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Determination of lead complexation in lake water by cathodic stripping voltammetry and ligand competition

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Abstract

A procedure is presented to determine lead complexing ligands in lake water by cathodic stripping voltammetry (CSV) with ligand competition using Calcein-blue (CB) (8-[*N*,*N*-bis(carboxyl-methyl)aminomethyl]-4-methylumbelliferone). The optimised conditions to determine dissolved lead in lake water by CSV using CB entails a CB concentration of 500 nM, a solution pH of 7.0 adjusted with TES buffer, an adsorption potential of −0.15 V, and an adsorption time of 90 s. Using these optimised conditions the 3σ limit of detection was 100 pM Pb. The complex stability of lead complexation by CB was calibrated by ligand competition against EDTA giving a value of $10^{4.8}$ for α_{PbCB_2} (=$[PbCB_2]/[Pb^{2+}]$), and of $10^{16.5}$ for the conditional stability constant ($\log \beta'_{PbCB_2}$) in lake water. The reactive lead concentration in lake waters was found to be lowered by complexation with unknown ligands. The concentration of these ligands in natural waters was determined by titrations with lead whilst monitoring the reactive lead concentration. The method was used to determine the concentration of lead complexing ligands in samples from a mountain lake (the Gossenkoellensee, Austria) revealing the presence of an excess of complexing ligands. The ligand concentration in the water column of this lake was found to vary between 1.6 and 2.7 nM, compared to lead concentrations between 0.6 and 1.1 nM, and with a value of 13.8 ± 0.3 for $\log K'_{PbL}$. The ionic lead concentration in equilibrium with the ligands was 14–33 fM. It is likely that this very strong complexation controls the geochemistry of lead in lakes.

Keywords: Cathodic stripping voltammetry; Lead; Complexation; Chemical speciation

1. Introduction

The geochemistry and availability to microorganisms of trace metals in natural waters are affected by the form in which they occur — their chemical speciation. The speciation of several metals has been determined in marine and freshwaters, and it has been found that copper [1–5], zinc [6–10] and iron [11–13] tend to occur fully complexed by organic matter. Little is known about lead — early studies using anodic stripping voltammetry have indicated about 90% complexation in estuarine waters, and to a greater extent in ocean waters [14–17].

A drawback of ASV is that an overpotential is applied during the plating step which causes labile species to dissociate so that only inert species are recorded as complexed. Cathodic stripping voltammetry (CSV), preceded by adsorptive deposition of metal

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species complexed with a specific adsorptive chelating agent, uses an adsorption potential more positive than the reduction potential of the metal and, therefore, does not induce electrochemical complex dissociation. Competition against the added ligand can be used to infer the stability of the natural complex, and the concentration of the natural complexing ligands can be determined by titration with the metal. Such methods exist for copper, zinc, iron and cobalt [8,11,18,19], but not yet for lead. Procedures to determine lead by CSV have been developed with reasonable success using several ligands [20–23]. These ligands (8-quinolinol, *o*-cresolphtalexone, Xylenol-orange, and Calcein-blue (CB), were tested, and CB was found to give best sensitivity. The CSV method using CB (8-[*N*,*N*-bis(carboxymethyl)-aminomethyl]-4-methylumbelliferone) [22] was optimised, and adapted to determine the chemical speciation of lead in freshwater. The method optimisation, its calibration against a known ligand (EDTA), and its first application to determine the chemical speciation of lead in a lake, are presented here.

2. Experimental

2.1. Instrumentation

The voltammetric investigations were performed in a 10 ml voltammetric cell (663 VA-Stand, Metrohm, Switzerland) connected via an IME-663 module to a computer controlled potentiostat (PGSTAT 10, Eco Chemie, The Netherlands). All measurements were done in the three electrode mode using a hanging mercury drop electrode (HMDE, drop surface area 0.38 mm^2) as working electrode, a double-junction Ag/AgCl, 3 M KCl, reference electrode, and a glassy carbon auxiliary electrode. The voltammetric cell was glass (borosilicate) (Metrohm).

Low-density polyethylene bottles (LDPE, Nalgene) were used to store samples. These bottles were cleaned by soaking sequentially with a hot detergent solution, 50% HCl, and 10% HNO_3 (1 week for each acid soak), and were subsequently stored partially filled with pH 2 Milli-Q water. Complexing capacity titrations were carried out in polystyrene "sterilin" tubes of 28 ml, which were cleaned by soaking in 1 M HCl.

