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Gold and Silver Micro-Wire Electrodes for Trace Analysis of Metals

Gabriel Billon, Constant M. G. van den Berg*

Department of Earth and Ocean Sciences, University of Liverpool, Liverpool L693GP (UK)

*e-mail; vandenberg@liv.ac.uk

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Abstract

Micro-wire electrodes were made from gold and silver wires (diameter: 25 μm ; length: 3–21 mm) and sealed in a polyethylene holder; micro-disk electrodes were made from the same wires and polished. The gold electrodes were electrochemically coated with mercury before use; the silver wires were used without coating. Comparative measurements demonstrated that the micro-wire electrodes had much higher sensitivity, and a much ($10\text{--}100\times$) lower limit of detection, than micro-disk electrodes, and the sensitivity increased linearly with the area and length of the electrodes. Using a gold micro-wire electrode of 21 mm and a deposition time of 300 s the limit of detection was 0.07 nM Pb in seawater of natural pH, compared to a limit of detection of 10 nM Pb (more than $100\times$ greater) using a gold micro-disk electrode of the same diameter. Using the silver micro-wire electrode the limit of detection of lead was improved by a factor of 10 to 0.2 nM in acidified seawater. It is expected that the improved sensitivity of micro-wire electrodes will lead to successful in situ detection of metals in natural waters.

Keywords: ASV, Micro-wire electrodes, Gold, Silver, Lead, Seawater

1. Introduction

In-situ measurement of trace elements in natural environments represents a challenge for analytical and environmental sciences. The use of voltammetry is attractive because of the high sensitivity of this technique for several metal pollutants like Cd, Pb and Zn, but the necessity to stir the solution and to renew the mercury drop for each measurement has inhibited its in situ application. A mercury film electrode could in principle be used for this purpose but this requires renewal of the diffusion layer by stirring. Microelectrodes are a good alternative for several reasons including: i) constant sensitivity without stirring because of a spherically expanding diffusion layer; ii) the surface can be activated electrochemically for many measurements; iii) the possibility to measure in low conductivity media such as freshwater due to the reduced resistivity per unit area and iv) they can be used in small volumes without greatly changing the ambient concentrations [1, 2]. The latter property is useful for measuring in sedimentary porewaters [3] or in samples as small as 2 μL [4].

Microelectrodes can be made conveniently from a short length of metal wire (mostly Au [5], Ag [6], Ir [7] and Pt [8]) or carbon [9], sealed in a glass capillary, and carefully polished to obtain a disk microelectrode (diameter 5–100 μm). Usually mercury is deposited, or bismuth [10], to move the hydrogen wave to a more negative potential. The surface preparation requires much care and time, and the measurement of low (pA) currents may be subject to interferences. For this reason alternatives are being developed such as arrays of micro-disk electrodes, prepared by printing techniques [11, 12], to produce greater currents.

In this paper, we report on a major improvement ($10\text{--}100\times$) in sensitivity, which is obtained by preparing micro-electrodes as micro-wires rather than as micro-disk for measurements in natural waters. Electrode preparation and testing are described, and their performance compared against disk electrodes. Our work demonstrates that mercury-plated gold, and bare silver, micro-wire electrodes (25 μm diameter and 0.3–21 mm long) can be used to determine lead with a much lower limit of detection and higher sensitivity than the usual micro-disk electrodes.

2. Experimental

2.1. Apparatus

Electrode coating with mercury was carried out using a $\mu\text{Autolab}$ voltammeter (Ecochemie, Netherlands) and the software GPES 3.0 was used for data treatment. The reference electrode and the auxiliary electrode were a calomel electrode (3 M KCl) and a platinum rod, respectively. A second voltammetric system was used for trace metal experiments to facilitate the preparation of one electrode whilst measurements were done with another electrode, and to minimize transfer of contaminants between plating and analytical solutions: the second voltammeter was a 757 VA Computrace (Metrohm, Switzerland) with a platinum rod as auxiliary electrode and a double-junction Ag/AgCl, 3 M KCl, reference electrode.

2.2. Chemicals

Solutions were prepared using MQ-water, which was purified by a Milli-Q Plus apparatus (Millipore, resistivity 18.2 M Ω). Lead standard solutions were prepared from a 1 g dm⁻³ standard (BDH; purity: 99.9%) diluted to 50 and 1 μ M, and acidified to pH 2 using HCl. Seawater used for the experiments (salinity 35) was previously UV-digested using a 125 W high-pressure mercury vapor lamp during 45 [13]. For measurements with the silver electrodes, the seawater was acidified using redistilled nitric acid (10 μ L per 20 mL).

Monohydrated mercury nitrate (BDH, p.a.) and perchloric acid (BDH, p.a.) were used to prepare the amalgamation solution (5 mM Hg(NO₃)₂ in 1 mM HClO₄).

Gold and silver wires for making the microelectrodes (diameter 25 μ m; purity: 99.99%) were obtained from Goodfellow Company (UK).

