Electrochemical Detection of Trace Cu (II) in Macro Algae Using an Antimony Thin Film Modified Glassy Carbon Electrode

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Abstract

This study describes the development of a robust method for the electro analytical quantification of trace copper(II) in non-deaerated organic samples of macro algae by square wave anodic stripping voltammetry (SWASV). The indicator electrode employed was an antimony thin film coated onto a glassy carbon electrode (SbFE) support. The modified electrode was successfully applied for the sensitive and selective detection of trace copper in real sea weed samples following acid digestion. Copper(II) calibrations in the range of 2-10 μgL^{-1} (LOD=0.53 μgL^{-1}) in model solutions of 0.01 M hydrochloric acid (pH 2) containing 1 mgl^{-1} of antimony(III) were made possible by the addition of 30 μgL^{-1} cadmium(II). The method proved to be robust by the quantification of copper(II) in a 25 ml cell, containing 5 ml of sample digest. Dried seaweed samples, *Palmaria palmata*, *Laminar digitata* and *Fucus vesiculosus* in the resulting cell were found to contain 3.06, 2.02 and 0.857 μgL^{-1} respectively (RSD=2.9%). Furthermore, 0.857 ± 0.1 μgL^{-1} copper(II) was determined in the *Fucus vesiculosus* sample with interferents, zinc(II), cadmium(II), lead(II) and arsenic(II), added at concentrations 15 times greater than the inherent concentration of copper(II).

Keywords: Electro analytical; Macro algae; Antimony; Voltammetry; Bismuth

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Introduction

The excessive intake of copper(30 mg/day) is known to cause liver failure, while lower concentrations are associated with Menkes Syndrome, Wilson disease and childhood cirrhosis [1-3]. Metals such as copper occur naturally in seawater, at low concentrations, as essential micronutrients for marine biota [4]. Elevated concentrations, as a result of industrial activity or other environmental contaminants, can pose a threat to marine life when absorbed or ingested by plants and animals in excess [5]. Limited bio monitoring of metals using shellfish was previously conducted [5]. A discussion document produced by the Environmental Protection Agency of Ireland proposed the inclusion of seaweed in an extended assessment of future monitoring programmes of metal concentrations in Irish coastal waters [2].

In relation to the quantification of heavy metals, in contrast to methods such as ICP-MS and GFAAS, portable electrochemical devices can be utilised for on-site applications [6]. Anodic stripping voltammetry (ASV) is among the most sensitive techniques available to the analytical chemist. Sensitivity can be attributed to both the pre-concentration step and co-deposition of a plating agent on various electrode materials. Traditionally the hanging mercury drop electrode (HMDE) and thin mercury film (TMF) had been the electrode of choice for the ASV determination of heavy metals in a large range of foods, sea foods and environmental samples [7]. Since then, HMDE and the co-deposition of TMF (on a glassy carbon support) have fallen out of favour, due to mercury's associated toxicity. Subsequent methods developed involve the modification of solid state surfaces such as carbon, gold, platinum, silver, and screen printed carbon inks with various modifications coated *in-situ* [8-12].

Bismuth coated working electrodes were introduced by Wang et al. at the turn of the century [12]. Being more environmentally friendly, bismuth electrodes have been the subject of various

novel studies including clinical and industrial applications on a broad range of electrode substrates [13,14]. In comparison to mercury, bismuth thin film offers advantages, which include: a slightly broader potential window, the complete resolution of thallium(III) in the presence of cadmium(II) and lead(II) due to slightly different oxidation potentials, is more practical in terms of non-deaerated solutions and complete electrochemical removal by oxidation of the pre-plated bismuth film [12]. Unlike the mercury thin film, where complete removal requires the addition of thiocyanate or physical cleaning [15].

