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Matthew T. Cox[a]; Lawrence R. Gahan[a]
[a] Department of Chemistry, The University of Queensland, Brisbane, QLD, Australia

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SEPARATION OF MERCURY (II), LEAD (II), AND SILVER (I) FROM AQUEOUS SOLUTION USING AN AMINOPOLYCARBOXYLATE SILICA

Matthew T. Cox and Lawrence R. Gahan*

Department of Chemistry, The University of Queensland,
Brisbane, QLD, Australia 4072

ABSTRACT

A quartz crystal microbalance modified by the attachment of silica particles derivatized with the aminopolycarboxylate ligand *N*-[(3-trimethoxysilyl)propyl]ethylenediamine-*N*,*N*′,*N*′-triacetic acid has been employed to assess conditions under which mercury (II), lead (II), and silver (I) nitrates may be separated in aqueous solution. The separation protocol, which involved removal of Hg(II), as $[HgI_4]^{2-}$, and Pb(II) with H^+ was successfully applied to a batchwise separation of the 3 metal ions.

Key Words: Quartz crystal microbalance; *N*-[(3-Trimethoxysilyl)propyl]ethylenediamine-*N*,*N*′,*N*′-triacetic acid; Silica; Mercury (II) nitrate; Lead (II) nitrate; Silver (I) nitrate; Selective separation

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*Corresponding author.

INTRODUCTION

Environmental problems associated with the presence of toxic heavy metals in natural waters are widely acknowledged and have resulted in interest in methods to determine concentrations and selective removal of heavy metals (1). Methodologies for the identification and separation of metal ions from water streams using polymeric materials as complexation reagents have been reported (1–9).

We have been interested in the preparation of a suitably modified material as an agent for the selective removal of mercury (II) from aqueous solution. Two approaches to this problem can be envisaged. In the first, a material that selectively complexes Hg(II) may be appended to the polymeric support and the highly selective complexation properties of the material can be employed to separate Hg(II) (5). In the second approach, a polymeric material is employed to complex many of the metal ions in solution, and then selective elution procedures are employed to separate the metal ions (10,11).

Suitably modified silica, which is generally easily prepared and relatively robust, has proved popular as a polymeric support for these separations (6,7,9,12). One example is the use of 2-mercaptobenzimidazole-modified silica, which has been shown to be particularly effective for the removal of Hg(II) from aqueous solutions containing Cu(II), Zn(II), Cd(II), and Pb(II) (10,11). In this case, the metals were easily employed through different concentrations of acid solution, 0.01 mol/L for Cu(II) and Zn(II), and 0.06 mol/L for Cd(II) and Pb(II). To recover Hg(II) completely from the column, 6 mol/L HCl were employed (10,11).

We report a study employing silica modified with an aminopolycarboxylate ligand as an agent for the separation of Hg(II) from a mixed aqueous solution of Hg(II), Pb(II), and Ag(I) nitrates. Rather than investigate separation protocols using batch or column methods, we have devised a methodology that employs a quartz crystal microbalance (QCM). A QCM consists of a thin circular quartz crystal with circular gold electrodes centrosymmetrically placed on opposite faces (13). Application of an electric field across the crystal, using an electronic oscillator, results in vibration of the crystal at its resonant frequency. The oscillation frequency of the crystal is decreased by deposition of mass on its surface (14). The application we explore is not consistent with the traditional role of the QCM as a mass sensor; instead, the QCM was used as a probe employed to assess the proficiency of an eluent solution in removing metal ions complexed on its surface, which has been modified with a multidentate aminopolycarboxylate-receptor sites for metal ion complexation. The device permitted investigation of different elution conditions and their efficacy for the decomplexation of the metal ions by allowing us to monitor the frequency changes of the QCM. The elution procedures developed through the use of the QCM were then applied on a larger scale to the separation of metal ions.

