

Reductive Galvanic Stripping Determination of Lead

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The feasibility of the determination of trace elements by anodic pre-concentration and subsequent reductive galvanic stripping is demonstrated using the determination of lead as an example. The technique is suitable for the determination of lead in the $\mu\text{g l}^{-1}$ range.

Keywords: Reductive galvanic stripping analysis; lead determination; platinum electrode

Cathodic stripping voltammetry (CSV) involves the anodic pre-concentration of analyte species followed by a linear cathodic potential scan.¹ During the cathodic reduction, the current flow between the working and counter electrodes is measured. However, this current consists of both capacitance and Faradaic components, of which only the latter is useful for analytical purposes. As in anodic stripping voltammetry (ASV), attempts to isolate the Faradaic current from the capacitance current have resulted in the introduction of sophisticated electroanalytical techniques such as normal pulse (NP) CSV,² differential pulse (DP) CSV³ and staircase stripping (SS) CSV.³

Recently Jagner⁴ described the technique of potentiometric stripping analysis (PSA), which is based on the chemical stripping of pre-concentrated elements using mercury(II) as an oxidant. This technique has been shown to be reliable and has several advantages over conventional ASV. Lead and manganese have been determined by anodic pre-concentration on to a platinum electrode, followed by chemical stripping using hydroquinone or pyrogallol.⁵ This technique was termed reductive potentiometric stripping analysis (RPSA). This paper reports the development of an electroanalytical technique, reductive galvanic stripping analysis (RGSA), which involves the pre-concentration of the analyte by anodic oxidation followed by stripping in an open-circuit position (OCP). An extension of the anodic stripping technique using a galvanic stripping method has been reported previously.⁶ In OCP mode, anodically pre-concentrated lead is stripped by a localised galvanic couple formation in the absence of any external electrical input or chemical reductant. The determination of lead by anodic deposition as lead dioxide and cathodic stripping voltammetry has been described by several workers.⁷⁻¹⁰ In this paper the determination of lead using a platinum working electrode is discussed as an illustrative example of the principles of the technique. This technique has also been found to be useful in the determination of manganese.¹¹

Experimental

Reagents

All solutions were prepared by dissolving analytical-reagent grade reagents in conductivity water.

A lead(II) solution (0.01 M) was prepared by dissolving 0.3312 g of lead nitrate in water and diluting to 100 ml. This stock solution was diluted with water as required.

Acetate buffer (1.0 M) was prepared by dissolving 12.6 g of sodium acetate and 6 ml of glacial acetic acid in 80 ml of water and diluting to 100 ml. The pH was adjusted to 5.

Apparatus

A conventional three-electrode cell with a platinum disc working electrode (JMC, 0.38 cm²), a bright platinum foil (12 cm²) counter electrode and a standard calomel reference electrode (SCE) was used.

A Wenking Model LB 75 M potentiostat coupled with a Wenking scan generator (Model VSG 72) was used.

An $X - Y/t$ recorder (Digitronic Model 2000) was used to record the potential - time ($E - t$) profiles. All the potentials were expressed with respect to SCE and the experiments were carried out at about 60 °C.

Procedure

To a 50-ml calibrated flask containing 5×10^{-8} – 1×10^{-5} M lead, add 5 ml of acetate - acetic acid buffer (pH 5) and dilute to the mark with water. Transfer the solution into the voltammetric cell and de-aerate with high purity nitrogen for 10 min. Electrolyse the solution at +1.4 V vs. SCE for 4 min at 60 °C (stirring the solution with a magnetic stirrer) in order to pre-concentrate the lead on to the platinum disc electrode as lead dioxide. Immediately after the completion of electrolysis, plot the $E - t$ profiles by recording the working electrode potential vs. SCE with time by switching over to the OCP (the E_r mode of the potentiostat). Draw a calibration graph by plotting the time required for galvanic stripping against the concentration of lead in solution.

Results and Discussion

Characteristics of $E - t$ Profiles

The feasibility of obtaining a reductive stripping signal for lead dioxide deposited on a platinum working electrode is demonstrated in Fig. 1. The typical $E - t$ profiles indicated in the

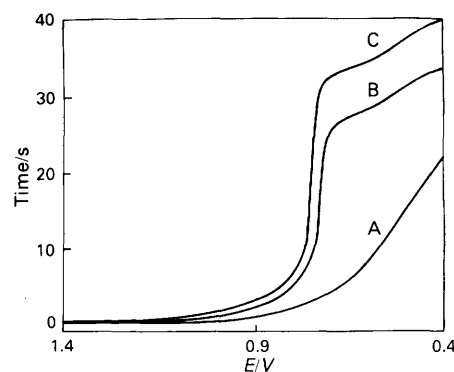


Fig. 1. Potential (E vs. SCE) - time profiles for A, 0.1 M acetate buffer and B and C, 5×10^{-6} and 1×10^{-5} M lead in acetate buffer. $E_d = 1.4$ V; $t_d = 4$ min; pH = 5