In 2007, Hocevar et al. demonstrated the efficacy of an antimony film, on a glassy carbon substrate, for the ASV determination of trace cadmium(II) and lead(II) [16]. Akin to bismuth, the antimony film was completely oxidised and the analysis was conducted in non-deaerated cells. Tesarova et al. produced similar findings with carbon paste substrates, using both, ASV and potentiometric stripping analysis [17,18]. Employing a boron-doped diamond substrate, Toghill et al. reported that the formation of antimony nanoparticles permitted the simultaneous quantification of cadmium(II) and lead(II) [19]. Various other substrates/mechanisms were reported for the effective and simultaneous detection of lead(II) and cadmium(II) in conjunction with an antimony film [20,21]. In comparison to bismuth or mercury, the oxidation of the antimony film produces only a small oxidation peak. Slavec et al. exploited this specific characteristic to detect copper(II) in a standard reference material of natural water [22]. The analysis of copper(II) was extended to real river samples by Ashrafi et al. using carbon paste electrodes [23,24]. Bobrowski et al. proved the efficacy of antimony film on a screen printed electrode for the detection of copper(II) in carbonate minerals and fly ash extracts [11].

One of the greatest limitations to ASV procedures is the matrix effect of real samples. In this study, macro algae was selected as a local marine and food sample that presents a challenging sample matrix. SbFE has never been utilised for such an analysis. The heavy metal content of such food stuff is under-represented in the literature [25]. Using a marine sample, both the salt content and organic matrix presents a challenge for electrochemical detection of a specific analyte. In this work, we exploited the characteristic SbFE intermetallic interactions with cadmium(II) for the quantification of copper(II) in the range of 2-10 µgL^{-1} in a model solution. The unique procedure was then successfully applied to the quantification of copper(II) in macro algae, collected locally, off the Donegal coast.

Experimental

Reagents

Nitric acid, sulfuric acid, hydrogen peroxide and hydrochloric acid used in this study were high purity reagents (99.999%) used as received from Sigma-Aldrich. Standard stock solutions of antimony(III), cadmium(II), Zinc(II), lead(II) and Cu (II) (1000 mgL^{-1}, atomic absorption standard solutions) were obtained from Merck and diluted as required. A solution of 0.01 M hydrochloric acid served as the supporting electrolyte throughout. All solutions were prepared from 18.2 MΩ Ultra-pure water provided by an ELGA System.

Apparatus

A Metrohm 797 VA Computrace and associated software was used for all voltammetric measurements. The conventional three-electrode configuration consisted of the antimony film modified glassy carbon rotating (2000 rpm) disc (2 mm in diameter) as the working electrode, an Ag/AgCl/1 M KCl as the reference electrode with a platinum wire counter electrode, all received from Metrohm, were used throughout. All measurements were performed at room temperature (20 ± 3°C) in either a 15 ml or 25 ml electrochemical cell.

Sample preparation

The crude samples were placed in plastic containers with 500 ml of deionised water, agitated at 125 rpm, 10°C, for 1 hour (using a Barnstead Lab-Line Max Q 4000 Digital Orbital Shaker). The procedure was repeated three times, with fresh water to remove excess NaCl. The sample was dried for 72 hours at 40°C, grinded for homogenisation, and digested according to the Metrohm Application Bulletin No. 113/2e [21]. As a brief summary of the digestion, 250 mg of sample was weighed into a round bottom boiling flask containing 4 ml concentrated H$_2$SO$_4$. The resulting mixture turned to brown colour. 1 ml w (H$_2$O$_2$)=30% was added via a dropping funnel returning the mixture to a clear colour. Following the initial reaction, the mixture was heated and returned to a brown colour. The process was repeated at ~100°C until the mixture remained clear. The mixture was then heated to 350-400°C. The addition of H$_2$O$_2$ was repeated until the solution stayed colourless at the boiling point of H$_2$SO$_4$ (>290°C). The colourless sulphuric acid was evaporated over a Bunsen burner to almost dryness. After cooling, the sample was made up to 100 ml with ultrapure water. An aliquot of 5 ml was diluted to volume and added to the electrochemical cell for trace analysis.