2.2. Reagents

Water was purified by reverse osmosis (Milli-RO, Millipore) followed by ion-exchange (Milli-Q). Ammonia and HCl were purified by sub-boiling quartz-distillation. Reagents were from Merck/BDH unless indicated differently. Solutions of lead were prepared by appropriate dilution of BDH atomic-absorption (Spectrosol) standard solutions, and acidified to pH 2 with HCl. Stock aqueous solutions of 50 μM CB, 1 M TES (*N*-tris(hydroxymethyl)methyl-2-aminoethansulfonic acid, 5 M ammonia added to adjust to pH 7), 2 M ammonium-acetate pH buffer, and 5 M sodium chloride, were purified by controlled potential (−1.3 V) electrolysis over a mercury pool electrode to remove traces of lead and simultaneously of copper, cadmium and zinc. The pH of an aqueous stock solution of 0.1 M EDTA was adjusted to neutral using ammonia.

2.3. Sample collection

Lake water samples were collected using a battery powered, peristaltic, pump, and immediately filtered through an in-line, 0.45 μm Millipore, filter into 500 ml, LDPE, sample bottles. Separate quantities were stored frozen at –20°C for speciation analysis, or stored at room temperature after acidification to pH 2.2 with HCl.

2.4. Procedure to determine dissolved lead

A total of 30 ml aliquots of acidified lake water were UV-irradiated for 3 h using a 100 W mercury vapour lamp. An aliquot of 10 ml of the sample was pipetted into the voltammetric cell, ammonia was added to approximately neutralise the pH, 100 μl of 50 μM CB (final concentration of 500 nM) was added and the pH was adjusted to pH 7 with 100 μl of 1 M TES (final concentration 10 mM). The solution was purged with water saturated nitrogen for 5 min. Voltammetric parameters were an adsorption potential of −0.15 V, a 90 s adsorption time from stirred solution, and a quiescence period of 10 s; the scan was made using the differential-pulse modulation: pulse rate of 10 s^{-1}, pulse height of 25 mV and a scan rate of 20 mV s^{-1}.

The analytical parameters were optimised in Milli-Q water containing 50 mM sodium chloride as background electrolyte.

Comparative determinations of dissolved lead were carried out by ASV of the acidified, UV-digested, samples using the mercury drop electrode. A square-wave frequency of 10 Hz was used, wave amplitude 50 mV, potential step 5 mV, and the scan from −1.1 to −0.4 V.

2.5. Procedure to determine lead complexing ligand concentrations

Prior to use, lake water samples were defrosted at room temperature and carefully swirled to ensure re-solution of any precipitates that might have formed. An aliquot of approximately 100 ml was transferred to a Teflon bottle; 1 ml of 50 μM CB (final concentration of 500 nM), and 1 ml of 1 M TES (final concentration 10 mM) were added to give pH 7. Lead was added to 10 Sterilin tubes giving a concentration range between 0 and 10 nM (in 10 ml lake water) in 10 steps, and 10 ml of the lake water mixture was pipetted into the tubes which were then capped and swirled for mixing. After overnight equilibration, the 10 ml aliquots were poured into the voltammetric cell and the labile lead concentration was determined by CSV using 90 s deposition at a deposition potential of −0.15 V. The sensitivity was evaluated from the sensitivity at lead concentrations where the natural ligands had been saturated with lead. The sensitivity was further corroborated by comparison with the slope obtained by further additions of lead standard to two cells at the high end of the lead titration where all organic complexing would likely to be saturated with lead.

The voltammetric cell was cleaned by soaking with 10% HNO_3 prior to first use, and was rinsed with Milli-Q water between titrations. The same order of Sterilins was maintained to condition these with lead and eliminate problems related to adsorption onto the walls. The Sterilin tubes were conditioned twice with lead titrations prior to first use.

