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# Anodic stripping voltammetry of lead and cadmium using a mercury film electrode and thiocyanate

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## Abstract

It is well known that lead and cadmium can be determined with good sensitivity using anodic stripping voltammetry (ASV) and a mercury film electrode. However, the mercury film formation is poorly reproducible and cannot fully be removed electrochemically. We have evaluated procedures to improve the reproducibility and sensitivity of the ASV method and found that in the presence of thiocyanate the film can be plated reproducibly and removed fully after each scan. Furthermore we optimised the analytical parameters pH, electrolyte composition, and deposition time and potential. Optimal analytical conditions were found to be a thiocyanate concentration of 5 mM, and a pH of 5.6. Optimisation of the deposition potential unexpectedly showed that the sensitivity was greatly improved by using a very negative potential of  $-1.5$  V, causing a 10-fold increase in the sensitivity of cadmium, and a 3-fold increase for lead. In these conditions the limit of detection ( $3\sigma$ ) was 5 pM cadmium and 8 pM lead (standard deviations of 1.7% and 2%) using a deposition time of 5 min. The method was successfully applied to the determination of cadmium and lead in lake waters and certified seawater after UV digestion. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Anodic stripping; Voltammetry; Mercury film electrode; Cadmium; Lead

## 1. Introduction

The determination of heavy metals such as cadmium and lead is important because they may be toxic through biomagnification, or to investigate their geochemistry. Although they can be detected by various analytical techniques, their concentrations in uncontaminated natural waters including seawater are so low that their determination is difficult. Without prior concentration they can only be determined using electroanalytical techniques including anodic strip-

ping voltammetry (ASV) and potentiometric stripping analysis (PSA). We have chosen to re-optimize the ASV method but the same procedure may be applicable to PSA.

The conventional procedure for the determination of these heavy metals involves using either a hanging mercury drop electrode (HMDE) or a mercury film-coated electrode [1–3]. The mercury film can be pre-plated and reused for some time. However, greatest sensitivity is obtained using in situ deposition of mercury: the mercury is then plated simultaneously with the metals, giving a thinner mercury film with a higher internal metal concentration, and which is less affected than the pre-plated film by interference by

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surfactants which are known to occur in natural waters. Glassy carbon is the usual conductive substrate for the electrode as it is inert and relatively easy to polish. The glassy carbon mercury film-coated electrode (GCMFE) is therefore the best choice to determine trace levels of cadmium and lead [4–6].

It is not usually mentioned in publications that use of the MFE can be tricky, due to the frequent manual pre-treatment (required to remove the film after each measurement and to prepare the electrode before the next measurement) and to irreproducibility of mercury film formation. The instability of the GCMFE is common [7], and the poor reproducibility of the mercury deposition and the laborious, frequent polishing of these electrodes are known [8]. Another disadvantage is the long deposition time: to achieve detection limits below 50–100 pM, plating times in excess of 30 min are typically required [3]. This is a problem because in water originating from uncontaminated oceanic conditions lead concentrations may be as low as 35 pM [9].

Recently a method was developed to determine trace levels of mercury (to sub-picomolar) in natural waters by ASV in the presence of thiocyanate [10]. Thiocyanate is also known to improve the reliability of mercury plating of iridium-based microelectrodes indicating that polishing can be avoided [8]. Thiocyanate was also used to aid the mercury film preparation prior to the voltammetric determination of nickel [11].

In this study we examined the application of thiocyanate to improve the reproducibility of the ASV determination of lead and cadmium using a conventional glassy carbon electrode, in situ plated with a mercury film. We also re-optimised the chemical (pH, thiocyanate concentration, supporting electrolyte, and pH buffer) and electroanalytical parameters, to improve the sensitivity. The success of the improved method is demonstrated by its application to the determination of lead and cadmium in uncontaminated lake waters and certified sea water.