2.3. Microelectrode Preparation

Disk and wire microelectrodes were homemade by sealing the wire in a polyethylene pipette tip similar to that done before [14]: approximately 4 cm silver or gold wire was attached to a shielded electrical wire using silver epoxy (Figure 1, step 1). The end of the shielding mesh was coated in non-conductive epoxy to avoid contact with the electrode wire. The electrode wire was introduced in a 200 μ L pipette tip (polyethylene) and heat-sealed by holding it above a homemade tubular oven (diameter ca. 1 cm). A second pipette tip was placed on the other, open, side and attached with epoxy glue to the first tip and to the electrical wire to prevent strain on the connection to the micro-wire (Figure 1, step 2).

To make a disk microelectrode, the electrode wire was cut close to the polyethylene seal and the tip was carefully polished first with sand paper and subsequently with diamond paste (diameter 1 μ m) to a mirror finish; the finish was checked with an inverted microscope (Zeiss) at a magnification of 500.

2.4. Mercury Plating

Before plating with mercury, the gold electrode was cleaned by dipping (2 min) in 2 M nitric acid, and in redistilled methanol; the electrode was rinsed with MQ-water and introduced in a 50 mL voltammetric cell containing 10 mL MQ-water acidified to pH ca. 2 using 10 μ L ca. 9 M nitric acid. Several scans were performed between -1 and 0 V to check for normal electrode behavior as apparent from a welldefined shape of the background and the position of the hydrogen wave (Figure 2).

The gold wire and disk microelectrodes were electrochemically plated with mercury: the acidified mercury solution (5 mM) was first purged with nitrogen during 600 s to eliminate the background current from oxygen as the mercury reduction current was monitored continuously

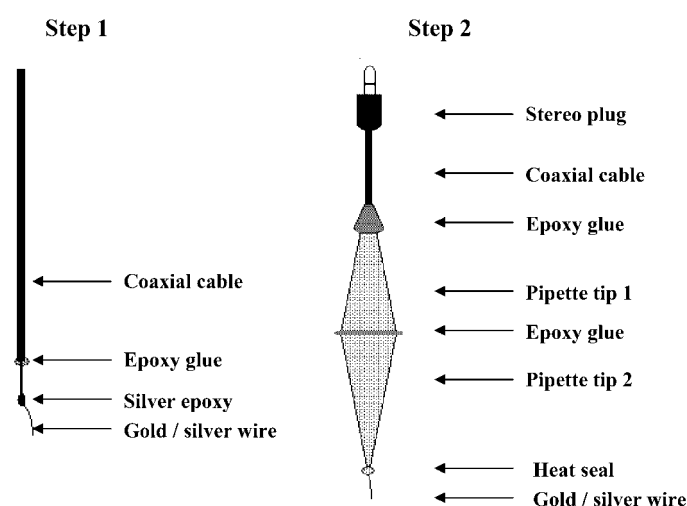


Fig. 1. Description of the wire microelectrodes.

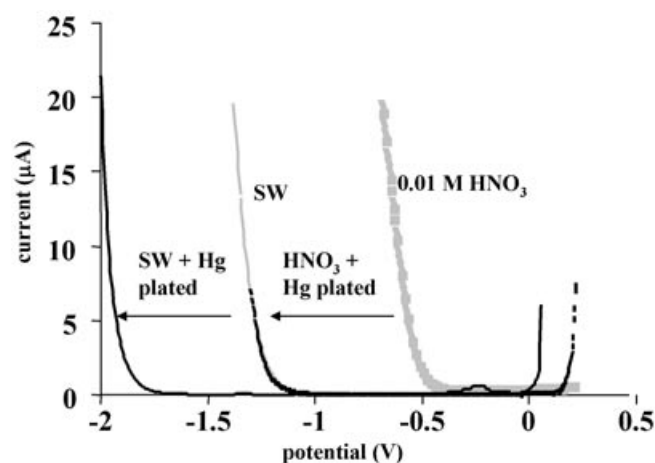


Fig. 2. Shape of the background current indicating the potential window available for analysis with a 3 mm/25 μ m gold wire microelectrode before and after the plating of a mercury coating.

and recorded as charge (coulombs) during the deposition step as a measure of the amount of mercury being deposited; purging was then stopped and deposition was carried out without stirring of the solution at a potential of -0.4 V until the same amount of mercury had been deposited per unit area of each electrode; this required a period of about 120 s for the disk, and 600 s for the wire, electrodes.

2.5. Voltammetric Measuring Parameters

2.5.1. Amalgamated Gold Micro-Wire Electrodes

Deposition time between 0 and 600 s at -1.0 V; start potential at -1.0 V and end potential at -0.3 V; frequency: 50 Hz, voltage step: 5 mV and amplitude: 25 mV; a "cleaning" period of 120 s was applied at -0.3 V after each scan to ensure that all lead and cadmium were re-oxidized, and the

electrode was kept at -0.3 V between measurements to prevent the formation of solid Hg_2Cl_2 .

