

Anodic stripping voltammetry of copper at insonated glassy carbon-based electrodes: application to the determination of copper in beer

César Agra-Gutiérrez, Joanna L. Hardcastle, Jon C. Ball and Richard G. Compton*

Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, UK OX1 3QZ. E-mail: richard.compton@chemistry.oxford.ac.uk

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The suitability of ultrasound-assisted anodic stripping voltammetry (*sono*-ASV) for the detection of total copper content in beer using both mercury thin film and glassy carbon electrodes has been investigated. An immersion horn probe is introduced into a small thermostatted conventional three electrode cell (20 cm³) opposite the working electrode: an *ex situ* mercury plated Nafion®-coated mercury film electrode or a bare glassy carbon electrode. Minimal sample pre-treatment is required which consists of acidification of the beer with dilute nitric acid and out-gassing with argon. After the deposition of copper (as the metal or its amalgam) on the electrode in the presence of ultrasound, a square wave scan is employed to get the analytical signal. In the absence of ultrasound, electrode passivation by organic species and lower rates of mass transport prevent the observation of any measurable signals. *In situ* cavitation cleaning of the electrode by insonation maintains the electrode activity. Total copper content levels in the range of 100 to 300 µg Cu L⁻¹ were determined by *sono*-ASV using both electrode substrates and showed excellent agreement with values provided by an independent method. This highlights the validity of the *sono*-ASV method as a useful electroanalytical technique in hostile media.

1. Introduction

Anodic stripping voltammetry (ASV) is a very sensitive and quick electroanalytical technique¹ which has been successfully applied to the detection and quantitative determination of various metals such as Pb, Sn, Cu, Zn, Cd, Bi, Sb, Au, Cr and Hg.^{1,2} ASV involves two stages. First is the pre-concentration step where the electrode is held at a suitably negative potential such that the target is reduced onto the electrode surface to form either an amalgam, if using a mercury electrode, or an adsorbed layer of the target, if using a solid electrode. Second, the electrode is subjected to a positive potential sweep causing the target on or in the electrode to be oxidised. This results in an anodic peak which is characteristic of the target being analysed. The position of the peak reveals the identity of the target and the area or height of the peak is related to its concentration. The technique is very sensitive and under favourable conditions can detect as low as 10⁻¹¹ M.^{1,2}

Mercury thin film electrodes (MTFEs) are well established electrode materials for ASV.²⁻⁶ These electrodes offer a large surface area to volume ratio and, as a result, greater sensitivity and resolution of neighbouring signals than those obtained with a mercury drop electrode are observed.² Glassy carbon is used as a common electrode substrate for MTFEs. Its advantages include³⁻⁶ the ease of preparation, high sensitivity, large potential window and low interaction with the mercury. However, the weak adhesion to mercury often results in poor mechanical properties.^{4,6,7} Other electrode materials such as platinum, copper and silver give rise to mercury thin films with more stable mechanical properties. However, the dissolution of these substrates in mercury and the resulting formation of intermetallic compounds with analyte metals deposited into the film can limit their utility.^{8,9} Mercury thin films on iridium have been shown to overcome this problem, due to the very low solubility of iridium in mercury.⁸⁻¹⁰ However, recent studies¹¹ have shown iridium-based mercury film electrodes to be less sensitive for the determination of lead and cadmium than

Nafion®-coated glassy carbon mercury film electrodes. Environmental and health issues concerning mercury and its toxicity have prompted the development of mercury-free solid electrodes, especially for on-line monitoring of foodstuff, clinical and field tests.¹²⁻¹⁴ In relation to this Sweden has recently banned the use of mercury from the year 2000;¹⁵ it is already prohibited in Japan. Carbon disc microelectrodes have been used for trace analysis of lead and copper in rain and wine samples using ASV.¹⁴ This technique has also been used to determine heavy metals in aqueous media using carbon screen-printed electrodes. Potentiometric stripping analysis for on-line monitoring has been successfully applied using gold-coated screen-printed carbon electrodes;¹⁶ interactions among the metals with the naked solid electrode still present problems. For example, unexpected or unexplained stripping voltammetric responses have been observed for electrodeposited copper and lead on glassy carbon and graphite electrodes due to inter-metallic interactions.¹⁷⁻²⁰ Both the enhancement^{17,18} and decrease or total suppression^{19,20} of the lead stripping peak have been observed in solutions with large copper to lead ratio.

