# Determination of Lead in Ice by Stripping Potentiometry

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**ABSTRACT**

In order to determine the amounts of lead in ice by stripping potentiometry, the 400 µl matrix modifying solution was added to an ice sample of total volume 30 ml in an electrochemical cell. The modified solution was 800.00 mg/l Hg(II) in 1.30 M hydrochloric acid. The working electrode was a glassy carbon disc, with Ag/AgCl as a reference electrode, and a platinum rod as a counter electrode. Stripping potentiometry was used on sample solutions and standard solutions which were electrolyzed for 3 min at −1.00 V. The peak potentials were set around −0.38 to −0.42 V. The concentrations of lead (II) standards were 0.10, 0.40, 0.70 and 1.00 µg/l. The calibration plot between peak areas and concentration of lead (II) standards was obtained with a correlation coefficient of 0.9969. A detection limit of 0.023 µg/l or 23.00 ng/l (3SD) was shown with a precision of 5.50 % RSD for a 2.0 µg/l standard (n = 5). The percentage recovery was found to be 95.50 %. The concentration range of lead (II) in ice samples was determined to be 0.09 to 0.53 µg/l.

**Keywords:** Lead, ice, stripping potentiometry, mercury film

## INTRODUCTION

Lead is a metallic chemical element; symbol Pb [Lat. *plumbum*]. One of the oldest metals used by humanity, lead was known to the ancient Egyptians and Babylonians. The Romans used it for pipes and in solder. It was one of the first metals mined in North America, where it was sought after especially for making shot. Continuing sources of environmental lead include water that has passed through old lead pipes, paint in older buildings, lead improperly disposed of in public landfills, and industrial sources such as mining, smelting, and recycling processes necessary to produce lead for batteries and other products. Drinking water can sometimes contribute to elevated blood-lead levels. All drinking water that does not come from wells is treated before it reaches the service line that directs the water to individual residences, thereby removing any lead that may be present in the water at its source. However, lead can still leach into drinking water from certain types of plumbing materials, such as lead pipes, lead solder, brass faucets and some water meter components. Chisholm et al. used ultra-clean procedures to measure an isotopic composition of < 1 pg of Pb in Polar snow and ice in Greenland and the Antarctic [1]. Boutron and co-workers have directly measured by laser excited atomic fluorescence spectrometry down to the pg/g level in the Antarctic core [2]. In addition, Doring and co-workers have used ICP-MS (Inductively Coupled Plasma Mass Spectrometry) to determine the concentration and isotopic ratios of lead in snow in Switzerland [3].

The determination of heavy metals in ice and beverages can be investigated by spectrometric techniques, in both absorption and emission and also by electroanalytical techniques. In recent years, stripping chronopotentiometry (SCP) has been employed for trace and ultra-trace metal determinations in water, SCP is the current name for the technique formerly known as potentiometric stripping analysis (PSA) [4-6]. SCP is a two-step technique. The first step, named "preconcentration", involves electrolysis of the solution containing the metal ions which are amalgamated on the mercury-coated glassy carbon electrode. The second step, named "stripping", is a chemical re-oxidation of the deposited metals. Potential and time data are digitally derived and E is plotted versus dt/dE in order to increase both sensitivity and resolution of this analysis. The aim of this work was rapid analysis of a trace metal (Pb) in ice. This method was applied to the detection of lead in ice water. The advantage of this technique is the reduction in the time which is taken for analysis (only 5 min per sample). Moreover, this technique does not require the sample preparation needed for GFAAS (Graphite Furnace Atomic Absorption Spectrometry) which is based on a pre-concentration step or the complete destruction of the organic matrix, that often causes a severe loss of the trace metal.

## MATERIALS AND METHODS

All solutions were prepared with deionized water. The mercury chloride ($HgCl_2$) and hydrochloric acid were supplied by Merck (Germany). A stock solution of 800.00 mg/l $HgCl_2$ was made in 1.30 M hydrochloric acid. Standard lead (II) (Radiometer S.A.) solutions were prepared by diluting with deionized water and stored in polyethylene bottles.