## 2. Experimental

### 2.1. Instrumentation

All voltammetric investigations were performed in a 10 ml glass voltammetric cell using a commercially

available electrode stand (663 VA-stand, Metrohm, Switzerland). The electrode was connected via an IME-663 module to a computer controlled potentiostat (PGSTAT-10 from Eco Chemie, Netherlands). Potentials were controlled using a 3-electrode configuration comprising a rotating, glassy carbon disc, working electrode (3 mm diameter, Metrohm, part number 6.1204.110), a double-junction Ag/AgCl (3 M KCl, saturated AgCl, and 3 M KCl in the bridge) reference electrode, and a glassy carbon rod counter electrode.

### 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 distillation using a quartz condenser, and made up to final concentrations of ca. ~6 M. Solutions of cadmium and lead were prepared by appropriate dilution of BDH atomic-absorption (Spectrosol) standard solutions, and acidified to pH 2 with HCl.

Ammonium acetate (NH<sub>4</sub>Ac), ammonium thiocyanate and mercury(II) nitrate were of analytical grade and purchased from Fluka. A stock ammonium acetate pH buffer was prepared containing 1 M NH<sub>4</sub>Ac/0.5 M HCl. Contaminating trace metals in the buffer were removed by electroplating over a mercury pool electrode. An aqueous stock solution of thiocyanate containing 1 M thiocyanate was prepared by dissolution of the salt in water; this solution was used without further purification.

### 2.3. Procedure

The glassy carbon electrode was polished at the beginning of the experiments with 0.05 μm aluminium oxide (particle size=0.1 μm, Metrohm, Switzerland), and was rinsed thoroughly with water, to obtain a clean, renewed electrode surface. The electrode was connected to the potentiostat and placed in a buffer solution; the potential was cycled 50x between –0.8 and +0.8 V using cyclic voltammetry at a scanning rate of 0.1 V s<sup>-1</sup>. The electrochemical pre-treatment was repeated daily, the polishing only when damage of the electrode surface was suspected. This happened only once during this investigation when the connection to the reference electrode was

broken causing the destruction of the glassy carbon electrode.

Seawater and lake water samples were UV digested for 3 h at pH 2 to decompose organic substances [10]. Ten ml of a sample was pipetted into the polarographic cell, the pH was adjusted to pH 5.6 by addition of 10  $\mu$ l of concentrated ammonia followed by the addition of  $\text{NH}_4\text{Ac}/\text{HCl}$  buffer to 0.01 M and thiocyanate to 5 mM, and 30  $\mu$ M mercury(II) was added. Oxygen was removed by a 5 min nitrogen purge, and deposition was carried out for 5–10 min at  $-1.5$  V, whilst the electrode was rotated at 1500 rpm. Subsequently after a 10 s quiescent period the stripping step was performed with a square-wave scan (frequency=50 Hz, amplitude=50 mV, potential step=5 mV) from  $-1.3$  to  $+0.6$  V. Each scan was preceded by an electrochemical cleaning step to remove the previous film using a conditioning potential of  $E_{\text{con}}=0.6$  V for a period of  $t_{\text{con}}=60$  s.

### 3. Results and discussion

Preliminary experiments showed that lead and cadmium could be determined using a GCMFE using in situ mercury plating without thiocyanate. However, the mercury could not be fully removed electrochemically, even after prolonged oxidation at 0.6 V. Subsequent scans showed therefore a mercury peak which increased with time. Furthermore, the plated mercury film did not always fully cover the electrode surface. In the presence of thiocyanate the mercury film could be readily plated and electrochemically removed: the formation of a new, shiny, mercury film, and its removal, could be seen from visual inspection of the electrode whilst it was submerged in the solutions. In order to optimise the conditions of film formation, and to obtain the greatest sensitivity and reproducibility for the determination of cadmium and lead, the influence of a number of analytical parameters was examined. For the preliminary investigations, a 10 ml water (Milli-Q) sample was spiked with 5 nM cadmium and 5 nM lead. Besides the parameters described below, also the mercury(II) concentration, stirrer speed, square-wave frequency, conditioning time and conditioning potential were optimised.

