

Detection of lead(II) and silver(I) in aqueous solution using a piezoelectric device

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The gold surface of a quartz crystal microbalance was modified by the attachment of silica particles derivatised with *N*-[(3-trimethoxysilyl)propyl]ethylenediaminetriacetic acid. The device was employed to study the kinetics of the interaction of aqueous solutions of lead(II) nitrate and silver(I) nitrate with the surface and for the selective separation of the metal ions.

The quartz crystal microbalance (QCM) consists of a thin, circular, quartz crystal with circular gold electrodes placed centrosymmetrically on opposite faces.^{1–5} Application of an electric field across the crystal, using an electronic oscillator, results in vibration of the crystal at its resonant frequency. The frequency of the oscillating crystal is decreased by deposition of mass on its surface and it has been shown that in the gas phase the change in frequency for a quartz crystal is related to change in mass by the Sauerbrey equation.⁶ These devices are radially sensitive, *i.e.*, it is the area under the gold electrode surface which is the most sensitive part, and the quartz surface projecting radially from the centre becomes less sensitive to mass deposited.⁷ The mass sensitivity of the QCM has been exploited in both the vapour phase and in liquids, and there are numerous reported applications.^{1–5,8–16}

Two areas of the application of QCM devices are of immediate interest. The first involves the monitoring of biomolecular reactions in the liquid phase, in particular kinetic immunoassays which can be followed by the change in frequency as the mass on the surface of the crystal increases.¹⁷ The piezoelectric device offers an alternative to the measurement of reaction kinetics of heterogeneous systems involving biomacromolecular interactions using the BIAcore™ instrument, although in the latter case the kinetic analyses have been more extensively investigated and developed.^{18–20} Second, we are interested in the development of piezoelectric devices for the detection and determination of metal ions in solution,^{14,21–27} where sorbents chemically attached to the crystal are employed in order to obtain the selectivity required to determine one metal ion in the presence of others.

We describe an application of the QCM which combines the two areas. The QCM device described in this work is not employed specifically as a mass sensor, in line with recent studies which question this aspect of their use,^{28,29} but more so as an event sensor. A QCM device, derivatised with an aminopolycarboxylate ligand covalently attached to spherical silica particles, is employed in the search for selective substrates and/or conditions under which it would be possible to separate metal ions under flow conditions. A combination of the determination of an adsorption isotherm and investigation of association and dissociation phase kinetic parameters has been employed to permit the prediction of the behaviour of two metal ions on the derivatised silica substrate.

Experimental

Materials and methods

N-[(3-Trimethoxysilyl)propyl]ethylenediaminetriacetic acid (ED3A) (50% trisodium salt in H₂O) was obtained from ABCR GmbH & Co., Karlsruhe, Germany. Glassclad RC was obtained from United Chemical Technologies, Inc., Bristol, PA, USA. LiChrospher Si 60 silica (5 μm spherical) was obtained from Merck (Darmstadt, Germany) and silica gel (200–400 mesh, 60 Å) from Aldrich (Milwaukee, WI, USA). AT-cut crystals (5 MHz) with polished surfaces and gold electrodes were purchased from International Crystal Manufacturing (ICM) (Oklahoma City, OK, USA). Flow cells (Model 1121, 70 μL chamber) were obtained from Universal Sensors (Metairie, CA, 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 (Palo Alto, CA, USA) JXA-8800L electron-probe microanalyser. The ED detector comprised a high purity germanium detector with a beryllium window. Standard samples (gold, chromium, quartz, lanthanum, silver and lead fluoride) were run at an accelerating voltage of 15.0 kV with a beam current of 10 nA for an acquisition time of either 30 s or 5 min. Actual QCM samples were analysed for a range of acquisition times (from 100 s to 20 min) at an accelerating voltage of 25.0 kV and a beam current of 10 nA, except for the lanthanum samples, which were acquired at an accelerating voltage of 15.0 kV. All QCM crystals were sampled at a minimum of four different regions on the central area of the crystal.

