of Hanford Defense Waste (HDW), which was accumulated during the processing of irradiated reactor fuels for nuclear weapon production continues to be a challenging analytical problem. Complexants in particular are difficult to analyze because in their free state, they are highly polar, exhibit low volatility, and exist in several charge states. In addition, they form complexes with metal ions resulting in multiple species. Analysis is also difficult because HDW is high in radioactivity, high in ionic strength, and high in hydroxide concentration. This account describes the first application of reverse polarity capillary zone electrophoresis (RPCE) for the determination of EDTA and HEDTA in HDW. In this report, RPCE parameters for a rapid separation of uncomplexed EDTA and HEDTA in aqueous solution were established. The buffer containing 25 mM borate and 25 mM hexamethonium bromide (HMB), an electroosmotic flow modifier, at pH 9.2, effectively separated EDTA and HEDTA in less than 6 min when \(-20\) kV was applied across a 50 \(\mu\)m i.d. \(\times\) 50 cm long bare capillary column. The separation of metal complexes of EDTA and HEDTA was achieved using an electrolyte of higher buffer capacity containing 25 mM borate/25 mM boric acid/25 mM hexamethonium bromide in aqueous basic solution. The stability of metal EDTA and HEDTA complexes in Synthetic Hanford Waste (SHW), a simulant for HDW, was tested for \(\text{Bi}^{3+}, \text{Ca}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Cr}^{3+}, \text{Cr}_2\text{O}_7^{2-}, \text{Hg}^{2+}, \text{UO}_2^{2+}, \text{Ni}^{2+}, \text{Fe}^{3+}, \) and \(\text{Th}^{4+}\) under basic conditions. It was observed that the metal complexes were unstable under the harsh conditions of SHW. Only \(\text{Pb}^{2+}\) formed stable EDTA and HEDTA complexes in SHW. Preliminary data from the analysis of real HDW samples by adding \(\text{Pb}^{2+}\) in basic citrate solution demonstrated the potential of RPCE for the determination of total EDTA and HEDTA in real samples. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Hanford Defense Waste; Radioactive/nuclear waste; Ethylenediaminetetraacetic acid; Reverse polarity capillary electrophoresis; Metal complexes; High ionic strength; \(\text{Pb(II)}\) complexes

1. Introduction

Organic complexants such as ethylenediaminetetraacetic acid (EDTA), \(N\)-hydroxyethylethylenediaminetriacetic acid (HEDTA) and citrate were used in copious amounts to treat wastes generated by the
processing of irradiated reactor fuels for plutonium production between 1944 and 1987 at the Hanford Site, located near Richland, WA [1]. Large volumes of mixed wastes known as Hanford Defense Waste (HDW), were generated in the process, and stored in 177 large underground tanks [2]. These tank wastes have unique characteristics of being extremely heterogeneous, highly basic, and high in ionic strength. The composition of the tanks includes radioactive constituents and various waste products from the plutonium recovery and waste treatment processes such as NaOH, NaAlO₂, NaNO₂, NaNO₃, metal ions, and organic complexants. EDTA and HEDTA were added to keep other metals in the aqueous solution during the removal of ⁹⁰Sr from the waste by solvent extraction. In addition, the complexants served to keep many of the polyvalent inert and radioactive metals in solution as coordination compounds [3]. The amounts of these complexing agents used in the Hanford Site have been estimated to be greater than 240 and 1500 tons of EDTA and HEDTA, respectively, with initial concentrations of 0.1 M EDTA and 0.2 M HEDTA in some tanks [4].

Complex chemical and radiological decomposition of the constituents occurs continuously in the tanks [2]. For example, HEDTA and other organic compounds undergo chemical degradation, producing flammable and inert gases such as hydrogen, nitrogen, nitrous oxide, and carbon dioxide [2,5,6]. Although the mechanism of the degradation reaction is not well understood, Delegard [2] suggested that the reaction was dependent on the concentrations of HEDTA, nitrate and/or nitrite, sodium aluminate and sodium hydroxide. Another decomposition process that contributed to the production of flammable gases but in a lesser extent was a radiolytic process [5,6].

In the past, the determination of EDTA and HEDTA in the HDW as iron(III) complexes was examined by Metcalf [4]. In that investigation, he used HPLC and ion exchange coupled with UV and atomic absorption detection methods. The most critical factor in the sample preparation was the effect of sample pH on the kinetics of complexant exchange reactions between Fe³⁺ and Al³⁺ [4,7], and between Fe³⁺ and Cr³⁺ [4]. To avoid precipitation of aluminum, the pH had to be adjusted to <4 or >11. To ensure that Fe³⁺ complexes were quantitatively formed, the sample had to be adjusted to a pH of 2 or less. The exchange reaction involving Cr³⁺ was complicated by side reactions with nitric acid and nitrite ion in the synthetic HDW. Moreover, the exchange reaction of CrEDTA⁻ and CrHEDTA with Fe³⁺ took more than 60 min even at pH 1.3. Also, Bi³⁺ interfered with the determination of HEDTA. This interference was removed by co-precipitation of Bi³⁺ (as the hydroxide) with Al³⁺ and Fe³⁺. Other metal ions considered to be in the HDW at 10⁻² M range included Ni²⁺, Pb²⁺, and UO₂²⁺. The above method involved rigorous, time-consuming, and tedious sample preparation and the detection limits were only 10⁻² M for both EDTA and HEDTA. Furthermore, large volumes of mixed waste, which were generated by the HPLC and ion exchange analysis (IEA), increased the overall cost of analysis per sample.