A commonly encountered problem in ASV is the deactivation of the electrode surface. The presence of organic substances in the sample matrix can cause peak depression or even complete fouling of the electrode.²¹⁻³¹ This leads to low sensitivity and poor reproducibility. As a consequence, it is often necessary to mineralise the sample to eliminate these interferences. These treatments consist in acidification or UV irradiation in the presence of an oxidant.²⁵ However, they complicate and lengthen the analytical protocol and introduce contamination risks. One method employed to prevent electrode fouling is to electrochemically activate or modify the electrode.³²⁻³⁷ A more efficient way of overcoming this problem is to use ultrasound-assisted electrochemistry. The use of ultrasound in electrochemistry has been exploited and is now emerging as a powerful technique in electroanalytical chemistry.³⁸⁻⁴⁷ Its major advantages include the extremely enhanced mass transport^{39,43,46,47} to and from the electrode surface and the activation and clean-

ing^{39,44,45,47} of electrode surfaces achieved under insonation. In particular, ultrasound has been successfully applied in ASV. For example, well defined and very sharp stripping responses have been obtained for lead, copper and cadmium using mercury containing electrodes in aqueous media and alcoholic beverages.^{38–40,42,48} Another way of overcoming electrode fouling is to use membrane-coated electrodes. Dialysis membranes, cellulose acetate and Nafion® have been used^{21–23,40–50} for this purpose. In particular Nafion®-coated electrodes have been successfully applied to the detection of heavy metals in aqueous^{11,48} and real media^{22,23,49,50} using ASV. These Nafion®-coated mercury thin film electrodes, usually on glassy carbon, often exhibit higher sensitivity and resistance to electrode fouling by excluding negatively charged organic species. In addition, the polymer coating provides a more mechanically stable mercury film under the presence of ultrasound.^{11,48} A major advantage of sono-electroanalysis is that cavitation effects can clean the surface during the pre-concentration stage preventing electrode fouling and also that insonation increases the mass transport to the electrode and hence the sensitivity of the experiment.

The aim of this paper is to assess the applicability of *sono*-ASV to the determination of total metal contents in dirty media using mercury-free electrodes in which other electroanalytical techniques fail to give accurate and reproducible results due to electrode fouling and matrix effects. For this purpose, a comparison of methodologies using both mercury thin film and glassy carbon electrodes is conducted using beer as a model dirty medium.

2. Experimental

The cell used is shown in Fig. 1. It has a volume of *ca.* 25 cm³. The working electrode is placed directly opposite the ultrasonic horn (Model CV26, Sonics and Materials, Danbury, CT, USA) and located near the cell bottom with a transducer probe to working electrode distance of 5 mm. The horn was equipped with a titanium alloy micro-tip (of diameter *ca.* 3 mm; Aldrich, Gillingham, Dorset, UK) and was operated at 20 kHz. The ultrasonic intensity was calibrated calorimetrically according to the procedure of Margulis and Maltsev⁵¹ and Mason *et al.*⁵² over the range 40–550 W cm^{−2}. The *sono*-ASV experiments were carried out at 200 ± 5 W cm^{−2} unless otherwise stated. Thermostating of the cell was accomplished by means of a

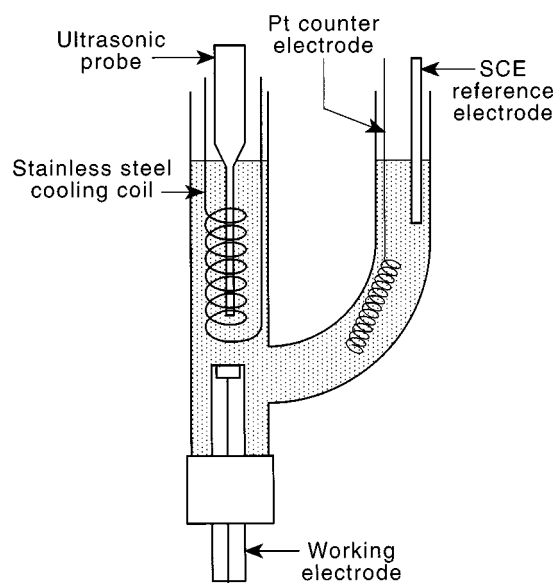


Fig. 1 Schematic diagram of the electrochemical cell employed in the *sono*-ASV determination of metals in beer.

stainless steel cooling coil inserted in the solution through which water was circulated from a constant temperature bath. By limitation of sonication time to less than 5 min this arrangement enabled the voltammetric measurements to be conducted at constant temperature (25 °C) to within ±2 °C.