Measurement procedure

Prior to each calibration/sample determination, the glassy carbon electrode was polished using a polishing pad with a 0.05 µm alumina slurry followed by a thorough rinsing with deionised water, then with 70% ethanol and finally with deionised water. All ASV measurements were conducted in a background solution of 0.01 M hydrochloric acid containing 1 mgL^{-1} antimony(III) unless otherwise stated. The electrochemical parameters were consistent for all experiments. The accumulation was performed at a rotating disc (2000 rpm) for 120 seconds at -1.2 V with a subsequent equilibrium period of 15 seconds. Square wave stripping voltammograms were recorded in a quiescent solution in the anodic direction with a frequency of 25 Hz, a potential step of 5 mV, with an amplitude of 25 mV. Prior to each measurement, the working electrode was electrochemically cleaned by applying 0.3 V for 30 seconds.

Results and Discussion

Evaluation of detectable metals using SbTF

Preliminary studies in model cadmium(II) solutions using SbTF produced linear calibration curves at concentrations from 10-100 µgL^{-1} (not shown). In contrast, model solutions of lead showed

poor linearity and distorted peaks over the same concentration range (not shown). However, in agreement with earlier studies by Slavec et al. [22], linear calibration curves were possible in model solutions which contained both cadmium(II) and lead(II) over the same concentration range **(Figure 1a)**. The antimony peak, at approximately 0.05 V, is seen to diminish as the cadmium(II) and lead(II) concentration increases and almost disappears at concentrations greater than 20 μgL^{-1}. Succesive additions of 10 μgL^{-1} copper(II) was shown to reduce both cadmium(II) and lead(II) oxidation peaks as shown in **Figure 1b**.

ASVs for model copper(II) solutions, using SbTF are shown in **Figure 2**. Linearity was only achieved for copper(II) at concentrations exceeding 20 μgL^{-1}. The copper(II) oxidation peak potential was -25 mV at 10 μgL^{-1}, which shifted to 0.0 V when the copper(II) concentration was increased to 20 μgL^{-1}, and shifted again to 40 mV at a concentration of 30 μgL^{-1}, where it remained stable at higher concentrations. The anodic peak shift may be attributed to repulsive interactions, at lower concentrations according to previous studies [26,27]. The reduced peak height and repulsive relationship suggests that low concentrations of copper(II) competes with excess Sb ions for deposition sites within the thin antimony film. Consequently, there is a limitation in regard to the determination of copper(II) at concentrations less than 20 μgL^{-1}, due to the dominant antimony peak. Furthermore, this limitation exists regarding the quantification of trace copper(II) in real samples, where much lower concentrations is often present [7,11].

Characterisation of Cu/Cd system

Figure 3 shows the ASVs recorded for 2 and 10 μgL^{-1} copper(II) in the presence of 1 mgL^{-1} antimony(III). No linearity was achieved at these concentrations and peak currents were, surprisingly, seen to diminish as the concentration of copper increased. It is demonstrable that at copper(II) concentrations between 2 and 10 μgL^{-1} the peak produced is dominated by antimony(III) oxidation (~6 μA), rather than copper(II).

Ashrafi et al. previously reported the formation of Cd/Sb complexes in the presence of excess antimony(III) [28]. Such Cd/Sb complexes compete more effectively than excess Sb ions for deposition sites within the antimony film, hence diminished antimony(III) oxidation peaks would be expected in the presence of cadmium(II). To collaborate the findings ASV's of cadmium(II), 10-40 μgL^{-1} in the presence of 1 mgL^{-1} antimony(III), were recorded **(Figure 4)**.

