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Detection and Quantification of the Presence of Lead using Screen Printed Electrode

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ABSTRACT
Industrial waste released directly into the environment, have the presence of heavy metals. This is one of the major potential health hazards. Therefore attempted in this paper is the development of simple procedure for one of the most perilous heavy metal, lead using Screen printed electrodes(SPE). These electrodes designed and developed using, silver as Reference Electrode and carbon as Working electrode as well as Counter electrode. When these electrodes comes in contact with the solution containing lead, a small amount of voltage is developed which is sensed by measuring or potentiostat circuit and displayed using high precision measuring unit. The response of the electrodes for varying concentrations of lead, zinc and copper were studied. The result confirms the sensitivity of the developed electrode is more for lead, (in the order of 0.1ng/ml) than the other two heavy metals. Various designs of electrodes were also used to test the lead to choose the best suited design for the proposed system. The output of this system is validated using the results obtained through inductively coupled plasma mass spectroscopy. The electrochemical cell functioning of the SPE was confirmed by performing, open circuit voltammetry and Cyclic Voltammetry analyses.

General Terms
Electro-Chemical reactions, Voltammetry, Potential development, Screen Printing.

Keywords
Screen-printed electrodes(SPE), silver, carbon, potentiostat, electrochemical.

1. INTRODUCTION
Many of the industries produce a gross amount of heavy metals in a daily scale which are dumped into the environment creating several issues where in the industrial workers as well as the residents in the vicinity are worst affected. Heavy metals impose a huge threat to the environment which in turn affects the human health varying from a simple head ache to complicated neurological problems. They have a high tendency

to accumulate biologically as well bio-magnify through food chain. They pose severe degradation of human health causing an unhealthy society. Improper treatment of the industrial wastes enriched with these heavy metals is so perilous that may even be carcinogenic. [1] Lead is one such heavy metal that causes several intricacies like decreased IQ level, learning and behavioral problems, cancer and other neurological problems that may be even fatal.

Especially young children are mostly affected by the lead causing developmental problems. [2]. Spectroscopic methods like inductively coupled plasma mass spectroscopy, inductively coupled plasma atomic spectroscopy, graphite furnace atomic absorption spectroscopy were approved by the regulatory agencies as the standard methods of detection of lead. [3] The detection of lead was calorimetrically performed where in several modifications like usage of nano gold particles were tried for higher detection sensitivity [4] Nano based detection were the turning point in the detection methodology, gold nano particles were used mainly because of their high extinction coefficient in visible range. The color change in gold particles may be observed even in naked eyes. Further negatively charged nano particles were used with positively charged quantum dots. [5] Later developed the theme of using DNAzymes that showed 100 fold better response than other methods. There has been considerable interest in developing portable and small devices for onsite testing. Miniaturized DNAzyme in a nanocapillary interconnected microfluidic device was yet another turning point in heavy metal detection. [6] This had the advantage that it was computer readable and was capable of being stored in CD’s. Later, developed a hybrid version utilisingDNAzymes along with nano particles where in monitoring was done by dynamic light scattering principle [6].This was further proceeded with miniaturisation of electrodes, as screen printed electrodes. The development of design and fabrication techniques of SPE, [7] for heavy metal detection answered several issues of sensitivity and portability that conventional methods could not. [8] SPEs were made with different materials and substrates, material properties were chosen and designed [9, 10, 11] for a variety of applications ranging from biomedical, pharmaceutical, industrial applications were used initially. [8] Screen printingtechnology used mercuric films as substrates [13]. Disposable SPEs were developed [14] for heavy metal detection, including cadmium, mercury, zinc and lead. [15] Later due to the health hazard that is being imposed upon the human beings as well as environment there was a trial to change the substrate. The detection of lead in foods [16] using SPE was developed, and then developed a screen printing technology that used a variety of carbon based materials. [17]

The proposed system describes the design and fabrication of silver basedSPE, along with measuring circuit to digitally display generated voltage due to lead. The total system is represented in figure 1.

The SPE are connected to the measuring circuit through a crocodile clip. A high precision voltmeter is used to display the potential generated.