#### 3.1. Effect of varying the concentrations of thiocyanate and mercury

Preliminary measurements of lead and cadmium by ASV using in situ mercury plating showed that the addition of thiocyanate slightly decreased the ASV sensitivity but it greatly reduced the variability of succeeding scans using the GCMFE: on the whole the standard deviation of the peak heights for cadmium and lead was therefore much improved. A concentration of 10 mM thiocyanate was used to minimise the concentration of mercury required to produce a mercury film and good sensitivity for lead: the peak height of lead was used as a measure for this optimisation. At mercury concentrations of 10, 15, 20, 30, 50 and 100  $\mu$ M the lead peak height increased as follows (using a 5 min plating time and 5 nM lead): 0, 62, 91, 100.9, 102.8, and 103.3 nA. There was very little improvement at mercury concentrations beyond 30  $\mu$ M so that concentration was selected for subsequent experiments. This concentration is slightly greater than that (10  $\mu$ M Hg) recommended by Mart et al. [12] but they used a longer plating time of 12 min, it is much less than that (1 mM Hg) used recently to initiate nucleation prior to the determination of copper [5].

The thiocyanate concentration was varied in order to establish its optimal concentration. The ASV peak heights and the calculated standard deviations (10 repeat scans) for cadmium and lead in water are shown as a function of the thiocyanate concentration in Table 1. An increase of the thiocyanate concentration from 0 to 20 mM caused the relative standard deviation (RSD) to be lowered from  $\sim 32\%$  to 1%, at a loss of sensitivity for cadmium and lead of around 50% (Table 1). The high RSD for the cadmium (31%) and lead (33%) peaks without thiocyanate was due to a systematic and continuous increase with each consecutive scan. In the presence of thiocyanate the peaks were essentially constant causing the RSD to be lowered to 1%. The systematic increase of the peak heights was caused by incomplete electrochemical removal of mercury from the electrode surface even using conditioning periods of 1–5 min before each new metal deposition.

The effect of thiocyanate is due to the formation of complexes with mercury(II) which prevents the formation of mercuric oxide on the electrode surface,

Table 1

Effect of thiocyanate on the peak height and standard deviation for cadmium and lead ( $n=10$ ) in water (Milli-Q) containing 0.1 M  $\text{NH}_4\text{Ac}$  (pH 4.6), 30  $\mu\text{M}$   $\text{Hg(II)}$ , 1 nM cadmium and 1 nM lead

Thiocyanate concentration (mM)	Cadmium		Lead	
	Peak height (nA)	RSD (%)	Peak height (nA)	RSD (%)
0.1	8.7	31.5	25.1	33.3
0.5	7.8	14.8	23.1	15.8
1	7.5	8.5	22.0	7.8
2.5	7.1	3.6	21.5	4.2
5	6.9	1.5	21.3	1.4
10	6.0	1.3	18.8	1.3
20	4.2	1.2	13.1	1

The deposition time was 300 s at  $-1.1$  V, the electrode was conditioned at 0.6 V for 60 s to remove the mercury film prior to each measurement.

furthermore it improves the reversibility of the reoxidation of mercury [8].

Further improvement of the RSD was small at thiocyanate concentrations above 5 mM whereas the sensitivity continued to decrease (Table 1). At 5 mM thiocyanate the sensitivity for cadmium was 79%, for lead 85%, of that at 0.1 mM thiocyanate. An optimal concentration of 5 mM thiocyanate was selected for the subsequent experiments as the sensitivity was then only slightly reduced.

### 3.2. Effect of varying the pH, and selection of pH buffer

The ASV peak current was measured as a function of the pH in Milli-Q water with 0.01 M  $\text{NH}_4\text{Ac}$ , 30  $\mu\text{M}$  mercury(II) and 5 mM thiocyanate. The pH value was varied between 2 and 8 by adjusting with HCl or ammonia, respectively, whilst measuring the pH in the voltammetric cell. The deposition potential was  $-1.1$  V and the deposition time 120 s. Whereas the peak height for lead showed a decrease with increasing pH, the corresponding peak for cadmium increased up to pH 7, at greater pH values the sensitivity for cadmium decreased again (Fig. 1). Greater sensitivity for cadmium was therefore obtained at pH 7, whereas for lead a pH between 2 and 4 could be selected. As a trade-off between the optimum conditions for these two metals pH 5.6 was selected for subsequent work. Advantage of this pH is that it is readily buffered using an acetate pH buffer.

