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Short communication

Determination of chromium in estuarine waters by catalytic cathodic stripping voltammetry using a vibrating silver amalgam microwire electrode

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ABSTRACT

Chromium (Cr^{VI}) in water can be determined by adsorptive catalytic cathodic stripping voltammetry in the presence of diethylenetriaminepentaacetic acid (DTPA) and nitrate on the hanging mercury drop electrode (HMDE). Predominately Cr^{VI} is detected and the water is UV-digested to convert all Cr to Cr^{VI} prior to analysis. We develop here an alternative to the HMDE by using a silver amalgam electrode based on a vibrating microwire. The microwire electrodes were 12.5 μm in diameter and electrochemically coated with mercury, and were stable for a week. Conditions were re-optimised, and we used a DTPA concentration of 5 mM, 30 mM acetate pH buffer (pH 5.5 in seawater and pH 5.8 in pure water), and 1.5 M nitrate solution. The microwire was reactivated prior to each scan by applying a negative potential (−3 V) for 2 s which removed all deposited Cr. The detection limit for chromium in pH buffer was found to be 0.2 nM Cr^{VI} and in seawater 0.3 nM Cr^{VI} at a deposition time of 30 s. The response increased linearly with the concentration of Cr^{VI} up to 60 nM Cr^{VI} in seawater. The limit of detection is less good than using the HMDE, but the linear range is good and the microwire electrode could form the basis of apparatus for flow-analysis. The method was successfully tested on water samples from the estuary of the river Mersey (Liverpool Bay) giving chromium concentrations between 1.48 nM and 2.29 nM.

1. Introduction

Chromium is an ecotoxic trace metal which is present in natural waters in two oxidation states: the reactive and toxic Cr^{VI} and the relatively inert Cr^{III}. Cr^{VI} is an inhaled carcinogen, toxic to humans and other mammals, while Cr^{III} is an essential mineral supplement at trace level [1]. Major sources of chromium contamination are metallurgy, electroplating industry, pigment production, tannery, mining and refractory materials [2]. Several sensitive methods exist in the literature for the determination of chromium, some of these based on voltammetry, which has advantages related to sensitivity and ability to measure in seawater. Cathodic stripping voltammetry (CSV) makes use of adsorption of an electroactive complex with an added ligand. CSV has good sensitivity and can be used to determine metal speciation as well as its concentration in seawater. The CSV procedure for Cr in natural waters typically makes use of diethylenetriaminepentaacetic acid (DTPA) which forms a species with Cr^{III} that adsorbs on a hanging mercury drop electrode (HMDE) [1,3,4]. The Cr^{III} is freshly produced by reduction of Cr^{VI} at potentials < -0.1 V. The freshly produced Cr^{III} is 30× more reactive than existing Cr^{III} in the solution, so Cr^{VI} is the main contributor to the voltammetric response [5]. Nitrate is added to increase the sensitivity through a catalytic reaction in which Cr^{III} is the catalyst, which causes reduction of nitrate when the voltammetric scan reaches its reduction potential. The CSV method mechanism has been developed further [1,5] and modified using a different ligand (cupferron), and different electrode materials including a bismuth film electrode [6,7] and a silver-amalgam film [8,9]. Methods were recently reviewed [2]. An interesting modification has been the introduction of a more negative deposition potential in which the Cr^{VI} is plated as metallic Cr, then re-oxidised and re-adsorbed as the Cr^{III} -DTPA species [10]. This modification is included in this work.

The CSV procedure using the mercury is a "batch analysis" method, which is laborious because reagents are added to the voltammetric cell, either manually or using automated burets, for each analysis separately. This method would benefit from the introduction of flow analysis, but this is complicated with a mercury drop electrode as it is not easily adapted to flow analysis. Automation has been achieved using an HMDE [10] making use of pumped medium exchange of a batch cell. Mercury drop electrodes have been incorporated in flow–cells [11] but this has not caught on generally probably because of difficulties of stabilising a mercury drop in flow conditions and of environmental risk

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when using it in the field. Here we develop a solid electrode to determine Cr^{VI} by CSV. A solid electrode can be readily converted to flow analysis by fitting in a flow-cell, which is much easier than with the HMDE. Another advantage of the solid electrode is that the use of mercury is much reduced although this electrode is mercury-coated.

