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Determination of trace levels of Pb(II) in tap water by anodic stripping voltammetry with boron-doped diamond electrode

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ABSTRACT: A simple and rapid method to determine traces of lead in the Hatyai city tap water by square wave anodic stripping voltammetry with boron-doped diamond (BDD) electrode has been studied. The parameters in the preconcentration steps studied included electrolyte influences, pH, concentrations, and volumes. Effective preconcentration of trace lead was achieved at pH 1.26. The appropriate electrolyte was found to be 0.2 M potassium nitrate (KNO_3) in 0.05 M nitric acid (HNO_3) to make all lead ionic. By scanning potential in the negative direction, the stripping peak was obtained at −0.460 V. Instrumental parameters including deposition potential, deposition time, scan rate, modulation amplitude, and equilibration time were optimized. The detection limit was found to be 0.3 µg/l. The accuracy was verified by analysing the standard reference material. Several interfering ions were studied and it was found that the method was not significantly affected by these coexisting ions and can be applied satisfactorily to lead determination in water samples. The results from determination of Pb^{2+} using the studied method and ICP-OES were compared and found to be in good agreement. The concentrations of lead in various water samples from eleven regions in Hatyai city were found to be in the range of 0.0–0.8 µg/l, lower than the drinking water contamination standard ($<$ 10.0 µg/l) issued by the World Health Organization.

KEYWORDS: voltammetry analysis, heavy metals, electrochemistry, square wave anodic stripping voltammetry

INTRODUCTION

Lead is a toxic heavy metal that appears in the environment mainly due to industrial processes. Lead pollution is one of the most serious environmental problems because of their stability in contaminated sites and the complexity of the mechanism for biological toxicity.

Hatyai city is an important travelling and business centre in the South of Thailand. Profits cause rapid development with the result of high population density in certain areas, increasing busy street traffic, and more air pollution from dust and Pb^{2+} exposure in the atmosphere from combustion[1]. Increasing dust and Pb^{2+} exposure causes widespread environmental contamination. The half-life of Pb^{2+} on the ground is about 90–100 years and it is not very soluble but the solubility can increase in clay acid conditions[2]. Drinking water can become contaminated by Pb^{2+}, either at the source due to deposition from environmental sources or in the water distribution system. A study of students aged 6–15 in primary schools in Pattani province revealed that the students of Municipality 3 School had elevated blood Pb^{2+} levels of over 25 µg/dl. Currently, the World Health Organization (WHO) limit is 10 µg/dl. These children live near boat plants where lead oxide is used to plug cracks of boat walls to prevent percolating water[3]. Effects of Pb^{2+} on the children's nervous system have been shown to reduce the IQ scale with the increased concentration in blood. In addition, consistent alterations were observed on attention, visual-motor reasoning skills, social behaviour, mathematics and reading abilities[4]. The biological half-life of lead in bone is more than 20 years[5]. The Environmental Protection Agency (EPA) estimates that nearly 20% of human exposure to lead occurs through contaminated drinking water[6]. It is therefore critical for humans to experience minimal exposure to these contaminants and this can be ensured through effective water quality monitoring.

Utaphao watercourse in Hatyai is the main route for wastewater from factories which are near watercourse branch. It also suffers from trash and wastewater from Hatyai city. The water used in Hatyai is 82 000 m^3/day, and the wastewater entering the Utaphao watercourse can be 66 000 m^3/day[7]. Therefore, the water from Utaphao watercourse used to produce tap water might be contaminated with heavy metals such as mercury, lead, and cadmium. Furthermore, lead is frequently used as a material for water supply pipes and so their is a possibility that tap water in contact with a lead pipe for a long time (e.g., overnight) can contain relatively high amounts of lead. Monitoring lead in drinking water is therefore increasingly recognized[8].

Sensitive methods for the determination of trace amount of lead have received much attention, and many techniques have been employed for the determination[9]. The current EPA-recommended methods for metal ion analysis in water supplies are atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and anodic stripping voltammetry (ASV). These methods, although highly sensitive, require relatively large volumes of sample for analysis, complicated operation, costly maintenance, expensive apparatus, and well-controlled experimental conditions. ASV is increasingly employed because of its wide linear dynamic range, low detection limit, and multi-element analysis capability. Additional advantages of ASV over AAS or ICP-MS include the simplicity of the instrumentation, high sensitivity, easy operation, relatively low cost, compactness, and low electrical power requirement[9]. This electrochemical method is one of the most favourable techniques to determine heavy metal ions, mostly carried out using mercury electrodes[10–13]. Due to environment concerns, mercury-free electrodes have become more attractive. Boron-doped diamond (BDD) electrodes have been shown to have a high sensitivity, good selectivity, and reproducibility for the determination of Pb^{2+} in tap water samples[8].