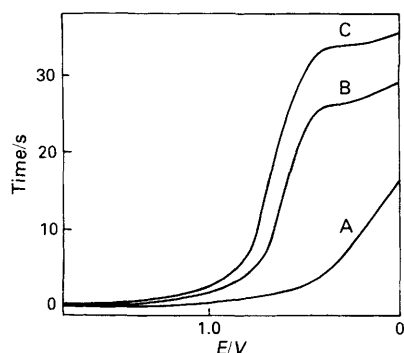


Fig. 2. Potential (E vs. Pt counter electrode) - time profiles for A, 0.1 M acetate buffer and B and C, 5×10^{-6} and 1×10^{-5} M of lead in acetate buffer. $E_d = 1.4$ V vs. SCE; $t_d = 4$ min; pH = 5

figure were recorded after an anodic pre-concentration at +1.4 V (vs. SCE) for 4 min in 0.1 M acetate buffer (pH 5). Lines A, B and C in the figure represent the $E - t$ profiles obtained when the potential changes of the working electrode vs. SCE were recorded in the E_r mode of the potentiostat for 0.0, 5 and 10 μ M concentrations of lead. It can be seen from Fig. 1 that the potential of the working electrode falls rapidly from 1.4 to 0.9 V (first break-point). A plateau is observed on the time axis, the length of which is proportional to the concentration of lead in solution. From the moment at which all the PbO_2 is reduced (the second break-point) the potential slowly drops further to the open circuit potential of the system (a Pt working electrode in 0.1 M acetate buffer, pH 5), i.e., +0.09 V. The time over which the plateau lasts is the time required for the stripping of the lead dioxide deposited earlier. The potential over which the plateau occurs (0.77–0.70 V) correlates well with the peak potential of the $\text{PbO}_2 - \text{Pb}^{2+}$ couple (0.74 V vs. SCE) obtained from the cathodic stripping voltammogram recorded under similar conditions in a separate experiment. This clearly indicates that PbO_2 dissolves as Pb^{2+} during the reductive stripping process, either in the presence of an applied potential sweep or in its absence.

Fig. 2 depicts the $E - t$ profiles obtained by following the changes in the potential of the working electrode (after PbO_2 deposition) against the counter electrode, under conditions similar to those described in Fig. 1. These graphs were recorded by connecting the working and counter electrodes directly to an $X - t$ recorder after disconnecting the potentiostat immediately after pre-concentration for 4 min at 1.4 V. As seen from Fig. 2, the potential of the working electrode drops immediately from 1.74 to 1.0 V. The $E - t$ graphs obtained in this instance are identical with those in Fig. 1 in that the plateau of the graphs are of the same length for both 5 and 10 μ M lead. Significantly, when the working and counter electrodes were connected externally through a sensitive ammeter, a current flow between the counter and working electrodes was observed during the plateau region of the stripping curves where reductive dissolution of PbO_2 occurs.

The following four observations, made in the absence of any externally added reagents that could react with PbO_2 , suggest the formation of a galvanic cell. (1) The attainment of the $E - t$ profiles of the working electrode either vs. SCE (Fig. 1) or the platinum counter electrode (Fig. 2) described above, in the absence of external polarisation. (2) The occurrence of a plateau on the time axis of the $E - t$ profiles. (3) A finite and constant current flow between the counter and working electrode in the plateau region. (4) The total charge passed during the reductive galvanic stripping is equal to the total charge passed during the anodic deposition of lead. This suggested galvanic cell is analogous to that set up during the dissolution of deposited cadmium from a mercury film⁶ and is presumed to provide the driving force for the observed $E - t$ responses as discussed below.

The dissolution of anodically deposited PbO_2 can also be thought of as being due to either the presence of reducing impurities or a chemical reaction with water. The former is ruled out by the fact that the magnitude of the stripping signal is unaffected by addition of 10^{-4} M hydroquinone and a change of rotation rate. Similar $E - t$ profiles are obtained in an electrolytically purified supporting electrolyte (i.e., by pre-oxidation). The possible chemical reduction of PbO_2 by water is insignificant under the experimental conditions employed as PbO_2 deposited anodically on a lead substrate remained stable even after 5–10 min in the OCP. A similar observation was reported by Kinard and Propst¹² during their studies of the OCP dissolution of PbO_2 deposited on a conducting glass electrode.

