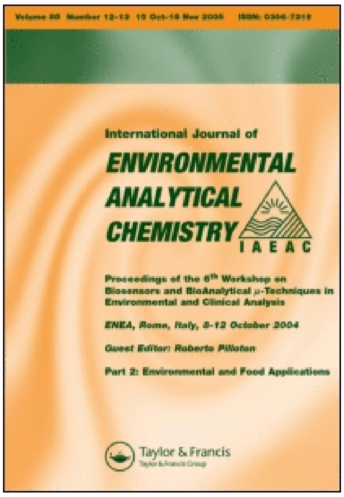

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Anodic stripping voltammetry: sn and pb analysis in archaeometallurgical samples

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**To cite this Article** Dirilgen, Neylan and Dogan, Fulya(2004) 'Anodic stripping voltammetry: sn and pb analysis in archaeometallurgical samples', International Journal of Environmental Analytical Chemistry, 84: 11, 855 — 864

**To link to this Article: DOI:** 10.1080/03067310410001730637

**URL:** http://dx.doi.org/10.1080/03067310410001730637

*Intern. J. Environ. Anal. Chem.*
Vol. 84, No. 11, pp. 855–864, 15 September 2004

# ANODIC STRIPPING VOLTAMMETRY: Sn AND Pb ANALYSIS IN ARCHAEOMETALLURGICAL SAMPLES

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*(Received 26 December 2002; In final form 5 March 2003)*

In most electrolytes the peak potentials of tin and lead are so close together that a voltammetric determination is impossible. Difficulties occur especially if one of the metals is present in excess. The simultaneous anodic stripping voltammetric analyses of lead and tin in ancient archaeometallurgical samples have been studied. Two different electrolytes were used; cetyltrimethylammonium bromide in a mixture of citrate and oxalate buffer, and methylene blue in oxalate buffer. Cetyltrimethylammonium bromide was found to be unsuitable for the determination of tin; the tin peak was asymmetric and often split. Methylene blue was studied at pH values of 1.35, 1.60, 1.80, 2.00, 2.68, 3.00 and 3.15. Differential pulse voltammograms were obtained between $-800$ mV and $-250$ mV. It was concluded that as pH was increased the corresponding half-wave potentials, $E_{1/2}$, for tin and lead were shifted to more negative values and the sensitivity of the simultaneous determination of tin and lead was decreased. However, tin and lead concentrations could be determined simultaneously in oxalate buffer and in the presence of methylene blue at about pH 1.6.

*Keywords:* Anodic stripping voltammetry; Archaeometallurgy; Tin; Lead; Methylene blue; pH effect

## INTRODUCTION

The most commonly used methods for determining trace amounts of tin include electrothermal atomic absorption spectrometry (ETAAS) [1], AAS with hydride generation [2] and electroanalytical methods, such as polarography and stripping voltammetry [3–5]. The determination of tin by voltammetric and polarographic methods in the presence of lead is difficult because of the overlapping stripping peaks [6,7]. The relatively narrow potential range over which tin and lead are oxidized makes it difficult to resolve the responses of these metals. Several reports have been published on the simultaneous determination of lead and tin. Voltammetric determination of lead and tin was performed in a wide range of supporting electrolytes, strong acids and buffers at various pH values [7]. Lead could be determined in a citrate buffer at pH 5.8 without interference from tin species (II or IV) whereas tin (IV) could be determined only in 0.1 M HCl.

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310410001730637

Also, the optimum conditions for the determination of lead, tin and molybdenum were reported to be the ethylenediaminetetraacetic acid–sodium acetate electrolyte at pH 3.5 [6]. The medium-exchange procedure was another method that was introduced to improve the selectivity of stripping analysis. It was reported that the mutual interference of tin and lead could be minimized by using a citrate buffer at pH 3.9 [8], a solution of methanol–isopropanol (50 : 50) containing 1 M hydrochloric acid [9], and a 0.1 M sodium tartarate solution at pH 3 [10]. Also, the polarographic behavior of tin and lead in the presence of the surfactant Hyamine-2389 was studied [11]. Surfactants can change the peak potentials for electroactive species and it is known that they suppress the stripping current peaks of metals deposited on a mercury electrode [12]. However, a cationic surfactant such as cetyltrimethylammonium bromide (CTAB) was reported to improve the sensitivity and the resolution of peaks in the determination of tin and lead [13].