Campbell et al. [8] also investigated the application of HPLC and LC/MS for the analysis of complexants in HDW. They observed that HDW matrix was too basic for a C₁₈ HPLC column to be used for the analysis because the column lost its ability to separate the analytes. They therefore surveyed LC and LC/MS methods that would involve carrying out the analysis under acidic conditions. Their general conclusion about using LC and LC/MS was that the techniques were costly, time-consuming, and required extensive sample preparation. Furthermore, a substantial amount of mixed waste was generated. In other studies, Campbell and co-workers [9,10,11] investigated the feasibility of analyzing HDW for EDTA and HEDTA by derivatization GC and GC/MS. These methods involved time-consuming and laborious sample preparation that at times took up to 5 days. In addition, due to high salt content, there were problems with drying of the samples. Detection limits were quite high and percent recoveries were in the 60% range. The methods were laden with interferences such as mixed metal complexes and nitroso-compounds arising from the derivatization procedures under acidic conditions. Thus there is a need for a better method for the analysis of EDTA and HEDTA in HDW. The ideal method would eliminate interferences arising from sample preparation, avoid pH adjustment, avert rigorous sample preparation, minimize waste generation, and cut down on time and cost of analysis.

Capillary zone electrophoresis (CZE) methods provide efficient separations with high resolution and can have excellent detection limits for small sample
sizes. Recently, Ballou and others reported the application of capillary zone electrophoresis for the determination of chelating agents in the Hanford tank waste simulant [12]. Their method, however, was not tested with a real HDW sample. In their method, a positive voltage was applied across the capillary column for the separation of Cu(II) complexes of EDTA, HEDTA, NTA, and other chelators in high pH phosphate and borate buffers. To achieve rapid migration, a low concentration of buffer and high electric fields were chosen for analysis. Due to peak distortion from the low ionic strength of the buffer relative to that of the sample, they could analyze only highly diluted samples. This required dilution could be a problem in the analysis of real samples that are low in chelate concentration.

Although many other publications on CZE measurements involving other aminopolycarboxylic acids have appeared in recent years [13–18], there have been only a few reports on capillary electrophoretic investigations involving EDTA and HEDTA [19–23]. None of these studies determined the concentration of EDTA and HEDTA. Instead, they used EDTA to determine cation concentrations. In addition, most of these investigations were carried out under acidic conditions. Hence, these methods are not ideal for the analysis of extremely basic and high ionic strength HDW.

RPCE, which involves the application of negative voltage at the injection position of the capillary electrophoresis instrument has the advantage of being anion-specific. Cations and neutrals migrated towards the cathode (away from the detector) and were not detected. Hence, the complexity and high cationic contents of the sample matrix did not constitute an interference problem. RPCE methodology has the potential of significantly reducing the overall time and cost of analysis, bringing about waste minimization and waste avoidance, and requiring minimal sample handling. The objectives of this study were to investigate the use of reverse polarity capillary zone electrophoresis (RPCE) for the separation of uncomplexed EDTA and HEDTA, the separation of metal complexes of EDTA and HEDTA, and the examination of the extent to which metal ions interfere with the separation of uncomplexed EDTA and HEDTA under high pH and high ionic strength conditions. The stability of the uncomplexed and complexed EDTA and HEDTA in Synthetic Hanford Waste (SHW), a simulant of HDW was investigated along with the preliminary analysis of real HDW.

2. Materials and method

2.1. Equipment

A Dionex capillary electrophoresis system (CES) I (Dionex Corporation, Sunnyvale, CA) was used for measurements involving the SHW samples. The instrument was equipped with a positive and negative polarity high voltage power supply of 0–30 kV, and had tunable UV/visible absorbance (190–800 nm) for on-column detection. The electrophoresis system was run in autosampler mode only. The CES I was interfaced to a Dionex Al-450 Laboratory Automation System, which was used for data acquisition and storage. A Waters model Quanta 4000E capillary ion analyzer (CIA) (Waters Millipore Corporation, MA) was used for the test analysis of the real HDW samples. Quanta 4000E CIA was connected to a 486 PC for instrument control, had a high voltage power supply (0–30 kV) suitable for both positive and negative polarities, and a capability of operating under constant electric current. The UV detector was based on a limited fixed-wavelength filter of which the 254 nm filter was used in this study. The gravity injection method was used for sample introduction.