2.5.2. Silver Micro-Wire Electrodes

Deposition times were between 0 and 300 s at -0.7 V; the start potential was -0.7 V and the end potential -0.2 V; frequency: 50 Hz, voltage step: 5 mV, and amplitude: 25 mV; a cleaning period of 120 s at -0.2 V was used to re-oxidize plated lead and cadmium. A rest potential of -0.2 V was applied between measurements to prevent the formation of AgCl(s) . In between experiments, or if it appeared that the sensitivity had dropped, the silver electrode was reactivated by conditioning 10 s at -2 V which was found to reverse the drift observed previously.

3. Results and Discussion

3.1. Electrode Preparation

The experiments were initiated with micro electrodes sealed in glass; however it was soon realized that many electrodes of different wire length had to be made, and it was found to be much more convenient to make these by sealing the wire in polyethylene, done here using pipette tips as described in the Methods section, adapted from an existing method [13]. The main advantage was the much lower temperature required for melting the polyethylene than for glass, and the ease with which they could be made. A problem with any method of making solid electrodes is that there has to be a good seal between the electrode and its non-conductive support to prevent the water from creeping in. In this case it was relied on the polyethylene making a seal as it melted and shaped itself around the microwire. The seal was tested in preliminary experiments by cutting the wire where it protruded out of the tip, followed by careful polishing to a microdisk. The microdisk electrode was tested by cyclic voltammetry in a solution of $\text{K}_3\text{Fe(CN)}_6$ to measure the surface area from the reduction current [7]; it was found that the surface area was that expected for a disk of a 25 μm wire indicating that there was no significant leakage at the electrode edge.

3.2. Mercury Plating of the Gold Microelectrodes

Only few studies exist on wire microelectrodes [2, 14, 15] and therefore experiments were carried out to optimize the analytical conditions for this kind of sensor. It was essential that mercury covered the entire surface of the gold wire as otherwise a mixed response was obtained, causing the baseline to be much higher. Gold is soluble in mercury (0.14% at 25 °C [16]) and it is usually necessary to do a new plating step when the sensitivity starts to decrease. It is known [15] that the stability of the deposit improves after several amalgamations and it is therefore not necessary to remove an old mercury deposit before plating a new one.

The stability was found to depend greatly on the potentials applied to the electrode, the mercury deposit disappearing when potentials more negative than -1.5 V were applied. In the optimized conditions, the stability of the electrode was about 2 days.

Preliminary experiments indicated that the lead peak on the mercury-gold electrode was very close, and overlapping, to that for cadmium at -0.58 V; however, the sensitivity for cadmium was much less (about $40\times$) than that for lead, and usually the lead concentration is greater than that of cadmium in natural waters, so this is not likely to be a problem for the determination of lead.

The mercury deposition time and potential, and the type of voltammetric scan, were varied, and the peak height for lead monitored, to optimize the analytical conditions. Coulometry was used to quantify the mercury deposition on the electrode surface during the plating step. Several scans were made after each mercury deposition to check that the electrode was well coated. Compared to an uncoated, or partially coated, electrode, the background current became progressively lower, and the hydrogen wave was shifted increasingly negative to -2 V, with increasing coverage with mercury (Figure 2).

In preliminary experiments the accuracy of using coulometry to monitor mercury deposition was evaluated using an iridium microelectrode in 0.01 M nitric acid. The current due to re-oxidation of the plated mercury during a voltammetric scan was found to be nearly the same (between 80 and 100%) as the plating current (in coulombs), indicating that no significant losses were occurring in these conditions, so monitoring of the charge (in coulombs) passing through the electrode during plating could be used to obtain a reasonable value for the amount of plated mercury. This charge (coulombs), corrected for the electrode size, was found to be equivalent to a mercury layer thickness of ca. 2 μm for an electrode of optimized composition. For a wire of ca. 1 cm length, the quantity of charge to get this thickness was ca. 20 mC. Comparative experiments showed the electrode stability was shortened to a few hours if the thickness was much less.

3.3. Microelectrode Behavior of the Wire Electrodes

Microelectrodes have special properties which make them more suitable than larger electrodes for in situ detection, due to the concentric nature of diffusion of reactive species to the electrode surface which should minimize stirring effects. Another measure of microelectrode behavior is that at a low scan rate, a cyclic voltammogram of a reversible reaction (such as for $\text{Fe(CN)}_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe(CN)}_6^{4-}$) should exhibit no hysteresis in the forward and backward scans [2, 7].

Experiments using the micro-wire electrodes demonstrated that the response for lead was increased two-fold by stirring of the solution during the deposition stage using a Teflon stirrer at 1000 rpm, and the cyclic voltammogram for a ferrous cyanide solution showed hysteresis, indicating that

true microelectrode behavior was not achieved by the wire electrodes. This compares to cyclic voltammograms using a mercury-coated iridium micro-disk electrode (diameter 7 μm) where the forward and backward scans were indistinguishable (scan rate 5 mV s^{-1}) in agreement with expected microelectrode behavior. However, this microelectrode also showed a stirring effect causing the sensitivity to increase by 50%. So, the stirring effect is probably not a good test for microelectrode behavior as it may cause the diffusion layer to be reduced to less than that occupied by the expanding diffusion layer of the electrode (see also theory below).