EXPERIMENTAL

Materials and Methods

N-[(3-trimethoxysilyl)propyl]ethylenediamine-*N*,*N*′,*N*′-triacetic acid (ED3A) (50% trisodium salt in H_2O) and Glassclad RC® were acquired from ACBR Chemical Co. (Karlscuhe, Germany) LiChrospher® Si 60 silica (5 μm spherical) was obtained from Merck (Darmstadt, Germany). 5 MHz AT-cut crystals with polished surfaces and gold electrodes were acquired from International Crystal Manufacturing Company, Inc (Oklahoma City, OK, USA). Flow cells (model 1121, 70 μL chamber) were obtained from Universal Sensors, Inc (Metairie, USA).

Energy dispersive spectroscopy (EDS) was undertaken at the Centre for Microanalysis and Microscopy at The University of Queensland, Brisbane, Australia with an energy-dispersive spectrometer attached to a JEOL JSM-6400F field emission electron-probe microanalyzer that incorporated both a scanning electron and compound microscope. This instrument utilized a lithium-drifted silicon detector (Si(Li)) with an atmospheric thin window (ATW) and was calibrated against a sample of pure copper metal. The samples were run at an accelerating voltage of 30.0 kV, with a beam current of 10 nA, for an acquisition time of 20 min. All QCM specimens were sampled in a minimum of 4 different areas on the central gold electrode of the QCM sensor.

ED3A-QCM crystals were analyzed for lead (II) and mercury (II) using a wavelength-dispersive (WD) spectrometer attached to a Jeol JXA-8800L electron-probe microanalyzer that incorporated both a scanning electron and an optical microscope. The WD instrument utilized a lithium fluoride crystal for diffraction crystal, while detection was achieved using a gas-filled counter. Standard samples (gold, mercury sulfide, and lead sulfide) were run at an accelerating voltage of 25.0 kV with a beam current of 10 nA, and a 50 micron step (dwell time 500 milliseconds) for a total acquisition time (per point) of 200 s. QCM samples were analyzed for a total acquisition time (per point) of 1 h at an accelerating voltage of 25.0 kV and a beam current of 60 nA with a 50 micron step and a dwell time of nine s. The QCM specimens were sampled in 3 different positions on the central gold electrode of the QCM sensor.

Solutions of mercury (II) nitrate, lead (II) nitrate, and silver (I) nitrate were prepared in Milli-Q water and analyzed with a Thermo Optek Corporation VG Plasma Quad ICP-MS (inductively coupled plasma–mass spectrometer) at the CSIRO Division of Tropical Agriculture, St. Lucia, Brisbane. Flame atomic absorption spectroscopy (AAS) was carried out in the Department of Chemistry at The University of Queensland, with a Varian SpectrAA 300 atomic absorption spectrometer. Standard solutions were either diluted from a commercially obtained standard solution or prepared from standard sources. All standards were calibrated by inductively coupled plasma (ICP) prior to use.

The activation and preparation of ED3A-silica and the preparation of an ED3A-silica QCM were undertaken as described previously (15).

Apparatus

The QCM was mounted between two O-rings in a Universal Sensors flow cell. One face of the crystal was exposed to a flowing aqueous solution in a 70 μL chamber; the other crystal face was exposed to air. The aqueous solutions were passed over the face of the crystal using a Minipuls peristaltic pump at flow rates from 5 mL/min to 14 mL/min, although most commonly the flow rate was maintained at 7 mL/min. Milli-Q water, dilute acid solutions, and aqueous solutions were in turn run across the face of the crystal through a series of taps connected to solution reservoirs. The crystal was powered by a 5 V direct current power supply giving an output that was recorded in real time on a Hewlett-Packard 5316B universal counter and visualized on an IBM compatible computer with software developed in-house. The oscillator was designed and built in-house. Both the oscillator and flow cell were housed within a Perspex box to maintain constant temperature and humidity. No other precautions were necessary to remove extraneous fields. Over the course of an experiment, which was of 1 or 2 h duration, the drift in frequency of the crystal was found to be less than ± 5 Hz. Pulsations in fluid flow due to the peristaltic pump were not found to disrupt the oscillation of the crystals.