2.6. Theory: evaluation of complexing ligand concentrations and calibration of the stability of lead complexes with CB

The theory of determining metal speciation in natural waters CSV with ligand competition has been described before [19]. Briefly, the complexation of lead by a natural ligand (L) can be defined as

$$K'_{\mathrm{PbL}} = \frac{[\mathrm{PbL}]}{[\mathrm{Pb}^{2+}][L']} \tag{1}$$

where K'_{PbL} is the conditional stability constant of the lead complex [L'], the concentration of L not complexed by lead [PbL] the concentration of lead complexed with the ligand L, and [Pb^{2+}] is the free lead ion concentration. The total ligand concentration (C_{L}) is defined as

$$C_{\mathrm{L}} = [\mathrm{PbL}] + [L'] \tag{2}$$

Substitution for [L'] in Eq. (1) using Eq. (2) and rearranging gives a relationship similar to the Langmuir equation [24,25]:

$$\frac{[\mathrm{Pb}^{2+}]}{[\mathrm{PbL}]} = \frac{[\mathrm{Pb}^{2+}]C_{\mathrm{L}} + 1}{K'_{\mathrm{PbL}}C_{\mathrm{L}}} \tag{3}$$

This equation is equivalent to a linear relationship between values of [Pb^{2+}]/[PbL] as a function of [Pb^{2+}]. A plot of these values for a natural water is linear in the presence of a single, dominant, ligand, with a slope equal to $1/C_{\mathrm{L}}$ and with the intercept yielding $1/(K'_{\mathrm{PbL}}C_{\mathrm{L}})$. The relationship is curved if more than one ligand is present which competes with the first ligand within the series of lead additions; in this case the stability of the other complexes could be calculated using an iterative calculation of linear portions of the data, or by fitting of the data to a non-linear equation [19] by extending the titration with more data pairs, however, the data gave no evidence for more than one ligand in this work.

The Pb^{2+} concentration is related to the current (i_{p}) measured at the hanging mercury drop by

$$[\mathrm{Pb}^{2+}] = \frac{i_{\mathrm{p}}}{S(\alpha_{\mathrm{Pb}} + \alpha_{\mathrm{PbCB}})} \tag{4}$$

where S is the sensitivity (peak current/lead concentration) of the system. S was estimated from the linear portion of the titration curve after effectively all of L has been titrated with lead. α_{Pb} is the inorganic side-reaction coefficient for lead, which was calculated to be 2.1 using an ion-pairing model and with constants corrected for the ionic strength [26]. α_{PbCB} is the side-reaction coefficient for lead complexed with the added competing ligand CB. In solution, α_{PbCB} is

fixed by the amount of CB added:

$$\alpha_{PbCB} = \beta'_{PbCB_2}[CB']^2 \quad (5)$$

where β'_{PbCB_2} is the conditional stability constant and [CB′] is the concentration of CB not complexed to lead. Normally the concentration of CB added to solution is much greater than that of lead, hence the total CB concentration (C_{CB}) added can be used instead of [CB′]. It was assumed here that lead formed a 1:2 stoichiometric complex with CB ($PbCB_2$). The stability of the PbL complex is still obtained corrected if this assumption is incorrect, for instance if a 1:1 (CB:Pb) complex were to be formed instead, as the value for α_{PbCB} was calibrated against EDTA at the same CB concentration as used in the titrations; for this reason, α_{PbCB} did not require recalculation for different CB concentrations and the estimated constant β'_{PbCB_2} was not used.

Finally, once C_L and β'_{PbL} had been determined, the concentration of Pb^{2+} in the lake water was calculated with the following quadratic equation

$$[Pb^{2+}]^2\alpha_{Pb}K'_{PbL} + [Pb^{2+}](K'_{PbL}C_L - K'_{PbL}C_{Pb} + \alpha_{Pb}) - C_{Pb} = 0 \quad (6)$$

where C_{Pb} is the total concentration of lead in solution.

2.7. Calibration of α_{PbCB}

The complex stability of lead with CB was calibrated against that with EDTA. Thereto, EDTA additions were made to lake water containing 500 nM CB, TES buffer and 5 nM Pb, the additions were allowed to equilibrate overnight before the peak height for labile lead was determined. The ratio X of the peak height with the EDTA addition over that without EDTA decreased from unity when the complex stability with EDTA increased to similar or greater than that with CB at higher EDTA concentrations [8]:

$$X = \frac{i_p}{i_{p^0}} = \frac{\alpha_{Pb} + \alpha_{PbCB}}{\alpha_{Pb} + \alpha_{PbCB} + \alpha_{PbEDTA}} \quad (7)$$

This equation has only one unknown (α_{PbCB}) for which a value was calculated for each data pair. The average was used to obtain values for α_{PbCB} and for the conditional stability constant, β'_{PbCB_2}, valid for the lake water to be investigated.

