

Development of a Portable Heavy Metal Ion Analyzer Using Disposable Screen-Printed Electrodes

Hong Seok Choi and Hai Dong Kim*

Department of Chemistry and Research Institute of Basic Science, Kyung Hee University, Seoul 130-701, Korea

*E-mail: haikim@khu.ac.kr

Received June 16, Accepted June 30

Key Words: Stripping analysis, Heavy metal, Screen-printed electrode

Environmental pollution with heavy metal ions is the worst poisoning material. Lead is the most common metal involved in chronic poisoning. Lead poisoning can affect nearly every system in the body. Elevated human blood lead concentrations are associated with damage to the kidney, the liver, and the gastrointestinal tract as well as with neurological damage and decreased hemoglobin production. It is often called silent epidemic because it occurs without obvious symptoms, it frequently goes unrecognized. Lead exposure occurs when lead dust or fumes are inhaled, or when lead is ingested via contaminated hands, food, water, or clothing. Lead entered the respiratory and digestive system is released to the blood and distributed throughout the body. Children are exposed to lead poisoning more easily through toys, soil which are already contaminated with heavy metals. Children begin to exhibit permanent neurological and behavioral dysfunctions at low blood lead levels (BLL), with significant neurological damage occurring over the 5 ~ 10 $\mu\text{g}/\text{dL}$ (0.25 ~ 0.5 μM) range.¹ At high BLL (> 40 $\mu\text{g}/\text{dL}$), adults experience fertility problems (lower sperm count and abnormal sperm for men; infertility and miscarriage for woman), as well as neurological dysfunction and anemia.² Therefore, monitoring blood lead level is very important for human health.

Lead in human body can be measured in blood, urine, bones, or hair. The most popular test is to measure the blood lead level. Blood lead levels are reported in micrograms per deciliter ($\mu\text{g}/\text{dL}$) of whole blood. BLL measurements show the amount of lead circulating in the blood stream, not the amount of lead stored in the body. In Korea, occupational exposure to lead is subject to the Industrial Safety and Health Act³ which places all workers with exposure to lead under special medical surveillance. Under this act, all workers are required to have their BLL measured at least every year. The standard elevated BLL for adult's set by the U. S. Center for Disease Control (CDC) is 25 $\mu\text{g}/\text{dL}$ of whole blood. However, the level for child is much lower, 10 $\mu\text{g}/\text{dL}$ of blood.⁴

Traditional laboratory methods such as atomic spectroscopy for lead screening are expensive, complicated, and time consuming to use.⁵ Field portable X-ray fluorescence analyzer have been used to determine the lead levels of painted surfaces,⁶ humane blood.⁷ However, X-ray can cause additional health hazard to humane body. Electrochemical analysis of metal ions using anodic stripping voltammetry (ASV) technique offers extremely sensitive results which allows the determina-

tion of heavy metal ions as low as ppb levels with inexpensive and simple instrumentation.^{8,9} Demand for a portable instrument capable of testing BLL is increasing for quick on-site analysis. Improved electrochemical techniques may offer promise of developing a portable, accurate, easy to use, and inexpensive method for BLL measurement.

We have developed a portable heavy metal ion analyzer using disposable electrochemical screen-printed electrode sensors based on anodic stripping voltammetry. By using disposable electrochemical screen-printed electrodes contamination problem of the sensor electrode between measurements can be eliminated. Preliminary results with the disposable electrochemical screen-printed electrodes showed that heavy metal ions can be measured without deoxygenation of the sample solutions with comparable accuracy and precision. By combining a low cost instrumentation employing a single chip microcontroller and disposable electrodes makes heavy metal ions can be measured easily with a hand-held portable electrochemical instrument just like a portable glucometer commercially available.

Experimental

Materials. All chemicals used in this work were reagent grade. The standard metal solution of lead for atomic absorption was purchased from Kanto Chemical Co. Hydrogen chloride was purchased from Duksan Co., Seoul, Korea. Silver paste (LS-506J) was purchased from Asahi Chemical Research Lab. Carbon paste (BQ902) was purchased from DuPont. Ag/AgCl paste from ALS Company was purchased for reference electrode and insulating paste was purchased from Asahi chemical research lab. All solutions were prepared with double-distilled water.