Silver-amalgam electrodes (made similarly to dental amalgam) have been proposed before for voltammetry [12] but that design is not readily made into a microelectrode. Solid electrodes have been used before for CSV. The mercury surface is particularly suitable for the adsorptive preconcentration step, but bismuth coated have also been used for several applications of cathodic stripping voltammetry [13,14]. A silver macro-electrode, physically coated with mercury prior to each scan, has been used before for the determination of Cr^{VI} [9] and cobalt and nickel [15] by CSV. Similarly a silver–bismuth alloy [16] and bismuth-coated carbon [17] have been used for CSV of nickel and cobalt, and mercury-coated gold for CSV of iron[18]. Alloys of silver and copper have been used for CSV of Ni[19].

Here we use a vibrating silver microwire electrode, electrochemically amalgamated with mercury, for CSV of Cr^{VI}. The surface is stable and suitable for CSV without requiring re-coating for a week, and its very thin diffusion layer thickness leads to rapid analysis with sensitivity sufficient for environmental monitoring.

2. Experimental

2.1. Apparatus

Electrochemical measurements were carried out using a μAutolabIII voltammeter (Ecochemie, The Netherlands) connected to an IME663 interface and a VA663 electrode stand (Metrohm, Switzerland). The working electrode was a 12.5 μm diameter silver microwire (Goodfellow Company, UK), the reference electrode was a double-junction Ag/AgCl, 3 M KCl, and the counter electrode was an iridium wire of 0.15 mm diameter and 2 cm length. The instrument was controlled by the software GPES 4.9 using subtraction mode for analysis. Seawater and nitrate solution used for the experiments were UV-digested using a 125 W high-pressure mercury vapour lamp during 45 min to remove dissolved organic matter prior to use.

2.2. Chemicals

All reagents were of analytical reagent grade and all solutions were prepared using Milli-Q deionised water (Elix/Gradient Milli-Q water purification system, resistivity 18 M Ωcm^{-1}). Standard solutions of Cr^{VI} were prepared either weekly or at the beginning of a set of experiments by dilution of metal atomic absorption stock solutions (1000 mg Cr L^{-1}) with water. An aqueous solution of DTPA (Acros Organics) was prepared containing 0.25 M DTPA. The pH was adjusted using a pH buffer containing 3 M ammonium acetate (AnalaR grade, England). Addition of 0.03 M of the ammonium acetate solution to seawater gave a pH of 5.5. An aqueous solution of 5 M sodium nitrate (Fisher Scientific) was employed for the catalytic effect. Contaminating Cr in the nitrate was removed by co-precipitation with 0.1 mM iron(II) chloride followed by filtration [4]. The mercury plating solution contained 2 mM monohydrated mercury nitrate (AnalaR grade, England) acidified with 10 mM HNO_3. Seawater samples (salinity 27–32) were collected using a polypropylene hand-pump in the Mersey Estuary in Liverpool Bay during a cruise with the Liverpool University research vessel Marisa in summer 2011. The samples were immediately gravity filtered through a 0.2 μm cellulose acetate filter cartridge (Sartobran 300, Sartorius) and stored under refrigeration.

2.3. Microwire electrode preparation

The fabrication of the silver microwire electrode was similar to that of gold wire electrodes [20]. A copper wire was passed through a 100 μL plastic pipette tip and dipped in a conductive silver solution. The end of the copper wire was then attached to a short length silver wire (12.5 or 25 μm) by gently touching it and subsequently withdrawing it into the tip, with ~1 mm protruding. The tip was melted by holding it for 8 s in the mouth of a tubular oven set to 450 °C. Good sealing between plastic and the silver wire ensures long-term stability, which is obvious from a lack of water build-up in the electrode tip and from scans without noise. To obtain a vibrating electrode, a vibrating device was placed in the back of the tip [21] using an adapted method [22].

2.4. Mercury plating

A scan in 10 mM HNO_3 was performed using cyclic voltammetry (CV) from 0 to +0.4 V to check for normal electrode behaviour, which showed silver oxidation beginning at +0.4 V. Subsequently mercury was added to the same solution to a final concentration of 2 mM Hg and purged with nitrogen for 5 min. Then, mercury was electrochemically plated on the silver microwire at −0.4 V (10 min) [23] resulting in a silver-amalgam electrode. The silver-amalgam electrode was used for about 1 week of experiments and was then replaced by a new one.