3. Results and discussion

3.1. Optimisation of analytical parameters

In the presence of CB and lead in water of neutral pH, a peak was obtained by CSV at −0.55 V. The parameters of the CSV method were varied to optimise the analytical conditions to determine lead in lake waters.

Variation of the CB concentration revealed that the height of the reduction peak for lead increased with the CB concentration and reached a maximum at around 1000 nM. The increased sensitivity is not explained by increased complexation of lead by CB as the lead–CB complex stability is very great, similar to that with EDTA (see below), and all lead is already complexed by CB at much lower concentrations of a few nM. A possible explanation is the formation of a specific, adsorptive, Pb–CB_2, species at the higher CB concentration, whereas a non-adsorptive Pb–CB species is formed at lower CB concentrations. At higher CB concentrations, the sensitivity was found to level off at 1 μM CB, and then decreased gradually whilst the background current deteriorated possibly due to competitive adsorption of free CB. An amount of 500 nM CB was selected as the optimum CB concentration for lead speciation analysis (Fig. 1a) as a compromise between good sensitivity and complex stability as at greater CB concentrations the complex stability could be greater than that of natural complexes of lead, the same concentration was used for the dissolved lead determination.

The effect of pH on the peak current showed (Fig. 1b) that the sensitivity increased with the pH at pH values between 2 and 7, whereas at higher pH values the sensitivity decreased. It is likely that this variation is due to changes in the relative distribution of adsorptive and non-adsorptive complexes with CB as a function of the pH. pH 7 was selected for the further optimisation as it is optimal for the speciation study in natural waters of neutral pH.

The effect of varying the adsorption potential on the peak height for lead is shown in Fig. 1c. The adsorption potential was varied between +0.2 and −0.5 V, the peak current was found to increase with decreasing deposition potential up to −0.15 V whereafter it decreased, therefore, a deposition potential of −0.15 V was chosen.

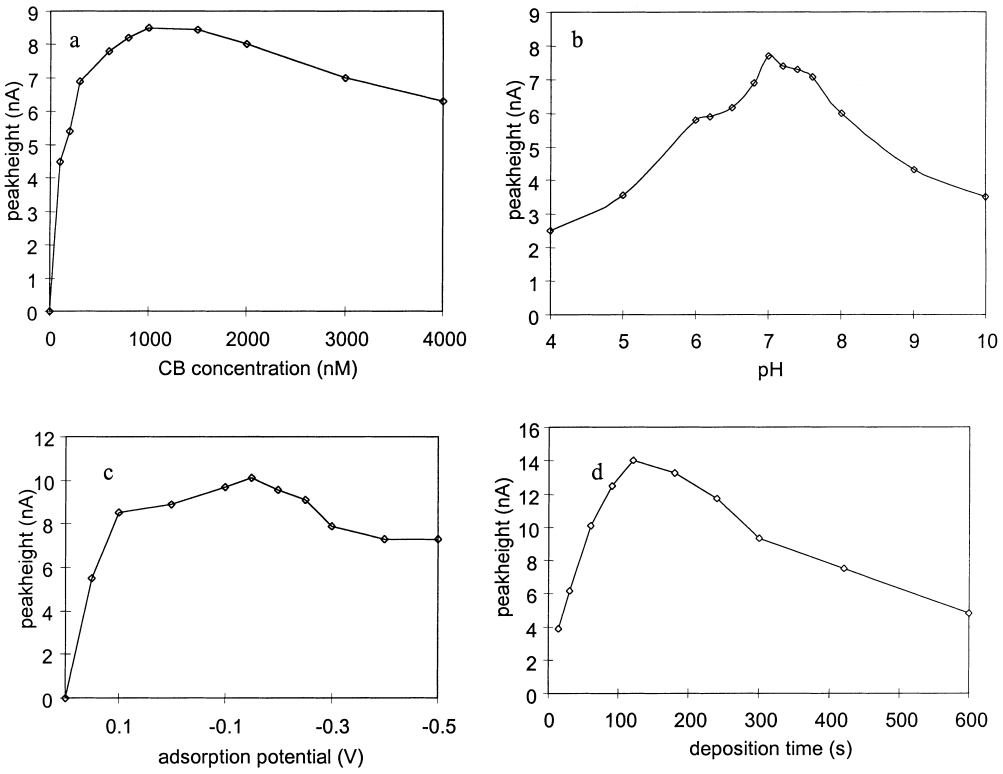

Fig. 1. Effect of varying voltammetric parameters on the peak height for lead in MQ-water containing 0.01 M TES buffer of pH 7: (a) variation of the CB concentration; (b) variation of the pH; (c) variation of the adsorption potential; (d) variation of the adsorption time.