A HP Diode Array Spectrophotometer (Hewlett Packard, Atlanta, GA), model 8452A, provided direct UV measurement of the samples. This instrument was a single-beam, microprocessor controlled UV/Vis spectrophotometer with collimating optics, and a UV/Vis wavelength range of 190–820 nm.

2.2. Reagents and standards

Nitrate salts of Al$^{3+}$, Bi$^{3+}$, Ca$^{2+}$, Cd$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Th$^{4+}$, and UO$_2$$^{2+}$ were used in this study. Sodium salt of Cr$_2$O$_7$$^{2-}$ was used in the preparation of the Cr(VI) solution. The nitrate salts were Baker Analyzed Reagent, ACS Specifications, (J.T. Baker, Phillipsburg, NJ), except Pb(II) nitrate (Sigma, St. Louis, MO), and Fe(III) nitrate (Mallinckrodt, St. Louis, MO). Disodium ethylenediaminetetraacetic acid (EDTA), (Baker Analyzed Reagent,
ACS Specifications, J.T. Baker, Phillipsburg, NJ) or tetrasodium EDTA, (Sigma, St. Louis, MO), and trisodium n-hydroxyethylethylenediaminetriacetic acid (HEDTA), (Aldrich Chemical Company, Milwaukee, WI), sodium citrate, (Baker Analyzed Reagent, ACS Specifications, J.T. Baker, Phillipsburg, NJ), were used for the preparation of complexant samples. Boric acid (Baker Analyzed Reagent, ACS Specifications, J.T. Baker, Phillipsburg, NJ), and sodium borate SX365 CB857 (Matheson Coleman and Bell, Norwood, OH), diethylene triamine (DETA), (Eastman Kodak, Rochester, NY), and hexamethonium bromide (ICN Biochemicals, Cleveland, OH) were used for buffer preparations. The Synthetic Hanford Waste (SHW) base was a mixture containing 1.02 M Na₂Al₂O₄, 1.61 M NaOH, 2.59 M NaNO₃, 2.24 M NaNO₂, and 0.42 M Na₂CO₃, pH > 13 (Westinghouse Hanford Company, Richland, WA)³. All other chemicals were Baker Analyzed Reagents, with ACS Specifications (J.T. Baker, Phillipsburg, NJ). The reagent water used was from 18 MW nanopure UV ultrapure water system (Barnstead/Thermolyne, Dubuque, IA) for the preparation of all standards and buffer solutions. Polyethylene bottles were used for the storage of all solutions.

2.3. Experiments

2.3.1. RPCE parameters for the separation of EDTA and HEDTA standards

A borate buffer containing 25 mM sodium borate and 25 mM of electroosmotic flow modifier, hexamethonium bromide (HMB), added to minimize the electroosmotic flow at pH 9.2 was used to separate a mixture of EDTA and HEDTA standards. The maximum applied voltage for borate/HMB buffer was determined by gradually increasing the voltage from −18 to −30 kV, until an electrical break down of the system occurred. The optimal voltage (unless otherwise stated) was −20 kV across the 50 μm i.d. (375 μm o.d.) x 50 cm long bare silica column. The gravity injection method was used to introduce the sample. The sampler head was raised to 100 mm above the buffer source vial for a 60 s injection time, resulting in the introduction of 21 nl volume of sample.

³ SHW supplied by Westinghouse Hanford Company, Richland, WA.

A small window for on-column UV detection was created on the capillary column by burning off the polyimide coating at 44.9 cm from the injection end. The wavelength for direct UV detection was 240 nm.

The pre-treatment of the capillary column involved flushing with 100 mM phosphoric acid for about 3 min to remove metal oxide precipitated on the silica walls during manufacture. It was then flushed with 500 mM NaOH for another 12 min in order to reactivate the inner surface of the column. Finally, the column was equilibrated with the operating buffer for another 12 min before sample injection. The column was rinsed three times with the buffer before each run. EDTA and HEDTA standard solutions were prepared and adjusted to pH > 12 with 2 M NaOH solution.

2.3.2. Preparation and RPCE separation of MEDTA⁻ and MHEDTA⁻ (M = Al³⁺, Cr³⁺, Ni²⁺, and Pb²⁺)

All concentrations used in this and subsequent sections for the metal complexes refer to their formal concentrations. A solution of 20.0 mM Cr³⁺ complexes of EDTA and HEDTA was prepared by boiling a mixture of Cr(III) nitrate with equimolar quantities of EDTA and HEDTA for about 10 min yielding an intense violet solution (pH 5.6) [24]. A solution of 20.0 mM NiEDTA²⁻ and NiHEDTA⁻ complexes was prepared by mixing equimolar quantities of Ni²⁺ solution with the complexants, forming a blue solution (pH 9.1). The preparation of 20.0 mM Pb(II) complexes was performed by mixing Pb²⁺ with equimolar quantities of EDTA and HEDTA and adding 0.10 M citrate (pH 12) until the precipitate re-dissolved and made up to 10 ml solution. Pb(II) complexes that did not contain citrate were prepared by making Pb(II) basic in sodium hydroxide solution (pH 12) and mixing with EDTA and HEDTA standards. A solution containing 2 mM of each complex was separated. The borate buffer used in this study was a mixture of 25 mM boric acid/25 mM borate/25 mM HMB at pH 9.1 ± 0.1. Applied voltage was −20 kV across a 50 μm i.d. (375 μm o.d.) x 50 cm long bare silica column. Gravity injection time was 60 s at a height of 100 mm above the detector.