Separation of Aqueous Solutions of Mercury (II), Lead (II), and Silver (I)

Experiments were conducted with mixed aqueous solutions of lead (II), mercury (II), and silver (I) nitrates with ED3A-functionalized LiChrospher® (functionalization = 0.95 mmol ED3A/g silica by C, H, and N microanalysis). ED3A-silica (0.53 g) and an equal amount of the nonfunctionalized silica were placed in separate centrifuge tubes. The tubes were filled with Milli-Q water and sonicated for approximately 2 min and then mechanically shaken for another 5 min to ensure mixing of contents. The tubes were then centrifuged for 10 min and the supernatant solutions carefully removed. This procedure was repeated using dilute nitric acid (0.1 mol/L), water, NaI (0.1 mol/L), and 2 water washes. To the silica thus prepared and in the centrifuge tubes, a mixed aqueous solution of mercury (II), lead (II), and silver (I) nitrates was added. The tubes were treated with sonication and mechanically shaken. The supernatant aqueous solution was removed. The silica samples were treated sequentially with NaI solution (0.1 mol/L) and dilute nitric acid (~ 0.1 mol/L), and at each step, aliquots were taken

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for analysis. Solutions were analyzed for mercury with ICP, while lead and silver content was determined by AAS. Experiments were undertaken with empty centrifugation tubes to ascertain the extent of metal ion uptake by the tubes.

RESULTS AND DISCUSSION

Reaction of *N*-[(3-trimethoxysilyl)propyl]ethylenediamine-*N*,*N*′,*N*′-triacetic acid (ED3A) with LiChrospher® silica (5 μm spherical silica) resulted in a polymeric material (ED3A-silica) containing 0.95 mmol ED3A/g silica. The aminopolycarboxylate ligands are well known for their capacity to form complexes with metal ions (16–19). The infrared spectrum of the modified silica shows prominent bands at 1587 cm^{-1} and 1412 cm^{-1}, which are indicative of the presence of COO^-.

To assess the conditions under which metal ions such as Hg(II), Pb(II), and Ag(I) can be removed from aqueous solution using the modified ED3A-silica, the particles were applied to the gold electrode of a QCM. We have previously employed this device to assess the conditions for the separation of Pb(II) and Ag(I), and others have used the technique to detect uranium and thorium (15,20–22). The silica beads act both as the solid support for the aminopolycarboxylate ligand and as a way to increase the surface area, and thus the number of receptor sites (21,22). The QCM device is particularly sensitive to the complexation and decomplexation of the metal ions. The changes in mass on the surface were reflected in the frequency change of the crystal (14). The response of the ED3A-QCM device in a flow cell to a stream of Milli-Q water in the presence of Hg(II) ions, as $Hg(NO_3)_2$, was similar to that described previously for lead (II) (Fig. 1) (15). Thus, initially upon introduction of the solution containing the metal ion, a large decrease in frequency of the crystal was observed. In the absence of any surface coverage, a bare crystal, the frequency change upon exposure of the crystal in the flow cell to an aqueous solution containing a metal ion was effectively instantaneous with no exponential decay evident. When coated with underivatized silica, the crystal attained a constant frequency within a period of 40 s. However, in the case of a crystal derivatized with ED3A silica, the rate of change in frequency was related to the concentration of the Hg(II) ion. As was observed with Pb(II), a prominent exponential region was evident as the frequency approached equilibrium (A→B in Fig. 1). Upon changing the flowing solution to water (B) a new equilibrium frequency was established (the plateau region) (C) (15). The difference in frequency between points A and C (Δf) was related to the mass deposited on the surface (14). In the case of Pb(II) studied previously, the application of a dilute acid solution at D, with subsequent washing of the ED3A-QCM with water, resulted in the reestablishment of the initial baseline frequency of the crystal; i.e., protonation of the ED3A ligand re-