Another important feature of microelectrodes for the purpose of in situ analysis is that the sensitivity is proportional to the deposition time; for macroelectrodes the sensitivity should flatten off due to the lowering of the diffusion gradient with the expanding diffusion layer. The equations of the diffusion current during unstirred deposition for the micro-disk and micro-wire electrodes produce different conditions for periods of around a second or so [17]. In the case of the micro-disk electrode, for which we can assume approximately microelectrode behavior the following is valid:

$$I(t) = \pi r^2 n F C_{\text{bulk}} [(D/\pi t)^{1/2} + (4 D/\pi r)] \quad (1)$$

where n is the number of electrons involved in the electrochemical reaction, F is the Faraday constant, D diffusion coefficient, C_{bulk} the concentration of the analyte in the bulk solution, t deposition time, and r is the radius of the electrode.

After prolonged plating the equation reduces to:

$$\lim_{t \rightarrow \infty} (I) = 4nFC_{\text{bulk}} r D$$

which means that there is a finite current which does not change with time.

In the case of the wire electrodes the current is described by:

$$I(t) = 2\pi n l F D C_{\text{bulk}} \times \left\{ \frac{e^{-0.1\sqrt{\frac{\pi D}{r^2}}}}{\sqrt{\frac{\pi D t}{r^2}}} + \left[\ln \left(5.2945 + 1.4986 \sqrt{\frac{D t}{r^2}} \right) \right]^{-1} \right\} \quad (2)$$

where l is the length of the wire. This equation reduces to the following after prolonged plating:

$$\lim_{t \rightarrow \infty} (I) = 0$$

which means that the current drops to zero with increased plating time.

According to this theory, the wire electrode should be less appropriate for measurement without stirring because the

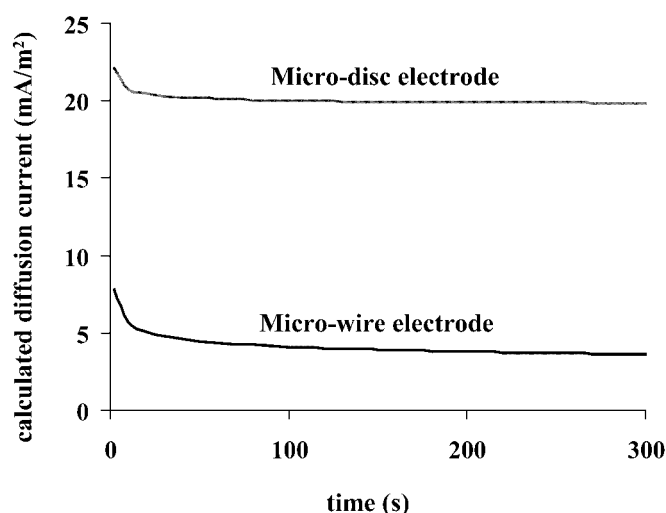


Fig. 3. Calculated diffusion current for micro-wire and -disk electrodes; a solution concentration of 1 μM was assumed for a 2-electron reaction, and the current is shown per unit area (m^2).

diffusion current approaches zero with increasing time. However, time appears only as an inverse logarithmic function and therefore the current declines only slowly. Calculation of the change in the diffusion current as a function of time shows relatively little difference between the micro-disk and -wire electrodes, and in particular little change in the sensitivity of the wire electrode over a typical plating time of 300 s (Figure 3), indicating that the increase in response as a function of time can be expected to be nearly linear. The wire electrodes can therefore be exploited experimentally in much the same way that steady-state currents are exploited at disk electrodes. In the literature, this case is sometimes called *quasi-steady state* [17]. On the other hand the calculation suggests that the response *per unit area* should be ca. 5 \times greater for the micro-disk electrode.

In practice the diffusion layer thickness does not increase indefinitely, and in fact is restricted by warmth related movement in the water. Assume that a wire electrode of length l μm and radius r μm is inserted in a quiescent (or stirred) solution and a plating potential is applied in the presence of electroactive species. Initially the current will follow Equation 2, but after a few seconds a diffusion layer of thickness d μm will build up, d being typically 10–50 μm . Electroactive substances will diffuse towards the electrode surface according to Fick's law, along the concentration gradient (from the bulk concentration of the analyte to zero at the electrode surface). The volume of the diffusion layer is given by $\pi((r+d)^2 - r^2)l$ and the total surface of the electrode by $2\pi r l$. The sensitivity is controlled by the ratio R of the volume of the diffusion layer divided by the surface area of the electrode, i.e., $R = (2rd + d^2)/2r = d^2/2r + d$.