An Eco-Chemie µAUTOLAB® (Utrecht, Netherlands) was employed to control the potential of the working electrode. The need for bipotentiometric⁵³ control of the titanium horn was eliminated by insulating the transducer from the probe with a thin Teflon™ disc and connecting the two with a screw thread machined from Delrin™ instead of titanium.

Experiments were conducted using two types of electrode materials. A bare glassy carbon electrode and an *ex situ* mercury-plated Nafion®-coated glassy carbon electrode. The substrate (a 3 mm diameter glassy carbon disc supplied by BAS, West Lafayette, USA) was carefully polished using diamond lapping compounds (Kemet, Kent, UK) of decreasing size down to 0.1 µm before use. A platinum counter electrode was used throughout the experiments. All potentials are quoted with respect to the saturated calomel electrode, SCE (Radiometer, Copenhagen, Denmark). Nafion® coating was achieved following the procedure described previously.^{11,40} Mercury plating of this electrode was conducted *ex situ* immediately before use. Mercury was deposited from a deaerated solution containing 0.1 M HClO₄ and 0.01 M Hg(ClO₄)₂ at −1.0 V vs. SCE until a charge of 1 mC had been passed through the electrode. Previous studies^{11,40} have shown that these films are composed of mercury micro-droplets deposited on the glassy carbon substrate and embedded in a compact, transparent Nafion® matrix. The electrode was refreshed by repeating this procedure for each measurement.

Reagents used were all of analytical grade or the highest commercially available purity. Nitric acid volumetric standards (1.0 M and 0.1 M), copper atomic absorption standard (990 mg Cu L^{−1}), lead volumetric standard (0.1 mg Pb L^{−1}), mercury(II) perchlorate, perchloric acid and dimethylformamide were supplied by Aldrich. Pedigree Bitter was purchased from Marston's Brewery (Burton-on-Trent, Staffs., UK). A Nafion® solution of 5% weight in low-weight alcohols (Sigma, Poole, Dorset, UK) was diluted with ethanol (analytical grade) prior to application. Solutions were prepared using UHQ grade water of resistivity not less than 18 MΩ cm (Elgastat, High Wycombe, Bucks, UK). Test solutions were prepared by adding 88 cm³ of beer to 162 cm³ of 0.1 M nitric acid unless otherwise stated. All solutions were thoroughly purged of oxygen by bubbling argon (PureShield, BOC, Guildford, Surrey, UK) through the solution prior to electrolysis.

For the comparison of total copper content, samples were analysed (standard addition method) using electrothermal atomic absorption spectrometry with no sample pretreatment. This was conducted by Rooney Laboratories Ltd. (Basingstoke, Hants., UK).

3. Results and discussion

3.1. Determination of copper in beer using mercury thin film electrodes

Anodic stripping square voltammograms for Cu²⁺ were obtained in a solution prepared by mixing 88 cm³ 0.1 M HNO₃ and 162 cm³ Pedigree Bitter beer using a mercury thin film electrode. Deposition of the lead amalgam was conducted for 240 s at −1.0 V vs. SCE under power ultrasound of intensity 200 W cm^{−2} emitted from a horn probe placed at 5 mm from a 3 mm diameter *ex situ* mercury-plated Nafion®-coated glassy carbon electrode (see Fig. 1). The square wave sweep parameters were as follows: pulse amplitude of 25 mV, potential step of 5 mV and a frequency of 60 Hz. Typical square

wave voltammograms are shown in Fig. 2. The anodic stripping peak at *ca.* 0.0 V vs. SCE increases and shifts anodically with increasing addition of copper. This wave corresponds to the oxidation of copper amalgam. Standard copper micro-addition experiments were conducted to determine the amount of copper in the beer using the method described above. A typical standard micro-addition plot is shown in Fig. 3, as a plot of the anodic stripping peak current vs. the amount of copper added per volume of beer. Results are shown in Table 1 and compared with analyses provided by an independent laboratory using electrothermal atomic absorption spectrometry. The standard addition method provides a copper content of $265 \pm 65 \mu\text{g Cu}$ per litre of beer (background corrected). A value for the total copper content in the beer sample was provided by an independent laboratory and shows excellent agreement (Table 1). Analysis of the standard addition data provided a theoretical limit of detection of $0.15 \mu\text{g Cu}$ per litre of beer, although