Solutions of lead(II) nitrate, silver(I) nitrate and lanthanum(III) nitrate were prepared using water obtained from a Milli-Q system (Millipore, Bedford, MA, USA) ('Milli-Q water') and analysed by ICP-MS (lead, lanthanum) at the CSIRO Division of Tropical Agriculture (St. Lucia, Brisbane, Australia) or AAS (silver) prior to use.

Activation of silica³⁰

LiChrospher® Si 60 silica (5 μm spherical) (0.5 g) was heated under reflux in concentrated HCl (5.0 mL) for 4 h. The silica

was filtered under vacuum and washed with Milli-Q water until the pH of the washings was approximately 5. The silica was washed with ethanol, and diethyl ether and then dried under high vacuum at room temperature.

Preparation of ED3A-silica

ED3A (50% trisodium salt in H₂O) was diluted with methanol to give a 10% solution. Activated LiChrospher silica (0.5 g) was mixed with the 10% ED3A solution (11.6 g; 2.5 mmol) and the mixture was agitated in a sealed vessel at room temperature. After 8 d the silica was separated by filtration, washed with methanol and dried under high vacuum (C, 8.26; H, 2.09; N, 1.73%; 0.62 mmol ligand g⁻¹ silica).

Preparation of an ED3A-silica QCM^{23,24}

A quartz crystal (5 MHz) was mounted on a crystal holder and dipped vertically into a 10% methanol solution of Glassclad RC and immediately held horizontally and permitted to dry in air. One side of the crystal was wiped with acetone-soaked tissue paper to remove the adhesive solution. The crystal was placed on a horizontal surface, the face with the air-dried adhesive uppermost. A copper template with a circular hole slightly larger than the circumference of the gold electrode was placed over the electrode. Derivatised LiChrospher silica was placed within the hole of the template so that it completely covered the exposed electrode area. The silica was pressed flat such that upon removal of the template a mound of silica remained on the electrode.

The crystal, adhesive layer and silica coating were placed in an oven and the temperature was raised slowly to 150 °C and the heating continued for 4 h. At the completion of the heating period, the crystal was permitted to cool to room temperature, excess silica was removed with a stream of Milli-Q water and the crystal dried in air. The crystal was mounted in a flow cell and permitted to oscillate in air for 12 h, and finally under a flow of Milli-Q water for 12 h prior to use.

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 and the other crystal face was exposed to air. The aqueous solutions were passed over the face of the crystal using a Minipuls peristaltic pump (Gilson, Worthington, OH, USA) at flow rates from 5 to 14 mL min⁻¹, although most commonly the flow rate was maintained at 7 mL min⁻¹. Milli-Q water, dilute acid solutions and aqueous solutions were in turn run across the face of the crystal by employing a series of taps connected to reservoirs of the solutions. The crystal was powered by a 5 V dc power supply giving an output that was recorded in real time on a Hewlett-Packard (Avondale, PA, USA) Model 5316B universal counter and visualized on an IBM compatible computer, using software developed in-house. The oscillator was designed and built in-house. The oscillator and flow cell were housed within a Perspex box in order to maintain constant temperature and humidity. No other precautions were necessary to remove extraneous fields. Over the course of an experiment, which may be of 1–2 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. The frequency *versus* time data for the relevant sections of the reaction profile were extracted and fitted using a non-linear curve fitting routine in SIGMAPLOT.³¹ The curve fitting process uses the Marquardt–Levenberg algorithm to find

the coefficients of the independent variables that minimize the sum of the squared differences between observed and predicted values of the dependent variable.³¹

Results and discussion

Derivatised silica was employed to produce a coating for a QCM device. The silica acts as a linker between the receptor ligand and the gold electrode and was employed because the high surface area enhances the sensitivity of the device by increasing the number of receptor sites per unit area on the electrode. In the present case we employed a commercially available silane, ED3A, in order to functionalise the silica, the resulting loading of ligand being 0.62 mmol g⁻¹ silica. Aminopolycarboxylate ligands are well known for their capacity to form complexes with metal ions.^{32–35} The application of an ED3A derivatised silica to the surface of a QCM for the detection of metal ions in solution has been utilised previously^{23,24} and zeolite monolayers have been applied also to the surfaces of surface acoustic wave devices.^{36,37}