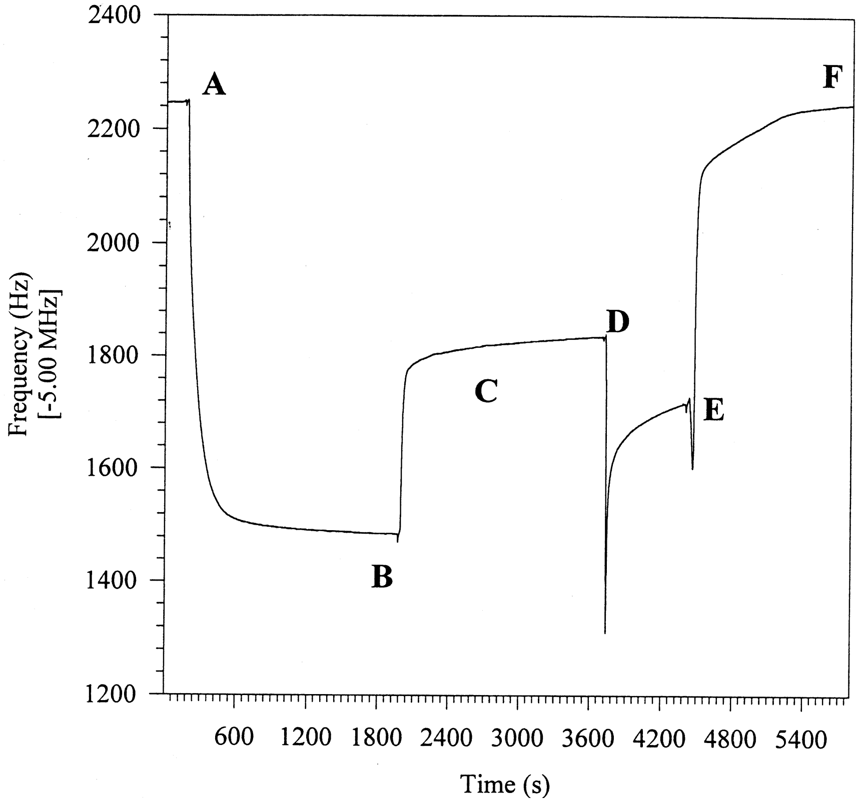

Figure 1. Frequency-time profile for the reaction of an aqueous solution of $Hg(NO_3)_2$ (9.3×10^{-5} mol/L) with ED3A-silica QCM. The labels are as indicated in the text.

sults in removal of the Pb(II). For Hg(II), addition of acid solution (0.1 mmol/L HNO_3) (D) had little effect on the magnitude of Δf. In contrast to both Pb(II) and Hg(II), when the ED3A-QCM was exposed to an aqueous solution of Ag(I), the metal ion was not retained by the ED3A-QCM device (15).

The lack of success in the removal of Hg(II) from the ED3A-QCM surface with H^+ suggested that it was not an efficient competitor for the metal ion with the ED3A ligand. This is consistent with observations made previously concerning the difficulty of removal of Hg(II) from 2-mercaptobenzimidazole-modified silica (10,11). In that case the difficulty was ascribed to the high affinity of sulfur for the Hg(II) (10), although it is more likely to be a reflection of the magnitude of the binding constant and the range of pH over which the complex is stable.

The lack of effect on the frequency of the Hg/ED3A-QCM of the H^+ wash procedure at point D (Fig. 1) prompted a search for conditions under which the metal ion could be successfully removed. Such conditions would result in the return of the frequency of the QCM device, after a final water wash, to the baseline frequency. It was found that application of a dilute (~ 0.1 mmol/L) solution of sodium iodide in place of the H^+ wash (D) resulted in the complete recovery of the baseline frequency (F) after a final water wash (E). Elution with an aqueous KI solution resulted in an erratic frequency response, suggesting contamination of the crystal surface.

Spectroscopic analysis of a solution of Hg(II) nitrate solution mixed with NaI indicated a band at 322 nm in the visible/UV spectrum; the species in solution was identified as $[HgI_4]^{2-}$ ($\lambda_{max} = 322$ nm; $\varepsilon = 1.97 \times 10^4$ $(mol/L)^{-1}\cdot cm^{-1}$) (23). Upon mixing KI and Hg(II) in aqueous solution, a bright red precipitate of $K_2[HgI_4]$ formed, suggesting that the erratic frequency response of the crystal when KI was employed as eluent was due to precipitation in the system. The binding constant for Hg(II) with an analogue of ED3A, *N*-methylethylenedinitrilotriacetic acid (24,25), has not been reported; however, the magnitudes of the binding constants with Hg(II) for the analogous aminopolycarboxylate ligands ethylenediamine-*N*,*N*′,*N*′-tetraacetic acid (EDTA) and imino-*N*,*N*-diacetic acid (IDA) ($\log_{10} = 21.5$ and $\log_{10} = 11.8$, respectively) (26) suggest that I^-, ($[HgI_4]^{2-}$ $\log_{10}\beta_4 = 29.8$, 25°C) (26) would be an efficient competitor with the ED3A-QCM for Hg(II).