2.5. Electrochemical reaction mechanism

During the deposition step at −1 V dissolved Cr^{VI} is reduced to Cr^{III}. The Cr^{III} forms a complex with the DTPA which is adsorbed on the electrode surface. This mechanism is the same as on an HMDE [4]. Subsequently, a potential scan was carried out to measure the amount of deposited Cr^{III} from its reduction current to Cr^{II} producing a peak at −1.2 V. The current was enhanced by a catalytic effect in the presence of nitrate ions, owing to the chemical reoxidation of Cr^{II} to Cr^{III} which is immediately re-reduced during the scan [4].

2.6. General procedure to determine chromium

The sample solution (10 mL) containing 5 mM DTPA, 0.03 M ammonium acetate buffer (pH 5.8 in Milli-Q water and 5.5 in seawater) and 3 mL 5 M nitrate (final concentration ~1.5 M nitrate) was pipetted into the voltammetric cell. The solution was deoxygenated by N_2-purging (5 min). The silver amalgam microwire electrode was activated at −3 V (2 s) (vibration on) and Cr^{III}-DTPA complexes were adsorbed at the deposition potential (E_{dep}) (30 s) (vibration on). E_{dep} was −1.0 V in seawater and −1.1 V in Milli-Q water due to a small difference in pH and peak potential. After a 2 s equilibration time (vibrator off) the voltammogram was recorded by applying a differential pulse scan (DP) from −1.0 to −1.35 V. The electrochemical parameters were as follows: interval time 0.1 s, step-potential 2 mV, modulation amplitude 50 mV and modulation time 0.002 s. The background scan used an adsorption time of just 1 s and was otherwise the same as the analytical scan. The background scan was subtracted from the analytical scan to obtain a background-corrected scan. This was automated using the Project function of the GPES software.

3. Results and discussion

3.1. Preliminary experiments

A peak was obtained for Cr^{VI} in water (seawater and pH buffers) using the silver amalgam electrode in the presence of DTPA and nitrate, under conditions used previously with mercury drop electrodes [3,4]. Preliminary experiments were performed to optimise the conditions with the silver amalgam electrode for the determination of Cr^{VI} in 0.03 M ammonium acetate buffer (pH 5.8) and subsequently in seawater (pH 5.5). Differential-pulse was selected as stripping mode, as it was found to give better peak shape than the square-wave modulation. Silver microwires of 12.5 μm and 25 μm diameter were plated (10 min in unstirred condition) at various Hg concentrations in the plating solution (from 0 to 5 mM Hg). No signal was detected for Cr^{VI} without Hg on the microwire. The peak height for Cr^{VI} was found to increase with the mercury concentration, producing best response using 2 mM Hg for the 12.5 μm silver wire and 5 mM of Hg for the 25 μm silver wire. However, a high concentration of Hg for the plating solution (5 mM Hg) made the electrode unstable, causing it to break. A possible explanation for this is the gradual dissolution of silver into mercury causing it to weaken. For this reason a plating concentration of 2 mM Hg was selected. Comparative scans for 10 nM Cr^{VI} using a fixed concentration of 2 mM Hg for the plating solution showed that the peak was greater using the 12.5 μM wire (Fig. 1A), which may have been caused by a greater thickness of Hg on this wire. This wire was selected for further experiments in combination with a plating solution of 2 mM Hg.

The surface of the electrode was re-activated between scans by briefly applying a negative conditioning potential. Variation of this conditioning potential between −1.3 and −3 V (in pH 5.5 buffer in seawater) gave best result for −3 V, as the measurements became poorly reproducible at more negative values. It is likely that all Cr^{III} which is adsorbed on the electrode is reduced to Cr^{II} and then expelled due to hydrogen generation upon switching to −3 V; it is not deposited as Cr^0 at −3 V as then it would not be removed at −3 V. Variation of the re-activation time between 1 and 10 s gave an optimal time of 2 s. Using this procedure scans were found to be reproducible and stable.

