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A Lead Sensor Based on Stripping Voltammetric Analysis Using Screen-Printed Electrode Modified with Polymeric Hydrogel Membrane

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Abstract. An electrochemical sensor for the determination of lead has been developed. The sensor transduction method was by stripping voltammetry and the best sensor response towards lead was obtained at pH 7, 0.3 M ammonia buffer with optimum pHEMA loading of 1.5 µg. The response to Pb^{2+} is at parts per billion range and linear response is from 100 – 1000 µg L^{-1} Pb^{2+} (R^2 = 0.9971) with a response time of 6 min at a stripping potential of -0.55 V. The addition of a poly(2-hydroxyethyl methacrylate) (pHEMA) membrane coated onto the screen-printed electrode was able to improve the response for the determination of Pb^{2+} in a blood serum matrix when compared with electrode without coated pHEMA.

Keywords: *Electrochemical sensor; lead(II); poly(2-hydroxyethyl methacrylate), blood serum*

Introduction

Among the toxic heavy metals, lead continues to be one of the most problematic. It is poisonous when accumulated and will cause effect to brain and the nervous system. Despite considerable effort to identify and eliminate Pb exposure sources, this metal still remains a significant health concern (1-4). It has been recognized that blood Pb concentration as low as 10 µg dL^{-1} can cause adverse effects in child development (5-7). The guidelines for potential health effects are linked directly to measured blood Pb levels (8).

Biomonitoring of Pb in individuals currently relies on collection of biological samples for subsequent laboratory analysis by means of standard spectroscopic techniques such as atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS). These analytical methods are generally conducted in centralized laboratories and require significant labor and analytical resources, potentially resulting in substantial delays in obtaining results. Electrochemical detection based on stripping voltammetry appears to be a promising technique (9-11), especially if the electrode is a low-cost disposable screen-printed electrode (SPE) that can be use for field-screening measurements.

For applications of electrochemical sensors to toxic metal analysis in biological samples, the complexity of the biological matrices such as urine, blood, and saliva often prevents successful measurements. The binding of target metals to proteins and macromolecules in the biological matrices can result in a low voltammetric response to known concentrations of the metals (12-13). Proteins also contribute to electrode fouling, which results in significant signal reduction and shortening of the electrode life-time. To overcome these issues, we develop an electrochemical sensor from screen-printed electrode (SPE) that was modified by using poly(2-hydroxyethyl methacrylate) (pHEMA) for the quantitative determination of Pb^{2+}. The SPE consisted of three printed electrodes; a carbon working electrode, a silver/silver chloride reference electrode and a carbon counter electrode. The pHEMA polymer is coated onto the working electrode and used as a membrane to provide protection for the electrode to reduce interferences especially from proteins or fats that are present in the biological samples. The pore size of the membrane may hinder the diffusion of these substances to the electrode surface. The measurement conditions were optimized with respect to pHEMA loading, pH, buffer concentration, accumulation time and deposition potential. The aim of this work is to examine the effect of pHEMA membrane on the response current of a lead sensor.

Materials and Methods

Reagents

Ultrapure water was obtained from ELGA (18.2 MΩ). Glassware was soaked in 12% nitric acid (R&M Marketing, Essex, U.K.) for 48 h, and then rinsed three times with ultrapure water before use. A 1.12 mL of ammonia 25% (Merck, Germany) stock solution was diluted in ultrapure water to prepare 50 ml 0.3 M ammonia solution, while 373 µL of ammonia 25% stock solution was diluted in ultrapure water to prepare 50 mL 0.1 M ammonia solution. Hydrochloric acid >30% was supplied by Fluka (Germany), 5 M and 0.1 M solutions of HCl were obtained by serial dilution in

ultrapure water. A concentration of 5 M HCl were titrated with the aid of a pH meter to give a buffer stock solution with desire pH. Stock solutions of Pb were prepared from $Pb(NO_3)_2$ (R&M Marketing, Essex, U.K.) by dissolving in ultrapure water. A 5 mL aliquot of Pb^{2+} stock solution was added with 400 µL of 0.1 M ammonia buffer of the suitable pH. In these studies the concentration of Pb^{2+} was fixed at 5 mgL^{-1}.