Potentiometric measurements were performed with a PGSTAT100 (Eco Chemie/AUTOLAB), equipped with a conventional three-electrode cell. All measurements were performed without removing oxygen from the solution. A glassy-carbon electrode was used as the working electrode, a Ag/AgCl electrode in 3.00 M KCl was used as the reference electrode and a platinum wire as the counter electrode. The glassy carbon electrode was polished and rinsed with deionized water prior to analysis. The mercury coating on the glassy-carbon electrode was prepared "*in-situ*" at the beginning of each analysis. The mercury film was prepared electrolytically from a solution containing 800.00 mg/l mercury (II) ions in 1.30 M hydrochloric acid. A 30 ml standard lead (II) solution of 100.00 µg/l was put directly into the electrochemical cell and optimum conditions of electrolysis potential, electrolysis time and the volume of mercury for the analysis were derived from this study. The samples of ice were collected in different places from the drinking store in Walailak University, and stored in plastic bottles in order to prevent contamination from metal and glass. The sample preparation involved melting at room temperature for an hour. The aliquots of ice samples (30 ml) were placed directly in the electrochemical cell and the program for plating the electrode was started under the optimized conditions.

## RESULTS AND DISCUSSION

The study was performed in a solution which contained 3.33 mg/l mercury (II) ions in 1.30 M HCl. Optimum conditions were obtained at an electrolysis potential of −1.00 V in **Figure 1**, an electrolysis time of 3 min in **Figure 2** and a volume of mercury (II) ions of 400 µl in **Figure 3** at which the sharpest and highest signals and the highest reproducibility were found. After each analysis the potential was switched to −0.60 V for 60 s for a cleaning period. The stripping curve of the standard lead (II) solution at 0.10, 0.40, 0.70 and 1.00 µg/l is shown in **Figure 4** and the calibration curve is shown in **Figure 5**. The results obtained by the PSA are given in **Table 1**.
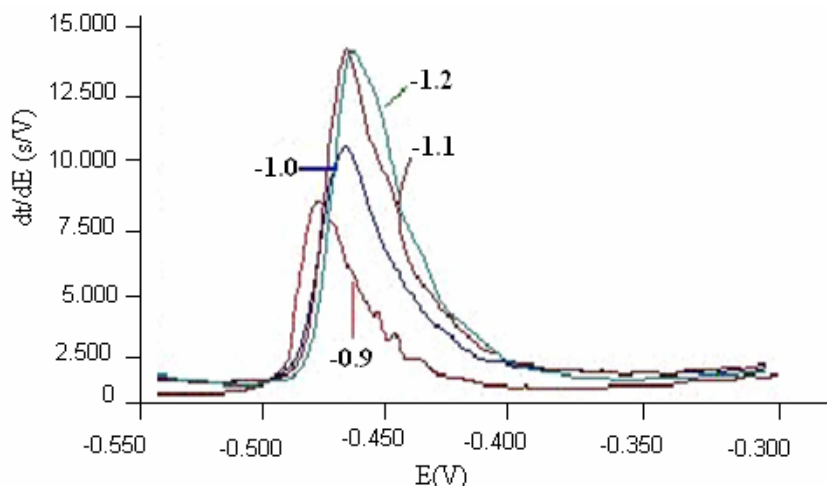
**Figure 1** The effect of varying the electrodeposition potential with a 100.00 μg/l Pb (II) standard solution.