Apparatus. Screen printing of the disposable electrode was printed with a commercial screen printer (KDS-300S, Kuckje Trade, Korea). Electrochemical signals of the electrodes were measured with a commercial electrochemical instrument (PEA-1000, Pimacs Co., Korea) for data verification during the portable instrument development.

Preparation of Sensors. Disposable screen-printed electrodes were prepared by integration of 3 electrodes (reference, working, and counter electrode) on a polypropylene sheet using screen printing technique as shown in Fig. 1. Three parallel conduction base patterns were printed first on a 0.5 mm thick poly-

propylene sheet (7 mm × 30 mm) with the commercial silver paste. Three conduction base patterns were designed for the formation of the integrated 3 electrodes on the one end of the polymer substrate strip, working, reference, and counter electrodes for later work. Ag/AgCl reference electrode was made by applying Ag/AgCl paste to the reference electrode pattern of the integrated 3 electrodes. After base pattern printing, the sensor was insulated with insulating paste except for the integrated 3-electrode assembly region and electrical connection strips at both ends. Electrode substrate (polypropylene) was cleaned with 0.1 M HNO₃ and deionized water before printing and baked in oven at 30 °C for 30 minutes to prevent shrink. After printing the electrode was dried further in a oven at 150 °C for 10 minutes.

Instrumentation. Schematic block diagram of the portable ion measurement system was shown in Fig. 2(a). A highly efficient 8-bit microcontroller unit (MCU) (C8051F040, Silicon Labs.) with built-in ADC (analog-to-digital converter), DAC (digital-to-analog converter), PGA (programmable gain ampli-

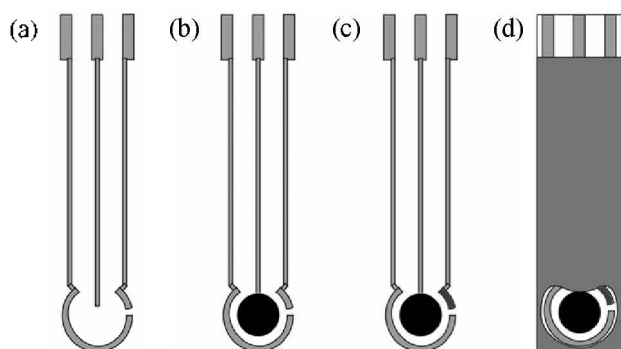
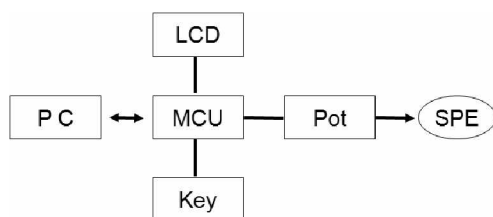


Figure 1. Preparation of the integrated screen printed electrodes. (a) conduction pattern with silver paste, (b) carbon working electrode, (c) Ag/AgCl reference electrode, (d) insulation layer.

(a) System



(b) Potentiostat

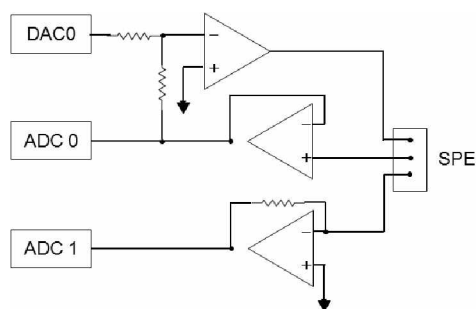


Figure 2. Schematic block diagram of (a) portable heavy metal ion analyzer, and (b) embedded potentiostat.

fier), RAM, flash memory for code, and digital peripherals was used to control electrochemical measurement system. The three major functions of the MCU were data transfer to PC, user interface (key, LCD), and control of the potentiostat. Program codes were written in C and downloaded into the built-in flash memory inside the MCU. Schematic of the potentiostat was shown in Fig. 2(b). By using a quad op-amp (LM324, National Semiconductor) a simple and efficient potentiostat was built for electrode control and signal processing. A 12-bit DAC built-in MCU was used for adjustment of the working electrode potential. Two built-in 12-bit ADC channels were used to read the potential and current signals of the working electrode respectively.