Several pH buffers were compared to see whether different sensitivities were obtained. Comparison of  $\text{NH}_4\text{Ac}/\text{HCl}$ ,  $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  and PIPES buffer (all prepared to give pH 5.6) showed that greatest sensitivity for cadmium and lead was obtained with acetate buffer: 8% greater than with the phosphate buffer, 15% greater than with the PIPES buffer. Variation of the acetate buffer concentration showed that optimal results were obtained at concentrations of 0.01–0.02 M: the lead peak increased from 24 nA at 0.001 M acetate to 40 nA at 0.005 M acetate, remained constant at 0.01 and 0.02 M, and then decreased to 35 nA at 0.05 M and to 33 nA at 0.1 M acetate.

### 3.3. Effect of variation of the deposition potential and time, and square-wave frequency

The deposition potential was varied between  $-0.7$  and  $-2.0$  V using a constant deposition time of 120 s; each ASV scan was initiated after 10 s of equilibration (without stirring) at  $-1.1$  V (Fig. 2). Unexpectedly the peak heights for cadmium and lead increased with more negative deposition potentials up to  $-1.5$  V and  $-1.7$  V, respectively, showing a decrease at more negative potentials. Normally one would expect the increase with the peak height to stabilise at potentials of  $\sim 0.2$  V < the peak potential of each metal, as then the current would equal to the diffusion limited current. The increase to potentials around  $-1.5$  V is therefore unexpected. However, the plating of cadmium and lead is simultaneous with that of the

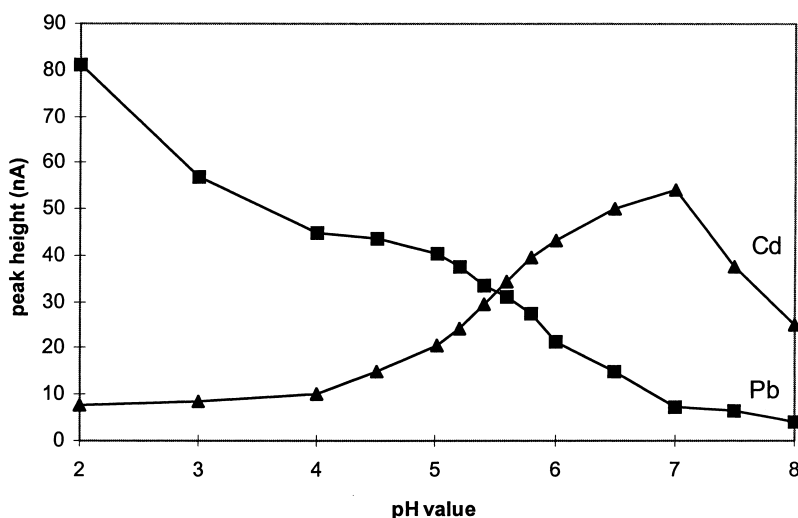


Fig. 1. Effect of varying the pH on the peak current for 5 nM cadmium and lead in Milli-Q water containing 0.01 M  $\text{NH}_4\text{Ac}$ , 30  $\mu\text{M}$  mercury(II) and 5 mM thiocyanate, using ASV with 120 s deposition at  $-1.1$  V vs.  $\text{Ag}/\text{AgCl}$ .