As noted earlier, the reaction occurring at the working electrode is the reduction of PbO_2 to Pb^{2+} in the plateau region. The coupling reaction of this reduction is identified as oxygen evolution at the platinum counter electrode (see Fig. 2), analogous with the hydrogen evolution reaction observed in galvanic stripping analysis.⁶ Thus, although the general $E - t$ profile pattern with the characteristic plateau region is indicative of a reductive galvanic stripping phenomenon in operation, the similar results shown in Fig. 1, in which the working electrode potential is recorded vs. SCE needs further investigation to be understood, as in this instance, the platinum counter electrode, the site for the galvanic coupling reaction, is disconnected from the circuit. Galvanic coupling can be envisaged even in this example by the formation of localised galvanic cells on the surface of the platinum working electrode (i.e., between the PbO_2 centres and the uncovered platinum surface sites constituting the necessary electrode pair for the galvanic cell), which provide the basis for the observed $E - t$ response. This proposition gains support from the facts that, (i) PbO_2 deposits as a non-uniform film; and (ii) a high impedance of the order of $10^{11} \Omega$ exists between the working and SCE electrodes in the E_r mode (thereby ruling out the possibility of current leakage through the reference electrode).

On the other hand, when the working electrode remains coupled to the counter platinum foil (as in Fig. 2) a galvanic cell is preferentially set up between them, thus shifting the site of anodic reaction to the counter electrode. This galvanic cell is due to the larger area of the counter electrode as compared with the uncovered area of platinum on the working electrode deposited with PbO_2 .

The performance of RGSA, i.e., the selectivity, accuracy, precision and detection limit, depends on a number of experimental parameters such as mode of electrode surface regeneration, temperature, the pH of the medium and the plating potential. The effect of these parameters on the procedure for the determination of lead are discussed below.

Electrode Regeneration

In order to obtain reproducible results for the determination of lead using RGSA, any oxide layer formed on the platinum electrode must be removed completely before each experiment. Various methods were attempted to achieve this. It was observed that treating the electrode with nitric or hydrochloric acid at room temperature for about 10 min was insufficient to regenerate the electrode surface. The recommended procedure involves the cathodic polarisation of the electrode at about 200 mV anodic to the hydrogen evolution potential in the given medium.⁵ The regeneration procedure was performed immediately after the stripping procedure until the cathodic current dropped to a stable value. This usually occurs after about 2–3 min.

Effect of Temperature

The re-dissolution of PbO_2 in the reductive galvanic stripping mode at room temperature is slow, with no clear break-points,

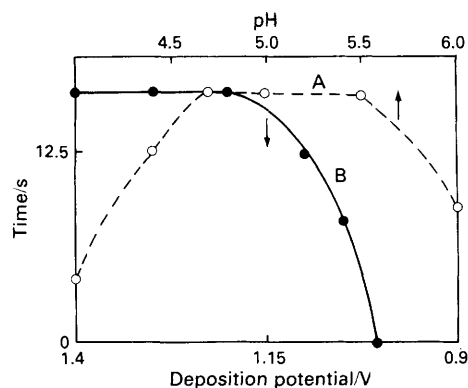


Fig. 3. Effect of pH (A) and plating potential (B) on the RGSA signal of 10^{-6} M lead. Conditions: pH 5, 0.1 M acetate buffer, $E_d = 1.4$ V vs. SCE, $t_d = 2$ min and temperature = 60°C

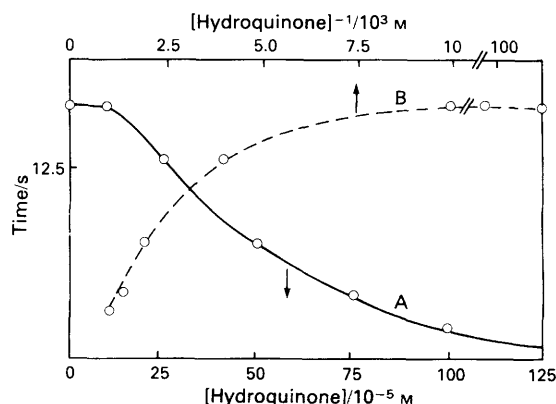


Fig. 4. Effect of hydroquinone (H_2Q) on the stripping signal of 10^{-6} M lead. Conditions: pH 5, 0.1 M acetate buffer, $E_d = 1.4$ V vs. SCE, $t_d = 2$ min and temperature 60°C . A, stripping signal vs. $[\text{H}_2\text{Q}]$ and B, stripping signal vs. $[\text{H}_2\text{Q}]^{-1}$

and the reproducibility of the stripping signal is also poor. At temperatures in the range $40\text{--}70^\circ\text{C}$, the quality and the reproducibility of the RGSA signal are improved significantly. The magnitude of the stripping signal reaches a maximum at a temperature of 50°C and remains constant with further increases in temperature up to 70°C . Hence subsequent experiments were carried out at *ca.* 60°C .