BDD has very similar electrochemical properties to those of Hg, but yields better detection figures of merit under conditions of several metal ions contaminants[9]. The lower background current and wider anodic potential limit are the main advantages of BDD over Hg[14–17]. ASV with a BDD electrode has been used to sensitively and accurately quantify contaminant metal ions in several real samples, such as lake, river, and tap waters, as well as digestions of river sediment, waste treatment sludge, and soil[14,16,18]. Conductive diamond represents an electrode material that has attracted great interest in electroanalysis, due to its outstanding electrochemical features: wide potential window in aqueous solutions, low background current, long-term stability of the response, and low sensitivity to dissolved oxygen[19]. These unique properties of polycrystalline diamond, together with its extreme robustness, strongly recommend this material as well suited for stripping voltammetry analysis of heavy metals, and the results reported thus far are promising[20,21].

This work was aimed at evaluating the potential analytical applications of boron-doped diamond (BDD) electrodes for the determination of Pb^{2+} within the nanomolar concentration range using ASV. In order to assess the practical utility of the method for tap water analysis, preliminary investigation concerning the effect of copper as possible interferent is also reported.

MATERIALS AND METHODS

Reagents

Potassium nitrate and lead atomic spectroscopy standard solution ($Pb(NO_3)_2$ in 0.5 M nitric acid; 1000 ppm) were obtained from Ajax Finechem and Fluka, respectively. $Pb(NO_3)_2$ was dissolved in ultrapure water to form 1 mg/l stock solutions. Working standards for calibration were prepared by diluting the primary stock solution with ultrapure water. All the other compounds were of analytical reagent grade, and all the solutions were prepared from ultrapure water (resistivity 18 MΩ) obtained by passing deionized water through an ELGA water purification system. Potassium nitrate solution (0.2 M) was used as the general supporting electrolyte, and in experiments the pH was adjusted to about 1.26 by adding appropriate amounts of concentrated HNO_3 solution. The glassware and plasticware were soaked in 10% (v/v) nitric acid for overnight, and then rinsed at least three times with ultra pure water[22].

NIST reference solution

A reference material (SRM 1640) was procured for testing from the National Institute of Standards and Technology (NIST). Aqueous samples were prepared as stated in the reference and contained certified amounts of Ag(I), Cu(II), Pb(II), Cd(II), and Zn(II), in addition to at least 24 other dissolved elements. The certified values of Pb(II) were 27.89 ± 0.14 ppb.

Apparatus

The BDD electrode had a 3 mm diameter (total diameter 7 mm) and the area of 0.07 cm^2 (Windsor Scientific Ltd., UK). The measurements were carried out in a conventional three-electrode cell at room temperature. All square wave anodic stripping voltammetries (SWASV) were carried out using an AUTOLAB PGSTAT 100 (Metrohm), 663 VA stand (Metrohm), IME663 interface (Metrohm), and GPES-µAUTOLAB software. The electrochemical cell containing a BDD electrode was used as the working electrode. Ag/AgCl

(3 M KCl) and platinum wire (Metrohm, 6.1204.120) were used as the reference and auxiliary electrodes, respectively. In all electrochemical experiments, the test solution was deaerated for at least 5 min using a stream of nitrogen. A Denver pH-meter (model 225) was used for the pH measurements.

Procedure

The BDD electrode was polished at the beginning of the experiments with 0.05 µm diameter alumina powder (Buehler) and was rinsed thoroughly with ultra pure water to obtain a clean, renewed electrode surface. The electrode was connected to the potentiostat and placed in ultra pure water. A constant potential of 600 mV was applied for 120 s after completion of the anodic sweep to fully oxidize all metal deposits prior to the next measurement. The electrochemical pre-treatment was repeated daily. The polishing was redone only when contamination of the electrode surface was suspected[14]. However, an electrode used for testing untreated tap water may need frequent polishing. Whenever the proper functioning of the electrode deteriorated, the treatment with the alumina was repeated. In previous work[23], a stable background and a stable response were obtained after a series of about 20 anodic stripping runs in the supporting electrolyte that were carried out under conditions typical for the determination of lead with 30 s deposition time.