The adsorption time was increased to find whether the sensitivity could be enhanced. Up to 2 min adsorption, the peak current was found to increase almost linearly with the adsorption time from a solution containing 10 nM Pb (Fig. 1d). However, at longer adsorption times, the peak current began to decrease suggesting that the electrode surface was saturated with free CB. An adsorption time of 90 s was selected as optimal.

3.2. Dynamic range of the calibration graph and limit of detection

Using the optimised conditions (500 nM CB, pH 7, and an adsorption potential of −0.15 V, 90 s adsorption time) the calibration graph was found to be linear up to 10 nM lead; at concentrations between 10 and 100 nM, the slope of the curve decreased, and above 100 nM, the calibration curve tended to level off because of adsorption saturation (Fig. 2).

The limit of detection was calculated from three times the standard deviation of six repeated measurements of 144 pM of lead giving a limit of detection of 100 pM Pb. This limit is slightly higher than that (40 pM) obtained previously with the same ligand [22]. The previous conditions used a slightly lower pH of 6.5 and a different pH buffer (PIPES) — that pH is less suitable for speciation studies of lakes with a typical pH around 7. However, in view of the pH effect shown in Fig. 1, the selected pH 7 should give slightly better sensitivity. It is, therefore, likely that this small difference in limit of detection is due to different instrumentation. The sensitivity of the CSV method is better than by ASV using a mercury drop electrode at the same deposition time, but the ASV sensitivity can be increased to be similar to that of the CSV method by using a much longer plating time of 5–10 min. Both methods are less sensitive than using a mercury film electrode by which