Crystals coated with derivatised or underderivatised silica were exposed, in the flow cell, to a stream of Milli-Q water, typically at a flow rate of 7 mL min⁻¹, the flow rate representing a compromise between volume of solution required per experiment and the total time taken per experiment. The baseline frequency of the crystal was monitored for a period of up to 10 min (fluctuations of less than ±2 Hz), then the stream was switched to a solution containing a metal ion at a concentration of 1 × 10⁻⁴ M. As the content of the flowing stream changes, the response of the QCM also changes. Initially in the presence of the solution containing the metal ion (in this case Pb²⁺) a large decrease in frequency of the crystal is observed. In the case of a crystal coated with underderivatised silica, the crystal attained a constant frequency within a period of 40 s whereas for a crystal derivatised with ED3A-silica the rate of change in frequency was related to the concentration of metal ion in solution with some reactions, employing the most dilute solutions, requiring upwards of 1 h to attain equilibrium, with a prominent exponential region evident as the frequency approached equilibrium (A–B in Fig. 1). In the absence of any surface coverage, *i.e.*, a bare crystal, the frequency change upon exposure of the crystal in the flow cell (7 mL min⁻¹) to an aqueous solution containing a metal ion was effectively instantaneous, with no exponential decay evident. Further,

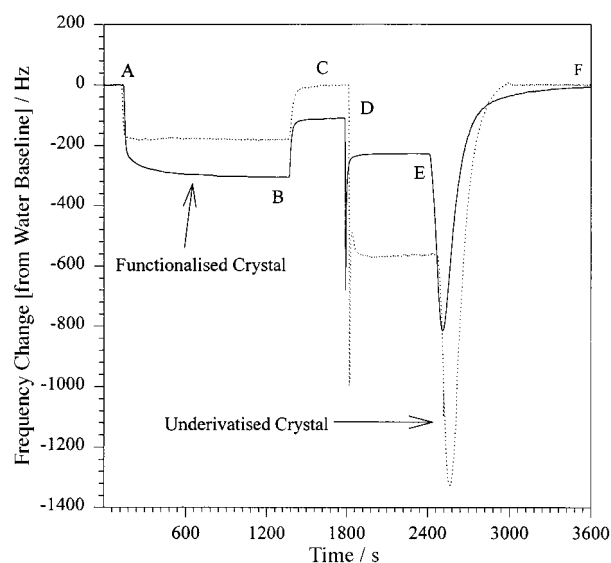


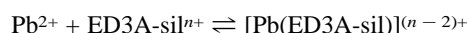
Fig. 1 Frequency–time profile for the reaction of an aqueous solution of Pb(NO₃)₂ with ED3A-silica QCM (functionalised crystal) and silica QCM (underderivatised QCM). The labels are as indicated in the text.

exposure of a crystal covered only with the glue material or a crystal derivatised with silica but having no metal ion receptor sites exhibited no region indicative of metal ion uptake.

The frequency *versus* time profile describing the interaction of the ED3A-silica QCM with an aqueous Pb(II) solution, illustrated in Fig. 1, may be interpreted in the following way.^{23,24,38} A constant frequency is replaced by a change in frequency as the aqueous solution is replaced by a solution of the metal ion (A). A constant frequency is obtained as equilibrium is established, the change in frequency reflecting both the change in density of the solution and uptake of metal ion by the bound receptor site. Changing the flowing solution to water (B) re-establishes a new equilibrium frequency (the plateau region) (C), the frequency difference between A and C (Δf) reflecting the uptake of metal ion by the supported ligand. Addition of acid solution (0.1 M HNO₃)(D) followed by aqueous solution (E) results in the removal of the metal ions from the substrate and the re-establishment of the initial frequency (F). The system is chemically reversible and robust. Indeed, we have successfully employed the same crystal in multiple sequences of metal ion loading and acid washings for periods extending over 1 month.