For all the stripping voltammetric measurements, a 25 ml aliquot of the analyte was transferred to a 50 ml cell and the pH was adjusted to 1.26 by adding an appropriate amount of concentrated HNO_3 solution to an electrochemical cell. A certain volume of supporting electrolyte and standard solution of Pb^{2+} were added into the cell. The solution was stirred and deaerated for 5 min and kept quiet for 10 s. The stripping voltammograms in the range of −0.80 to 0.00 V were recorded in the square wave mode, for which the scan rate was 1 V/s, the pulse amplitude was 50 mV, and the duration was 10 min. The stripping peaks were observed at −0.460 V. All measurements were made at room temperature (25–35 °C).

Voltammetric behaviour of Pb^{2+}

In the preconcentration step, the accumulated Pb^{2+} was found to be reduced at −1.30 V at which the lead ion is electrochemically deposited at the electrode surface. The deposited lead is oxidized, i.e., electrochemically stripped off by square wave voltammetry. The whole mechanism comprises of accumulation, reduction, and stripping stages which can be represented, respectively, by the following:

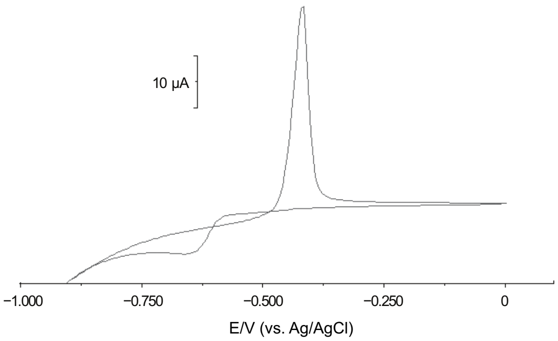

Fig. 1 Cyclic voltammogram of 50.0 mg/l Pb^{2+} in 25 ml 0.01 M HNO_3 (pH 1.93), recorded with the potential range from −0.900 to 0.000 V versus Ag/AgCl (3 M KCl) with the scan rate of 50 mV/s.

$$(Pb^{2+})_{solution} + (BDD)_{surface} \longrightarrow (Pb^{2+}{-}BDD)_{adsorption},$$
$$(Pb^{2+}{-}BDD)_{adsorption} + 2\,e^- \longrightarrow (Pb{-}BDD)_{adsorption},$$
$$(Pb{-}BDD)_{adsorption} \longrightarrow (Pb^{2+})_{solution} + (BDD)_{surface} + 2\,e^-.$$

RESULTS AND DISCUSSION

Stripping voltammogram of Pb^{2+}

The cyclic voltammogram of 50.0 mg/l Pb^{2+} in 0.01 M HNO_3 solution (pH 1.93) as a supporting electrolyte was recorded (Fig. 1). Reduction/oxidation processes were clearly exhibited. The reduction peak appears at −0.659 V with $I_{pc} = 6.526 \times 10^{-6}$ A. When the scan was reversed, the oxidation peak occurred at −0.420 V with $I_{pa} = 4.082 \times 10^{-5}$ A. The scan was intended to start from 0.000 V which was high enough to drive the reduction of Pb^{2+} ($Pb^{2+}_{(aq)} + 2\,e^- \longrightarrow Pb_{(s)}$). Lead ions in the solution gain electrons and to become Pb metal at the surface of the electrode. After that, the oxidation reaction ($Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2\,e^-$) occurs, i.e., lead atom loses electron and returns to $Pb^{2+}_{(aq)}$.

Effects of electrolyte and pH

The electrochemical behaviours of Pb^{2+} are only slightly different in different electrolytes. Various electrolytes including KNO_3, $NaNO_3$, KCl, NaCl, CH_3COONH_4, and CH_3COONa in a concentration of 0.2 M (pH 1.26) were evaluated for their suitability for Pb^{2+} determination at the electrode surface, and 0.2 M KNO_3 was found to provide the best current and peak shape.