Effect of pH

The effect of pH on the deposition of PbO_2 and the subsequent reductive galvanic stripping analysis was studied using 10^{-6} M Pb^{II} , adjusting the pH of the acetate-buffered medium. The pH dependence of the RGSA signal vs. time of stripping is shown in line A of Fig. 3. It is clear from this figure that a constant and maximum signal is obtained in the pH range of 4.7–5.5, which decreases either on decreasing or increasing the pH beyond this range. Hence a pH 5.0 acetate buffer (0.1 M) was used in subsequent experiments.

Effect of Deposition Potential

The magnitudes of the RGSA signals obtained by the described procedure for a 10^{-6} M lead solution in 0.1 M acetate buffer (pH 5, 60°C) at various deposition potentials (2 min each) are shown in line B of Fig. 3. It is clear from Fig. 3 that the deposition of PbO_2 begins only when the deposition potential is above 1.0 V, *i.e.*, 0.25 V more positive than the dissolution potential of the $\text{PbO}_2\text{--Pb}^{2+}$ couple. The deposition reaches a maximum when the deposition potential is maintained above 1.2 V and then remains unaltered on further increases up to 1.4 V. Hence, for maximum deposition, the potential should

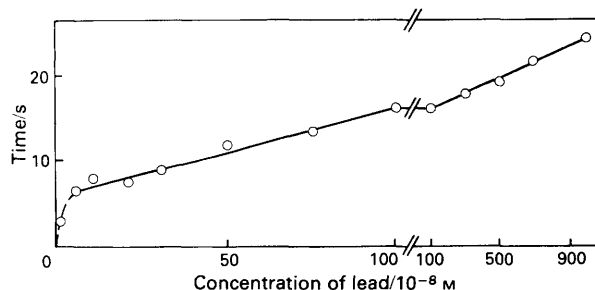


Fig. 5. Calibration graph consisting of two linear segments obtained for lead in $0\text{--}10^{-6}$ M solutions

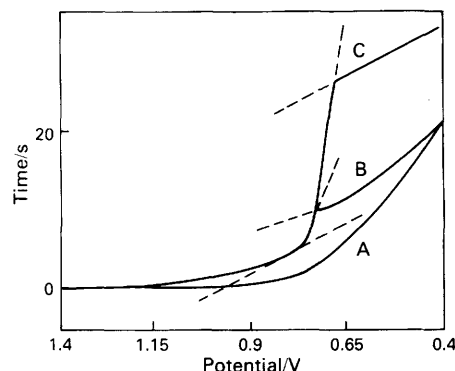


Fig. 6. Typical stripping profiles recorded for A, blank solution, B, solution containing 1×10^{-8} M and C, 5×10^{-6} M lead in solution

be at least 0.45 V more positive than the potential of PbO_2 dissolution.

Effect of Hydroquinone Concentration

Hydroquinone has been used as a reductant in RPSA.⁵ Hence, a study was carried out to investigate the effect of the addition of different amounts of hydroquinone on the reductive stripping signal. The results of the investigation (*e.g.*, line A, Fig. 4) show that in the presence of $\geq 10^{-4}$ M hydroquinone, chemical stripping of PbO_2 predominates. In more dilute solutions of hydroquinone, however, the presence of hydroquinone does not affect the stripping signal, as evidenced from the fact that identical signals were recorded both in the presence and absence of hydroquinone. This observation suggests that stripping of PbO_2 occurs by galvanic couple formation in these solutions. It is also seen from line B, Fig. 4, that the stripping does not occur entirely by chemical means even in the presence of $10^{-4}\text{--}10^{-3}$ M hydroquinone, as evidenced by the non-linearity of the graph.

Interference Studies

The effect of various cations, either singly or in combination, in the RGSA of Pb^{II} was examined by the addition of a 100-fold excess of each of these ions to 10^{-6} M Pb^{II} . Of the ions studied, *i.e.*, Cd^{II} , Co^{II} , Tl^I , Fe^{III} , Zn^{II} , Cu^{II} , Mn^{II} and Hg^{II} , only Hg^{II} and Mn^{II} were found to interfere.

Detection Limit, Precision and Calibration Range

The detection limit depends on the deposition time. Thus, a 2-min pre-concentration time for 10^{-8} M lead on Pt produces a significant signal, *i.e.*, twice the standard deviation of the background signal.

The precision of the technique was obtained by carrying out five successive experiments, each with a 2-min deposition time

and 10^{-6} M solutions of lead(II), as described under Procedure. The relative standard deviation was 1.5%.

The calibration graph (Fig 5.) was linear in the range 5×10^{-8} – 1×10^{-5} M Pb^{2+} in solution. Stripping profiles in typical dilute solutions of lead are shown in Fig. 6.

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