Previously we had shown that Pb(II) ions could be removed from ED3A-silica (on a QCM) with H^+ and that Ag(I) ions were not retained (15). The present result suggests that a combination of elution conditions alternating between water, H^+, and I^- may permit separation of Ag(I), Pb(II), and Hg(II) on the ED3A-silica. To explore the separation scheme more closely, a series of ED3A-QCM crystals was prepared and exposed to a mixed solution of Hg(II), Pb(II), and Ag(I) nitrates in the flow cell with the same conditions previously described. A crystal was removed from the cell at point C (Fig. 1) after exposure to the mixed-metal solution after the I^- wash, after the H^+ wash, and following the final water wash and recovery of the baseline frequency. Analysis of the surfaces of the crystals with wavelength dispersive spectrometer (WDS) indicated that both Hg(II) and Pb(II) were present on the surface of the ED3A-QCM removed at point C; lead (II) but not mercury (II) was present after the I^- wash; and no metal ions were detected following the acid/water wash. The Ag(I) ions were not retained by the ED3A-QCM (15).

The elution methodology developed with the QCM device should permit separation of a mixture of Hg(II), Pb(II), and Ag(I) from aqueous solution using ED3A-silica. The procedure is predicated on the fact that Hg(II) and Pb(II) could be separated by differential elution while Ag(I) should not be retained by the ED3A-silica. Thus separation on a larger scale was attempted on a mixed aqueous solution of lead (II), mercury (II), and silver (I) with ED3A-functionalized

Table 1. Separation of Hg(II), Pb(II), and Ag(I) on ED3A-LiChrospher Silica[a]

Sample	Average Pb(II) Concentration[b]	Average Hg(II) Concentration[c]	Average Ag(I) Concentration[b]
Stock solution	266.9 ± 1.4	139.5 ± 1.8	248.1 ± 0.6
Mixed solution exposed to blank LiChrospher	266.8 ± 1.4	137.0 ± 1.8	240.4 ± 0.7
Solution following exposure to ED3A-LiChrospher	<1.0	<1.0	235.0 ± 0.9
I^- wash solution	<1.0	140.9 ± 1.5	<1.0
H^+ wash solution	250.6 ± 1.4	<1.0	<1.0

[a] All concentrations have been corrected for adsorption of the metal ions by the containers; the limit of detection was 1.0 ppm.

[b] Determined from AAS (ppm).

[c] Determined from ICP-MS (ppm).

LiChrospher®. A batch separation technique, described in the experimental section, was employed. The results are summarized in Table 1. Blank tests, in which the metal solutions were run through the experimental procedure in centrifuge tubes not containing silica, indicated that an amount of each metal was being adsorbed by the tubes themselves and the results presented in Table 1 have been corrected to account for this adsorption. The results in Table 1 suggest that, at the limits of detection of the instrumentation, the respective eluents I^- and H^+ can discriminate between Pb(II) and Hg(II) on the ED3A-silica.

The results of both the surface studies and the aqueous separations reported here demonstrate that, when anchored to silica, the aminopolycarboxylate ligand ED3A is capable of separating three environmentally important heavy metal ions in aqueous solution. While this sort of separation does not represent a new idea, it has two novel aspects. The first is the use of a QCM sensor, modified with a receptor layer containing the coordinating ligand of interest, in a predictive role to develop a separation scheme. The second is the development of extremely mild conditions (0.1 mol/L I^-) for the removal of Hg(II), in contrast to previous methods where concentrated acid solutions were employed (10,11). The large extinction coefficient of the $[HgI_4]^{2-}$ ion ($\varepsilon = 1.97 \times 10^4$ (mol/L)$^{-1}\cdot$cm^{-1}) offers an added advantage for spectrophotometric detection.

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