For large electrodes (r is large) R is similar to the diffusion layer thickness d , whilst R is greater for thinner electrodes. To evaluate the effect of microwire thickness, values were calculated for R at different values of r , and at realistic

Table 1. Modelled effect of varying the microwire thickness on the value of R , where $R = (2rd + d^2)/2r = d^2/2r + d$; r is the electrode radius, and d the diffusion layer thickness, both in μm .

r (μm)	d (μm)	R
1	20	220
2	20	120
5	20	60
10	20	40
25	20	28
100	20	22
250	20	21
1	50	1300
2	50	675
5	50	300
10	50	175
25	50	100
100	50	63
250	50	55
1	200	20200
2	200	10200
5	200	4200
10	200	2200
25	200	1000
100	200	400
250	200	280

values for the diffusion layer thickness d , and are shown in Table 1. For a typical diffusion layer thickness (d) of 50 μm R approaches d for thick wires ($> 100 \mu\text{m}$) and considerably greater values are obtained for R for thinner wires. This demonstrates that it is worthwhile to use thin wires as it should increase the sensitivity from unstirred conditions as would be the case for measuring in situ conditions. Furthermore the response should increase in proportion with the wire length as this is directly related to the volume of the diffusion layer.

3.4. Lead Detection Using Micro-Wire and -Disk Electrodes

The electrodes were tested on lead to evaluate their use for trace metal analysis. A pseudo-polarogram of lead was obtained by plotting the peak current for 2.6 nM lead in seawater as a function of the deposition potential (Figure 4). The lead peak can be seen to be increasing with increasingly negative deposition potentials, stabilizing at deposition potentials between -1 and -1.4 V. At more negative deposition potentials (< -1.4 V), mercury entered in the body of the electrode due to amalgamation with gold [15] causing the sensitivity to diminish; when such negative potentials were maintained for 10 min at -2 V, the sensitivity decreased drastically also when a more positive plating potential was used (dot A on Figure 4). For this reason the deposition potential for lead was set to -1 V.

The oxidation peak of lead was located at around -0.47 V, which was more negative than that (-0.4 V) obtained with a conventional mercury drop electrode. Cadmium can usually be co-determined with lead when a

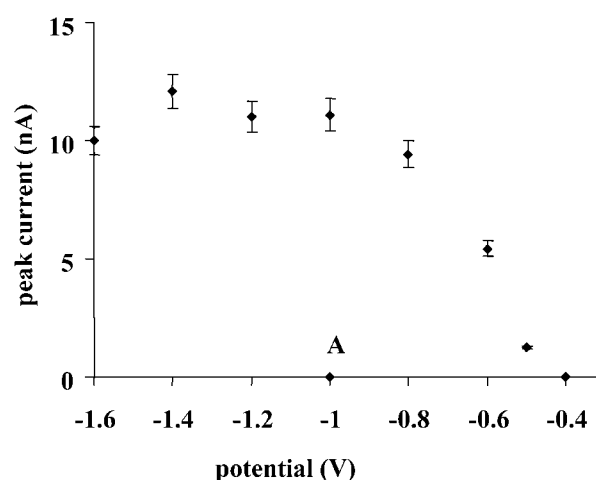


Fig. 4. Pseudo-voltammogram of 2.6 nM Pb in UV-digested seawater. Deposition time 300 s; the 8 mm/25 μm gold wire had been mercury plated; point A: after setting the potential to -2 V during 10 min which caused the mercury layer to disappear.

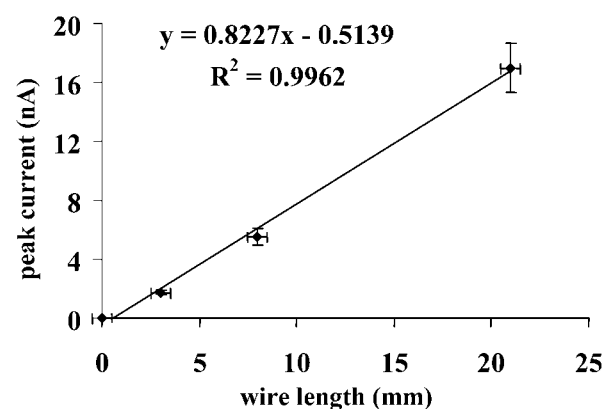


Fig. 5. Plot of the sensitivity for lead in UV-seawater against the length of the mercury plated gold wire electrodes in UV seawater; the deposition time was 300 s at -1 V.

mercury electrode is used, but the response with the mercury-plated gold electrode was very poor: the sensitivity for cadmium was about 40 times lower than for lead, and the response of a low level of lead was not affected by cadmium additions of 10 nM although the peak potential was located at -0.58 V, only about 0.1 V more negative than that for lead.