A 40-fold decrease in peak height, from 6 μA to 150 nA, can be observed for 1 mgL^{-1} antimony(III) in the presence of cadmium(II) at a concentration of 40 μgL^{-1} **(Figure 4)**. The residual peak of 150 nA is most likely a result of the oxidation of the thin antimony film from the carbon substrate. A copper(II) calibration, in the presence of cadmium(II), diminished the cadmium(II) oxidation peak, as shown previously in **Figure 1b**. Hence, Cu/Sb complexes previously reported by Dal Borgo et al. compete favourably against the Cd/Sb complexes, for deposition sites using SbFE [29]. The sensitivity of such a system can then be characterised as favouring Cd/Sb oxidation over antimony(II), then Cu/Sb oxidation

over Cd/Sb. Therefore, the antimony(II) oxidation interference around the 0.0 V region can be almost completely eliminated by the presence of cadmium(II), increasing the systems sensitivity towards the detection of copper(II).

Optimisation of cadmium(II) concentration

To find the optimum concentration of cadmium(II) required, four copper(II) calibrations, from 2-10 μgL^{-1}, were performed in duplicate. Each calibration contains 25, 50, 75 or 100 μgL^{-1}

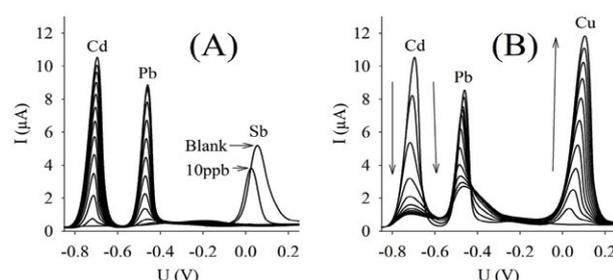**Figure 1** (A) ASV curves for consecutive additions of 10 μ L^{-1} of cadmium (II) and lead (II) to the background solution. (B) ASVs for successive 10 μ L^{-1} additions of copper (II) to the background solution containing 120 μ L^{-1} cadmium (II) and lead (II).
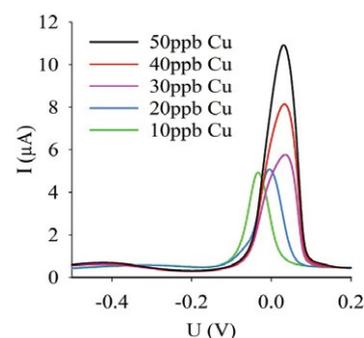

Figure 2 ASV response for successive additions of 10 μ L^{-1} copper (II) illustrating the non-linear response of copper (II) at concentrations less than 30 μ L^{-1}.
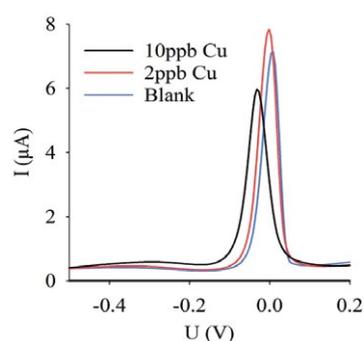

Figure 3 ASVs illustrating the antimony (III) oxidation peak obtained in the background solution (blue line) and after subsequent additions of 2 and 10 μ L^{-1} copper (II) (red and black lines respectively).

cadmium(II) in the background solution as shown in **Figure 5**. The solution containing 100 µgL⁻¹ cadmium(II) produced the smallest copper(II) peaks **(Figure 5a)**. 75 µgL⁻¹ cadmium(II) produced a dual oxidation peak most evident at 2 µgL⁻¹ copper(II) **(Figure 5b)**. Using cadmium(II) concentration of 50 µgL⁻¹, the peak height of 10 µgL⁻¹ copper(II) increased 4-fold, relative to 75 µgL⁻¹ **(Figure 5c)**. The lowest concentration, 25 µgL⁻¹ cadmium(II) produced similar results but with less reproducibility at 2 µgL⁻¹ copper(II) **(Figure 5d)**.