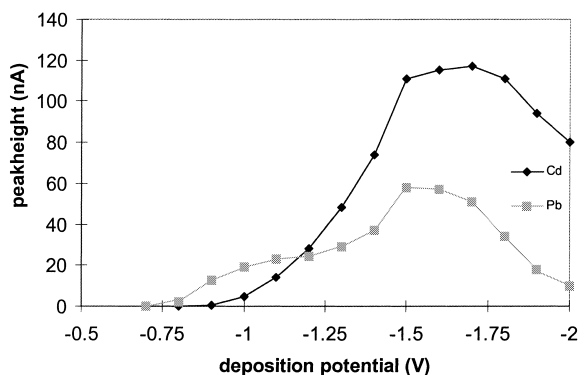


Fig. 2. Effect of varying the deposition potential on the cadmium and lead peak current for 5 nM cadmium and 5 nM lead in Milli-Q containing 0.01 M  $\text{NH}_4\text{Ac}/\text{HCl}$  buffer (pH 5.6), 30  $\mu\text{M}$   $\text{Hg}(\text{II})$  and 5 mM thiocyanate, using ASV and a 120 s deposition.

mercury film. These plating potentials are also much more negative (about 1.5 V) than the reduction potential of mercury. At these negative potentials hydrogen formation must occur. Possibly the molecular hydrogen formation assists with the nucleation of the mercury droplets which form the beginning of the mercury film, thus improving the film formation, and with it a concomitant increase in the lead and cadmium peaks.

At potentials between  $-1.5$  and  $-1.7$  V there was little change in the peak height, but at potentials more negative than  $-1.6$  V the background current gradu-

ally deteriorated. For this reason a deposition potential of  $-1.5$  V was selected as the optimum condition for the determination of cadmium and lead. The sensitivity for cadmium is about 10 times, and of lead three times, higher at this deposition potential than using the conventionally selected deposition potential of  $-1.0$  V or  $-1.1$  V [13–15].

The deposition time dependence of the peak heights for cadmium and lead was examined for deposition times in the range of 30–600 s, in the presence of 5 nM cadmium and lead. As the results in Fig. 3 show, the peak currents increased almost linearly with the deposition time. In separate experiments it was established that saturation of the electrode did not occur for much higher concentrations of cadmium and lead up to 50 nM and deposition times of 600 s. The sensitivity for low (or high) levels of these metals can therefore be readily increased by using a longer deposition time.

Variation of the square-wave frequency showed a non-linear increase of the peak heights with increasing frequency: for instance the lead peak increased from 54 to 110 nA when the frequency was raised from 10 to 25 Hz, and to 183 nA at 50 Hz, to 242 nA at 75 Hz, and to 300 nA at 100 Hz. However, the baseline thickened at frequencies above 50 Hz due to mains interference, so a frequency of 50 Hz was optimal. The non-linear increase with increasing frequency is typi-

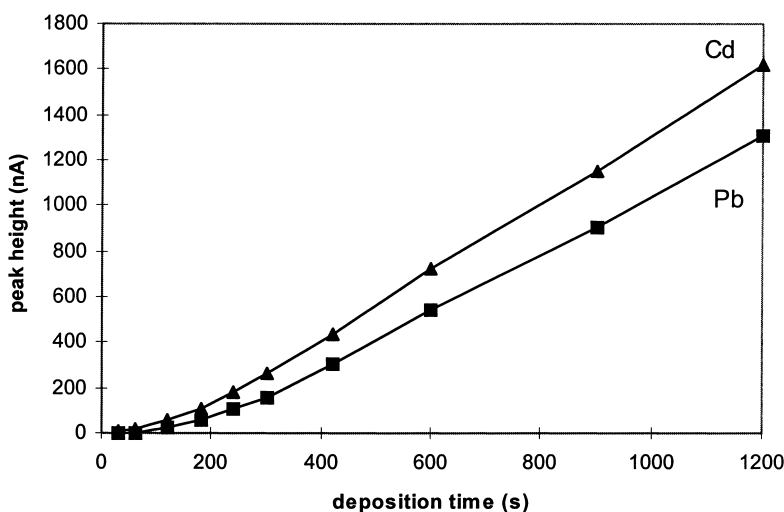


Fig. 3. Effect of increasing the deposition time on the peak height for 5 nM cadmium and lead in 0.01 M  $\text{NH}_4\text{Ac}/\text{HCl}$  buffer (pH 5.6), 30  $\mu\text{M}$   $\text{Hg}(\text{II})$  and 5 mM thiocyanate, using ASV and at a deposition potential of  $-1.5$  V vs.  $\text{Ag}/\text{AgCl}$ .

cal for diffusion currents and is due to the elements having to diffuse through the mercury.