Evidence for metal uptake by the system was obtained by EDS. In an experiment using aqueous La³⁺ [La(NO₃)₃] solutions and an ED3A-silica QCM, three crystals were subjected to the experiment described in Fig. 1. The crystals were removed at points corresponding to just prior to A, at C and at F and were examined by EDS. No La³⁺ was detected at points A and F and nanomolar levels of La³⁺ were detected at C. The results suggest that this system is capable of reversibly binding a metal ion. More complete data concerning the interaction of La³⁺ with the ED3A-silica QCM will be reported subsequently.³⁸

A more quantitative analysis of the uptake of metal ions was undertaken. A series of aqueous solutions of lead(II) nitrate at concentrations from 1×10^{-6} to 1×10^{-3} M were exposed to the surface of an ED3A-silica QCM. The sequence of exposure was as described above, with the frequency change at the plateau region (C in Fig. 1) recorded. In each experiment, subsequent exposure of the crystal to 0.1 M HNO₃, then water, resulted in the recovery of the frequency of the QCM to its starting value. The same crystal was employed for the series of experiments with solutions of lead(II) and typically duplicate or triplicate analyses were undertaken for each concentration. A plot of Δf (at the plateau region) *versus* [Pb(II)] indicates that, at the higher concentrations, saturation of the metal ion coordination sites had occurred (Fig. 2). Assuming that the model for reaction can be described as



where the state of protonation of the complex is undefined, the data can be fitted to a Langmuir isotherm expression of the form³⁹

$$\Delta f = f_{\text{max}} \left\{ \frac{K[\text{Pb(II)}]}{1 + K[\text{Pb(II)}]} \right\} \quad (1)$$

The fit to the data resulted in $\log K = 6.0$ (Fig. 2), essentially the binding constant for lead(II) to the derivatised surface.

The experiments were repeated with aqueous solutions of silver(I) nitrate. A typical frequency *versus* time profile for reaction of an ED3A-silica QCM with Ag(I) solutions (1×10^{-6} to 1×10^{-3} M) is shown in Fig. 3. Differences between the profiles for lead(II) and silver(I) are immediately obvious with the plateau region (C) not present for the profiles with the latter metal ion. For Ag(I) solutions, dissociation of the metal ion from the surface of the crystal appears to contribute to the shape of the curve, with the final frequency of the crystal essentially identical with the frequency at the commencement of the experiment. It was not possible to obtain an adsorption isotherm for Ag(I) with this system.

An analogue of ED3A, *N*-methylethylenedinitriacetate, is known,^{40,41} although binding constants with Pb(II) and Ag(I) have not been reported.⁴²

The response of the QCM in the region represented by A–B (Fig. 1) was dependent on (i) the presence of the ED3A-silica and (ii) the concentration of lead(II) in the solution. In the absence of receptor sites on the silica the exponential region extended for approximately 40 s and in the analysis which follows the data included were collected after this period. In the presence of the receptor sites the rate of change in frequency was related to the concentration of metal ion in solution. Reactions at low concentration ($< 1 \times 10^{-6}$ M) were typically left for approximately 60 min, although sufficient data can be obtained after 30 min to permit a successful kinetic analysis. At higher concentrations, *e.g.*, 5×10^{-5} M, equilibrium results after 10 min. The equilibration time may be improved by employing higher flow rates,¹³ at the expense of increased volume of solution required. Thus, aqueous solutions of lead(II) nitrate (1×10^{-6} to 1×10^{-3} M) were exposed to the surface of the ED3A-silica QCM in the flow cell at a flow rate of 7

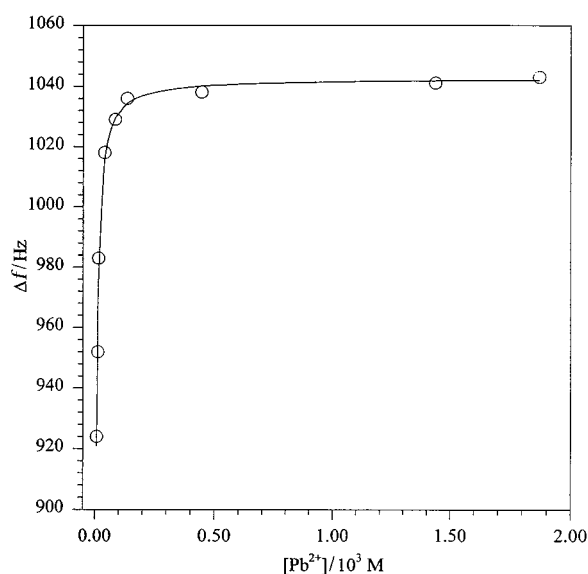


Fig. 2 Isotherm for the reaction of an aqueous solution of Pb(NO₃)₂ with ED3A-silica QCM. The line represents the best non-linear least-squares fit to the experimental data using the parameters given in the text.