The goal of the present work is to carry out voltammetric analyses on early metallurgical finds from 4000–1700 BC which were excavated in North Central Anatolia, Turkey. The metals which have given their names to various periods in human history have been analyzed by physical and chemical methods. These analyses reveal details of the objects such as where, how and from which metal they were made and the ore source used to manufacture them. As a result, information can be gained on the technological and cultural stage of the ancient society which manufactured the artifact. Tin and arsenic alloying with copper, cupelling silver from lead and smelting lead were the common techniques used in Prehistoric Anatolia. Since, tin was one of the metals that was known and used in antiquity along with copper, silver, gold, lead, mercury and later iron, its accurate and rapid quantitation is very important. The present work aims to deal with the chemical aspect of the problem rather than its archaeometallurgical aspect.

Anodic stripping voltammetry provides high selectivity and low detection limits. No analogous work has been reported for simultaneous determination of tin and lead in metallurgical samples.

## EXPERIMENTAL

Two different methods were applied for the simultaneous determination of tin and lead. The first method involved the addition of cetyltrimethylammonium bromide (CTAB) to a mixture of citrate and oxalate buffer and the second method used the addition of methylene blue to an oxalate buffer.

### Apparatus

A Metrohm Model 757 VA Computrace Analyzer (Metrohm Ltd., Switzerland) was used. A typical three-electrode system consisted of a platinum wire auxiliary electrode, a saturated Ag/AgCl reference electrode and a hanging drop mercury working electrode (HDME). The pH values were measured with a WTW model pH meter (WTW-GmbH, Germany).

## Reagents and Standard Solutions

All reagents were of the purest quality possible (analytical grade or suprapur). Only ultrapure water was used.

### *CTAB Method*

Hydrochloric acid (HCl) 30% w/v, base electrolyte at a pH value of 2.5 (trisodium citrate dihydrate 0.1 mol/L, oxalic acid monohydrate 0.1 mol/L, HCl 0.2 mol/L) and CTAB solution 0.005 mol/L were used.

### *Methylene Blue Method*

Hydrochloric acid (HCl) 30% w/v, base electrolyte (di-ammonium oxalate monohydrate 0.14 mol/L, ammonium chloride 0.17 mol/L, HCl 0.15 mol/L) and methylene blue solution 0.1 g/L were used. Stock standard lead solution (1 g/L) was ready to use $Pb(NO_3)_2$ from Metrohm. Stock standard tin solution (1 g /L) was prepared by dissolving 1.000 g of tin metal in 100 mL concentrated HCl. Tin stock solution was heated to 60°C, cooled and diluted to 1 L.

Method parameters were optimized with a reference sample, B.C.S. 18/3 which was composed of Cu 84.5, Sn 6.69, Pb 3.40, Zn 3.25, Ni 1.52, As 0.15, Sb 0.25, Bi 0.008 and Fe 0.028%. B.C.S. 18/3 was purchased from the British Chemical Standards, Bureau of Analytical Samples Ltd., England.

## Sample Preparation

Archaeometallurgical samples were classified into four main groups; weapons, tools, jewelry and emblems. Each group contained various objects. The first included spearheads, daggers and arrowheads; the second contained blades, axes, harpoons, needles and fishing hooks; jewelry consisted of necklaces, rings, beads, bracelets and hairpins. Samples were treated in two main categories as ore–slag samples, and as metallic samples.

### *Ore–Slag Samples*

About 20 mg of samples were ground to 200 mesh (75 μm) in a Teflon beaker. A mixture of $HClO_4$ and HF in 1 : 3 (v/v) ratio was added and heated to dryness on a hot plate. 5 mL of aqua regia were added, the Teflon beaker was covered with a watch glass and heated on a hot plate for about 20 min. The solution was diluted to 50 mL with 6 M $HNO_3$. A 1-mL aliquot of solution was pipetted and made up to 100 mL with ultrapure water.