2.3.3. Preparation and separation of EDTA and HEDTA in SHW

The pH of the samples prepared from SHW was kept above pH 11 because precipitation of Al(OH)₃...
occurred at a lower pH. Direct preparation of EDTA and HEDTA in the synthetic waste with solid EDTA and HEDTA led to precipitation of Al(OH)₃. For this reason, the EDTA standard was adjusted to pH > 12. The complexants were prepared in the SHW to contain 100 mM EDTA and 200 mM HEDTA for high complexant, and 10 mM EDTA and 20 mM HEDTA for low complexant concentration in the SHW. A 1:100 dilution of the SHW sample was analyzed with borate/HMB buffer. Other components of the SHW such as anions and metal ions were added during interference studies of each compound.

2.3.4. Metal ion interference study

The experiments described below were run in a borate buffer containing diethylene triamine (DETA) or hexamethonium bromide (HMB), electroosmotic flow modifiers, added to minimize the electroosmotic flow at pH 9.2. As DETA reacted with PbHEDTA⁻, its use was discontinued and HMB used for the rest of the investigation. Borate buffer containing DETA was a mixture of 200 mM boric acid, 20 mM sodium borate, and 100 mM DETA, while the buffer containing HMB was a mixture of 25 mM sodium borate and 25 mM HMB at pH 9.2. Metal ions (Bi³⁺, Ca²⁺, Cd²⁺, Cr³⁺, Cr₂O₇²⁻, Hg²⁺, UO₂²⁺, Ni²⁺, Pb²⁺, Fe³⁺, and Th⁴⁺) of 25 mM concentration, were tested at high complexants concentration in SHW. As Cu²⁺ precipitated in the buffer solutions it was not further investigated. The interferences were studied at concentration levels of 25 mM of metal ion in SHW because this level of each metal ions has been suggested to be present in some of the HDW [4]. EDTA and HEDTA solutions were first mixed with the metal ions to form metal complexes. The metal complex was then mixed with SHW such that the final concentrations of EDTA and HEDTA were 100 and 200 mM, respectively, in the SHW sample. A 1:100 dilution of the sample was used for the RPCE runs. The final pH of each SHW sample was pH 11 or higher.

Another series of experiments was carried out to examine whether the addition of Pb(II) solution to a sample containing EDTA and HEDTA complexes of Bi³⁺, Cr³⁺, Ni²⁺, and Fe³⁺ would quantitatively form Pb(II) complexes in SHW. All concentrations for the metal complexes are given as formal concentrations. A sample of 50 mM BiEDTA (pH 1.2) was prepared by mixing 1 ml of 0.50 mM Bi³⁺ and 5 ml of 0.10 M EDTA and then made up to 10 ml solution. SHW was added to 1.0 ml of this solution as shown in Table 1. To Sample A was added 0.0 ml SHW, to B 1.0 ml, to C 2.0 ml, etc. as shown. To Sample F, only dilute NaOH solution was added. The filtrate of Sample F (pH 10.8) was used for further investigations as also shown in Table 1. To 1 ml of Solution F was added 9 ml SHW. This solution became Sample G. 1 ml of Solution G was (i) treated with excess Pb²⁺ and made up to 10 ml of solution, (ii) treated with excess citrate and made up to 10 ml of solution, and (iii) made up to 10 ml of solution in reagent water. The UV spectra of Sample G(i)–(iii) were taken in a photodiode array spectrophotometer. For FeEDTA⁻, 2.0 ml of 50 mM FeEDTA⁻ was mixed with 2 ml of 1.0 mM Pb²⁺ and 5 ml of SHW. RPCE of the mixture was performed. Similarly, mixtures of 10 mM NiEDTA²⁻ and 10 mM NiHEDTA⁻; and 10 mM CrEDTA⁻ and 10 mM CrHEDTA⁻ were, respectively, treated with SHW and then with excess basic Pb²⁺ solution.

2.3.5. Analysis of real Hanford Defense Waste

The real HDW sample used in this study was from tank U-107. The RPCE analysis of real HDW sample was performed in the following manner. A serial dilution of 50 μl HDW sample to 1:100 in reagent water was made. Another serial dilution of 50 μl HDW sample to 1:100 was carried out by treating the sample with an excess Pb(II) in high pH citrate solution. No further pH adjustments were made. The UV wavelength of 254 nm was used for detection. A 75 μm i.d. bare silica column, 40 cm in length, was used with −18 kV potential to the injector.