In **Figure 1** the effect of varying the electrodeposition potential on the stripping curve is shown in **Figure 1** the stripping curve related to the lead determination in the standard solution is reported and the potential E (V) is shown by varying electrodeposition potential. It is found that, the more negative the accumulation potential the higher peak. At more negative potentials, lead was reduced more completely. Thus, the peak height increases. When the accumulation potential exceeds −1.10 V, the peak was not in the form of a Gaussian curve and it was unsymmetrical. Finally, −1.00 V was chosen as the accumulation potential for further measurements.
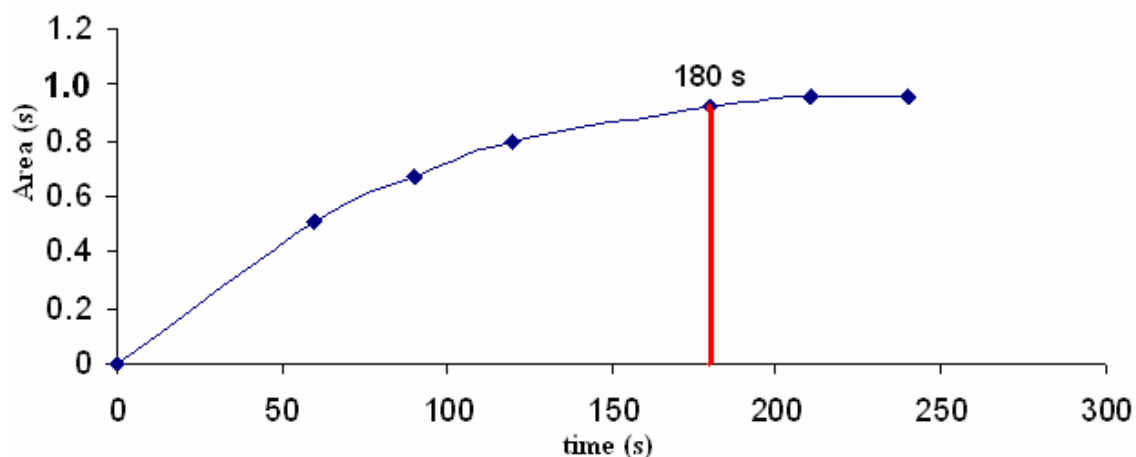


**Figure 2** The effect of varying the electrolysis time with a 100.00 μg/l Pb (II) standard solution.

The influence of electrolysis time is shown in **Figure 2**. The longer electrolysis time will cause more reduction and will cause the peak area to increase. But when the electrolysis time was longer than 180 s, the peak area changed slowly. Thus, an electrolysis time of 180 s was selected in our experiments.
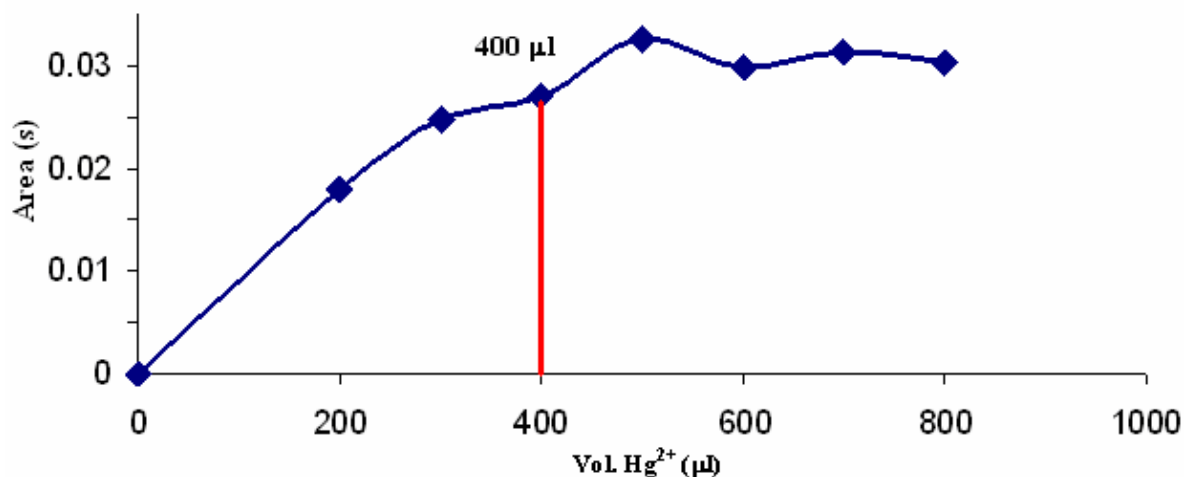


**Figure 3** The effect of varying the volume of the Hg (II) solution with a 100.00 μg/l Pb (II) standard solution.

The thickness of the mercury-electrode film affected the stripping response. The dependence of the peak area on the volume of $Hg^{2+}$ added to the glassy carbon electrode (GCE) surface was examined over the range 0 - 800 μl (**Figure 3**). It is clear that the peak at 500 μl had the highest peak area. But it has lower reproducibility than the peak at 400 μl. Thus, in our experiment, the mercury-electrode films were prepared using 400 μl of $Hg^{2+}$.