To find the minimal optimum concentration of cadmium(II) required, a further two copper(II) calibrations, 2-10 µgL⁻¹, in the presence of 30 and 35 µgL⁻¹ cadmium(II) were performed. 30 µgL⁻¹ cadmium(II) yielded a peak with the narrowest base width and greatest peak height of 2.32 µA for 10 µgL⁻¹ copper(II) **(Figure 6)**. Increasing the cadmium(II) concentration to 35 µgL⁻¹ increased the base width by ~30 mV and reduced peak height to 1.84 µA.

According to studies by Mirceski et al. the cathodic drift of the oxidation peak potential, as a result of increasing concentrations of copper(II) in **Figure 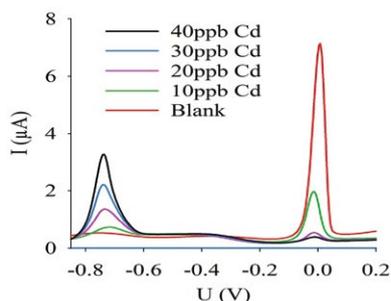5a**, may be attributed to repulsive forces at the electrode interface [27]. Reducing the concentration of cadmium(II) in solution had a profound effect on this phenomenon causing the oxidation peak potential to drift in the opposite direction (indicating attractive interactions occurring). Hence, there may be a direct relationship between the concentration of cadmium(II) and interactive forces occurring at the electrode surface.

Based on voltammograms (peak height, shape and width) and linearity **(Figure 6b)**, a concentration of 30 µgL⁻¹ cadmium(II) was selected as the optimum for the determination of the copper(II) in real samples. **Figure 6b** illustrates that the linear relationship with an LOD of 0.53 ppb (3.3 σ/slope).

Determination of copper(II) in macro algae

Three macro algae samples, *Palmaria palmata*, *laminar digitata* and *Fucus vesiculosus* were digested according to Metrohm Application Bulletin No.113/2e (21). An aliquot of 5 ml *Laminar digitata* sample digest was made up to a 15 ml in 0.01 M hydrochloric acid containing 1 mgL⁻¹ antimony(III) and 30 µgL⁻¹ cadmium(II).

Successive additions to this solution of 2 µgL⁻¹ copper(II), resulted in distorted voltammograms, most prominent in the final addition as shown in **Figure 7a**. This distortion and non-linear response shown in **Figure 7b** was attributed to electrode fouling. To overcome this, ASVs were recorded under the same conditions

Figure 4 ASVs demonstrating the effect of cadmium (II), 10-40 µg L⁻¹, on the inherent oxidation peak of 1 mg L⁻¹ antimony (III) in 0.01 M hydrochloric acid.

Figure 6 (A) Duplicate ASVs of 2-10 µg L⁻¹ copper(II) in 0.01 M hydrochloric acid, 1 mg L⁻¹ antimony(III) and 30 µg L⁻¹ cadmium(II). (B) Corresponding calibration plot (R²=0.9961).

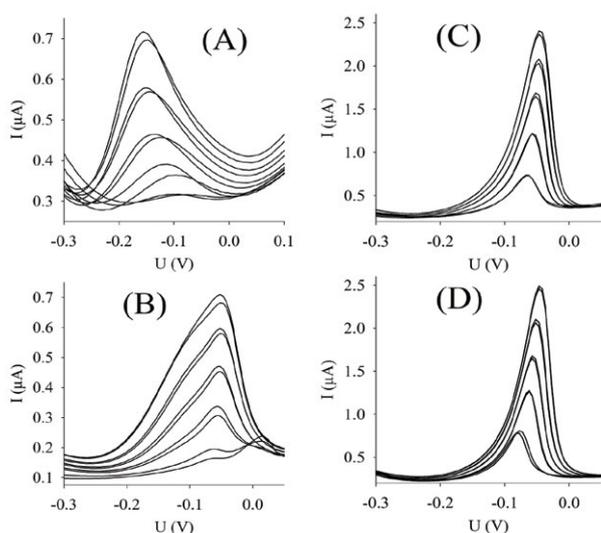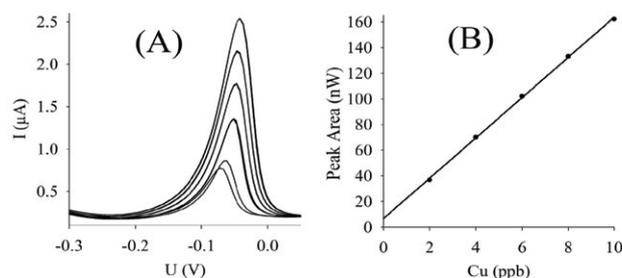**Figure 5** Effect of cadmium (II) concentration, ranging from (A) 100, (B) 75, (C) 50 and (D) 25 µg L⁻¹ on the ASV response to successive additions of 2, 4, 6, 8 and 10 µg L⁻¹ copper (II).