3.2. Optimisation of analytical parameters (DTPA, nitrate and modulation time)

The effect of varying the concentration of DTPA in pH buffer containing 10 nM Cr^{VI} showed an optimal concentration of 5 mM of DTPA (Fig. 2A), which is similar to slightly higher than that (2.5 mM DTPA) on the mercury drop electrode [4]. At higher ligand concentrations, the Cr^{VI} peak height was found to decrease, possibly due to competitive adsorption of the DTPA without Cr.

3.3. Effect of varying the nitrate concentration

The concentration of nitrate was varied at constant levels of Cr and DTPA. The peak height for Cr^{VI} was found to increase linearly with the nitrate concentration (Fig. 2B). This is to be expected as the current is due to the reduction of nitrate, catalysed by the Cr^{III}/Cr^{II} redox couple: the current therefore is directly dependent on the diffusion of nitrate and therefore on its concentration. The downward curvature at high levels of nitrate in Fig. 2B is due to sample dilution. A nitrate concentration of 1.5 M was used for further experiments (3 mL of 5 M nitrate per 10 mL of sample) to maximise the sensitivity with relatively minor sample dilution. Greater sensitivity could be achieved by increasing the nitrate concentration further. This concentration of nitrate is 3× higher than used previously using the HMDE [4] in order to maximise the sensitivity of the silver-amalgam wire electrode.

Preliminary experiments in which the concentration of nitrate was raised were found to give a smaller increase in the peak height, the increase strongly diminishing with greater nitrate levels, which was suspected to be due to the presence of interfering organic matter in the nitrate salt. This was removed by UV-digestion of the nitrate stock solution after which the linear response was obtained (Fig. 2B). It was also found to be necessary to remove contaminating Cr^{VI} in the nitrate (by co-precipitation with Fe-hydroxide after reduction to Cr^{III}) as the background level contributed significantly to the water concentration of Cr^{VI} at low nM levels.

3.4. Effect of modulation time

The modulation time of the differential-pulse modulation was varied between 0.002 and 0.05 s. The peak height was found to decrease with the increasing modulation time. Highest peak current was obtained with the shortest modulation time of our instrumentation (0.002 s) which was selected for the Cr method. The decreasing response at longer modulation time is probably caused by a depletion of the diffusion layer as the reduction of Cr^{III} –DTPA is diffusion controlled [5].

3.5. Optimisation of the deposition potential

The deposition potential was varied in seawater containing 4 nM Cr^{VI}, from −0.5 to −2 V. Interestingly the response was best at two different potentials (Fig. 2C): the first maximum was obtained at −1.0 V, which is similar to that found using the older HMDE

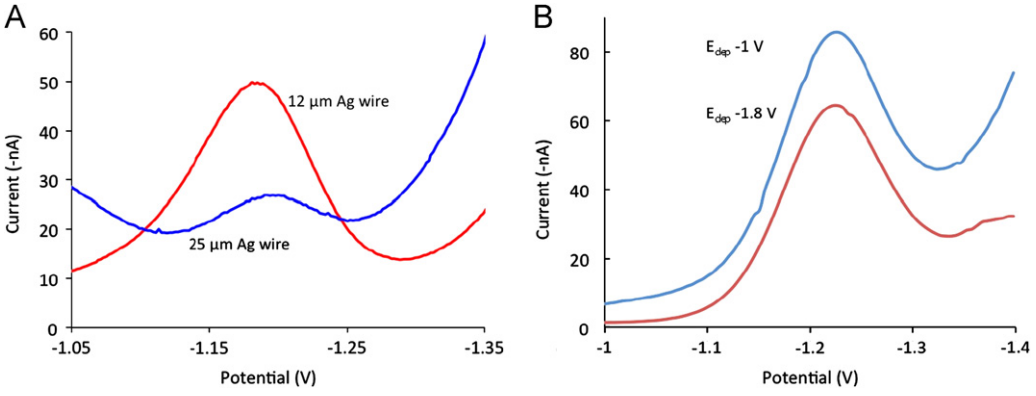

Fig. 1. Voltammetric scans for Cr^{VI}. (A) Effect of the diameter of the silver amalgam wire on the response for 10 nM Cr^{VI} in pH 5.8 buffer. The silver wires had been coated by plating (10 min at −0.4 V) from a solution containing 2 mM Hg. Deposition time 10 s at −1 V; and (B) Effect of the deposition potential on the scan shape for 7 nM Cr^{VI} in seawater (pH 5.5). The deposition time was 30 s at the indicated potential using a 12.5 μm silver amalgam wire. Each scan was initiated from −1 V.