Apparatus

Differential pulse voltammetry (DPV) was performed using 1-(2-pyridylazo)-2-naphthol (PAN) modified screen-printed electrode (PAN-SPE). The SPE consisted of three printed electrodes on a substrate; a carbon working electrode, a silver/silver chloride reference electrode and a carbon counter electrode (Scrint Technology). The measurement of current was performed on a potentiostat (Pstat12) interfaced to a PC for data acquisition. A general purpose electrochemical system software package (GPES) version 4.9 was used for such purpose (Eco Chemie B.V., Utrecht, The Netherlands). The polymer modified lead sensor was fabricated by coating 1.5 µL pHEMA solution on the working electrode surface of the PAN-SPE and left to dry at room temperature. The polymer solution was prepared by dissolving pHEMA with 1,4-dioxan solution in the ratio of 1 g pHEMA : 1 mL 20 % (v/v) 1,4-dioxan. Rotary magnetic stirrer (IKA-WERKE, Staufen, Germany) was used to control stirring rate. All pH measurements were carried out using a HANA pH meter.

Electrochemical measurements

A 5 mL aliquot of Pb(II) standard solution was mixed with 400 µL of 0.3 M ammonia buffer at pH 7. In the optimization studies, the concentration of Pb^{2+} was fixed at 5 mgL^{-1}. Polymer (pHEMA) modified electrode was placed in the solution and accumulation of Pb was performed at closed circuit under stirred condition with a accumulation potential of -1.4 V. For the Pb measurement step, the pHEMA modified electrode with accumulated Pb was first rinsed in ultrapure water and Pb reduction was then performed in a voltammetric cell containing 5 mL of 0.1 M HCl. The accumulated Pb was then oxidized by scanning the potential from -1.4 to 0.00 V (versus SCE) and resulted a peak to appear at -0.55 V. The differential pulse waveform that employed was a step height of 2.4 mV, pulse repetition time of 0.2 s, pulse amplitude of 50 mV and pulse duration of 50 ms.

Evaluation of performance of the lead sensor

Several standard Pb^{2+} solutions in the concentration range of 100–1000 μgL^{-1} Pb^{2+} were prepared in ammonia buffer solution (0.3 M, pH 7) and determined using the lead sensor under optimized conditions to construct the sensor calibration curve. For the testing on blood serum samples, a fixed volume of serum was added to the buffer solution spiked with 1 mg L^{-1} Pb^{2+} and the response of the sensor was evaluated after each addition.

Results and Discussion

Effect of polymer loadings on lead response

A study was carried out to establish the relationship between the DPV current and pHEMA loadings. Figure 1 shows that the voltammetric response reaches a maximum value when pHEMA coated on the sensor was 1.5 µg (1.5 µL of pHEMA solution). The increase in current over this range of loading may be related to the good hydrophilicity of the pHEMA. As the thickness of pHEMA increases, slow transport processes of the metal ions through the coated membrane leads to a decrease of the current and hence a reduction in the overall conductivity of the sensor. From this data, 1.5 µg of the polymer provided the best sensor response and this was used for further studies involving the accumulation of the Pb^{2+} followed by stripping voltammetry.