At high concentrations of electroactive species, overcharging phenomena such as non-linear standard addition curves or splitting into multiple peaks occurred. They were due to the enrichment of species at polarized electrodes. Dilution factor was determined by trial and error.

### *Metallic Samples*

About 15–20 mg samples were drilled out and put into a beaker. They were dissolved by the addition of 5 mL of aqua regia and the beaker was covered with a watch glass. The resulting solution was diluted to 50 mL with 6 M $HNO_3$. A 1-mL aliquot of solution was pipetted and made up to 100 mL with ultrapure water.

### *B.C.S. 18/3 Standard Sample*

A 34.7 mg sample was drilled out and put into a beaker. The digestion procedure and the dilution factor were the same as for the metallic sample and ore–slag sample treatments. The standard sample solution yielded a tin concentration of 23.21 μg/L and a lead concentration of 11.79 μg/L.

## Voltammetric Measurements

### *CTAB Method*

5-mL aliquots of each diluted sample solution and a base electrolyte were transferred into the voltammetric cell. After the addition of 0.05 mL of CTAB, the solution was deaerated by bubbling ultrapure nitrogen for 300 s. The differential pulse voltammograms were obtained between −800 mV and −300 mV with the following parameters: deposition potential −700 mV, deposition time 90 s, equilibration time 20 s, pulse amplitude 50 mV, voltage step 4 mV, voltage step time 0.2 s, sweep rate 20 mV/s. The corresponding peak potentials for tin and lead were expected to be at −550 mV and at −420 mV, respectively. The detection limit was 1 μg/L for lead and 2 μg/L for tin.

### *Methylene Blue Method*

5-mL aliquots of each diluted sample solution and a base electrolyte were transferred into the voltammetric cell. After the addition of 5 mL of methylene blue, the solution was deaerated by bubbling ultrapure nitrogen for 300 s. The differential pulse voltammograms were obtained between −800 mV and −250 mV with the following parameters: deposition potential −580 mV, deposition time 20 s, equilibration time 20 s, pulse amplitude 50 mV, voltage step 4 mV, voltage step time 0.2 s, sweep rate 20 mV/s. The corresponding peak potentials for tin and lead were expected to be at −540 mV and at −400 mV, respectively. The detection limit was 1 μg/L for both lead and tin.

Lead and tin concentrations were determined by standard addition using both the CTAB and methylene blue methods. Additions were made with 0.05 mL of stock lead and tin solutions at concentrations of 5 mg/L and 3 mg/L, respectively. Also, standard additions for the blank determinations were run with 0.05 mL of stock lead and tin solutions at concentrations of 0.50–0.75 and 0.25–0.50 mg/L, respectively.

## RESULTS AND DISCUSSION

The anodic stripping voltammetric curve of a model archaeometallurgical sample solution for tin and lead determination in CTAB is shown in Fig. 1. The solution