The length of the micro-wire electrodes was varied to evaluate its effect on the sensitivity for lead. Increasing the wire length from 3 to 8 and 21 mm showed that the sensitivity for lead was directly proportional to wire length (Fig. 5) indicating that the limit of detection can be brought down by extending the wire length. Long wires may cause spatial problems in small sample sizes, and a length of 1–2 cm is probably a good compromise between sensitivity and convenience, but longer wires could be used to achieve a lower limit of detection. A possibility is that pickup from radio sources will increase electronic noise at longer wire

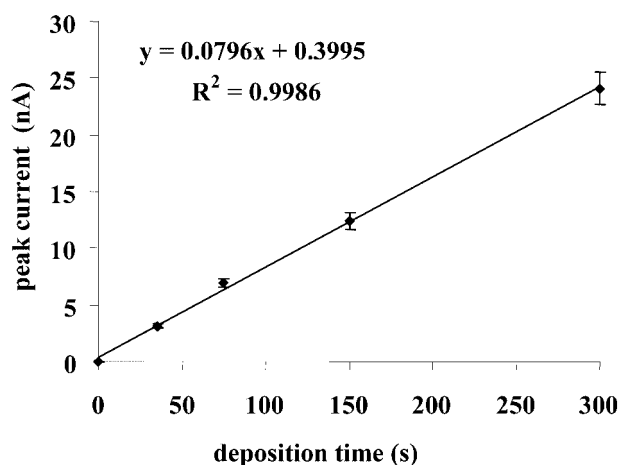


Fig. 6. Plot of the peak height (nA) for 3.7 nM lead in UV-seawater as a function of the deposition time (at -1 V) using an mercury plated gold wire electrode (8 mm/ 25 μ m).

lengths than tested but no increased background noise was noticed within the ranges tested.

Variation of the deposition time demonstrated that the response, in unstirred conditions, increased linearly with the deposition time (Figure 6), causing the response to approximately double with the deposition time over tested periods up to 600 s. This indicates that the deposition was not limited by the expected non-linearity in the diffusion rate as a function of time (Eq. 2 and Fig. 3), confirming experimentally that this is a minor effect within this time domain and that deposition on micro-wire electrodes achieves a quasi-steady state.

3.5. Limit of Detection

The limit of detection was calculated from the standard deviation ($3 \times \text{SD}$) of repeated determinations of the lead concentration at a low level of lead (between 0.2 nM for a 21 mm wire and 20 nM for the micro-disk electrode), with calibration of the sensitivity by lead standard additions. Voltammetric scans for lead using a 8 mm electrode wire are shown in Figure 7. This was repeated with micro-wire electrodes of various lengths and with the micro-disk electrode. The comparative measurements indicated clearly the analytical advantage of a micro-wire over that of a disk: the limit of detection was much lower using the micro-wire electrodes (0.07 nM Pb, 140 fold lower, and the sensitivity much greater, than using the micro-disk electrode (Table 2). The sensitivity for lead increased approximately linearly with the length of the wire which makes sense as this can be expected to be directly related to the surface area of the electrode: the sensitivity was 5 nA nM⁻¹ Pb per cm of wire electrode, 1700 \times higher than that (0.003 nA nM⁻¹) using the micro-disk electrode; this ratio was very similar to the ratio of the surface area of the micro-wire (from $2\pi rl$) over that of the micro-disk (from πr^2) which was ca. 1600 confirming that

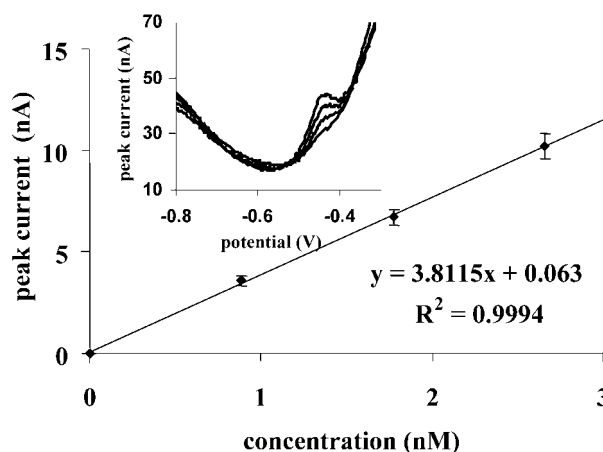


Fig. 7. Calibration plot in UV seawater using a 8 mm/25 μ m gold wire electrode; the deposition time was 300 s at -1 V.

the sensitivity was directly related to the surface area of the electrode.

Normalization of the lead peak current to the surface area of each electrode (Table 2) showed that the same current per unit area was obtained (6 nA nM⁻¹ mm⁻²) for the wire and the disk electrodes. Theoretically the micro-disk electrode should have been more sensitive per unit electrode-area than the micro-wire (Fig. 3), but this assumed that the micro-disk electrode behaved more as a microelectrode than the micro-wire electrodes. The fact that nearly the same sensitivity for lead was obtained using both types of electrode suggests that the behavior of the disk electrode was nearer to that of a macroelectrode due to its relatively large diameter of 25 μ m.