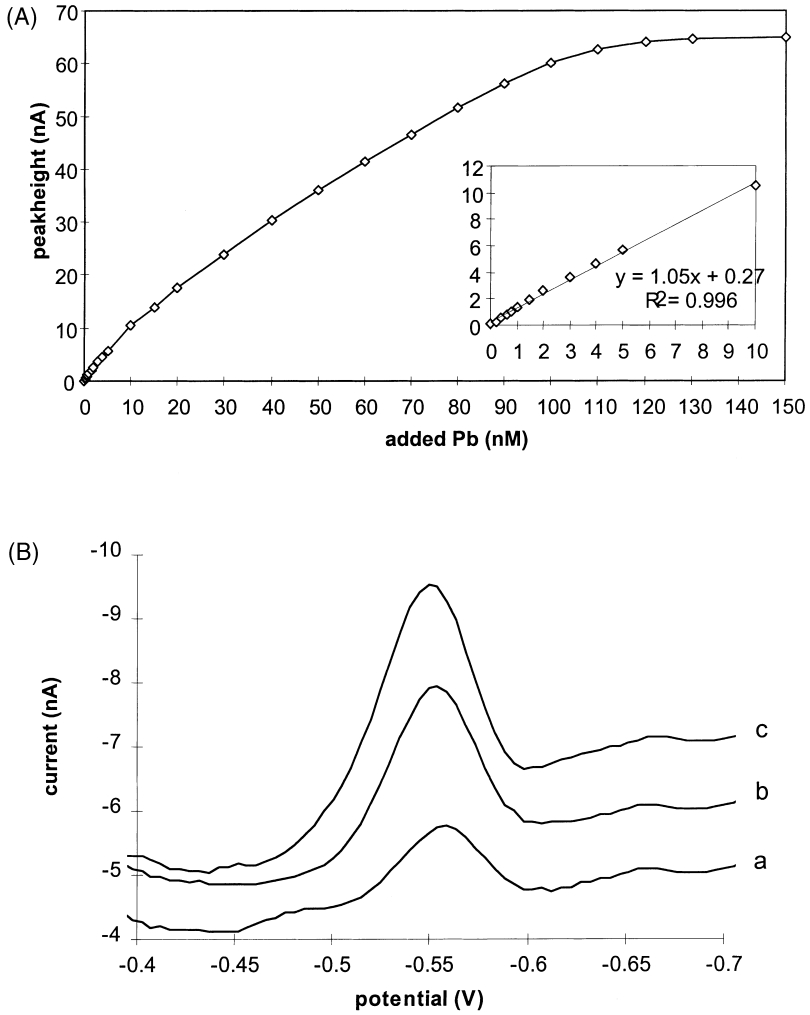

Fig. 2. CSV of lead in lake water using 0.5 μM CB, 0.01 M TES buffer at pH 7, and an adsorption time of 90 s. (A) Peak height as a function of the lead concentration in MQ-water. (B) Voltammograms for water from the Gossenkoellensee (1 m depth): (a) sample containing 0.75 nM Pb; (b) after addition of 1 nM Pb; (c) of 2 nM Pb.

a limit of detection of 8 pM Pb can be achieved [27].

The accuracy of the method to determine total dissolved lead in lake water was tested by comparative determinations of lead by the CSV method and by ASV using the mercury drop electrode, in samples from the water column of the Gossenkoellensee. Prior to the analysis, the water was UV-digested at pH 2 to destroy natural complexing ligands and to release all complexed lead. Then lead was determined by ASV at pH 2 using a 5 min plating time at –1.2 V, with a voltammetric scan using the differential-pulse modulation (10 Hz), with calibration by internal standard additions to each sample aliquot. The CSV determination used the here optimised conditions, and included the addition of ammonia to each sample to approximately neutralise the pH prior to the buffer addition. The lead concentration was found to be between 0.59 ± 0.07 and 1.2 ± 0.18 nM at various depths, and good agreement was found between the concentrations found by ASV and CSV (Table 1), demonstrating that the accuracy of this CSV method is identical to that of ASV which has

Table 1
Comparison of concentrations of dissolved lead at different depths in the Gossenkoellensee, determined by ASV and the new CSV technique after UV-digestion[a]

Depth (m)	Pb (nM) ASV	Pb (nM) CSV
1	0.71	0.75
2	0.61	0.65
3	1.11	1.20
4	0.95	1.02
5	0.99	1.00
6	0.73	0.75
7	0.92	0.87
8	1.13	1.15

[a] Parameters for the ASV technique were: pH 2; deposition potential −1.1 V; plating time of 420 s; a square-wave frequency of 10 Hz; amplitude 50 mV; potential step 5 mV; scan from −1.1 to −0.4 V. CSV parameters: pH 7.0; 0.5 μM CB; an adsorption potential of −0.15 V; adsorption time of 90 s.

been shown to give the same results as other analytical methods for lead in trace metal certifications [28]. The CSV scans obtained for lead in the Gossenkoellensee at a depth of 1 m and for two additions of lead standard to this water are shown in Fig. 2.

3.3. Calibration of the complex stability of CB with Pb (α_{PbCB} and β'_{PbCB_2})

The complex stability of $PbCB_2$ was calibrated against EDTA by measurement of the peak height of a lead concentration fixed at 10 nM in the presence of 500 nM CB, at increasing concentrations of EDTA, in the lake water being investigated. The peak height decreased with increasing EDTA as a result of the competition between the two ligands. Values of the ratio X in Eq. (7) were obtained from the peak height in the presence of EDTA over that in its absence. The decrease in X with increasing concentration of EDTA is shown in Fig. 3. The stability of the EDTA complex of lead was calculated using stability constants from a compilation [29], and concentrations of 10^{-6} M Mg^{2+}, and 10^{-5} M Ca^{2+} [30] giving a value of 11.37 for K'_{PbEDTA}.

The complex stability of $PbCB_2$ (α_{PbCB}) was calculated from the average of the X-ratios at EDTA concentrations between 100–400 nM, covering X-ratios between 0.9 and 0.1 where the complex stabilities of lead with EDTA and CB are relatively similar. A value for log α_{PbCB_2} was found of 4.83 ± 0.37; a corresponding value for the conditional stability constant of log $\beta'_{PbCB_2} = 16.48 \pm 0.37$ is valid assuming that the $PbCB_2$ species is predominant.