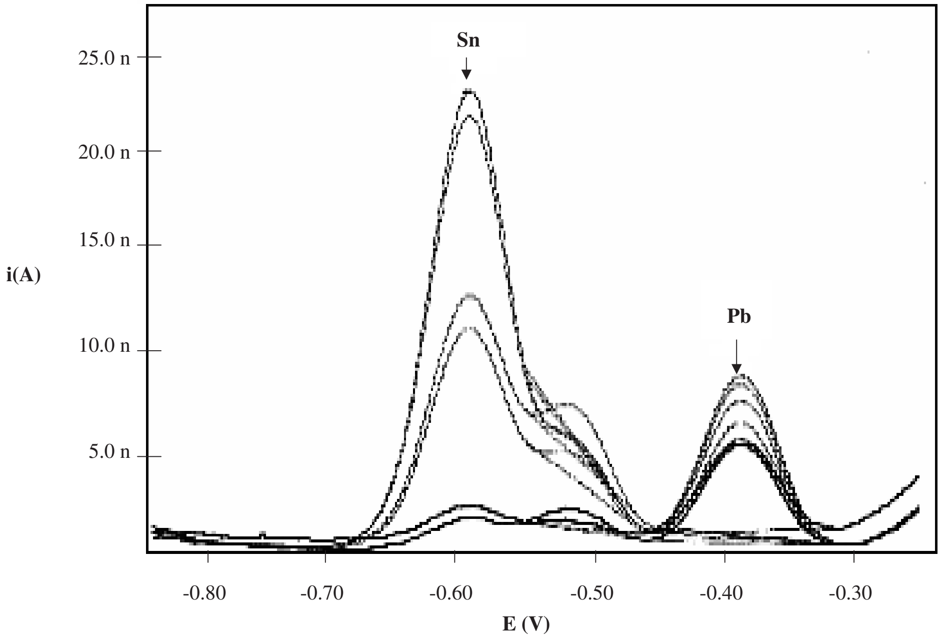

FIGURE 1 Voltammetric stripping curve of Sn (1.92 µg/L) and Pb (6.07 µg/L) in a model archaeometallurgical sample solution by the CTAB method.

matrix was Cu 85.50, Zn 1.50, Ni 0.33, Fe 0.47, Sb 0.54 and As 0.015%. Also, Sn 0.23% (9.62 µg or 1.92 µg/L) and Pb 0.72% (30.35 µg or 6.07 µg/L ) were present in the matrix. The corresponding pH value of the solution was 1.40. The voltammetric curve showed that peak currents appeared at approximately −600 mV and −418 mV for tin and lead, respectively. The standard addition method registered the blank-corrected lead concentration as 9.24 ± 1.05 µg/L, and the concentration of tin could not be determined. In general, in the presence of CTAB the rates of electrode reactions and the current signals are decreased; thus CTAB is usually considered to interfere in polarography and voltammetry. However, CTAB is a cationic surfactant and at negative potentials, owing to the formation of ion-pairs or micellar congregations in solution, a marked improvement in accumulation efficiency for the determination of titanium and vanadium was observed [14]. A similar enhancement effect in CTAB was observed using a mercury electrode [15]. Mendez *et al.* [13], reported sensitization of the simultaneous determination of tin and lead at a hanging drop mercury electrode in a 0.1 M hydrochloric acid–0.1 M oxalic acid medium in the presence of CTAB. In the present work, CTAB was found to be unsatisfactory for the determination of tin; the tin peak was asymmetric and often split. Modifying either the pH value or the deposition time did not improve the result. Faller *et al.* [5] reported that tin and lead peaks could be improved by displacement of the tin peak potential through formation of a complex compound with an organic reagent added to the electrolyte solution in the presence of various solid electrodes – a glassy carbon electrode, an ultra trace electrode and a disposable thick-film graphite electrode. However, many metal ions interfered with the sensitivity of the simultaneous determination of tin and lead in such an electrolytic media and these metal ions happened to be the main matrix constituents

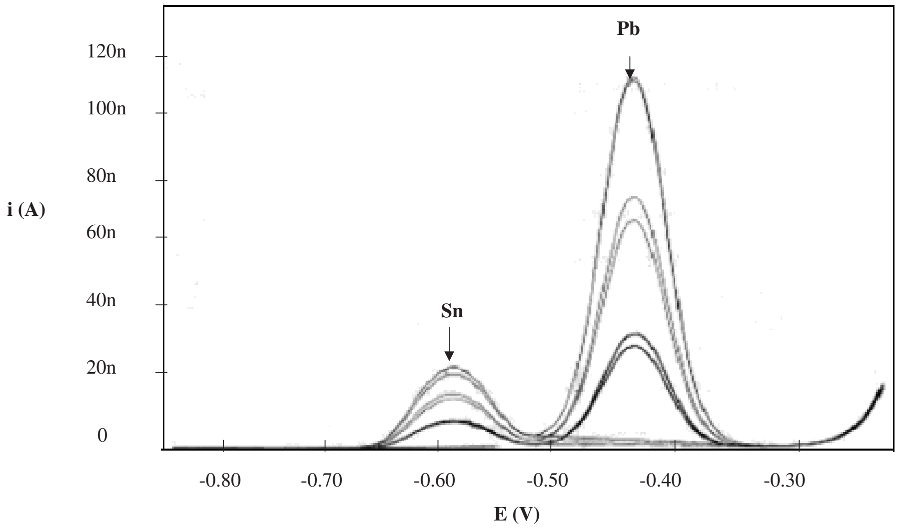

FIGURE 2 Voltammetric stripping curve of Sn (23.21 µg/L) and Pb (11.79 µg/L) in B.C.S. 18/3 sample at pH 1.6 by the methylene blue method.