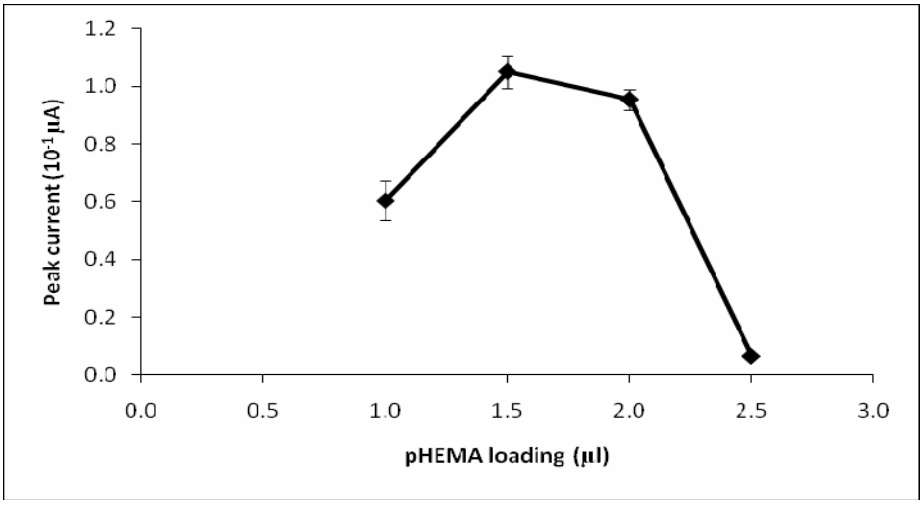

Figure 1. The effect of pHEMA loadings on the differential pulse stripping voltammetric peak current of a Pb sensor in 5 mgL^{-1} Pb^{2+}. (1 µL pHEMA = 1 µg)

Effect of pH on lead response

The stripping peak currents were found to increase as the pH of the accumulation solution (ammonia buffer) was increased from the acidic to neutral pH range. This is because Pb^{2+} is not precipitated in acid to neutral conditions (Fig. 2). The maximum stripping current was at pH 7. After pH 7, the stripping current was found to decrease rapidly, probably attributed to the precipitation of insoluble lead compounds under more alkaline conditions. Thus, pH 7 was selected as a condition of lead determination using this the lead sensor.

Effect of buffer concentration and accumulation time on the lead response

The effect of buffer concentration on the lead sensor response was also studied. To investigate the accumulation behaviour of Pb^{2+} at different ammonia buffer concentrations, ammonia buffer (pH 7) at different concentrations ranged from 0.1 to 0.5 M were used. The maximum response to Pb^{2+} occurred at buffer concentration of 0.3 M (Fig. 3). Thus 0.3 M as suitable to obtain the best lead sensor response. The dependence of the differential pulse stripping peak of Pb on the accumulation time was also investigated and the current clearly increased with time (Fig. 4) until 6 min after which the response decreased. Thus, 6 min was suitable accumulation time for best lead response.

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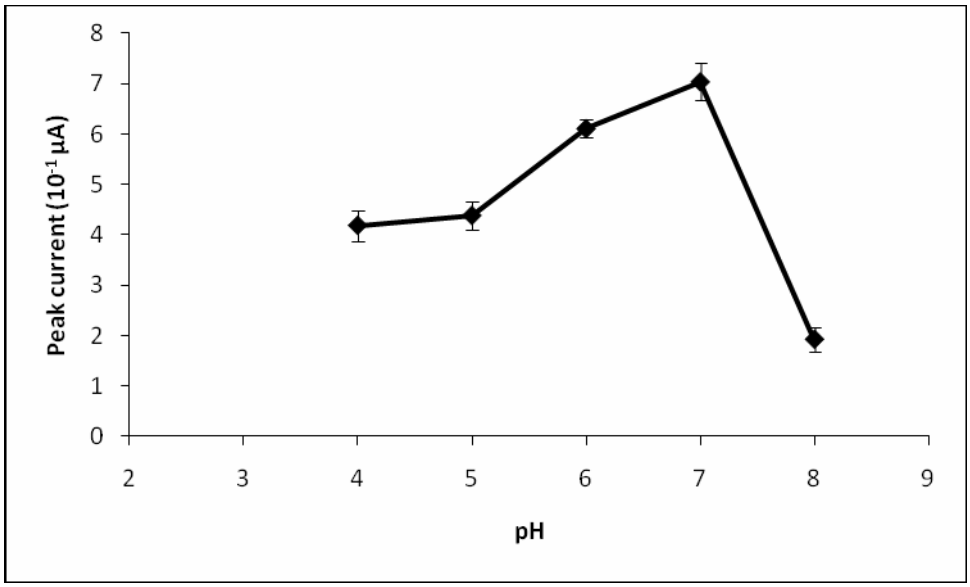