General Procedure. Standard solutions of lead were made by diluting a commercial standard lead solution made for atomic spectroscopy to make 10 ~ 100 µg/dL sample solutions. All lead analysis were performed without removal of oxygen. Sample solution was made by adding appropriate amount of standard solution into 0.1 M HCl solution. Electrolyte used was 0.1 M KCl and no buffer solutions were used for sample preparation. Lead solutions were preconcentrated at -1.1 V for 100 ~ 400 s. Measurement and control conditions for differential pulse stripping voltammetry were step potential 5 mV, pulse amplitude 50 mV, and scan rate 6 mV/s. After signal measurement, the area of the current peak was calculated automatically by MCU and used for quantitative analysis.

Results and Discussion

The major functions of the portable heavy metal ion test instrument are setting of electrode potential and measurement of electrode current through working electrode. To test the potentiostat, potential of the working electrode was scanned in the range of ±2000 mV with a dummy electrode. Potential of the working electrode was increased linearly from -2000 mV to +2000 mV, and resulting current was read as shown in Fig. 3. The current-voltage (I-V) curve showed linear response which indicates that the instrument functions as a potentiostat properly.

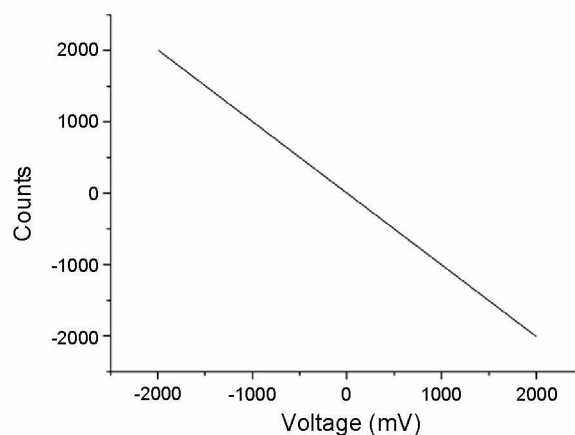


Figure 3. Calibration curve of the instrument obtained by using a dummy electrode (register). As potential increased linearly resulting current through a dummy register increased linearly.

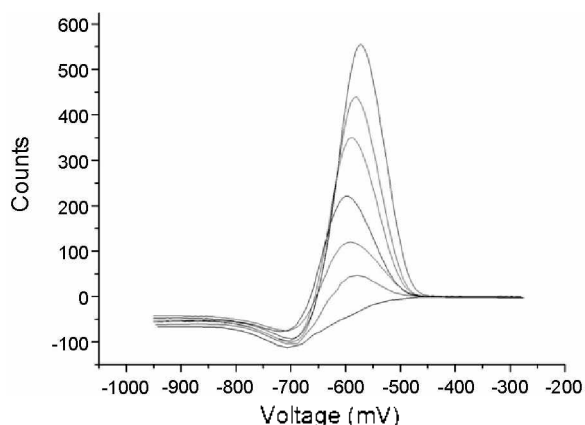


Figure 4. Stripping voltammogram of lead standard solutions (10 ~ 60 µg/dL) obtained with the portable heavy metal ion analyzer using disposable screen printed electrodes.

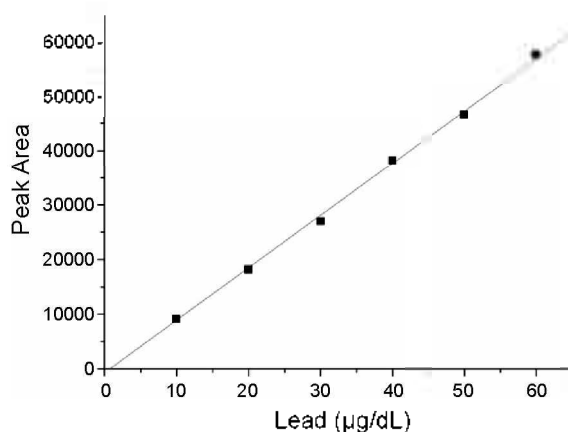


Figure 5. Calibration curve of lead standard solutions (10 ~ 60 µg/dL) obtained with the portable heavy metal ion analyzer using disposable screen printed electrodes. Data showed good linearity with correlation coefficient of 0.999.