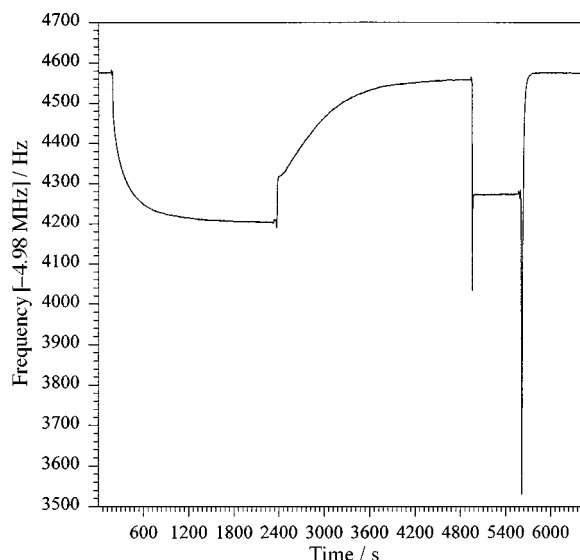
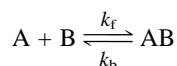


Fig. 3 Frequency–time profile for the reaction of an aqueous solution of Ag(NO₃) with ED3A-silica QCM.

mL min⁻¹. For each concentration the association phase (A–B in Fig. 1) of the data was fitted, assuming the model



where k_f and k_b are the association and dissociation rate constants, respectively, using a non-linear least-squares fitting routine, to an integrated rate equation of the form^{18–20}

$$f_t = f_{\text{eqm}}(1 - e^{-k_{\text{obs}}t}) \quad (2)$$

where f_t is the frequency at time t , f_{eqm} is the frequency at equilibrium (at B) and $k_{\text{obs}} \{k_{\text{obs}} = k_f[\text{Pb(II)}] + k_b\}$ is obtained from the fit to the curve. Typically duplicate or triplicate runs were taken for each concentration. The plot of k_{obs} versus $[\text{Pb(II)}]$ was linear (Fig. 4) with the association rate constant obtained from the slope of the plot ($k_f = 82.5 \text{ L mol}^{-1} \text{ s}^{-1}$) and the dissociation rate constant ($k_b = 3.7 \times 10^{-5} \text{ s}^{-1}$) from the intercept on the y-axis, although the accuracy of this number is low.⁴³ $\text{Log } K(k_f/k_b) = 6.3$, similar to the result obtained from analysis of the isotherm. Mass transport effects were shown to be negligible by running the experiments employing ED3A-silica QCMs with significantly lower loadings of receptor sites. In these cases the k_{obs} were within experimental error of those obtained above, at the same flow rate. The acid dependence of the dissociation phase of the experiment (D–E in Fig. 1) was not investigated.

For reactions of Ag(I) with the ED3A-silica QCM the exponential regions of the curve, the association phase and the dissociation phase, were also investigated. Attempts to fit the association phase to eqn. (2) were not successful, with deviations from pseudo-first-order kinetics apparent. The lack of success in fitting the association phase of the data suggests that factors including ligand-site heterogeneity, mass transport effects and rebinding may be important.¹⁹ Previously in situations where deviations from first-order behaviour have been observed in BIAcore experiments, attempts were made to fit the data with inclusion of a second exponential term¹⁹ which acts to deconvolute partly the multi-exponential form of the data. We chose not to extend the analysis to this extent.