of the archaeometallurgical samples (copper in major quantities, arsenic, zinc, antimony, iron, bismuth, cobalt, gold and nickel in trace quantities).

Figure 2 presents an anodic voltammogram of tin and lead deposited from the B.C.S. 18/3 at pH 1.6 with the methylene blue method. The peak currents appeared at approximately −584 mV and −443 mV for tin and lead, respectively. The standard addition method gave the blank-corrected concentration values for tin and lead as 22.92 ± 3.37 µg/L and 11.15 ± 2.21 µg/L, respectively. The voltammetric measurements were run three times each with two replications for the tin and lead determinations in B.C.S. 18/3 at pH 1.6. The 95% confidence intervals were 22.92 ± 3.54 µg/L for tin and 11.15 ± 2.32 µg/L for lead. The results were reproducible and a systematic error was absent. Hence, the precision and the accuracy of the method parameters were established.

The effect of pH on the resolution of peaks for tin and lead was evaluated by adjusting the oxalate electrolyte to pH values of 1.36, 1.80, 2.00, 2.68, 3.00 and 3.15 in B.C.S. 18/3 reference runs. The results are given in Table I. At pH 1.36, the resolution of tin and lead peaks was not sufficient to allow the precise determination of the corresponding concentration values and the alignment of base lines for sample and standard addition curves as either whole, front or rear peak did not yield further improvement in the results (Fig. 3). It was concluded that as pH was increased the corresponding values of half-wave potentials, $E_{1/2}$ for tin and lead were shifted to more negative values. Also, the observed concentrations of both tin and lead were registered to be much higher than the true ones. At pH 3.00 and 3.15, the actual tin peak in the blank runs completely disappeared, and the identity of the lead peak could not be established due to shifts in $E_{1/2}$ values.

Acetates, oxalates, tartrates and citrates are commonly used as supporting electrolytes in voltammetry. It was reported that the shape of potentiometric stripping signals was unaffected by the type of anion in the electrolyte in case of lead determination alone [7]. Also, the effect of pH was not significant in the acidic pH range while a

TABLE I Effects of pH on simultaneous determination of Sn and Pb in oxalate buffer in methylene blue