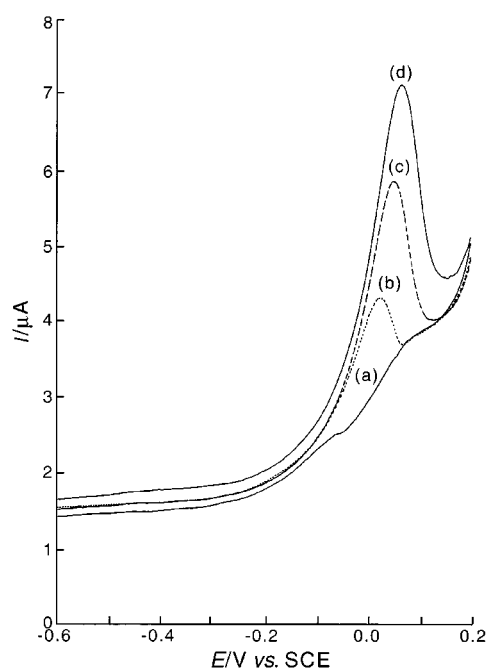


Fig. 2 Square wave anodic stripping voltammograms of aqueous solutions prepared by mixing 88 cm^3 0.1 M HNO_3 and 162 cm^3 Pedigree Beer: (a) blank, and after addition of (b) $507 \mu\text{g Cu L}^{-1}$, (c) $1522 \mu\text{g Cu L}^{-1}$, and (d) $2536 \mu\text{g Cu L}^{-1}$. The deposition step was conducted for 240 s at -1.0 V vs. SCE under power ultrasound of intensity 200 W cm^{-2} emitted from a horn probe placed at 5 mm opposite a 3 mm *ex situ* mercury-plated Nafion®-coated glassy carbon electrode. Square wave sweep parameters: pulse amplitude of 25 mV, potential step of 5 mV and a frequency of 60 Hz.

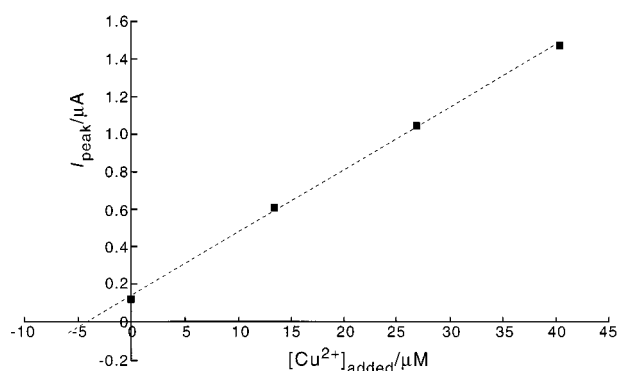


Fig. 3 Standard micro-addition plot for copper(II) in a solution prepared by mixing 88 cm^3 0.1 M HNO_3 and 162 cm^3 Pedigree Beer. The deposition step was conducted for 240 s at -1.0 V vs. SCE under power ultrasound of intensity 200 W cm^{-2} emitted from a horn probe placed at 5 mm opposite a 3 mm *ex situ* mercury-plated Nafion®-coated glassy carbon electrode. Square wave sweep parameters as in Fig. 2.

practical detection limits are somewhat higher depending on the minimum detectable peak and the purity of the reagents.⁴⁰

3.2. Determination of copper in beer using solid electrodes

Mercury-free electrodes were used to determine the amount of copper in Pedigree Bitter using a 3 mm diameter glassy carbon electrode. Pre-conditioning of the electrode was conducted at -2 V vs. SCE for 10 s. This treatment reduces the fouling of the electrode improving the stability and the size of the signal. Deposition of copper on the glassy carbon substrate was conducted at -1.5 V vs. SCE under power ultrasound of intensity 200 W cm^{-2} emitted from a horn probe placed at 5 mm from the working electrode (see scheme in Fig. 1). The stripping step was carried out using a square wave scan with the same parameters as for experiments in Section 3.1. Typical square wave voltammograms for a solution containing 162 cm^3 0.1 M HNO_3 and 88 cm^3 Pedigree Bitter with and without added copper are shown in Fig. 4. Note the different current scale