Because the dissociation phase for Ag(I) did not require the presence of acid, these data were more easily analysed than in the case of the Pb(II). The dissociation phase data were fitted to the integrated expression^{18–20}

$$f_t = f_{\text{eqm}}(e^{-k_b t}) \quad (3)$$

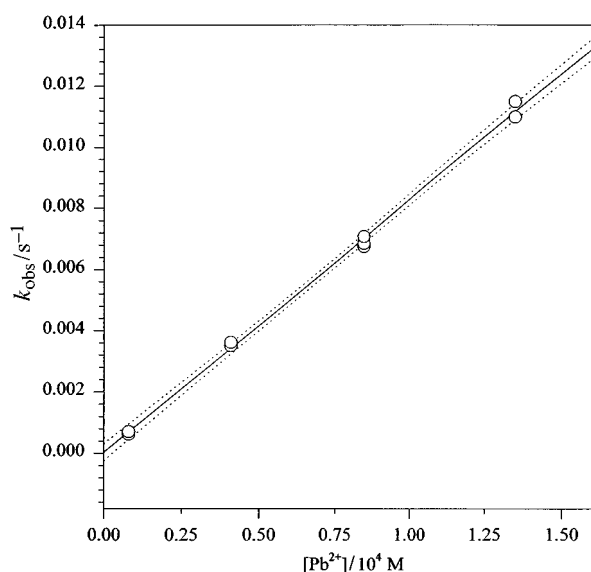


Fig. 4 Plot of k_{obs} versus $[\text{Pb}^{2+}]$. The solid line represents the best least-squares fit to the experimental data using the parameters given in the text and the dotted lines represent the 95% confidence limits.

where k_b is the dissociation rate constant. For a series of aqueous AgNO₃ solutions, with concentrations from 8.29×10^{-6} to $9.56 \times 10^{-4} \text{ M}$, k_b was found to be independent of initial Ag(I) concentration [$k_b = 2.7 (\pm 1.1) \times 10^{-3} \text{ s}^{-1}$]. Dissociation phase data have been shown to exhibit biphasic, double exponential behaviour and it has recently been shown that transport limitations rather than multiple binding sites may contribute to this behaviour.⁴⁴ Models for dissociation and rebinding, including corrections for the influence of mass transport, have been published.⁴⁵ Employing these models⁴⁶ resulted in $k_b = 2.8 (\pm 1.1) \times 10^{-3} \text{ s}^{-1}$.

Comparison of the k_b obtained for Pb(II) ($3.7 \times 10^{-5} \text{ s}^{-1}$) and Ag(I) ($2.8 \times 10^{-3} \text{ s}^{-1}$) indicate that the 'off' rates for these two metal ions differ by at least two orders of magnitude. The comparison also suggests that (i) rebinding may be a significant contributor to the inability to describe mathematically the association phase of the Ag(I) interaction with the ED3A-silica QCM and (ii), not unexpectedly, the different interactions of these two metal ions with the QCM might largely be dictated by the 'off' rates.

The frequency versus time profiles, the isotherms and the kinetic analyses for the interaction of an ED3A-silica QCM with lead(II) and silver(I) suggest that the ED3A-silica QCM device should be able to discriminate between the two metal ions. Therefore, an aqueous solution containing both Pb(NO₃)₂ ($8.12 \times 10^{-5} \text{ M}$) and AgNO₃ ($5.66 \times 10^{-5} \text{ M}$) was passed over the ED3A-silica QCM at a flow rate of 7 mL min^{-1} . The concentrations were chosen such that they should result in >95% saturation but less than 100% of available complexation sites, based on the previous isotherms. The resulting frequency-time profile exhibits the characteristic pattern seen for Pb(II) with an obvious plateau, and at the completion of the acid-water wash sequences the frequency of the QCM returns to its original value. Based on the previous results the frequency difference at the plateau region should reflect the uptake of Pb(II) and not Ag(I).