Effects of deposition potential and time

Deposition potential is an important parameter for stripping techniques and it has a substantial influence on the sensitivity of the determination. The effect of

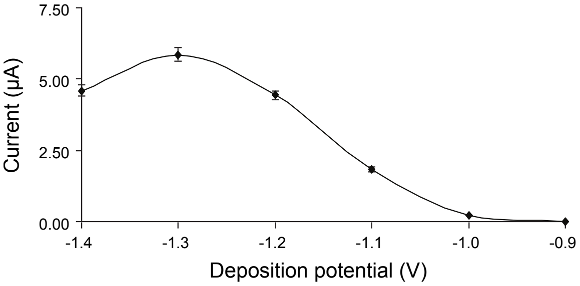

Fig. 2 Effect of deposition potentials on the SWASV peak currents. Conditions: 20.0 μg/l Pb^{2+} in 25 ml 0.05 M HNO_3 (pH 1.26) and 0.2 M KNO_3; deposition potential, −1.3 V vs Ag/AgCl; deposition time, 7 min; pulse amplitude, 50 mV.

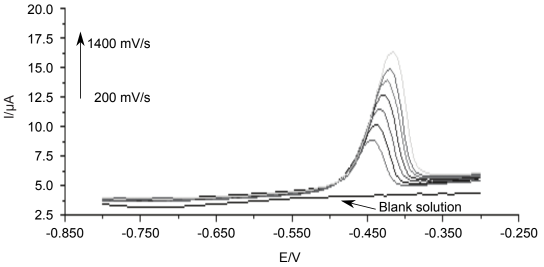

Fig. 3 Effect of scan rates on the stripping voltammograms. Conditions: 20.0 μg/l Pb^{2+} in 25 ml 0.01 M HNO_3 (pH 1.93) and 0.2 M KNO_3; deposition potential, −1.3 V vs Ag/AgCl; deposition time, 7 min; pulse amplitude, 75 mV.

deposition potentials on the stripping peak currents of Pb^{2+} is shown in Fig. 2. The deposition potential was varied from −0.9 to −1.4 V with a constant deposition time of 420 s. It is obvious that the negative shifts of electrode potential can improve the oxidation of Pb^{2+} on the surface of the electrode and increase the peak current up to the potential of −1.3 V. Beyond that point, the intensity goes down. Therefore, the optimum value of the deposition potential used in this work is −1.3 V. The deposition time dependence of the peak heights for lead ions was examined in the range from 300 to 660 s. In the presence of 20.0 μg/l Pb^{2+}, the peak current increased almost linearly with deposition time. The sensitivity for low levels of this metal can be increased by using a longer deposition time. Hence, a 600 s deposition time was employed in all subsequent experiments since this deposition time was sufficient to assess tap water contamination within a reasonable period and was a lot higher than that required for determining the WHO drinking water contamination limit (10.0 μg/l).

Effect of scan rate and step potential

The scan rate was varied from 200 to 1400 mV/s. The scan rate is related to the step potential. When the step potential is changed, the scan rate is also altered automatically by the instrument. The scan rate from 200 to 1400 mV/s corresponds to a step potential of 1.20–8.85 mV. The peak current increases up to a scan rate of 1000 mV/s, after which the peak becomes broad peak with lower stability (greater %RSD value) as shown in Fig. 3. Therefore, a scan rate of 1000 mV/s was chosen for further studies.

Calibration graph, detection limit and precision

The square wave anodic stripping voltammetric determination of a series of standard solutions of Pb^{2+} was performed under the optimized working conditions described above. The results show that stripping peak current has a linear relationship with concentration in the range of 2.0–30.0 μg/l of Pb^{2+} (Fig. 4). The linear correlation coefficient is 0.9994. The detection limit (three times signal to noise ratio (S/N)) was found to be 0.3 μg/l at a deposition time of 10 min. For 10 successive determinations of 2.0 μg/L and 30.0 μg/l Pb^{2+}, the relative standard deviations were 5.4% and 4.2%, respectively. The results indicate that the BDD electrode has excellent reproducibility.