**Figure 4** shows the stripping potentiograms recorded in derivative standard by adding increasing concentration of $Pb^{2+}$ with a mercury ion volume of 400 μl. The electrodeposition time and electrodeposition potential were fixed at 3 min and −1.00 V, respectively. The lead was oxidized at approximately −400 mV.
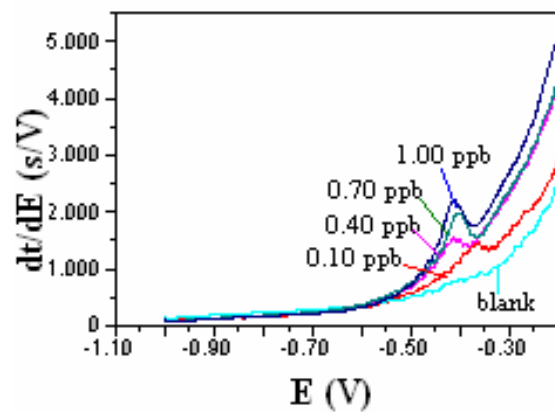
**Figure 4** Potentiogram of the lead (II) standard solution; accumulation potential −1.00 V, accumulation time 3 min, amount of $Hg^{2+}$ 400 µl.
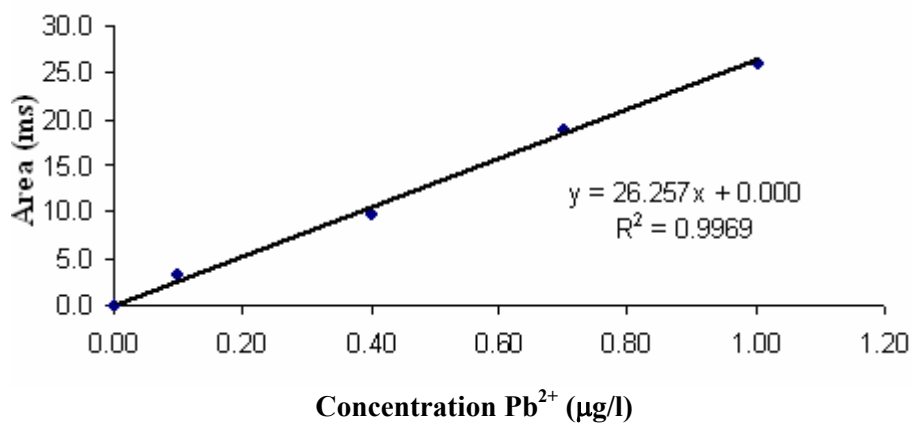


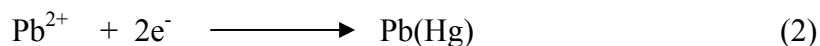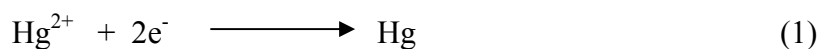**Concentration Pb$^{2+}$ (µg/l)**

**Figure 5** The calibration curve of lead (II) standard solution.

**Table 1** Concentration of lead in the ice samples as determined by PSA.

| Sample | Concentration (µg/l) |
|--------|----------------------|
| B1 | $0.22 \pm 0.01$ |
| B2 | $0.10 \pm 0.01$ |
| S1 | $0.16 \pm 0.01$ |
| S2 | $0.21 \pm 0.01$ |
| S3 | $0.21 \pm 0.01$ |
| S4 | $0.51 \pm 0.02$ |
| S5 | $0.53 \pm 0.03$ |
| S6 | $0.23 \pm 0.01$ |
| S7 | $0.18 \pm 0.01$ |
| S8 | $0.09 \pm 0.01$ |
| S9 | $0.14 \pm 0.01$ |
| S10 | $0.21 \pm 0.01$ |
| S11 | $0.40 \pm 0.01$ |
| S12 | $0.43 \pm 0.05$ |

Using a working electrode consisting of a material insoluble in mercury with a high hydrogen overvoltage, a sample containing mercury (II) ions and mercury soluble lead ions ($Pb^{2+}$), the reactions are shown in the following equations:

$$Hg^{2+} + 2e^- \longrightarrow Hg \tag{1}$$

$$Pb^{2+} + 2e^- \longrightarrow Pb(Hg) \tag{2}$$

$$Pb(Hg) - 2e^- \longrightarrow Hg + Pb^{2+} \tag{3}$$

The reactions will occur simultaneously by keeping the electrode surface small, in order to decrease lead concentration, but will occur very slowly.