In order to assess the extent of selective uptake, EDS measurements were undertaken. Three separate ED3A-silica QCM crystals were prepared. The crystals were separately exposed to different degrees of the flow experiment. A crystal (a) was mounted in the flow cell and exposed to a flow of Milli-Q water, then removed. A second crystal (b) was exposed to a flow of Milli-Q water and then exposed to a mixed Pb(II)–Ag(I) solution in the flow cell and removed at the plateau region. A third crystal (c) was exposed to the conditions as described for the previous two crystals as well as the final acid-water wash sequences, then removed for analysis. Analysis of the surfaces of the three crystals by EDS indicated that no metal ions could be detected from crystal (a) after the initial water wash, Pb(II) (L α 10.55 keV, M α 2.345 keV) but not Ag(I) (L α 2.984 keV)⁴⁷ was detected on the surface of crystal (b), and no metal ions were detected on the surface of crystal (c) (Fig. 5). The results suggest that, at the limits of detection of EDS, the QCM device selectively takes up Pb(II) ions in the presence of Ag(I). The frequency difference observed for crystal (b) (984 Hz) suggests that approximately 6 nmol of Pb(II) are present on the surface of the ED3A-silica QCM,⁶ although this analysis does not take into account solvent effects.^{11,12,14} The results indicate that, for this particular QCM system, one metal ion may be sensed and separated from another, in a chemically reversible process.

These results extend studies on QCM devices past their application as simple mass detectors. A combination of adsorption isotherms and analysis of adsorption and dissociation phases during metal ion uptake with the ED3A-silica QCM device permit the prediction of conditions under which metal ions may be separated and/or concentrated on a derivatised silica substrate in aqueous solution. The approach employed presents an alternative methodology to the methods traditionally employed for assessing the suitability for derivatised silica substrates for metal ion separation.^{30,48–50} The preparation of

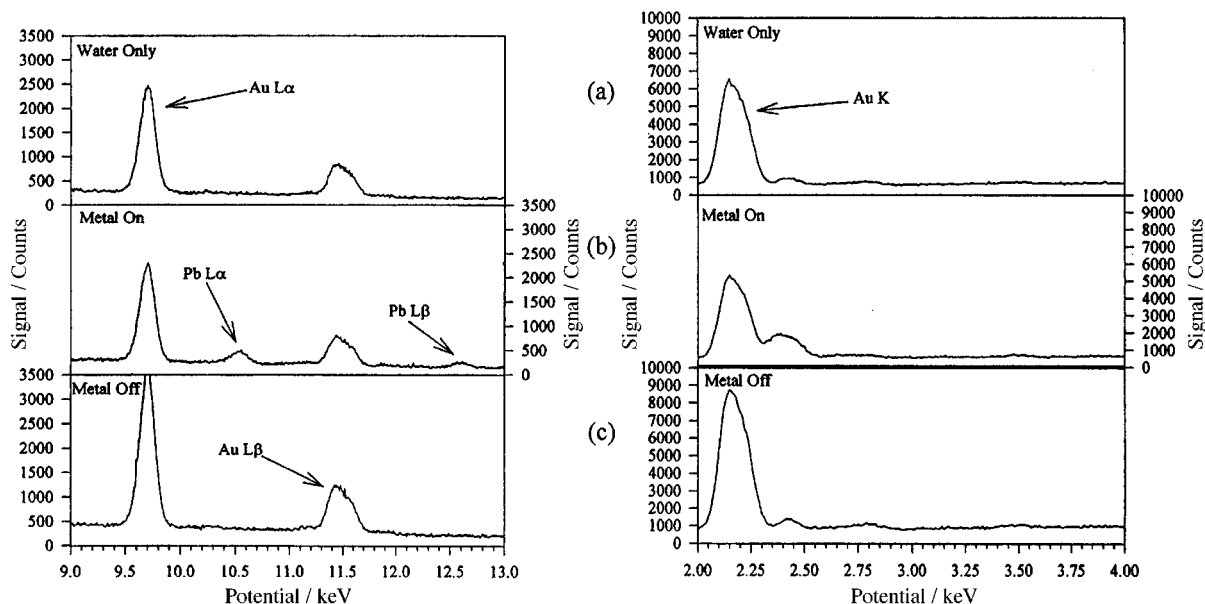


Fig. 5 EDS showing the presence and absence of Pb and Ag: crystal (a) after the initial water wash, crystal (b) Pb(II) ($L\alpha$ 10.55 keV, $M\alpha$ 2.345 keV) present, crystal (c) Ag(I) ($L\alpha$ 2.984 keV) absent.

more specific metal binding substrates should lead to more selective and elaborate separation and analysis methodologies.

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