In spite of the obviously increased surface area it is perhaps unexpected that the limit of detection using the micro-wire electrode was improved as much as it did: a more similar limit of detection might have been expected if the background current had become increased by the same amount as the analytical current in the same conditions: the background current should have been about 1600 times smaller for the disk if it was related to the surface areas alone. The actual experimental ratio of the residual currents was about 200 (per cm micro-wire), which may be the reason for the relatively poor detection limit using the disk electrode compared to that using the micro-wire: the detection limit using the gold micro-wire (0.07 nM Pb) was 140 \times lower than that (10 nM Pb) achieved with the micro-disk electrode, using a deposition time of 300 s; no peak was observed using the micro-disk electrode at concentrations of 1–2 nM Pb.

3.6. Silver Microelectrodes

Some of the experiments were repeated with a micro-wire of a different metal, silver, and without mercury coating, for

Table 2. Comparison of sensitivities and limits of detection for lead in UV-digested seawater using micro-disk and -wire electrodes of gold and silver. The limit of detection was calculated from $3\times$ the standard deviation of repeated (5) measurements at a low concentration of lead (between 0.3 nM for the 21 mm/25 μ m gold wire to 20 nM for the 25 μ m diameter gold disk microelectrode) using a 300 s deposition time.

	Units	Au wire	Au disk	Ag wire	Ag disk
pH		8.3	8.3	2	2
Peak potential	V	−0.46	−0.48	−0.40	−0.40
Background current near the lead peak	nA	ca. 100 cm^{-1}	ca. 0.3	ca. 100 cm^{-1}	ca. 1
Surface area	mm^2	0.79 cm^{-1}	4.9×10^{-4}	0.79 cm^{-1}	4.9×10^{-4}
Sensitivity	nA nM^{-1}	5 cm^{-1}	0.003	10 cm^{-1}	0.04
Sensitivity per unit surface area	$\text{nA nM}^{-1} \text{mm}^{-2}$	6	6	12	80
Standard deviation at low lead level	%	6	10	3	3
Detection limit	nM	0.070	10	0.2	2

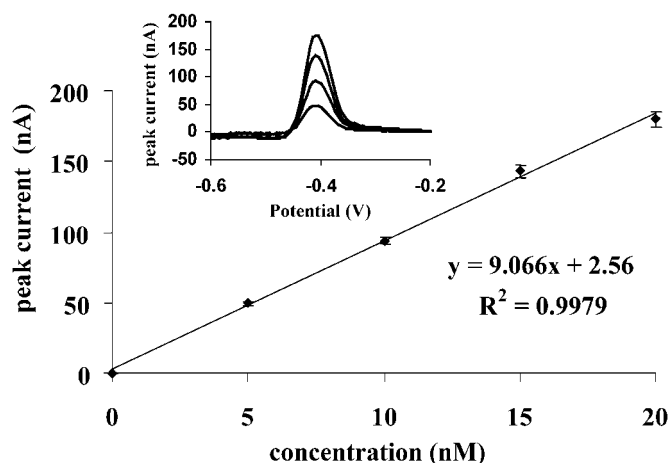


Fig. 8. Calibration plot for lead in acidified UV-seawater (pH 2) using a silver wire microelectrode (8 mm/25 μ m) and a deposition time of 300 s at -0.7 V; the scans are shown in the inset.

reasons of comparison. Silver was used for these wire and disk microelectrodes because this metal allows a determination of lead without the need of mercury whilst our preliminary experiments demonstrated peak overlap between cadmium and lead using the mercury-film-on-gold-microwire electrode. The lead deposition is known to be improved due to adsorption of the metal on the silver surface causing the so-called under-potential-deposition (UPD) [18, 19].

The experiments were carried out in pH 2 seawater as no signal could be obtained without the acid in agreement with previous findings [19] possibly because lead hydroxide formation in pH 8 seawater caused the peak to be irreversible, or the higher pH was for other reasons not conducive for the UPD process possibly due to substitution of $\text{Pb}(\text{OH})_2$ for PbCl_3^- .

Figure 8 shows a calibration plot with a silver micro-wire (diameter 25 μ m and 8 mm long). The sensitivity for lead was higher than using the gold wire but the limit of detection was greater (Table 2) because of a less reproducible and more noisy background current. The peak height increased approximately linearly with the deposition time until at least 600 s, similar to that with the gold wire electrode.

The sensitivity for lead using the silver wire electrode was $250\times$ greater than that using the silver disk, and the background current was ca. 100 greater; the limit of detection using the silver wire electrode was $10\times$ lower than using the disk. Like the gold micro-wire, the silver micro-wire gave therefore a major improvement in analytical performance over the micro-disk alternative. The sensitivity *per unit area* for the silver micro-disk electrode was much ($6.5\times$) greater than that of the silver wire electrode, which may have been due the polishing process which is known to enhance the sensitivity of silver disk electrodes [20] whereas the silver micro-wire electrode was not polished.