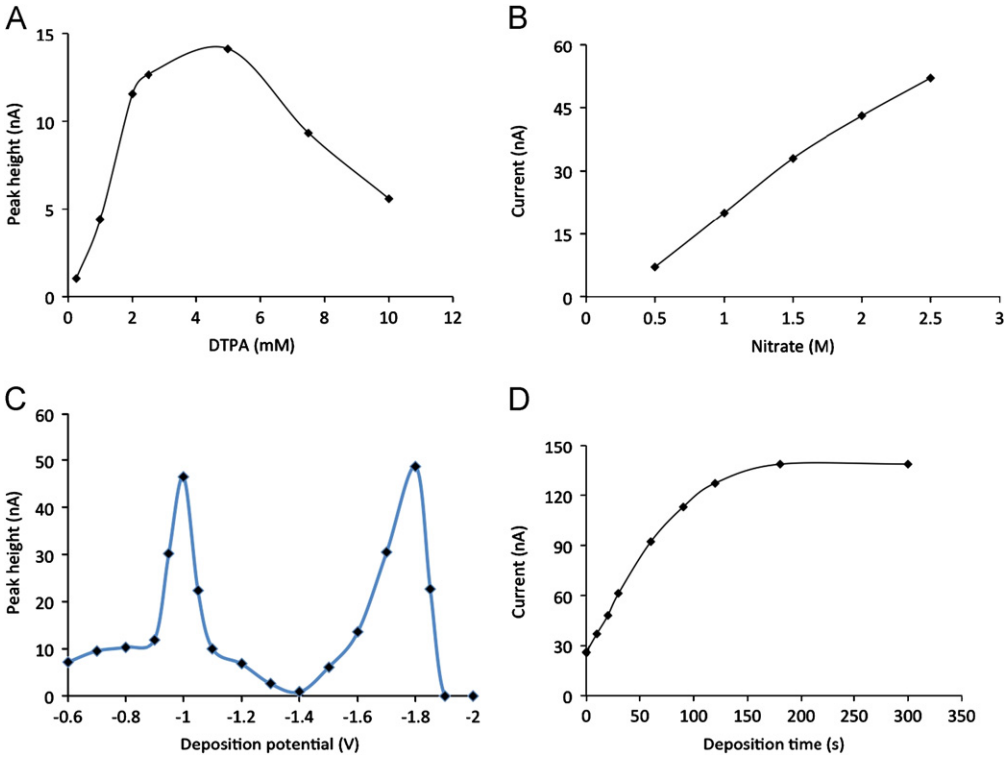

Fig. 2. Experiments to optimise the voltammetric parameters of CSV using the vibrating amalgamated silver wire electrode of Cr^{VI} in seawater. The solutions contained 5 mM DTPA, 30 mM NH_4Ac, 1.5 M $NaNO_3$ and 10 nM Cr^{VI} unless indicated differently. The deposition time was 30 s with vibration on using an adsorption potential of −1 V; scans were in the differential-pulse mode after a 2 s quiescence time at −1 V. (A) Variation of the concentration of DTPA, (B) variation of the concentration of $NaNO_3$, (C) variation of the deposition potential on the response for 6 nM Cr^{VI} in seawater, and (D) variation of the deposition time on the response of 4 nM Cr^{VI} in seawater after plating at −1.8 V and 5 s equilibration at −1 V.