Table 1 Determination of copper in Pedigree Beer using *sono*-SWASV. Results for two types of electrodes are shown: NCMFGCE corresponds to an *ex situ* mercury-plated Nafion®-coated glassy carbon electrode; GC corresponds to a glassy carbon electrode. Deposition was carried out at -1.5 V vs. SCE in the case of GC and at -1 V vs. SCE in the case of the NCMFGCE for 240 s under ultrasound of intensity 200 W cm^{-2} at a horn to electrode distance of 5 mm (see scheme in Fig. 1). Glassy carbon electrodes were pre-conditioned at -2 V vs. SCE for 5 s. Values are expressed as the average values for 3 determinations $\pm$ their standard deviation

Electrode	Sample	$[\text{Cu}]^a/\mu\text{g Cu L}^{-1}$	$[\text{Cu}]^b/\mu\text{g Cu L}^{-1}$
NCMFGCE	Pedigree sample 1	265 ± 65	230
GC	Pedigree sample 1	222 ± 31	230
GC	Pedigree sample 2	139 ± 4	140

^a As determined by *sono*-SWASV. ^b As determined by independent laboratory.

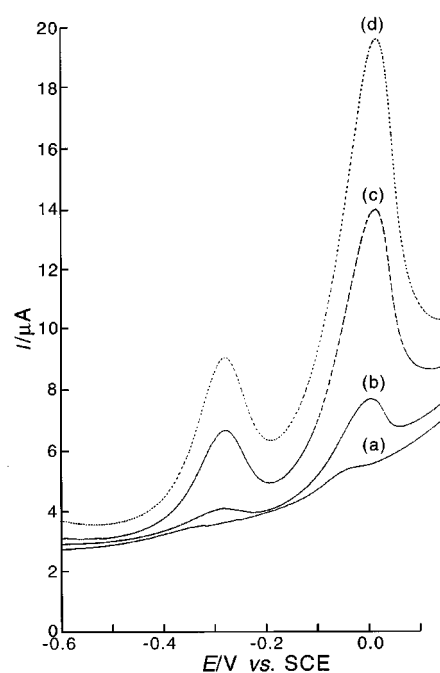


Fig. 4 Square wave anodic stripping voltammograms of aqueous solutions prepared by mixing 162 cm^3 0.1 M HNO_3 and 88 cm^3 Pedigree Beer: (a) blank, and after addition of (b) $47.7 \mu\text{g Cu L}^{-1}$, (c) $143 \mu\text{g Cu L}^{-1}$, and (d) $190.6 \mu\text{g Cu L}^{-1}$. The deposition step was conducted for 240 s at -1.5 V vs. SCE under (a) silent conditions, and (b), (c) and (d), power ultrasound of intensity 200 W cm^{-2} emitted from a horn probe placed at 5 mm opposite a 3 mm glassy carbon electrode. Square wave sweep parameters as in Fig. 2.

compared with Fig. 2 for analysis using different electrode substrates. Results in the absence of ultrasound are shown for comparison. The wave at ca. 0 V vs. SCE increases with increasing concentration of added copper and corresponds to the anodic stripping peak of solid copper deposited on the glassy carbon electrode. The wave at ca. -0.3 V vs. SCE also increases with added copper concentration and is related to copper-lead interactions which will be further discussed in the next section. In the absence of ultrasound both the copper and copper-lead alloy stripping peaks are not observed; application of ultrasound is essential for the ASV procedure. This is due to the surface activation^{39,42,43} observed in the presence of ultrasound which removes organic adsorbates thought to preclude measurement under silent conditions. This highlights one major benefit of using ultrasound coupled to ASV; in addition the high mass transport ensures that large SWV signals are seen for relatively short accumulation times.

Several determinations of copper in Pedigree Beer were obtained as described above and analysis of the standard addition data provided the values shown in Table 1 together with values provided by an independent laboratory. The excellent agreement between the two methods confirms the reliability of *sono*-SWASV to give the total copper content in beer.