The sensitivity for lead of the silver micro-disk electrode at pH 2 was $10\times$ greater than the mercury-coated gold micro-disk electrode at pH 8, which may have been caused similarly by the polishing activation of the silver disk; by the pH difference (the silver electrode does not give a peak for lead at the original pH of seawater (pH 8)); or by diffusion of the plated lead away from the electrode surface into the 1 μ m layer of mercury (assuming an even mercury distribution): during the scan such amalgamated lead would not have oxidized quite as quickly as the lead on the silver electrode. This aspect was not further investigated.

3.7. Possible Application to In Situ Metal Detection in the Environment

The high limit of detection when working with silver microelectrode, and the requirement for sample acidification, are major problems which eliminate the possibility of in situ measurements. On the other hand the mercury-plated gold wire is suitable for possible in situ detection as it can be used at the original natural water pH, and because of the very low limit of detection which can be achieved.

As a preliminary test of the suitability of the gold micro-wire for lead detection in natural waters, a 21 mm length wire electrode was used to determine lead in a sample (salinity 30) from the Mersey estuary, collected next to Liverpool Marina. The sample was filtered (0.45 μ m) to enable comparison of analysis before and after UV-digestion, and analyzed by ASV using a 10 min plating time (Fig. 9); the sensitivity was calibrated with a 1 nM lead

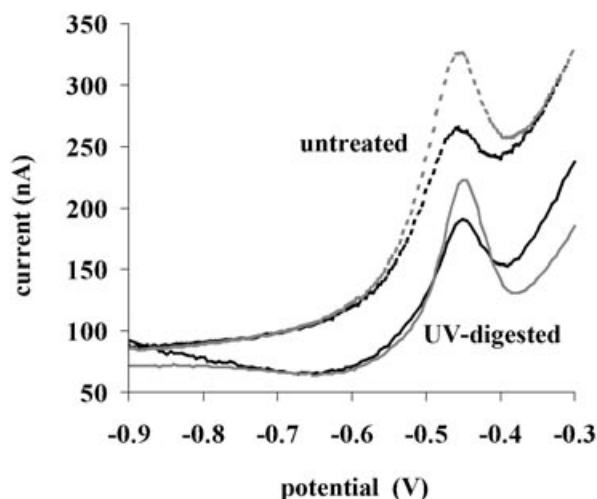


Fig. 9. Voltammograms for lead in a sample from the Mersey estuary before and after UV-digestion using a gold wire micro-electrode (21 mm/25 μm) and a deposition time of 600 s: After UV-digestion: —; after addition of 1 nM lead: —. Before UV-digestion: ----; after addition of 1 nM lead: ----.

addition in each case. The peak height was unaltered by the UV-digestion although the height of the baseline changed, and the same lead concentration (1.0 ± 0.1 nM) was obtained, indicating that the lead, if initially organically complexed, was mostly dissociated and detected as total lead at the plating potential (-1.0 V) used here; this is perhaps not surprising as the plating potential was 0.5 V more negative than the lead reduction potential. The sensitivity was not affected by the UV-digestion, and was the same as that obtained in clean seawater (Atlantic) just before measuring the samples.

The concentration of lead in the open ocean is 0.1–0.2 nM [21] and higher in coastal waters; the limit of detection of 0.07 nM lead using the micro-wire and a 300 s deposition time can be brought down further by increasing the plating time, and is sufficient for most seawater samples. However a drawback for in situ detection is the large background current due to dissolved oxygen which reaches ca. 250 μM in air-equilibrated water. This drawback is particularly great when using micro-electrodes for in situ analysis as the interference of dissolved oxygen is then maximized due to its optimized diffusion. In the past this interference has been overcome by passing the water via semi-permeable tubing through an in situ oxygen trap [22]; the same could be done with the micro-wire electrodes whilst benefiting from the much improved sensitivity and the reduced diffusion of oxygen per unit area.

4. Conclusions

The work demonstrates that

The sensitivity for metals using a micro-wire electrode is much greater than using a micro-disk electrode of the same diameter;

The sensitivity for metal detection is directly related to the wire length, and the surface area, of the wire electrodes;

The sensitivity *per unit area* of a silver wire electrode is less than that of a disk electrode of the same diameter due to the polishing treatment; however on the balance the absolute sensitivity of the wire electrode is much greater due to its greater surface area;

The theory shows that the increase in the sensitivity with deposition time of the wire electrodes is nearly linear with plating time in spite of the popular belief that it is necessary to use a flat microelectrode for this purpose; for this reason the sensitivity can be increased by plating over long time periods without stirring of the solution;

The in situ detection of low lead (sub-nM) levels using wire electrodes suffers from interference of dissolved oxygen like using other electrodes but the interference is significantly less than using disk electrodes.

On balance the use of micro-wire electrodes provides much improved sensitivity, and much reduced detection limits, over micro-disk electrodes of equivalent diameter.

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