method [3,4]. However, at more negative potential a second maximum was obtained at −1.8 V, corresponding to deposition of metallic Cr^0 [10]. On an HMDE the response is the same after deposition at potentials between −1.5 and −1.7 V [10] (more negative potentials were not tested, presumably due to instability of the HMDE). Our data shows that on the silver amalgam electrode the response is marginally greater at −1.8 V after which it decreases again after deposition at lower potentials. Other ions (major ions in seawater such as Na and Mg) could interfere with the Cr^{VI} deposition at these very negative potentials, which is perhaps the cause for the decrease, or hydrogen generation interferes with the complex adsorption at the negative potentials. The data shows that Cr^{VI} can be deposited on the amalgam silver wire with similar sensitivity at −1.0 V and at −1.8 V: at −1.0 V the deposition is as Cr^{III} -DTPA whilst it is as Cr^0 at −1.8 V. The deposition step at −1.8 V has to be followed by a reoxidation step at −1.0 V to generate the signal for Cr^{III} -DTPA. A repeat of this experiment in pH 5.8 acetate buffer showed that the maximum in response after deposition at −1.0 V shifted to more negative as −1.1 V, along with similar shift of the peak potential, due to the slightly higher pH.

Though the peak height showed little difference between deposition at −1.0 and −1.8 V, the baseline under the peak tended to be flatter after deposition at −1.8 V (Fig. 1B). Also, measurement of Cr^{VI} in estuarine water samples showed that there was less interference from organic matter using deposition at −1.8 V. A possible reason for this is that organic matter tends to be rejected at negative deposition potentials (< -1 V). For this reason −1.8 V is preferred in the presence of organic matter.

3.6. Influence of deposition time

The deposition time was varied to evaluate at which point the wire electrode would be saturated. Using a deposition potential of −1.1 V the response for 4 nM Cr^{VI} in seawater was found to increase until about 60 s after which it first levelled off and then started to decrease. This was possibly caused by competitive adsorption of the free DTPA as this is also known to adsorb [5]. Interestingly, using a deposition potential of −1.8 V, where the Cr^{VI} is reduced all the way to Cr^0, the peak height continued to increase for a longer period, then stabilised and did not decrease (Fig. 2D). The longer gradual increase is due to the continued accumulation of Cr^0 in the silver-amalgam of the electrode: possibly the free DTPA adsorbs less efficiently at this potential.

3.7. Linear range and limit of detection

The linear range and limit of detection for chromium was determined in both Milli-Q water and seawater, using ammonium acetate buffer and a deposition time of 30 s. Background subtraction was used to correct the scans for curvature in the baseline using the GPES software of the instrumentation. In Milli-Q water, the response was found to increase linearly with the concentration of Cr^{VI} to ~20 nM and non-linearly after that due to electrode saturation. The detection limit in this condition was ~0.2 nM Cr^{VI} (from 3 x the standard deviation). In seawater the peak height increased linearly to higher Cr^{VI} (60 nM) than in acetate buffer (Fig. 3). The sensitivity in the seawater was about 25% less than that in the acetate buffer. The detection limit for chromium in seawater in this condition was ~0.3 nM Cr^{VI}. The detection limits found here for MQ and seawater are higher than those found previously (0.01 nM Cr^{VI} in MQ and 0.1 nM Cr^{VI} in seawater) using the HMDE [4]. The difference would be greater if the same concentration of nitrate had been used (we used 1.5 M nitrate using the silver amalgam wire, whereas the previous HMDE work used 0.5 M nitrate). The reason for the higher limits of detection using the solid (silver-amalgam) electrode is probably related to interference by dissolved organic matter that

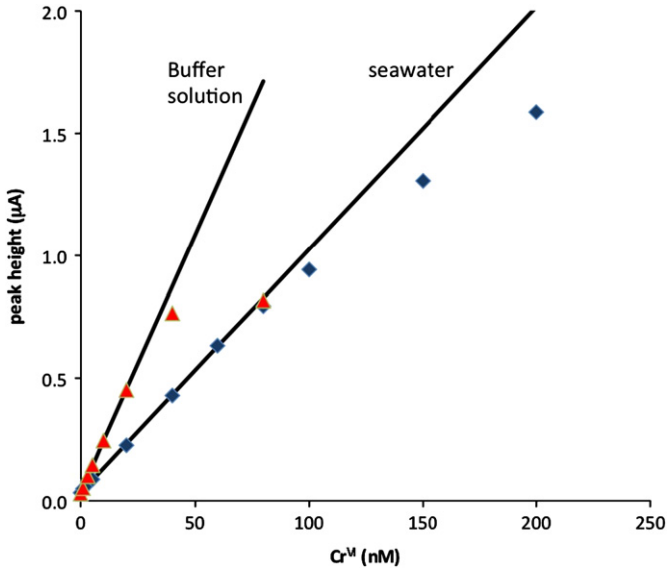

Fig. 3. Response as a function of the concentration of Cr^{VI} in acetate pH buffer (A) and in seawater (B). Deposition 30 s at −1.1 V (A) and −1.8 V (B).