Figure 2. The effect of pH on the differential pulse stripping voltammetric peak current of a Pb sensor in 5 mgL^{-1} Pb^{2+}

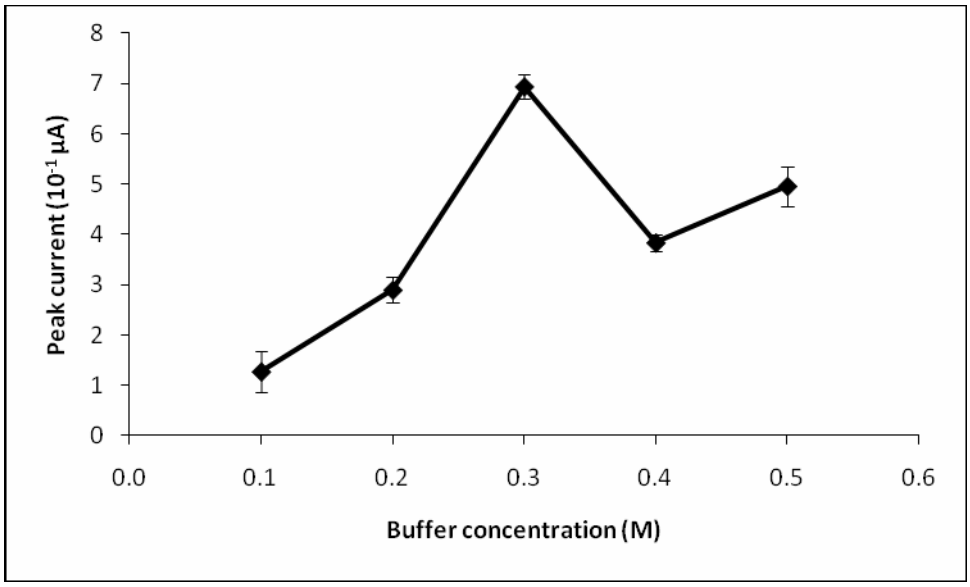

Figure 3. The effect of ammonia buffer concentrations on the differential pulse stripping voltammetric current of the Pb sensor in 5 mgL^{-1} Pb^{2+}.