3. Results and discussions

3.1. RPCE separation of uncomplexed EDTA and HEDTA

The RPCE separation of uncomplexed EDTA and HEDTA was accomplished by using 25 mM borate/25 mM HMB such that the complexants were separated in less than 6 min with −20 kV. As expected, (Fig. 1), the electropherogram of EDTA and HEDTA, showed that EDTA migrated faster, due
Table 1
The decomposition of BiEDTA− in SHW in the presence of excess Pb(II) added at high pH

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Sample treatment</th>
<th>SHW added (ml)</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50 mM BiEDTA− pH 1.2 + SHW 0.0</td>
<td>No ppt formed</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>50 mM BiEDTA− pH 1.2 + SHW 1.0</td>
<td>Heavy white ppt of Bi(OH)3 and Al(OH)3 formed</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>50 mM BiEDTA− pH 1.2 + SHW 2.0</td>
<td>Heavy white ppt of Bi(OH)3 and Al(OH)3 formed</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>50 mM BiEDTA− pH 1.2 + SHW 9.0</td>
<td>Heavy white ppt of Bi(OH)3 and Al(OH)3 formed</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>50 mM BiEDTA− + 200 mM Pb2+ + SHW 3.0</td>
<td>Slight ppt of Bi(OH)3 Filtrate became sample G. Sample pH=10.5</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>50 mM BiEDTA− pH 1.2 + dil NaOH 0.0</td>
<td>Slight ppt of Bi(OH)3 Filtrate became sample G.</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>5.0 mM BiEDTA− pH 10.5 + SHW 9.0</td>
<td>No ppt formed. UV spectra of solution showed BiEDTA peak</td>
<td></td>
</tr>
<tr>
<td>G(i)</td>
<td>G + Pb2+ excess diluted to 1:10 0.0</td>
<td>UV spectra showed PbEDTA2− peak but BiEDTA− peak disappeared.</td>
<td></td>
</tr>
<tr>
<td>G(ii)</td>
<td>G + excess citrate diluted to 1:10 0.0</td>
<td>UV spectra showed that BiEDTA peak disappeared</td>
<td></td>
</tr>
<tr>
<td>G(iii)</td>
<td>1:10 dilution of G 0.0</td>
<td>UV spectra showed BiEDTA− peak</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. RPCE electropherogram of 1 mM EDTA and 2 mM HEDTA. Conditions for the separation were 25 mM borate/25 mM HMB buffer at pH 9.2 with −20 kV applied across a 50 μm i.d. × 50 cm long capillary column. Gravity injection for 60 s at 100 mm injector head height was used as method of sample introduction and detection was by direct UV absorption at 240 nm wavelength.

electroosmotic flow modifier, HMB, in reducing the electroosmotic flow in addition to the high buffer ionic strength decreased EOF and gave a rapid migration of the complexants in less than 6 min.

3.2. RPCE separation of MEDTA and MHEDTA: (M=Al3+, Cr3+, Ni2+, and Pb2+)

Metal complexes in low ionic strength basic aqueous solution were separated in reagent water prior to the study of their chemistry in high ionic strength SHW. The formation of metal HEDTA complexes under basic conditions allowed the detection of trivalent metal complexes under RPCE conditions because the ionization of the hydroxy group of HEDTA gave the complexes a net negative charge. It has been shown that under basic conditions, the ethanolic proton of the hydroxy group of HEDTA takes part in bond formation with metals that form hexadentate structures [26,27].

Fig. 2 is the electropherogram showing the separation of a mixture of metal complexes of EDTA and HEDTA. The migration behavior of the complexes generally followed the charge number and the mass of the complexes. In addition, equivalent ionic conductances of metal ions have been suggested to affect the migration behavior with metal complex ions that have higher equivalent ionic conductance migrating faster [23]. Hence, although AlEDTA− has a lower charge number, it migrated faster than PbEDTA2− because of its small mass. For EDTA complexes, \( \mu_{obs}(\text{AlEDTA}^-) > \mu_{obs}(\text{PbEDTA}^{2-}) > \mu_{obs}(\text{CrEDTA}^-) \)
> \mu_{\text{obs}}(\text{NiEDTA}^{2-})$. For HEDTA complexes, the free hydroxy group in \(\text{Pb}^{2+}\) and \(\text{Ni}^{2+}\) complexes affected their migration behavior because the hydroxy group probably interacts with the ionized silanol groups on the capillary wall leading to broader peaks and peak tailing as evident in Fig. 2. Hence, \(\mu_{\text{obs}}(\text{AlHEDTA}^{-}) > \mu_{\text{obs}}(\text{CrHEDTA}^{-}) > \mu_{\text{obs}}(\text{PbHEDTA}^{2-}) > \mu_{\text{obs}}(\text{NiHEDTA}^{2-})\).