Table 1
Determination of Cr (nM) by CSV using the silver-amalgam electrode in water samples from the high salinity end of the estuary of the River Mersey (England). The samples were UV–digested prior to analysis. Samples stored at natural pH were analysed the day after sampling. Due to the adsorption of Cr^{III} on the bottle walls these values represent the concentration of Cr^{VI}. Two samples were stored acidified to pH 2.2 to obtain the total dissolved Cr ($Cr_T = Cr^{III} + Cr^{VI}$); these were neutralised to neutral pH prior to UV-digestion.

Station	1	2	3	4	5	6
Natural pH (Cr^{VI})	1.5 ± 0.1	1.7 ± 0.1	1.9 ± 0.1	2.3 ± 0.2	2.2 ± 0.1	2.2 ± 0.1
Acidified (Cr_T)	2.7 ± 0.1	2.5 ± 0.3	–	–	–	–
Salinity	31.8	31.3	30.2	29.9	28.8	27.3

adsorbs on the electrode surface in spite of the negative potential (−3 V) used to regenerate the electrode between scans. A completely fresh surface is obtained prior to each measurement using HMDE, which contrasts with the regenerated surface of the silver-amalgam microwire.

Sensitivity using the silver-amalgam wire is sufficient for the monitoring Cr in fresh and coastal waters (typical concentrations of 2–4 nM Cr). The measurements using the silver-amalgam wire are quicker than using the HMDE because of the thin diffusion layer thickness (~1 μm) [24]. The response on the wire became non-linear after a deposition time of ~30 s at −1.1 V, which was extended to >60 s at −1.8 V. It becomes non-linear after 1–2 min on the HMDE [4,9], which was only slightly longer. So, an advantage of using a microwire is a shorter analysis time, but the overall sensitivity is less than achievable using the HMDE.

3.8. Application to seawater samples from Liverpool Bay

The method was tested on water samples collected from the estuary of the river Mersey. The samples had been UV-digested (45 min) at natural pH to remove organic matter and also to convert Cr^{III} to Cr^{VI} [4]. In view of the particle-reactivity of Cr^{III} and the high particle load of the Mersey estuary, it is likely that most dissolved Cr in the estuary is Cr^{VI}. Any Cr^{III} in the water is likely to adsorb on the bottle walls upon storage, and would not be recovered by the UV-digestion. The filtered samples that were stored at natural pH therefore represent Cr^{VI}. The results (Table 1) show a concentration of Cr^{VI} between 1.48 nM and 2.29 nM. Some samples were stored acidified; the pH of these was neutralised immediately prior to UV-digestion and analysis, to obtain total dissolved Cr ($Cr^{III} + Cr^{VI}$). The total Cr in the acidified samples was greater than that in the samples stored at natural pH, indicating that samples should be stored acidified to prevent losses of Cr^{III}. The concentrations found are typical in clean coastal waters [25]. It was attempted to determine Cr^{VI} in these samples without UV-digestion but this was not possible due to interference by dissolved organic matter. Separate experiments showed that measurement of Cr^{VI} without UV-digestion was possible using a HMDE (data not included) when a negative deposition potential (−1.8 V) was used due to better sensitivity with an HMDE.

4. Conclusions

The work shows that CSV of Cr^{VI} can be carried out using a silver amalgam microwire electrode. The solid electrode has advantages over the mercury drop electrode in that it should be easy to use as the basis for a flow cell, and that very little mercury is released into the environment. Testing of the electrode on estuarine water samples showed that the wire electrode is sufficiently sensitive to monitor Cr in coastal waters. The work is an example of a replacement of a mercury drop based method to a solid electrode. It may be possible to apply the mercury drop substitution with the silver-amalgam wire to other metals that are detectable by CSV. A drawback is that the method has a higher limit of detection than the original method based on the mercury drop electrode.

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