### 3.4. Linear range and limits of detection

The linear ranges and limits of detection of the ASV responses for cadmium and lead were determined in Milli-Q water containing 5 mM thiocyanate, 30  $\mu\text{M}$  mercury(II) and 0.01 M acetate buffer (pH 5.6). Using the optimum conditions (a conditioning potential of 0.6 V, a conditioning time of 60 s, and a deposition potential of  $-1.5$  V) the calibration graph was linear up to 10  $\mu\text{M}$  of cadmium and lead with 5 min deposition. The linear range could be extended by using a shorter deposition time.

The limit of detection was calculated from three times the standard deviation of six repeated scans of cadmium and lead (87 pM cadmium and 168 pM lead) in water, using a 5 min deposition period. The limit of detection was 5 pM cadmium and 8 pM lead. These limits may be reduced by increasing the deposition period.

The contribution of the reagents to the background concentrations were investigated by doubling the concentrations of the  $\text{Hg}(\text{II})$ , thiocyanate and acetate buffer solution separately. The obtained reagent blanks were for each compound below the detection limits for cadmium and lead from six replicate analyses.

### 3.5. Determination of lead and cadmium in lake water samples and in certified seawater (NASS4)

The accuracy of the method was tested by analysis of certified seawater (there is no certified lakewater): NASS4 seawater (National Research Council, Canada). This commercially available sea water is acidified to pH 1.6 with nitric acid, and the concentrations of a number of metals are accurately certified. The seawater was UV digested (2 h), and the acid partially neutralised by addition of ammonia (40  $\mu\text{l}$ , 6 M ammonia to each 10 ml of water) followed by reagent addition. The ASV response, using the optimised conditions and with a 5 min deposition time, of the certified sea water analyses is shown in Fig. 4. Concentrations of  $146 \pm 2$  pM cadmium and  $65 \pm 3$  pM lead ( $n=6$ ) were found, which compare very well with the certified values of 142 and 63 pM, respectively, showing that the method does not have a bias.

The method was used without modification to determine lead and cadmium in samples from a mountain lake (the Gossenköllersee, Austria). The samples were filtered (0.4  $\mu\text{m}$  polycarbonate membrane filter), acidified to pH 2 with HCl, and UV digested for 2 h. Concentrations were found to lie between 27 and 300 pM cadmium, and 100 and 1500 pM lead. The lake data (Fig. 5) for cadmium