The \(\text{Pb}^{2+}\) complexes were more sensitive than the other metal complexes because the EDTA and HEDTA complexes of \(\text{Pb}^{2+}\) have high absorption at 240 nm. The CrHEDTA\(^{-}\) peak was small because it began to dissociate when the sample was mixed with \(\text{Pb(II)}\) complexes under basic conditions. These results demonstrated that the determination of the complexants as \(\text{Pb(II)}\) complexes were more sensitive than the other metals complexes.

3.3. Measurement of EDTA and HEDTA in the Synthetic Hanford Waste (SHW)

Measurement of EDTA and HEDTA in SHW was carried out separately for each complexant at concentration levels of 1.0 and 100.0 mM for EDTA and 2.0 and 200.0 mM for HEDTA. In each experiment, SHW gave a high absorbance background. Dilution of the sample, however, enabled the detection of the complexants which reacted with metal species in the SHW and formed stable EDTA or HEDTA complex. The migration times of the complexes were longer than the EDTA\(^{4-}\) and HEDTA\(^{3-}\) standards. Fig. 3(a,b) show the electropherograms of these SHW samples of EDTA and HEDTA, respectively. The EDTA and HEDTA reacted with SHW matrix to form AIEDTA\(^{-}\) and AIHEDTA\(^{-}\) which were identified by running AIEDTA\(^{-}\) and AIHEDTA\(^{-}\) standards at high pH as shown in Fig. 2. Al\(^{3+}\) formed AIHEDTA\(^{-}\) rather than AIHEDTA\(^{0}\) because of the participation of the ethanolic proton of the hydroxy group of HEDTA at high pH as mentioned earlier [26,27]. A rough estimate of the detection limits for EDTA and HEDTA in SHW as AIEDTA\(^{-}\) and AIHEDTA\(^{-}\) was 3 mM each in a sample of 1:10 dilution. Moreover, the peaks were broad and diffuse due to the low buffer/sample ionic strength ratio [25]. EDTA and HEDTA cannot, therefore, be measured in their uncomplexed forms in SHW because of the high aluminum content of the SHW matrix.
Fig. 4. RPCE electropherograms showing the behavior of metal–EDTA in SHW. (a) Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}, (b) Bi\textsuperscript{3+}, (c) Cr\textsuperscript{3+}, (d) Ca\textsuperscript{2+}, (e) Cd\textsuperscript{2+}, (f) Pb\textsuperscript{2+}. The final concentration of each metal ion and EDTA were 0.025 and 1.0 mM, respectively after a 1 : 100 dilution of the SHW sample. RPCE conditions were 100 mM boric acid/20 mM borate/100 mM diethylene amine buffer at pH 9.2 with −24 kV applied across a 50 \( \mu \)m i.d. \times 50 cm long capillary column. Gravity injection for 60 s at 100 mm injector head height was used as the method of sample introduction and detection was by direct UV absorption at 240 nm wavelength.

3.4. Metal ion interference study

Potential interferences from metal ions other than aluminum such as Bi\textsuperscript{3+}, Ca\textsuperscript{2+}, Cd\textsuperscript{2+}, Cr\textsuperscript{3+}, Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}, Hg\textsuperscript{2+}, UO\textsubscript{2}\textsuperscript{2+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+}, Fe\textsuperscript{3+}, and Th\textsuperscript{4+} ions, were investigated. Figs. 4 and 5 are some of the electropherograms from these investigations for each metal complex that was examined separately. The final pH of the SHW sample was 11 or higher throughout the investigation in order to keep Al\textsuperscript{3+} in solution (as its hydroxy complexes). When SHW was added to the solution of the EDTA and HEDTA complexes of Bi\textsuperscript{3+}, Cr\textsuperscript{3+}, Hg\textsuperscript{2+}, UO\textsubscript{2}\textsuperscript{2+}, Ni\textsuperscript{2+}, Fe\textsuperscript{3+}, and Th\textsuperscript{4+}, the complexes decomposed forming precipitates of metal hydroxides. No peaks were observed in the migration time region of EDTA and HEDTA metal complexes and SHW. Similarly, in Fig. 5, the migration time and the peak height of uncomplexed HEDTA\textsuperscript{3−} were 5.6 min and ~0.0038 absorbance unit for the samples of (a) UO\textsubscript{2}\textsuperscript{2+}, (b) Ni\textsuperscript{2+}, and (c) Th\textsuperscript{4+} in SHW. In Fig. 5(d), the migration time of PbHEDTA\textsuperscript{2−} formed in SHW was longer (13.6 min) and its peak was higher (~0.09 AU) than that of uncomplexed HEDTA\textsuperscript{3−} as shown in Fig. 5(a–c). The results indicate that only Pb\textsuperscript{2+} formed stable HEDTA complex in SHW and hence interferes in the determination of uncomplexed HEDTA in SHW.