Effect of other ions

The influence of other ions present in the analyte solution on the current response of Pb^{2+} is shown in Table 1. The interference is referred to in terms of percentage current change whereas the peak potentials were found to stay unchanged. At the coexisting ion concentration that affected the stripping peak current of Pb^{2+}, only a 5% change of peak current is allowed. Several ions such as Mg^{2+}, Ca^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, and Mn^{2+} have only negligible effect on the determination of Pb^{2+}. However, 20.0 μg/l of Co^{2+} and Al^{3+} was found to decrease the determination response significantly. Cu^{2+} at 20.0 μg/l interferes significantly by decreasing the Pb^{2+} signal due to strong competition of copper with lead in the deposition at the electrode. However, the interfering effect of Cu^{2+} can be eliminated by the addition of 0.001 M KCN as a masking reagent[24]. If sufficient KCN was added to the solution of Cu^{2+} ions (with K_f of 1.4×10^4) the complexed ions $[Cu(CN)_3]^{2-}$ are formed more easily than Pb^{2+} ions (with K_f of 4.9×10^4). Hence the KCN forms a complex with Cu^{2+}, while it does not interact with Pb^{2+}. Furthermore, the influence of weakly interfering ions can easily be eliminated by applying the standard addition method for the evaluation of the concentration of Pb^{2+}.

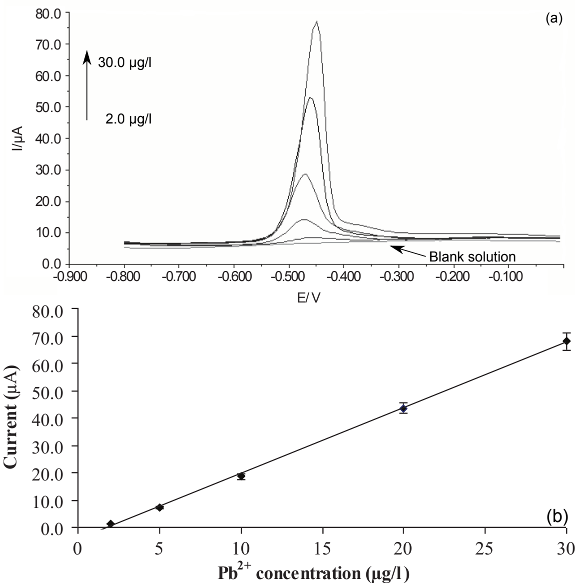

Fig. 4 (a) Square wave anodic stripping voltammograms of Pb^{2+} deposited BDD electrode. Pb^{2+} concentration: 0.0, 2.0, 5.0, 10.0, 20.0, and 30.0 μg/l. (b) The related calibration graph. Conditions: accumulation potential, −1.30 V; accumulation time, 10 min; 0.2 M KNO_3 and 0.05 M nitric acid solution pH 1.26 as and supporting electrolytes; scan rate, 1.0 V/s; pulse amplitude, 50 mV.

Table 1 Interferences of some metal ions with the determination of 20.0 μg/l Pb^{2+}.

Interfering ions	Concentration (μg/l)	Peak current change (%)
Ca^{2+}	3000	−5.09
Mg^{2+}	1000	−6.25
Mn^{2+}	500	−5.50
Al^{3+}	20	−4.93
Zn^{2+}	100	−5.77
Fe^{2+}	200	+5.15
Cu^{2+}	20	−5.80
Co^{2+}	20	−5.20
Ni^{2+}	50	−5.36
Cd^{2+}	50	−5.50

The working conditions are as in Fig. 4.

Analysis of a NIST reference solution

Fig. 5 shows a square wave anodic tripping voltammetric i–E curve for the NIST sample, overlaid with curves for standard solutions of Pb^{2+} at equal concentrations ranging from 2.0 to 10.0 μg/l ($r^2 > 0.9972$). Stripping peaks for lead in the NIST sample (complex sample with > 24 ionic species present) are present at potentials of around −0.42 V. The sensitivity of current peak for the SRM 1640 is clearly less than that of the prepared standards in Fig. 4 due to the fact that there are several other metals in the media. The concentrations were determined by the standard addition method. As an example, a plot of peak current versus the concentration of standard additions is shown in Fig. 5(b). Good linearity is observed with a linear regression correlation coefficient of 0.9967. The concentration of the unknown is determined from the intercept on the negative x-axis, which in this case is 5.51 μg/l.