3.4. Determination of lead complexing ligands in lake water

Ligand competition in the presence of complexing matter in lake water samples caused the reactive lead concentration to be much less than the total lead concentration. Preliminary measurements showed that this effect was removed by UV-digestion indicating

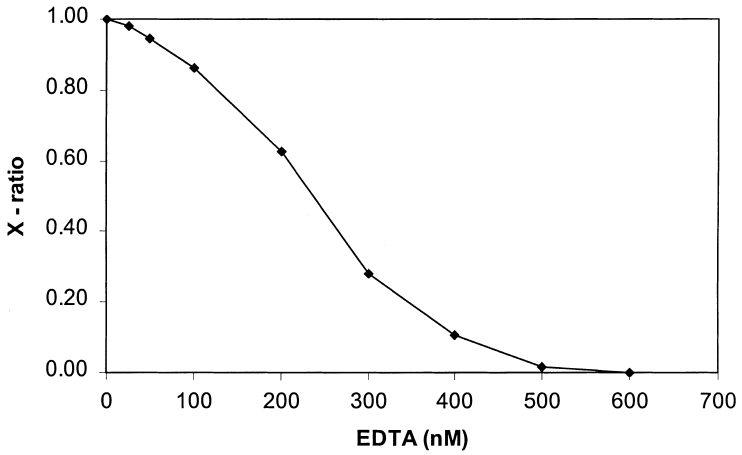

Fig. 3. Calibration of the complex stability of Pb–CB by competition against EDTA in water from the Gossenkoellensee containing 0.01 M TES buffer (pH 7.0), 10 nM Pb, and 0.5 μM CB, the adsorption time was 90 s, and the adsorption potential −0.15 V.

that it was caused by organic matter. Titrations with lead were used to determine the concentration of these lead binding ligands, whilst monitoring the reactive lead concentration by CSV. The lead additions were allowed to equilibrate overnight to ensure full equilibration, and the vials used for the titrations were conditioned by setting in the same titration twice, and maintaining the same order of the vials, before running the first lake titration. Polystyrene (Sterilin) tubes were used for the titrations as these are cheap and adsorption of lead or its complexes with CB was eliminated by conditioning. Work in our laboratory using lead and other metals has indicated that adsorption on these tubes is no worse than on Teflon and they have an advantage in being transparent, they are easy to clean by soaking in dilute acid prior to first use except for a silicone ring (which can be removed) in the cap which releases small amounts (low nM) of zinc which presents a problem for studies using that metal.

Samples collected from a mountain lake were used for this study, but the same method should be valid for other freshwaters. These mountain lake waters differ from low-land lakes in lower typical levels of organic matter and primary productivity. These lakes are oligotrophic and tend to have a high transparency to UV. It is likely that the concentration of natural complexing matter in oligotrophic mountain lakes is less than in more eutrophic, low-land, lakes.

Samples between 1 and 8 m depth of the Gossenkoellensee, Austria, were titrated with lead additions between 1 and 9 nM, and the concentration of $PbCB_2$ (i.e. the CSV peak height) was determined after overnight equilibration. A typical complexing ligand titration for one of the samples (4 m depth) is shown in Fig. 4a, and the linearisation of the results is shown in Fig. 4b. The titration (Fig. 4a) shows clear curvature demonstrating that at low lead concentrations the added lead is masked by complexation with the natural complexing ligand(s) until these are saturated at higher lead concentration when the CSV response becomes equivalent to that for all added lead. The curvature indicates that the complex is chemically reversible, releasing lead when CB is added, and forming new PbL species when lead is added. The plot of the data according to Eq. (3) (Fig. 4b) is straight indicating that the complexation is dominated by a single ligand or complexation site. The concentration of the ligand was calculated using Eq. (3), giving