Most metals did not interfere with the direct determination of EDTA and HEDTA due to the high level
of hydroxide concentration (>2 M) and the high ionic strength (>11 M) of SHW. Table 2 lists the $K_{sp}$ values of the metal hydroxides used in this study [28]. The formation of Bi(OH)$_3$ (log $K_{sp} = -30.4$) for example, was preferential to the formation of BiEDTA$^-$ (log $K_f = 22.8$). Metal hydroxides of Bi$^{3+}$, Cr$^{3+}$, Hg$^{2+}$, UO$_2^{2+}$, Fe$^{3+}$, and Th$^{4+}$ are quite insoluble and precipitate in solutions containing >1 M[OH$^-$] and 25 mM of the metal ion. EDTA and HEDTA complexes of Fe$^{3+}$ and Cr$^{3+}$ are known to decompose in highly alkaline solution resulting in rapid formation of Fe(OH)$_3$ and Cr(OH)$_3$ as discussed in a review by Bermejo-Martinez [29]. The Ni(II) complex also degrades in the alkaline solution [30]. Therefore, in the presence of high concentrations of hydroxide ion ([OH$^-$] > 2 M) in SHW, the decomposition of EDTA and HEDTA complexes becomes more pronounced than in dilute alkaline solution [30]. Another factor that contributed to the decomposition of some metal EDTA and HEDTA complexes in SHW was its high ionic strength (I > 11 M). High ionic strength decreases the coulombic attraction of the metal ions and complexing reagents. The effect of the dielectric constant of the solution therefore becomes more important at high ionic strength [31,32].

Since Pb$^{2+}$ EDTA and HEDTA complexes were stable in SHW, a series of experiments was carried out to determine the stability of Bi$^{3+}$, Cr$^{3+}$, Ni$^{2+}$, and Fe$^{3+}$ EDTA and HEDTA complexes in SHW in the presence of Pb$^{2+}$. The experiments involving Bi$^{3+}$ could not be measured by RPCE because Bi$^{3+}$ complexes formed a precipitate with the electrolyte which plugged the capillary column during the electrophoretic runs. A summary of the experiments and results involving Bi$^{3+}$ complexes is shown in Table 1. At high concentrations of Bi$^{3+}$ ([Bi$^{3+}$] > 5 mM) and under acidic conditions, BiEDTA decomposed when SHW was added to the solution. All the BiEDTA samples to which SHW was directly added formed Al(OH)$_3$ and Bi(OH)$_3$ precipitates, and liberated a brown gas thought to be nitrous oxide (Samples B to E of Table 1). The precipitation of Bi(OH)$_3$ in all the samples containing high [Bi$^{3+}$] is in agreement with the literature [30]. The sample of BiEDTA$^-$ that was made basic by the addition of dilute sodium hydroxide solution (without adding SHW) was found to be moderately soluble, forming only a slight precipitate (Sample F). When SHW was added to Sample F a solution was formed (Sample G), which was further tested as follows: G(i) was a 0.5 mM BiEDTA$^-$ in SHW mixed with excess Pb(II) solution, G(ii) was a 0.5 mM BiEDTA$^-$ in SHW mixed with excess citrate solution, G(iii) was a 1:10 dilution of 0.5 mM BiEDTA$^-$ in SHW. Fig. 6 is the UV spectra of samples G(i) to G(iii). The dilution of Sample G by the addition of basic Pb$^{2+}$ solution resulted in the disappearance of the BiEDTA$^-$ peak and the formation of a PbEDTA$^{2-}$ peak as shown in the UV spectra in Fig. 6(i). A similar disappearance of the BiEDTA$^-$ peak was observed when excess citrate was added to another aliquot of sample G, i.e. Fig. 6(ii). However, when 0.5 mM BiEDTA$^-$ in SHW was diluted in water, there was no disappearance of the BiEDTA$^-$ peak as shown in Fig. 6(iii). These results seem to show that when the basic solution of Pb$^{2+}$ and citrate were added, the formation of bismuth polynuclear hydroxo complexes [33,34] such as Bi$_9$(OH)$_{12}$$^{6+}$ (log $K = 168$) [35] were favored over the formation of bismuth EDTA complexes. Thus, the formation of PbEDTA$^{2-}$ occurred. Fig. 6(iv) is the UV spectra of the aqueous solution of the BiEDTA$^-$ standard which was not treated with SHW.

When FeEDTA$^-$ was treated with excess Pb$^{2+}$ and with SHW, a mixture of greenish crystals and brownish precipitate was observed, implying that FeEDTA$^-$ decomposed in the presence of SHW. The RPCE of the filtrate showed only a PbEDTA$^{2-}$ peak indicating that the freed EDTA$^{4-}$ preferentially complexed with Pb(II). Analogously, when more than five-fold excess Pb$^{2+}$ in basic citrate was added to a solution of EDTA and HEDTA complexes of Cr$^{3+}$ and Ni$^{2+}$, PbEDTA$^{2-}$ and PbHEDTA$^{2-}$ were formed. The implication of these results is that the total EDTA and

<table>
<thead>
<tr>
<th>M(OH)$_n$</th>
<th>$K_{sp}$</th>
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<tbody>
<tr>
<td>Bi(OH)$_3$</td>
<td>$4.0 \times 10^{-31}$</td>
</tr>
<tr>
<td>Cr(OH)$_3$</td>
<td>$6.3 \times 10^{-31}$</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
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<td>Th(OH)$_4$</td>
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</tr>
<tr>
<td>UO$_2$(OH)$_2$</td>
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</tr>
<tr>
<td>Ni(OH)$_2$</td>
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</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>$5.5 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

$^a$ From Ref. [25].
HEDTA as Pb(II) complexes could be determined in the presence of Bi$^{3+}$, Fe$^{3+}$, Cr$^{3+}$, and Ni$^{2+}$.