Lead analysis was performed using differential pulse anodic stripping voltammetry (DP-ASV) by adding standard lead solutions into 0.1 M HCl with 0.1 M KCl as an electrolyte without dissolved oxygen removal process. The electrode potential was maintained at -1100 mV for 400 seconds for the lead deposition, and the electrode potential was scanned from -1000 mV to -200 mV by DP-ASV method with step potential 5 mV, pulse amplitude 50 mV, scan rate 6 mV/s. The current-voltage curve showed a peak around -600 mV and shifted as increasing lead concentrations shown in Fig. 4. Background current was not noticeable using the blank solution of 0.1 M HCl with 0.1 M KCl as an electrolyte. We did not remove oxygen in the sample solutions and no buffer solutions were used throughout measurements. Calibration data with standard samples showed excellent linearity with correlation coefficient of 0.999 as shown in Fig. 5. Under proper experimental conditions, linearity between the analytical signal and concentrations was observed in 5 ~ 70 µg/dL range with detection limit of 2 µg/dL, which is sufficient for BLL measurement.

Heavy metals such as lead, cadmium, mercury, can be measured by anodic stripping voltammetry down to ppb

levels with high precision.^{10,11} However, normal procedure for analysis of heavy metals by ASV requires deoxygenation and the use of mercury. Portable instrument for on-site measurement of BLL in the field requires simple instrument to use and easy sample preparation. Working electrodes used in our experiments for lead detection were screen printed carbon electrodes. Precision of the results among screen printed carbon electrodes showed good results with minimum inter-sensor errors. Inter-sensor mismatch depends largely on the screen printing conditions and printer operation. We are also currently testing other working electrodes such as noble metal electrodes.

In this study, we developed a compact and very inexpensive portable heavy metal ion analyzer based on electrochemical stripping voltammetry. The portable electrochemical instrument developed needs no sample deoxygenation and need not any mercury for sample treatment before sample analysis. The most troublesome work in electrochemical voltammetric analysis is the sensor contamination by fouling of the electrode. Fouling of the electrode with various chemicals including metal ions dissolved in the sample solutions requires cleaning of the electrode surface each time. By using a disposable screen printed electrode the troublesome electrode contamination and fouling problems can be eliminated. Users without any knowledge or experience in electrochemistry can use the portable instrument with minimum efforts for determination of heavy metal ions. Once sample is loaded and user press 'Measure' key, all the measurements and data processing are carried out automatically by the embedded intelligent microcontroller and measurement results are displayed on LCD. User can save the data in flash memory and can be downloaded to a PC for later use.

Acknowledgments. This work was supported by a research grant from Kyung Hee University (2008). We wish to thank Pimacs Co., Ltd., Seoul, Korea, for their cooperation with electrochemical instrumentation.

References

1. Flegal, A. R.; Smith, D. R. *Environ. Res.* **1992**, *58*, 125.
2. Canfield, R. L.; Henderson, C. R., Jr.; Cory-Slechta, D. A.; Cox, C.; Jusko, T. A.; Lanphear, B. P. *N. Engl. J. Med.* **2003**, *348*, 1517.
3. Korean Occupational Safety and Health Agency (KOSHA), *Industrial Safety and Health Act*, KOSHA, 2003.
4. Dept. of U. S. Labor and Industries, *Occupational Lead Exposure*, 1999, October, Report #17-6-1999.
5. Subramanian, K. S. *Sci. Total Environ.* **1989**, *89*, 237.
6. Clark, C. S.; Thuppil, V.; Clark, R.; Sinha, S. *et al. J. Occupational and Environmental Hygiene* **2005**, *2*, 38.
7. Kuruvilla, A.; Pillay, V. V.; Venkatesh, T.; Adhikari, P.; Chakrapani, M.; Clark, C. S.; D'Souza, H.; Menezes, G.; Nayak, N.; Sinha, S. *Indian. J. Pediatrics* **2004**, *71*, 495.
8. Wang, J. *Stripping Analysis, Instrumentation and Applications*; VCH Publishers Inc.: Deerfield Beach FL, 1985.
9. Brainina, K.; Neyman, E. *Electroanalytical Stripping Methods*; J. Wiley and Sons: New York, 1993.
10. Yantasee, W.; Timchalk, C.; Lin, Y. *Anal. Bioanal. Chem.* **2007**, *387*, 335.
11. Brainina, K.; Schafer, H.; Ivanova, A.; Khanina, R. *Anal. Chim. Acta* **1996**, *330*, 175.