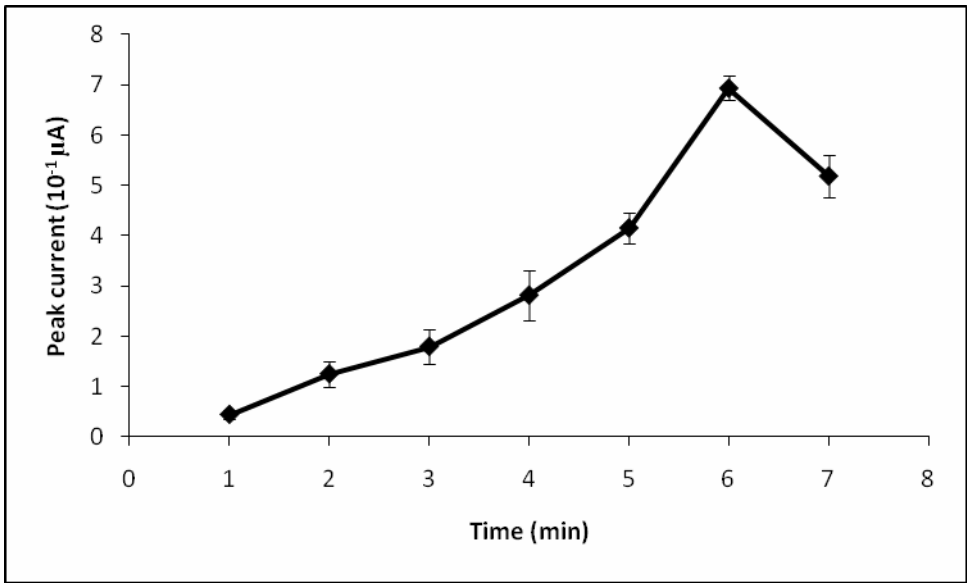

Figure 4. The effect of accumulation time on the differential pulse stripping voltammetric peak current of a Pb sensor in 5 mgL^{-1} Pb^{2+}.

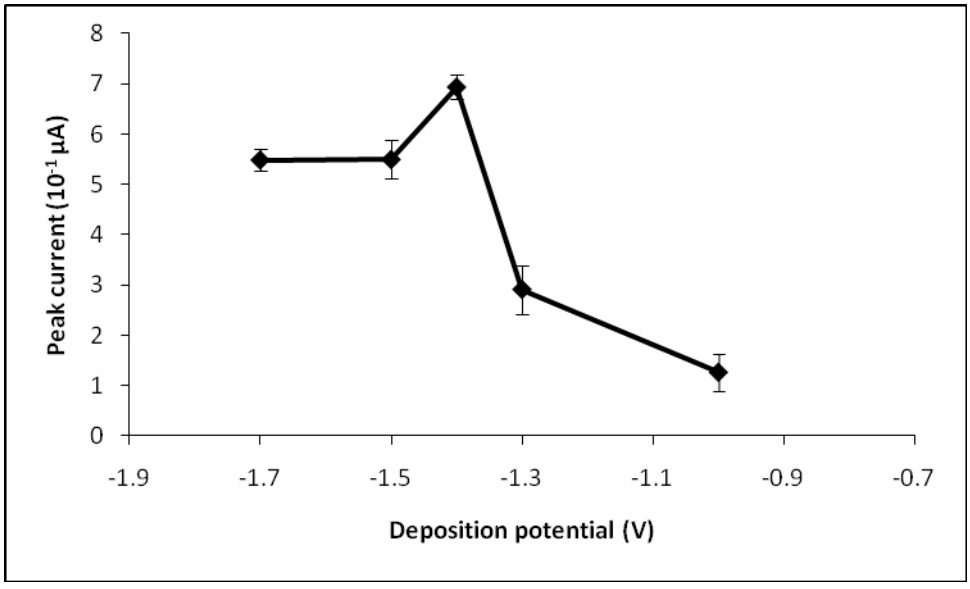

Figure 5. Effect of accumulation potential on the differential pulse stripping voltammetric peak of a Pb sensor in 5 mgL^{-1} Pb^{2+}.

Effect of accumulation potentials on the Pb sensor response

Under the optimum conditions for accumulation of Pb^{2+} at the pHEMA-SPE, e.g. 0.3 M ammonia buffer, pH 7 and accumulation time of 6 min, the optimum stripping potential for Pb was determined. After the Pb accumulation period, the sensor was transferred to 0.1 M HCl and the reduction potential varied between −1.0 and −1.7 V for a time of 5 s at each potnetial. Fig. 5 shows the maximum response for Pb occurs at a potential equal to −1.4 V and this is the operation potential for the lead sensor.

Application of the pHEMA modified lead sensor

A calibration curve of the pHEMA modified lead sensor under optimized conditions is shown in Fig. 6. The calibration curve demonstrated a large linear range of response towards lead ion, i.e. between 100 to 1000 μgL^{-1} Pb^{2+} (r = 0.9971).