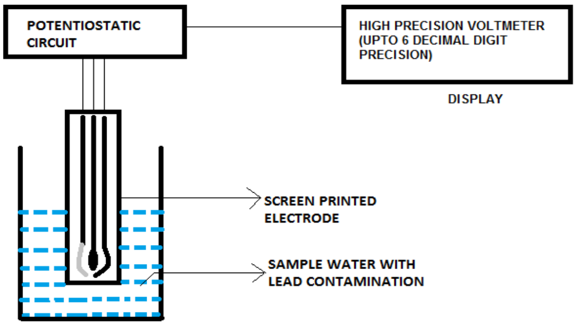

Figure. 1. Experimental setup of lead detection system

2. SCREEN PRINTED ELECTRODES

The fabrication process is simple and easy, initially the SPE are to be specifically designed, to standardize them. For the fabrication we need a stencil, which is prepared as the similar method as the screen printing. After the stencil preparation we finally coat ink (carbon and silver) one after another as shown in Figure 2. The final process is the curing, to attain the conductivity of the material.

Choosing the substrate is also an important task; the ink should not peel off from the substrate, such as in PVC. [14] The substrate used is polyester sheet of thickness 0.75 microns.

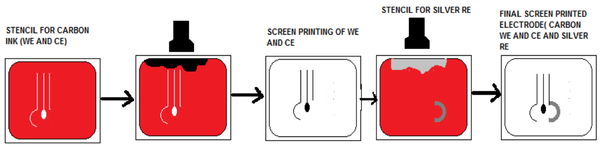

Figure 2. Screen printing, coating the ink

2.1 Preparation of solutions for testing

Various concentrations of lead were prepared using lead nitrate of analytical quality. Successive dilution method was chosen to prepare 10 concentrations in the multiples of 10 ranging from10 ng/dl to 10g/dl. Similarly copper sulphate and zinc sulphate were used to prepare test solutions for testing copper and zinc.

2.2 Mechanism of potential development

The mechanism of potential development is indicated in Figure.3 .

The oxidation reaction occurs at the carbon working electrode, and reduction occurs at the silver reference electrode. The reaction that takes place is:

Oxidation

$Pb \rightarrow Pb^{2+} + 2e^-$

Reduction

$2Ag^+ + 2e \rightarrow 2\ Ag$

Net Reaction

$Pb + 2Ag \rightarrow Pb^{2+} + 2\ Ag$

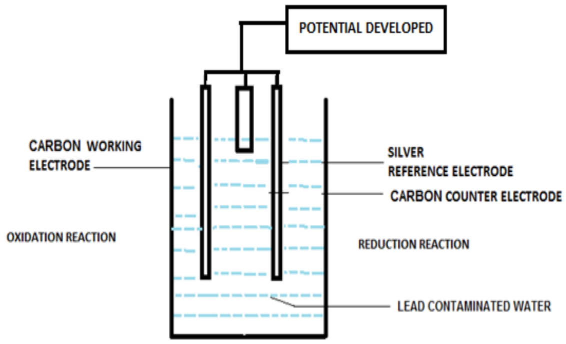

Figure.3 Mechanism of potential development

The electron transfer causing a development of a small potential is amplified using a potentiostat circuit. The potentiostat circuit has two functions mainly to amplify the developed potential due to lead and nullify the voltage developed between the reference electrode and counter electrode so that the potential developed due to lead can be measured accurately. Figure 4. shows the potentiostat circuit.

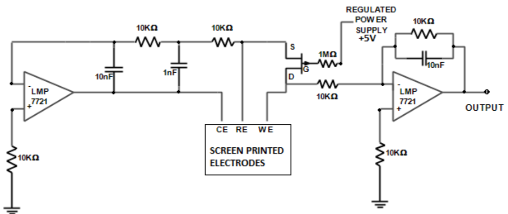

Figure 4. Potentiostat circuit

As the voltage need to be precisely noted, Agilent Precision source/measure unit B2912A is used that have a precision of 5 digits after the decimal.

The voltage reading is to be taken as the maximum peak voltage value immediately after placing the lead solution (within 30 seconds) in the tip of SPE.