The effect of the linearity of the analytical signal on the lead PSA was examined for mass concentrations in the range of 0.10 - 1.00 µg/l. From the obtained high values of the correlation coefficient 0.9969, relative standard deviation was 5.50 % and the detection limit (3SD) was 0.023 µg/l. The percentage recovery was found to be 95.50 %. The concentration range of lead (II) in ice samples was found to be 0.09 to 0.53 µg/l. This method works in non-deoxygenated solution because the potential to deposit was not more than $-1.20$ V. Nevertheless, when mercury (II) is used as an oxidizing agent, it must be added to the working solution just at the end of the deposition period, in order not to disturb the chemical equilibrium in the solution. As the stability of thin mercury film electrode is very good, the sensitivity of the method can be established before beginning the analysis.

## CONCLUSIONS

Potentiometric stripping analysis has been successfully applied to the determination of trace amounts of lead in ice with acceptable accuracy and precision. The proposed method is inexpensive and fast. The levels found are not harmful to consumers.

## ACKNOWLEDGEMENTS

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## บทคัดย่อ

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**การวิเคราะห์ตะกั่วในน้ำแข็งโดยวิธีวัดศักย์ไฟฟ้าคืนรูป**

การวิเคราะห์ตะกั่วในน้ำแข็งด้วยวิธีวัดศักย์ไฟฟ้าคืนรูป โดยการเติมสารละลายปรับสภาพ 400 ไมโครลิตร ลงในสารละลายตัวอย่างน้ำแข็ง 30 มิลลิลิตร ที่อยู่ในเซลล์เคมีไฟฟ้า ซึ่งสารละลายปรับสภาพที่ใช้ คือ เมอร์คิวริก คลอไรด์เข้มข้น 800.00 มิลลิกรัมต่อลิตรในสารละลาย 1.30 โมลาร์ของกรดไฮโดรคลอริก การวิเคราะห์นี้ใช้กลาสสิ-คาร์บอนเส้นผ่านศูนย์กลาง 3 มิลลิเมตรเป็นขั้วไฟฟ้าทำงาน ซิลเวอร์-ซิลเวอร์คลอไรด์เป็นขั้วไฟฟ้าอ้างอิง และลวดทองคำขาวเป็นขั้วไฟฟ้าช่วย โดยให้ศักย์ไฟฟ้าในขั้นอิเล็กโตรไลซิสนาน 3 นาที ที่ -1.00 โวลต์ พบว่า ศักย์ไฟฟ้าคืนรูปของตะกั่วอยู่ในช่วง -0.38 ถึง -0.42 โวลต์ และมีกราฟมาตรฐานของตะกั่วในช่วงความเข้มข้น 0.10 - 1.00 ไมโครกรัมต่อลิตร ค่าสัมประสิทธิ์สหสัมพันธ์มีค่า 0.9969 ความสามารถในการตรวจวัดต่ำสุดเท่ากับ 0.023 ไมโครกรัมต่อลิตร หรือ 23.00 นาโนกรัมต่อลิตร (3SD) ที่ค่าความแม่นยำเท่ากับ 5.50 ของค่าร้อยละของค่าเบี่ยงเบนสัมพัทธ์ สำหรับความเข้มข้นของสารละลายมาตรฐานตะกั่ว 2.00 ไมโครกรัมต่อลิตร (n = 5) และร้อยละการกลับคืนเท่ากับ 95.50 จากการวิเคราะห์สารตัวอย่างพบว่ามีความเข้มข้นของตะกั่วในน้ำแข็งจาก 0.09 ถึง 0.53 ไมโครกรัมต่อลิตร

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