Application of the lead sensor to blood serum lead determination showed that in the absence of serum, a maximum current is obtained but when blood serum is present, the sensor response is gradually suppressed (Fig 7). As the volume of blood serum increases, the current response decreases further. At the amount of serum below a dilution of 500 times, the current response of the lead sensor was almost suppressed completely. However, the response of the lead sensor coated with a layer of pHEMA appeared to yield higher signal when compared to lead sensor without pHEMA, especially in the presence of blood serum. The presence of pHEMA may be able to block some interferences from proteins and fatty substances from the serum and avoid complete surface fouling of the electrode. Hence, a better signal is obtained.

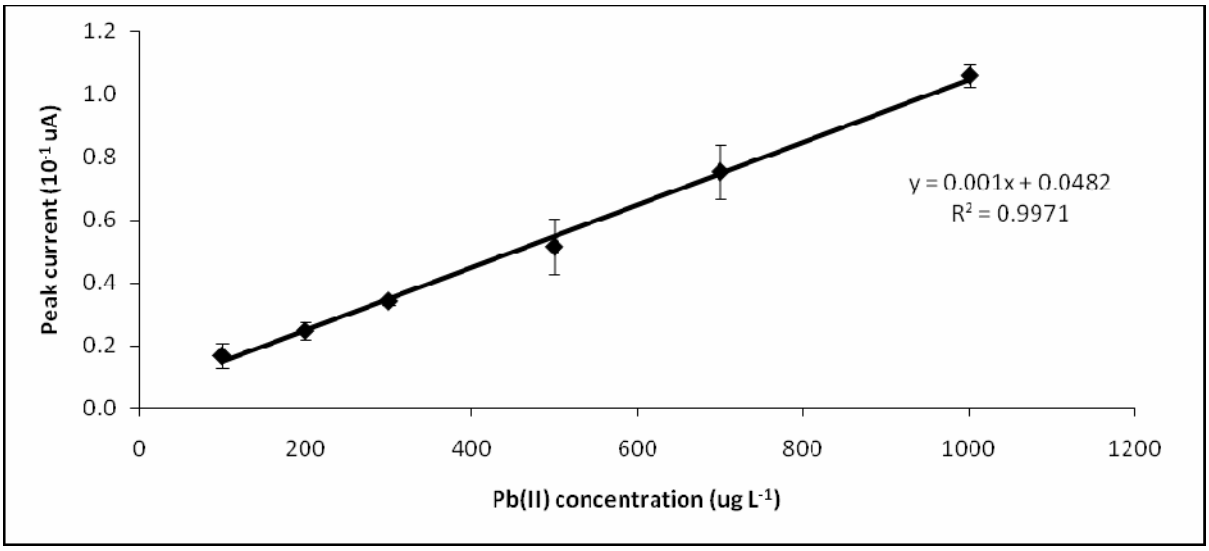

Figure 6. The calibration curve of the lead sensor for lead ion concentrations of 100 – 1000 µg L^{-1} Pb^{2+}