| | *Blank* | | | | *B.C.S. 18/3*[a] | | | | *Blank-corrected results* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *Sn* | | *Pb* | | *Sn* | | *Pb* | | *Sn* | *Pb* |
| *pH* | $E_{1/2}$ (V) | *Concentration* (μg/L) | $E_{1/2}$ (V) | *Concentration* (μg/L) | $E_{1/2}$ (V) | *Concentration* (μg/L) | $E_{1/2}$ (V) | *Concentration* (μg/L) | *Concentration* (μg/L) | *Concentration* (μg/L) |
| 1.36 | −0.546 | 5.82 ± 0.11 | −0.419 | 44.47 ± 1.08 | −0.538 | 34.15 ± 1.60 | −0.419 | 54.87 ± 2.75 | 28.33 ± 1.61 | 10.40 ± 1.67 |
| | −0.546 | | −0.423 | | −0.538 | | −0.419 | | | |
| | −0.546 | | −0.423 | | −0.542 | | −0.419 | | | |
| | −0.546 | | −0.423 | | −0.542 | | −0.419 | | | |
| | −0.546 | | −0.423 | | −0.542 | | −0.419 | | | |
| | −0.542 | | −0.423 | | −0.542 | | −0.419 | | | |
| 1.6 | −0.538 | 3.40 ± 0.41 | −0.419 | 29.57 ± 1.41 | −0.538 | 26.32 ± 3.37 | −0.419 | 40.72 ± 4.67 | 22.92 ± 3.37 | 11.15 ± 2.21 |
| | −0.538 | | −0.419 | | −0.538 | | −0.419 | | | |
| | −0.538 | | −0.419 | | −0.542 | | −0.419 | | | |
| | −0.538 | | −0.419 | | −0.542 | | −0.419 | | | |
| | −0.542 | | −0.419 | | −0.542 | | −0.419 | | | |
| | −0.542 | | −0.419 | | −0.542 | | −0.419 | | | |
| 1.8 | −0.562 | 3.40 ± 0.41 | −0.427 | 40.69 ± 0.78 | −0.562 | 34.76 ± 0.70 | −0.431 | 62.28 ± 1.61 | 31.36 ± 0.82 | 21.59 ± 1.34 |
| | −0.562 | | −0.431 | | −0.562 | | −0.431 | | | |
| | −0.562 | | −0.431 | | −0.562 | | −0.431 | | | |
| | −0.582 | | −0.431 | | −0.562 | | −0.431 | | | |
| | −0.582 | | −0.431 | | −0.562 | | −0.431 | | | |
| | −0.582 | | −0.431 | | −0.562 | | −0.431 | | | |
| 2 | −0.578 | 26.07 ± 1.10 | −0.439 | 37.89 ± 0.72 | −0.578 | 52.69 ± 1.47 | −0.439 | 51.28 ± 2.01 | 26.62 ± 1.84 | 13.39 ± 1.46 |
| | −0.582 | | −0.439 | | −0.578 | | −0.439 | | | |
| | −0.582 | | −0.443 | | −0.578 | | −0.439 | | | |
| | −0.582 | | −0.443 | | −0.578 | | −0.439 | | | |
| | −0.582 | | −0.443 | | −0.578 | | −0.439 | | | |
| | −0.582 | | −0.443 | | −0.578 | | −0.439 | | | |
| 2.68 | −0.613 | 26.39 ± 4.49 | −0.459 | 26.46 ± 1.45 | −0.609 | 60.34 ± 6.45 | −0.455 | 44.08 ± 0.806 | 33.95 ± 7.86 | 17.62 ± 1.29 |
| | −0.617 | | −0.459 | | −0.609 | | −0.455 | | | |
| | −0.613 | | −0.459 | | −0.605 | | −0.455 | | | |
| | −0.613 | | −0.459 | | −0.605 | | −0.455 | | | |
| | −0.609 | | −0.459 | | −0.605 | | −0.455 | | | |
| | −0.613 | | −0.459 | | −0.605 | | −0.455 | | | |
| 3.15 | | Not determined[b] | | Not determined[b] | | Not determined[b] | | Not determined[b] | Not determined[b] | Not determined[b] |

[a] Certified values were 23.21 μg/L Sn and 11.79 μg/L Pb.

[b] Tin peak disappeared, lead peak potential shifted.