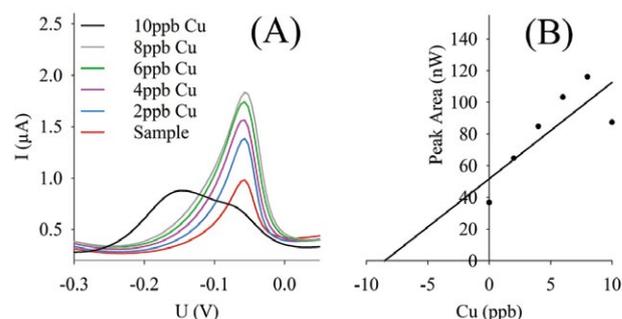**Figure 7** (A) ASV determination of copper(II) by the method of standard addition (2-10 µg L⁻¹ copper(II) in 5 ml of sample digest, made up to 15 ml in 0.01 M hydrochloric acid, 1 mg L⁻¹ antimony and 30 µg L⁻¹ cadmium(II). (B) Corresponding calibration plot.

using 5 ml of the sample digest diluted to 25 ml. Using the higher dilution factor, no evidence of electrode fouling was observed and good linearity was evident from the standard addition curves as seen in **Figure 8a** and **8b**. This allowed a value of 2.02 µgL^{-1} copper(II) to be successfully determined for the sample. Under the same conditions, the concentration of copper(II) using the samples *Palmaria palmata*, and *Fucus vesiculosus* in a 25 ml cell were determined to be 3.06 µgL^{-1} and 0.857 µgL^{-1} respectively. Repeat ASVs under the same conditions without the addition of 30 µgL^{-1} cadmium(II) are shown in **Figure 8c**. This illustrates the requirement for the addition of cadmium(II) for the determination of sub-µgL^{-1} concentrations of copper(II) in real samples.

Ten replicate ASVs of the sample, after addition of 10 µgL^{-1} copper(II), shown in **Figure 8d**, illustrates that a 1 in 5 dilution of the sample is sufficient to minimise the effects of electrode fouling from the sample matrix. The repetitive measurement (n=10) yielded a relative standard deviation of 2.9%. The copper(II)
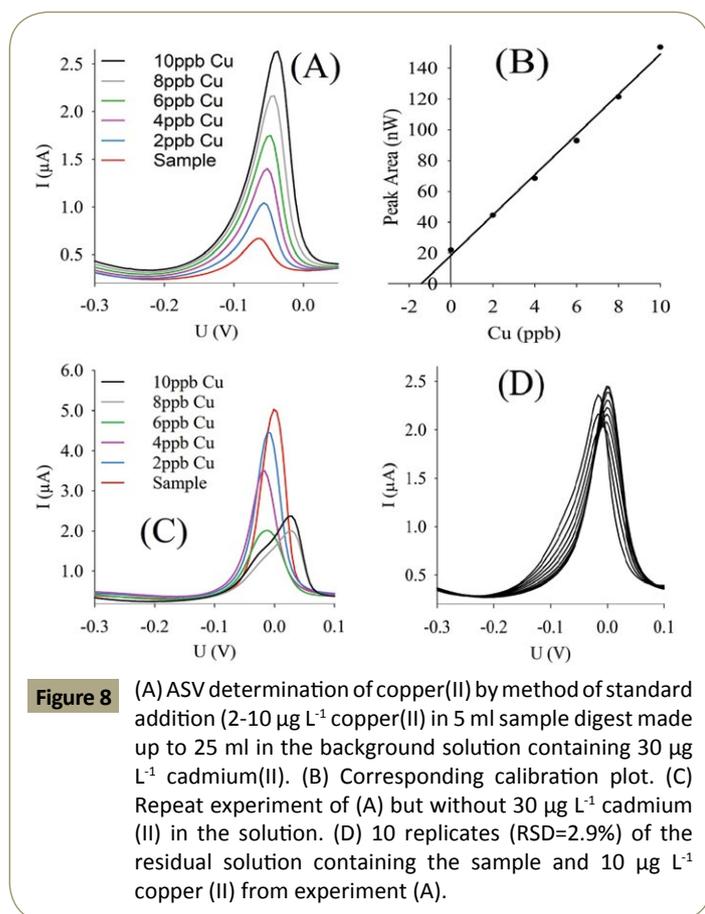
Table 1 Results of the ASV determination of copper (II) in macro algae using SbFE and 30 μg L^{-1} cadmium (II) compared to GF-AAS.