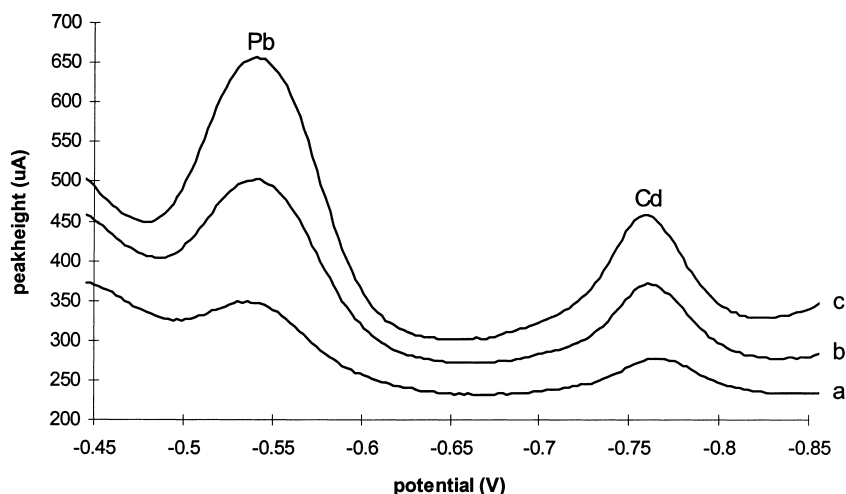


Fig. 4. Anodic stripping voltammograms for certified seawater (NASS4) using the new method without modification. The seawater pH was neutralised with ammonia, and reagent (0.01 M  $\text{NH}_4\text{Ac}/\text{HCl}$  buffer (pH 5.6),  $30 \mu\text{M}$   $\text{Hg}(\text{II})$  and 5 mM thiocyanate) was added; the deposition time was 300 s at  $-1.5$  V: (a) original, (b) after addition of 150 pM cadmium and 150 pM lead, and (c) after addition of 300 pM cadmium and 300 pM lead.

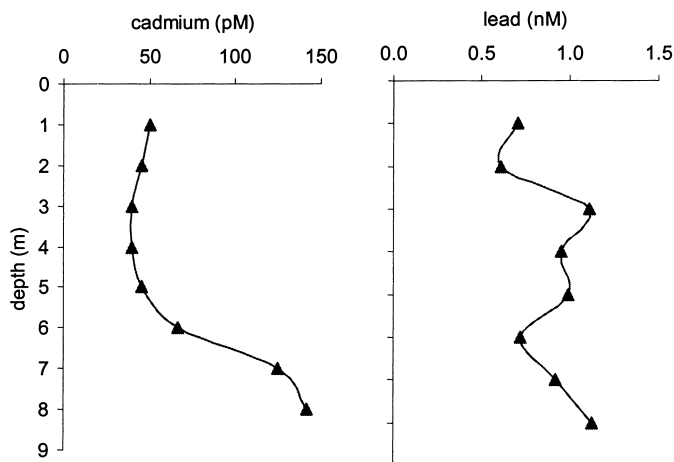


Fig. 5. The distributions of lead and cadmium in a lake (the Gössenkollersee) as determined by the new ASV method. The metal concentrations were either close to, or below, the limit of detection by ASV using a HMDE, whereas they were well above the limit of detection of the new method.

appear to be of very good quality, showing a smooth and systematic trend for very low cadmium concentrations. The lead data appear to show some variation which is possibly related to adsorption and desorption processes in the presence of suspended particulate material. The geochemistry of lead and cadmium is subject to further investigation using the new method. The cadmium concentrations were largely undetectable (below 0.1 nM) by ASV using a HMDE, illustrating the advantage of the new method.

#### 4. Conclusions

The use of thiocyanate greatly facilitates the formation, and its subsequent electrochemical removal, of an in situ plated mercury film prior to ASV of lead and cadmium. Electrode preparation is much simplified to an electrochemical pre-treatment once a day, and a polish with aluminium oxide only if damage to the electrode surface is suspected. The presence of thiocyanate causes a small decrease in the sensitivity

when the conventional deposition potential ( $-1.1$  V) is used. However, the thiocyanate causes a large improvement in the reproducibility of the measurements (the relative standard deviation is lowered from 32% to 1%). The addition of thiocyanate prevents the formation and deposition of mercuric oxide on the electrode surface during the electrochemical removal of mercury, which eliminates the time intensive polishing steps between each mercury film deposition and greatly improves the reproducibility.

The sensitivity is greatly increased (10-fold for cadmium and 3-fold for lead) by plating at a very negative potential ( $-1.5$  V), in the region of hydrogen formation. It is likely that the combination of thiocyanate with atomic hydrogen formation facilitates the nucleation of mercury.

Using the optimised conditions (a deposition potential of  $-1.5$  V and a deposition time of 5 min in 10 ml sample containing 0.01 M  $\text{NH}_4\text{Ac}/\text{HCl}$  buffer (pH 5.6), 5 mM thiocyanate and 30  $\mu\text{M}$  mercury(II)) the detection limit was 5 pM cadmium and 8 pM lead. The method was successfully employed for the determination of lead and cadmium in various lake water samples and, without modification, in certified seawater.

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