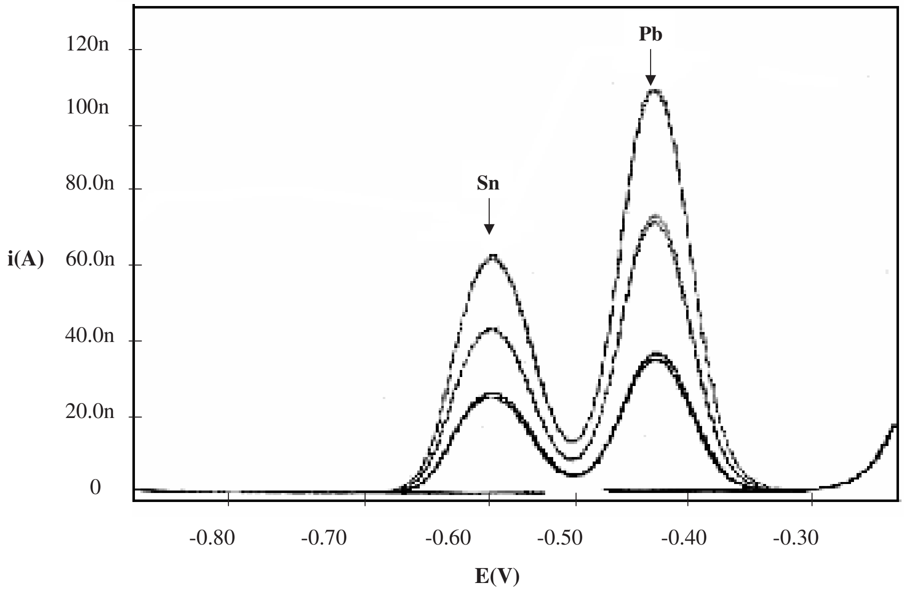

FIGURE 3 Voltammetric stripping curve for Sn (23.21 μg/L) and Pb (11.79 μg/L) in B.C.S. 18/3 at pH 1.36 by the methylene blue method.

decrease in sensitivity was observed in neutral and basic media in the presence of 0.1 mol/L $Na_2C_2O_4$, 0.1 mol/L tartaric acid plus 0.1 mol/L citric acid, 0.1 mol/L citrate buffer and 0.1 mol/L HCl. The influence of the electrolyte concentration and migration current on the deposition and stripping of lead were investigated by cyclic voltammetry at a microdisc electrode with and without addition of $KNO_3$ electrolyte. It was reported that both deposition and stripping were enhanced in the absence of added supporting electrolyte, relative to the case where 0.1 M $KNO_3$ has been added [16]. Also, in low ionic strength media neither deposition nor stripping currents varied in a simple manner with added supporting electrolyte. Hence, the anodic stripping voltammetry technique was subject to error when conventional calibration procedures were employed to minimize the unknown matrix problems. The cathodic stripping voltammetric method was developed for determination of lead with pyrogallol red on to a hanging mercury drop electrode. It was reported that tin at 10-fold, zinc at 400-fold, copper, manganese, iron and palladium at 100-fold, nickel and cadmium at 250-fold, nitrate, acetate, carbonate and silver at 1000-fold did not interfere with the determination of 20.0 ng/mL of lead [17]. Also, cathodic stripping voltammetry for simultaneous determination of lead and tin was studied in an acetic acid–ortho phosphoric acid–boric acid mixture, having a differential pulse voltammetric peak separation of 72 mV. Recently, bismuth-coated carbon electrodes have been developed and they offered comparable performance to mercury-film electrodes in anodic stripping voltammetry [18–20]. Detection limits of 1.1 and 0.3 μg/L lead were obtained on the glassy-carbon or carbon-fiber substrate. A comparison between the two electrodes in a solution containing 20 μg/L each of lead, cadmium and zinc in 0.1 M acetate buffer (pH 4.5) showed that the sensitivity for lead was better on the bismuth-film electrode than on the mercury-film electrode [21].

TABLE II Results from archaeometallurgical samples.

| *Sample ID* | *Samples* | *Pb* (μg) [a] | *Sn* (μg) [a] | *Pb* (%) | *Sn* (%) |
|---|---|---|---|---|---|
| 02/104 | spearheads | 0.00 | 0.00 | 0.00 | 0.00 |
| 02/105 | dagger | 8.89 ± 0.41 | 0.100 ± 0.004 | 0.12 | 0.013 |
| 02/106 | axe | 16.08 ± 1.09 | 4.55 ± 0.21 | 0.23 | 0.064 |
| 02/107 | axe | 9.28 ± 0.50 | 2.52 ± 0.08 | 0.076 | 0.018 |
| 02/108 | spearheads | 14.00 ± 1.10 | 5.48 ± 0.22 | 0.069 | 0.027 |
| 02/109 | spiral plaque | 17.67 ± 1.38 | 6.67 ± 0.34 | 0.10 | 0.038 |
| 02/110 | spearheads | 13.44 ± 1.17 | 2.58 ± 0.09 | 0.075 | 0.015 |
| 02/111 | spearheads | 12.90 ± 1.23 | 1.65 ± 0.04 | 0.076 | 0.010 |
| 02/112 | spiral plaque | 33.69 ± 2.56 | 3.09 ± 0.13 | 0.32 | 0.030 |
| 02/113 | spearheads | 15.52 ± 1.01 | 1.97 ± 0.09 | 0.19 | 0.025 |
| 02/114 | spiral plaque | 7.24 ± 0.43 | 3.07 ± 0.10 | 0.042 | 0.018 |
| 02/115 | earrings | 8.06 ± 0.63 | 0.48 ± 0.02 | 0.034 | 0.002 |
| 02/116 | earrings | 14.01 ± 1.25 | 23.85 ± 1.39 | 0.056 | 0.60 |
| 02/117 | spiral plaque | 10.88 ± 0.68 | 3.10 ± 0.11 | 0.059 | 0.017 |
| 02/188 | spearheads | 31.16 ± 2.88 | 4.70 ± 0.16 | 0.14 | 0.021 |
| 02/189 | dagger | 30.35 ± 2.49 | 9.45 ± 0.43 | 0.72 | 0.23 |
| 02/190 | spearheads | 124.90 ± 8.98 | 2.42 ± 0.03 | 0.86 | 0.017 |