Sample	Concentration in solution (GF-AAS) (µg L^{-1})	Concentration in solution (ASV-SbFE) (µg L^{-1})	Contents (mg kg^{-1}) (Based on ASV-SbFE)
Fucus vesiculosus	5.25	4.29±0.1	1.72
Laminar digitata	8.29	10.1±0.3	4.04
Palmaria palmata	16.97	15.3±0.4	6.12

concentration in the sample extracts were also compared with values recorded using GF-AAS **(Table 1)**.

Interference study

To test for the effect of common interfering ions often present in real samples, zinc, cadmium, lead and arsenic was added to the cell, containing the sample of the lowest concentration of copper(II), *Fucus vesiculosus*. Results showed copper(II) determined in the presence of aforementioned ions at concentrations 15-fold greater. The calculated concentration of copper(II) in samples with 5, 10 and 15 µgL^{-1} of interferents (Zn(II), Cd(II), Pb(II) and As(III)) were 0.756, 0.933 and 0.761 µgL^{-1} respectively. The interferents caused a broader oxidation peak for copper(II) than in the original sample.

Conclusion

A robust method for the detection of copper(II) in organic marine samples of macro algae, using a SbFE, has been demonstrated for the first time. It was shown Cd/Sb complexes compete favourably with antimony(III), reducing the antimony(III) oxidation peak, 40-fold, from 6,000 nA to 150 nA. In addition, copper(II) has been shown to compete favourably against cadmium(II), in terms of forming antimony complexes for oxidation within the SbFE. This fundamental concept and subsequent optimisation has led to the accurate and reproducible quantification of copper(II) at concentrations of less than 1 µgL^{-1} in organic samples. Furthermore, this was achieved at relatively short pre-concentration times without the need to deaerate the sample solution. In addition to the sample matrix, copper(II) was quantified in the presence of, the added interferents, zinc(II), cadmium(II), lead(II) and arsenic (III) at concentrations 15-fold greater. The procedure takes approximately 90 minutes when the sample is dried. Further development is required to optimise and adapt this system, for an *in-situ* portable device. This study in combination with emerging technologies has the potential to determine copper(II) in various types of organic samples on site.

Figure 8 (A) ASV determination of copper(II) by method of standard addition (2-10 µg L^{-1} copper(II) in 5 ml sample digest made up to 25 ml in the background solution containing 30 µg L^{-1} cadmium(II). (B) Corresponding calibration plot. (C) Repeat experiment of (A) but without 30 µg L^{-1} cadmium (II) in the solution. (D) 10 replicates (RSD=2.9%) of the residual solution containing the sample and 10 µg L^{-1} copper (II) from experiment (A).

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