3. TEST RESULTS

3.1 For Various Concentrations Of Lead, Copper And Zinc

The test was performed to determine the response of lead in giver sample of water. A drop of the test sample is placed in the screen printed electrodes, which is connected through the crocodile clip with the potentiostat circuit integrated with the digital display.

The test was performed for various concentration of lead which is represented in Figure. 5.

The response of the SPE to the other heavy metals, copper and zinc were tested. The response is plotted as concentration-voltage plot in Figure 5.

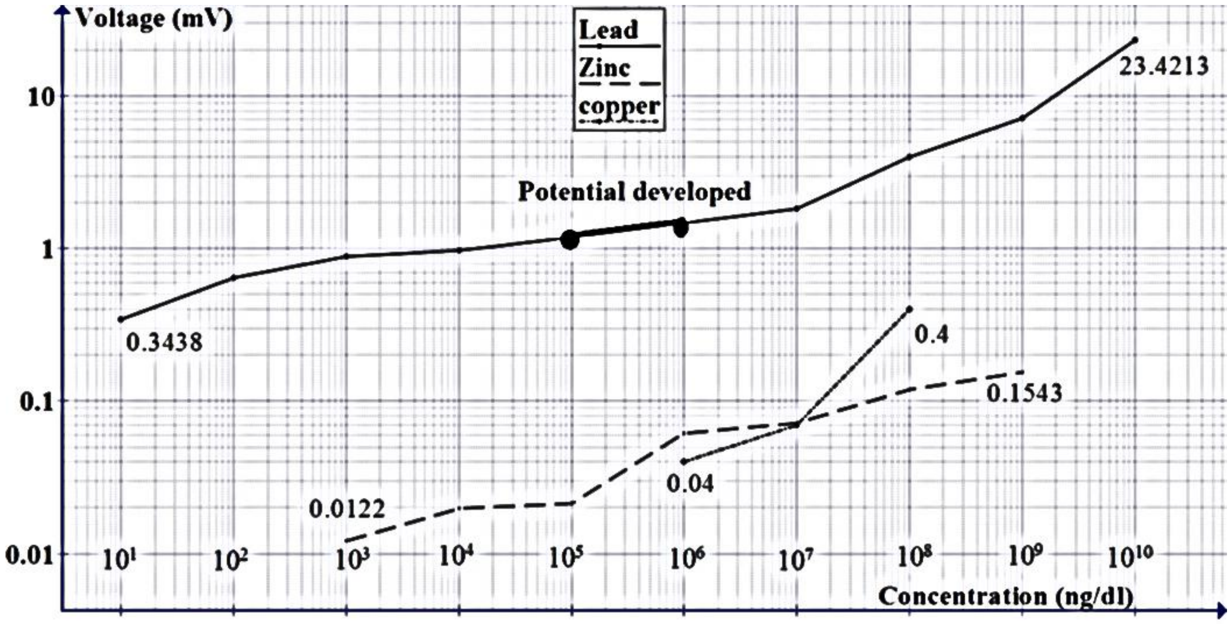

Figure 5 Concentration-Voltage characteristics of lead, copper and zinc

3.2 For various designs

The test for three other designs, along with standard design was taken to find out the best suited design for detection of lead. These designs are shown in Figure 6.