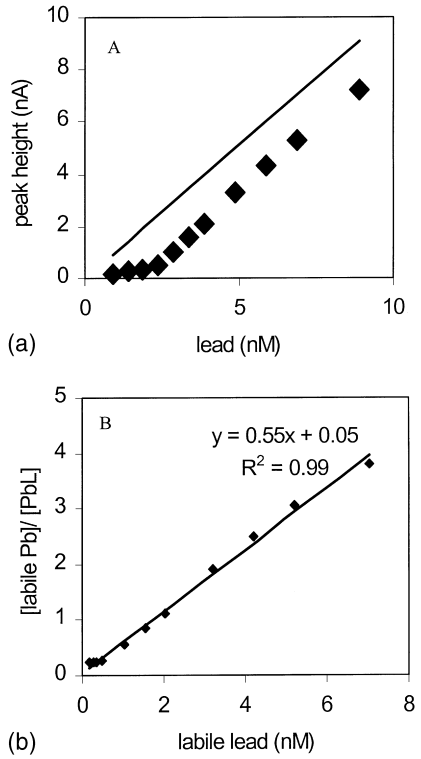

Fig. 4. Complexing ligand titration of a sample from Gossenkoellensee (8 m depth) containing 0.01 M TES buffer (pH 7.0) and 0.5 μM CB, using an adsorption time of 90 s: (a) labile lead as function of total dissolved lead; (b) linearisation of the data.

a value of 1.80 ± 0.04 nM for C_L, with a value of 13.9 ± 0.4 for the conditional stability constant (log K'_{PbL}). The standard deviation of the log K'_{PbL} value (± 0.4) was relatively large due to the ligand being partially saturated with lead initially in the lake water prior to the lead additions.

Ligand concentrations in excess to the lead concentrations were detected in all samples tested, demonstrating that the lead occurred fully complexed throughout this lake. The ligand concentrations in the lake have been plotted along with the lead concentrations in Fig. 5. The average ligand concentration was 2.0 nM, compared to an average lead concentration of 0.9 nM. The stability constant (log K'_{PbL}) was $13.8 \pm 0.3\ M^{-1}$, and the average binding strength of the complexes (log α_{PbL}) was 5.1 ± 0.26. It is not clear what the origin is of these ligands, or their composition — the lead is bound very strongly as the stability constant

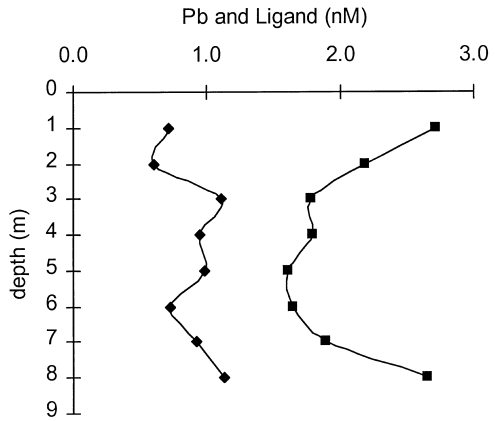

Fig. 5. Distribution of the concentrations of dissolved lead and lead-complexing ligands (C_L) in the water column of Gossenkoellensee, measured in the presence of 0.01 M TES buffer (pH 7.0) and 0.5 μM CB.

is more than two orders of magnitude greater than for EDTA for this lake water, causing a ratio of organically bound lead over inorganic lead of $10^{4.8}$ at a ligand concentration of a few nM. Seasonal variations in the distribution of these ligands, and a comparison with other lakes, are part of a further study using this new method.

Application of this method to determine lead speciation in saline waters with a high magnesium content is not without complications as this causes the sensitivity to be diminished [22] presumably due to competitive complexation of CB. For a suitable speciation method of lead in seawater, it may, therefore, be necessary to find an alternative ligand, unless its effect can be overcome otherwise.

4. Conclusions

The optimised conditions to determine lead in lake water by CSV are a CB concentration of 500 nM, pH 7.0, and an adsorption potential of −0.15 V with an adsorption time of 90 s. The limit of detection is 100 pM Pb. Comparative measurements showed that the accuracy of the method was the same as that of conventional ASV.

The complex stability of lead with CB was calibrated against EDTA in lake water giving a value of 4.83 ± 0.37 for α_{PbCB_2}, and a value of 16.48 ± 0.37 for the conditional stability constant ($\log \beta'_{PbCB_2}$).

A method was developed to determine complexation of lead by natural complexing ligands in lake water by taking advantage of ligand competition against CB. The concentration of natural ligands as well as the complex stability were determined by titrations of lake waters with lead. Preliminary measurements revealed the presence of strong lead binding ligands in the water column of a mountain lake, the Gossenkoellensee in Austria. These ligands cause the lead to occur fully bound by organic matter in the lake water. This complexation may affect the chemistry and bioavailability of lead in natural waters.

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