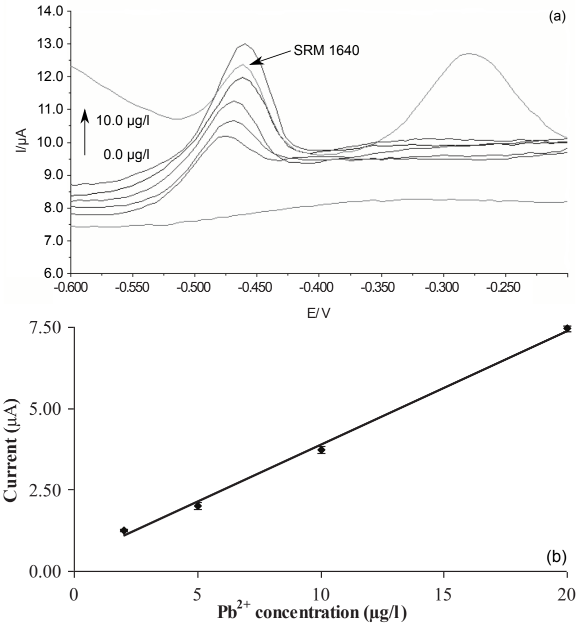

Fig. 5 (a) Square wave anodic stripping voltammetry i–E curve for a NIST sample (SRM 1640) overlaid with curves for standard solutions of Pb^{2+} ranging in concentration from 2.0 to 10.0 μg/l, each line represents: (1) 0.0, (2) 2.0, (3) 4.0, (4) 6.0, (5) 8.0, (6) 10.0 corresponding to 0.10 M KNO_3 (pH 1.00). (b) The related standard addition calibration curve of Pb^{2+} in tap water samples from first region at Hatyai city. Conditions: accumulation potential, −1.30 V vs Ag/AgCl; accumulation time, 10 min; 0.2 M KNO_3 and 0.05 M nitric acid solution pH 1.26 as and supporting electrolytes; scan rate, 1.0 V/s; pulse amplitude, 50 mV. The peak height were determined by integration over the range −0.550 to −0.400 mV.

Analytical applications

The studied method was applied to the determination of Pb^{2+} in tap water samples from eleven regions at Hatyai city, in February 2008. The tap water sample showed a distinct peak for Pb^{2+}. Hence the

Table 2 Recovery test for the studied method using tap water samples ($n = 3$) spiked with 2, 10, and 20 µg/l of Pb^{2+}.

Sample	Added (µg/l)	Expected (µg/l)	Measured (µg/l)	Recovery (%)
Tap water	0	-	BDL	-
9th region	2	-	2.84 ± 0.13	-
	10	10.84	10.51 ± 0.35	96.97
	20	20.84	20.17 ± 0.28	96.77
Tap water	0	-	BDL	-
10th region	2	-	2.68 ± 0.17	-
	10	10.68	10.26 ± 0.62	96.08
	20	20.68	21.10 ± 0.67	102.03
Tap water	0	-	BDL	-
11th region	2	-	2.59 ± 0.14	-
	10	10.59	10.57 ± 0.44	99.85
	20	20.59	20.05 ± 0.42	97.36

Mean ± S.D. ($n = 3$); BDL: below the detection limit.

concentration of lead in the tap water sample was easily determined by the standard addition method. Three determinations were made on each addition. The plot of peak current against lead concentration was linear ($r = 0.9967$). The concentrations of Pb^{2+} in sample were deduced from the stretched range of the regression equation. All of the samples were measured without any further treatment. The concentrations in the real sample are significantly higher than the limit of detection (Table 2). The excellent average recoveries of three water samples suggest that the studied method developed in this work has practical significance and is able to satisfactorily determine of Pb^{2+} in tap water samples.

Comparison with previous studies

The proposed sample preparation method in this study was satisfactory due to simplicity, speed and efficiency compared with the previous studies as shown in Table 3. It can be successfully applied to determination of lead in tap water samples. The results were in good agreement with those obtained by ICP-OES, demonstrating the practical analytical utility of the method. Tap water samples, that have been kept in contact for several hours with a solder wire and ink contaminate, were analysed for the lead content by ASV at the diamond electrode.

The BDD was found to give good and selective response for lead without only modification with the advantage of being so rugged therefore perfect for practical use. Further studies using various chemically modified electrodes may improve the conditions of the polycrystalline diamond films on the analytical performance characteristics for lead detection by ASV.

Table 3 Comparison of the proposed method and previous studies for anodic stripping voltammetry (water determination using BDD electrodes).

	Previous studies		Proposed
	Ref. 15	Ref. 8	method
Limit of detection (µg/l)	72.5	0.4	0.3
Deposition time (min)	2	15	10
Linear range (µg/l)	0–1000	0.4–20.7	2.0–30.0

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