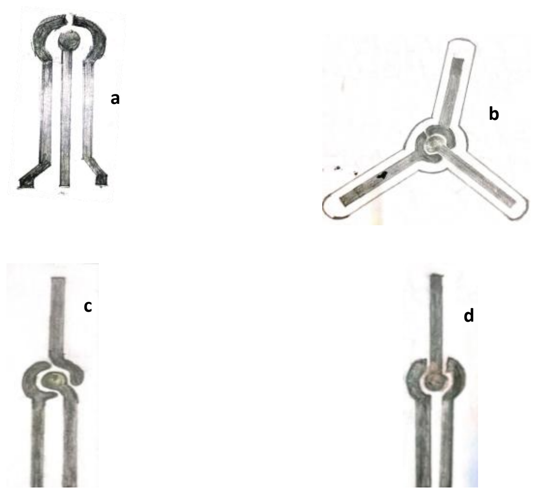

Figure 6. Various designs a. Design I b. Design II c. Design III d. Design IV

3.3 Electrochemical analyses

Electrochemical analysis of the SPE was performed using BIOLOGIC SP240 instrument. Two analyses were performed namely, open circuit voltammetry and cyclic voltammetry. Open circuit voltammetry describes the time taken for stabilization of the output, without the usage of the potentiostat circuit. Cyclic voltammetry describes the ability of the developed SPE to form a complete electrochemical cell. The result of these analyses is shown in Figure 7.

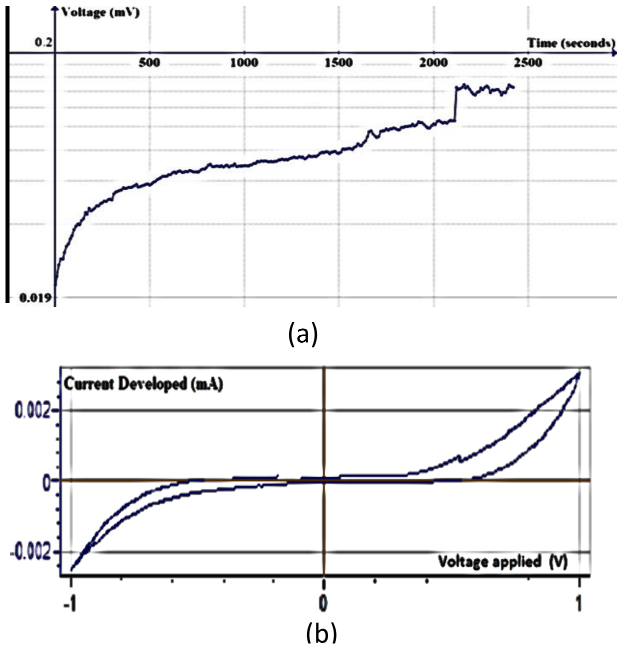

Figure 7. Responses of a. Open circuit voltage plot b. Cyclic voltammogram

3.4 Experimental Validation

A test solution was prepared by diluting 6g of zinc, 6g of copper and 6g of lead in 1 liter of water and was tested for lead using inductively coupled plasma mass spectroscopy, in Bureau VERITAS, Chennai.

The lab results proved the amount of lead in test solution is 0.6mg/dl. Same was also tested using SPE and potentiostat circuit as proposed in this paper. Voltage obtained was between potential developed with the concentration of 100µg/dl (or 0.1 mg/dl) and 1 mg/dl. (in between two points as indicated in the figure 5)Thus the standard lab test result is in concurrence with the results obtained through the method and hence validated.

4. CONCLUSIONS

Figure 5 shows the response of SPE for different concentration of lead, copper and zinc. For example the in potential obtained when tested with 10mg/dl and 1 g/dl of copper, zinc and lead are 0.36mV, 0.0571mV, 5.2826mV. From this it is clear that the response of the SPE is more sensitive to lead.

Various designs of the SPE were developed to choose which design suits the best for detection of lead. The designs based on the area of electrode interface with the lead solution and ease of crocodile clip placement. Design I had better area, but placing crocodile clip was a challenge. Design II III and IV had better area as well ease of crocodile clip placement. The ability to dip is possible for design I. The response of design II was very much comparable to the design I which is standardized [15]. Thus two designs, design I and II are suitable for detection of lead.

The responses of open circuit voltage plot and cyclic voltammogram is shown in the Figure 7.The open circuit voltage plot shows that the voltage obtained from the SPE for lead solution of concentration 0.6 mg/dl becomes constant near to 2400 seconds (40 minutes). This takes a really longer period of time to stabilize the voltage indicating the importance of using potentiostat, where external voltage is applied to get quick response. The cyclic voltammetry indicates the equilibrium of the two half cells, the oxidation and reduction half cells. There by the developed SPE forms a complete functional electrochemical cell. The performance of this system still can be improved by using nano ink and by surface modification of SPE.

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