[a] Mean values of three measurements.

In case of tin alone in solution, it was reported that the sensitivity of determination decreased with increasing pH of media; sensitivity attained a minimum in neutral solutions [5]. In an acetate buffer at pH greater than 4, hydroxide ions involved in tin ionization; $Sn(OH)_4$, $HSnO_2^-$, $HSnO_3^-$ and $SnO_4^-$ were formed depending on the pH of the solution. Consequently, the potential of the tin electrodissolution current maximum was displaced toward more negative potentials compared to the potential of the lead peak. It was reported that under these conditions separation of tin and lead responses was possible by using solid modified electrodes [5].

The results of the present work for the simultaneous voltammetric measurements of tin and lead in various ancient archaeometallurgical samples are presented in Table II. They are the mean values of three measurements. From the experimental results it is concluded that tin has a stable and well-defined peak in oxalate buffer in presence of methylene blue at about pH 1.6, and that tin and lead concentrations can be determined simultaneously. The experiments showed that tin oxalate and methylene blue could form an adsorptive ionic complex at the dropping or hanging dropping mercury electrode surface [22]. Since, methylene blue shows adsorption, the ionic complex of methylene blue and tin oxalate were adsorbed on the mercury surface and changed the surface tension of the mercury drop. Accordingly, a sensitive peak resulted from the reduction of tin(IV) to tin(II) and further reduction of tin(II) to tin(0). The possible mechanism was [22]:

$$\text{(Methylene blue)}^+\text{–Sn(IV)} \rightleftharpoons \text{(Methyleneblue)}^+ - \text{Sn(IV)ads}$$

$$\text{(Methyleneblue)}^+\text{–Sn(IV)ads} + 2e^- \rightleftharpoons \text{(Methyleneblue)}^+\text{–Sn(II)}$$

$$\text{(Methyleneblue)}^+\text{–Sn(II)} \rightleftharpoons \text{(Methyleneblue)}^+\text{–Sn(II)ads}$$

$$\text{(Methyleneblue)}^+\text{–Sn(II)ads} + 2e^- \rightleftharpoons \text{(Methyleneblue)}^+\text{–Sn(0)}$$

## CONCLUSION

Archaeometallurgists investigate metal objects and the byproducts of metallurgical activities to understand the technological ability of the early metallurgists. The present work demonstrates that tin and lead can be analyzed in archaeometallurgical samples by anodic stripping voltammetry at HMDE in the presence of oxalate electrolyte and methylene blue. The method was characterized by reproducibility and convenience in sample preparation. The chemical analyses of the excavated objects revealed that the tin content was very low, and therefore arsenic alloying with copper might have been the context of metalworking. Hence, voltammetric measurements for arsenic determination in archaeometallurgical samples will be investigated in future work.

### *Acknowledgements*

The authors wish to thank Prof. Dr. Hadi Özbal and Bilge Gedik for their valuable cooperative work. This work is supported by Boğaziçi University Fund, Project Number 01S102.

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