3.5. Analysis of EDTA and HEDTA in real Hanford Defense Waste

Uncomplexed EDTA and HEDTA standards gave very low responses at 254 nm. Other wavelengths were not attempted because of instrumental limitations. The result of a 1:100 dilution of the sample from tank U-107 in water is shown in Fig. 7. Essentially, at 254 nm, no uncomplexed EDTA and HEDTA or any other forms of the complexants were observed. Fig. 8 is the electropherogram of PbEDTA$^{2-}$ and PbHEDTA$^{-}$ standards in basic citrate solution. The peaks were well separated from each other, migration times were 6.4 and 14.9 min, respectively. Fig. 9(a) is the electropherogram of a 1:100 dilution of sample U-107 treated with Pb(II) in a 20 mM citrate solution. Citrate was added to ensure that the complexants bound to Al$^{3+}$ were released as previously discussed. The peaks at 2.3 and 2.5 min were the nitrite and nitrate peaks. The peaks at 6.3 and 15.1 min were PbEDTA$^{2-}$ and PbEDTA$^{-}$, respectively. These migration times were used for peak identification of PbEDTA$^{2-}$ and PbHEDTA$^{-}$ in the real HDW sample and were within 2% deviation of the migration time of the standards. The HDW sample was spiked with PbEDTA$^{2-}$ and PbHEDTA$^{-}$ standards and resulted in a proportional increase in the peak areas for both PbEDTA$^{2-}$ and PbHEDTA$^{-}$ as shown in Fig. 9(b). The RPCE runs resulted in a stable baseline and good peak shapes indicating that the method gave a high separation efficiency.

4. Conclusions

The RPCE separation of EDTA and HEDTA gave sharp peaks whose effective electrophoretic mobilities were $3.97 \times 10^{-4}$ and $3.26 \times 10^{-4} \text{cm}^{2} \text{V}^{-1} \text{s}^{-1}$, respectively, in a reduced electroosmotic flow mo-
Fig. 8. RPCE electropherogram of PbEDTA$^{2-}$ and PbHEDTA$^{-}$ standard in basic citrate solution (pH 12). Other electrophoretic conditions were the same as in Fig. 7.

Capacity of $-1.9 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. Separation efficiencies of 80 000 and 120 000 theoretical plates were obtained for EDTA and HEDTA, respectively. Metal EDTA complexes were found to separate due to a combination of the effects of molecular size, conductivity, and charge number. Hence, $\mu_{\text{obs (AlEDTA}^-)} > \mu_{\text{obs (PbEDTA}^{2-})} > \mu_{\text{obs (CrEDTA}^-)} > \mu_{\text{obs (NiEDTA}^{2-})}$ was observed. The hydroxyethyl group of the HEDTA complexes affected the migration behavior and peak shape of divalent metal complexes. Hence, $\mu_{\text{obs (AlHEDTA}^-)} > \mu_{\text{obs (CrHEDTA}^-)} > \mu_{\text{obs (PbHEDTA}^-)} > \mu_{\text{obs (NiHEDTA}^-)}$.

The EDTA and HEDTA complexes of Bi$^{3+}$, Cr$^{3+}$, Cr$_2$O$_7^{2-}$, Hg$^{2+}$, UO$_2^{2+}$, Ni$^{2+}$, Fe$^{3+}$, and Th$^{4+}$ decompose in the presence of SHW due to the high hydroxide concentration and high ionic strength of SHW. The EDTA and HEDTA complexes of Pb$^{2+}$, however, are stable in SHW and HDW and more sensitive than the other metal complexes. Hence, in the analysis of SHW and HDW for total EDTA and HEDTA, basic citrate should be used as an effective masking agent for Al(III) ion in the sample preparation process and should be measured to increase sensitivity.

**Acknowledgements**

We are grateful to Dr. W.F. Siems, Department of Chemistry, Washington State University, Pullman, WA, for helpful discussions during the course of this work. We also thank Professor K. Mopper, Department of Chemistry, Washington State University, Pullman, WA, for permitting the use of the photodiode array spectrophotometer in his laboratory and Susan Bentjen for her help in editing and preparation of the final draft. This work was supported in part by a grant from Westinghouse Hanford Company, Richland, WA.
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