3.3. Observations on the use of solid electrodes: copper-lead alloys

Fig. 4 shows a wave at ca. -0.3 V vs. SCE which is attributed to a copper-lead alloy. Further experiments were conducted to corroborate this inference. *Sono*-ASV experiments were conducted in a solution containing 0.1 M HNO₃ and 0.5 μ M Pb²⁺ to which certain amounts of Cu²⁺ and Pb²⁺ were successively added using a glassy carbon electrode. The working electrode was pre-conditioned at -2 V vs. SCE for 5 s. The deposition step was then conducted at -1.5 V vs. SCE for 120 s under power ultrasound of intensity 200 W cm⁻² emitted from a horn probe placed at 5 mm from the working electrode. The stripping step was carried out using a linear sweep voltammetric scan at a scan rate of 50 mV s⁻¹. Results are shown in Fig. 5 as a plot of current vs. applied potential for (a) micro-additions of Cu²⁺, and (b) micro-additions of Pb²⁺ solutions. Fig. 5(a) shows linear sweep voltammograms upon additions of Cu²⁺ solutions. The peak at ca. 0.0 V vs. SCE corresponds to the oxidation of copper deposited on the glassy carbon electrode and increases with the micro-additions. The peak at ca. -0.5 V corresponds to the oxidation of lead deposited on the electrode and decreases with increasing amount of copper added. The third wave, at ca. -0.3 V, increases with increasing concentration of copper added and corresponds to the oxidation of a lead-copper alloy. Fig. 5(b) shows linear sweep voltammograms upon additions of Pb²⁺ to a solution containing 0.1 M HNO₃, 0.5 μ M Pb²⁺ and 3 μ M Cu²⁺. The anodic copper peak at ca. 0.0 V remains initially constant upon addition of up to 150.1 μ g Pb L⁻¹. Further addition of lead results in a decrease of the copper peak and an increase of both the lead and alloy peaks which broaden and merge. These results clearly indicate the occurrence of a copper-lead alloy, in the form of an intermetallic compound or a solid solution. These observations are in agreement with earlier reports about the deposition of copper and lead on solid electrodes.^{14,20,25} On comparison with the results obtained using mercury film electrodes reported in this paper it can be concluded that copper-lead interactions are less important in the presence of mercury. This is in agreement with previous observations.^{17,20} Nonetheless, the occurrence of these interactions does not affect the applicability of *sono*-ASV to the detection of total copper in beer using mercury-free glassy carbon electrodes, as evidenced by the excellent agreement with copper content values provided by the independent laboratory.

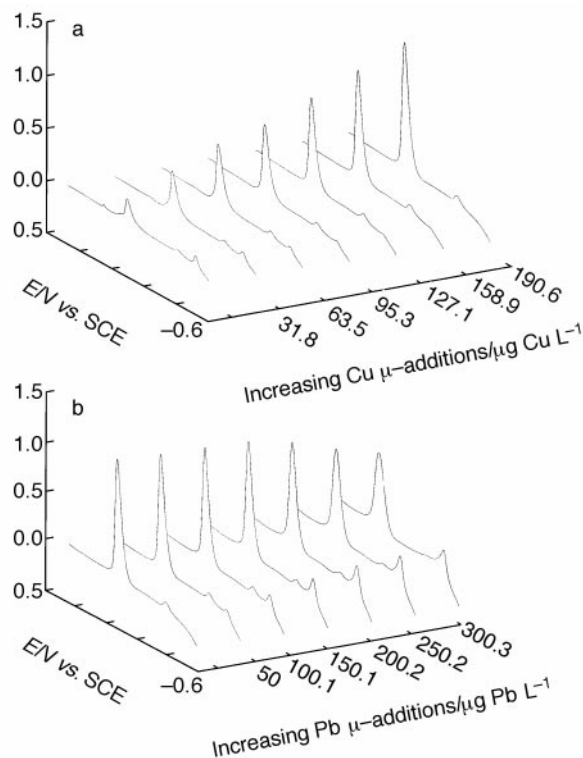


Fig. 5 Linear sweep voltammograms (50 mV s⁻¹) obtained in aqueous solutions of 0.1 M HNO₃, 0.5 μ M Pb²⁺ and: (a) after several micro-additions of copper (0 to 190.6 μ g Cu L⁻¹); (b) 190.6 μ g Cu L⁻¹ and several micro-additions of lead (0 to 300.3 μ g Pb L⁻¹). The deposition step was conducted for 120 s at -1.5 V vs. SCE under power ultrasound of intensity 200 W cm⁻² emitted from a horn probe placed at 5 mm opposite a 3 mm glassy carbon electrode.

4. Conclusions

Sono-ASV has been shown to be an effective electroanalytical technique to determine total copper contents in dirty media using both mercury thin film and unmodified glassy carbon electrodes. Both electrodes give excellent agreement with values obtained using atomic absorption spectroscopy conducted by an independent laboratory. In the absence of ultrasound, electrode passivation by organic species and lower rates of mass transport prevent the observation of any measurable signals. *In situ* cavitation cleaning of the electrode by insonation maintains the electrode activity and is fundamental to the success of the experiment.

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