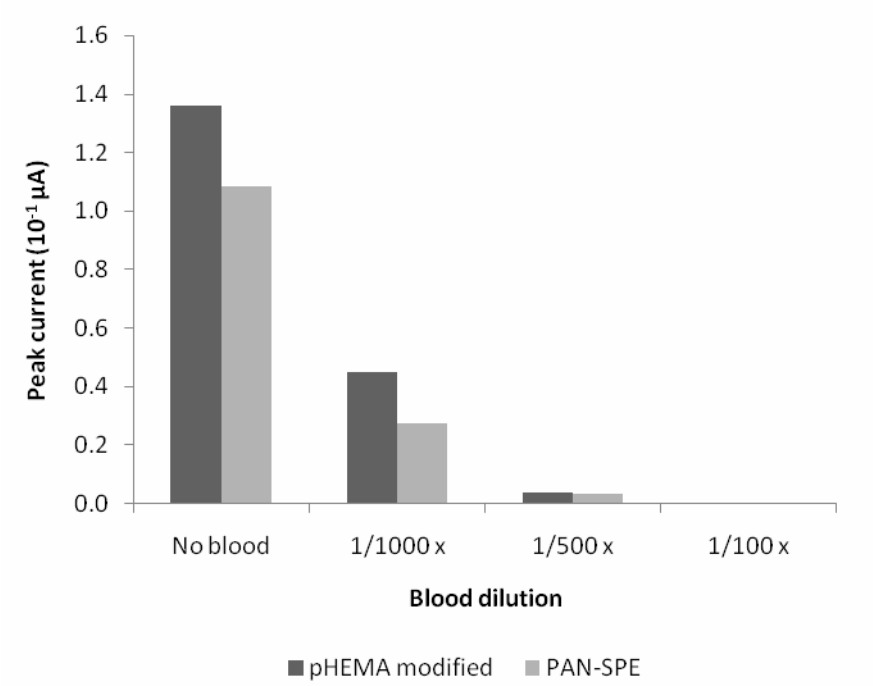

Figure 7. The effect on the lead sensor response when various volumes of blood serum was added to a buffer solution containing 1 mg L^{-1} Pb^{2+} (1/1000x refers to 1 part of blood serum is diluted to 1000 times)

Conclusion

This work has demonstrated that a PAN-SPE that is coated with pHEMA can be applied to determine trace levels of Pb^{2+}. Under optimized conditions, the sensor can detect lead in the parts per billion range and this enable the sensor to be used for environmental monitoring of Pb ions. The use of pHEMA can reduce slightly the interferences from biological matrices when compared with in the absence of this protective polymer layer.

Acknowledgement

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References

1. Banks,E.C., Ferretti,L.E., Shucard,D.W. (1997). *Effects of low level of lead exposure on cognitive function in children: a review of behavioral, neuropsychological and biological evidence.* Neurotoxicol **18(1):**237–281.
2. Grigg,J. (2004). *Environmental toxins; their impact on children's health*. Arch Dis Child **89**:244–250.
3. Juberg,D.R., Kleiman,C.F. & Kwon,S.C. (1997). *Position paper of the American Council on Science and Health: lead and human health.* Ecotoxicol Environ Saf **38**:162–180.
4. CDC (U.S. Centers for Disease Control and Prevention). (2000). *Blood lead levels in young children - United States and selected states, 1996–1999*. MMWR **49**:1133–1137.
5. Davis,J.M. & Svendsgaard,D.J. (1987). *Nature* **329**: 297.
6. Mushak,P., Davis,J.M., Crochetti,A.F. & Grant,L.D. (1989). Environ. Res. **50** : 11.
7. Honeychurch,K.C., Hart,J.P. & Cowell,D.C. (2001). *Voltammetric studies of lead at a 1-(2-Pyridylazo)-2-Naphtol modified screen-printed carbon electrode and its trace determination in water by stripping voltammetry.* Analytica Chimica Acta **43**: 89-99.
8. Jakubowski,M., Trzcinka-Ochocka,M. (2005). *Biological monitoring of exposure: trends and key developments.* J Occup Health **47**:22–28.
9. Lin,Y., Zhao,R., Thrall,K.D., Timchalk,C., Bennett,W.D. & Matson,M.D. (1999). *Integration of microfluidics/electrochemical system for trace metal analysis by stripping voltammetry*. Proc Soc Opt Eng (SPIE) **3877**:248-256.
10. Wang,J. (1994). *Analytical Electrochemistry*. New York:VCH Publishers, Inc
11. Wang,J., Lin,Y. & Chen,L. (1993). *Organic-phase biosensors for monitoring phenol and hydrogen peroxide in pharmaceutical antibacterial products*. Analyst **118**:277.
12. Timchalk,C., Poet,T.S., Lin,Y., Weitz,K.K., Zhao,R. & Thrall,K.D. (2001). *Development of an integrated micro-analytical system for lead in saliva and linkage to a physiologically based pharmacokinetic model describing lead saliva secretion*. J Am Ind Hyg Assoc. **62**:295-302.
13. Wang,J. (1982). *Stripping analysis of trace metals in human body fluids*. J Electroanal Chem **139:**225-232.