

# Heavy metals detection using nanostructured screen printed electrodes

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## Abstract

This work deals with the problematic of heavy metals dissolved in aqueous solution detection using standard electrochemical methods. The problematic of low signal response of miniaturized electrochemical electrodes for electrochemical analysis is mentioned here. Finally some solutions for electrodes miniaturization and examples of fabricated electrodes and their heavy metals detection capabilities on a real sample are shown and discussed here.

**Keywords:** Screen-printed electrode, Carbon nanotubes, Heavy metals analysis

## Introduction

Recently heavy metals analysis is one of the most discussed problems (Ouyang, et al. 2011; Kokkinos et al. 2011; Krystofova et al. 2010). Formerly, since prof. Heyrovsky discovered polarography (1922), heavy metals were detected electrochemically using polarography as a great tool for cheap and fast trace detection in sub ppm and later sub ppb concentrations. From a nowadays point of view, this method in advanced versions is still one of the most reliable and accurate for wide field of usage. The problem is that this method uses toxic mercury as a working electrode material which is in the list of dangerous chemical elements that cannot be used for production in industry. Therefore there is an effort to substitute toxic mercury drop electrode by solid electrodes (Danhel et al. 2011; Atta et al. 2011).

The disadvantage of standard solid electrodes is their robustness which predestines them to be used in laboratories only. The necessity of fast on field or in-vivo detection pushed the electrochemistry to the scene of miniaturized electrochemical systems which usually use planar solid electrode systems. The electrode area of such electrochemical systems usually called as

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sensors is in the range of tens of square millimetres (eg. Teng, et al. 2010) The current response of such systems is usually smaller in comparison with standard electrochemical systems due to the active electrode area size of working electrodes which is according to Cottrel equation equal to current response of such systems. In many cases the response of such small electrochemical system is sufficient, but in the case of next miniaturization of electrodes, the signals from the system begin to be insufficient for proper evaluation.

This paper tries to show some possibilities how to solve this problem. Finally an example of heavy metals analysis using modified miniaturized working electrode on a real biological sample is shown here too.

## Solutions

One possibility how to solve the problem with the low signal from the miniaturized electrochemical systems mentioned in the introduction is a modification of working electrode. There could be modified material of a working electrode with some biological species that can easily select detected species from the solution. Another possibility is its active area increasing preserving the original geometrical size of the working electrode. This could be achieved using some techniques for 3D structuring of the electrode that could increase the electrode active area several times (Hu et al. 2010; Kalimuthu et al. 2010).

Lithography represents one of the possibilities for nanostructuring process that is usually used for microelectronic devices, but cheaper methods for electrode surface nanostructuring exist. For example vertically aligned direct grown carbon nanotubes on the electrode surface using CVD techniques (Prasek et al. 2006; Wang et al. 2011), aligned nanowires, nanotubes or nanorods created by anodization process (Klosova et al. 2007; Ismail et al. 2011), etc. could be created on the surface of miniaturized electrodes.

One of the most commonly used techniques of nanostructured electrodes preparation is use of nanocomposition made of nanopowder and suitable vehicle. Such nanocomposition could be deposited using screen-printing, dip-coating, drop-coating, spray-casting and other techniques.

### Nanostructured electrode example

Example of screen-printed working electrode that was made using a nanocomposition mixture of multi-walled carbon nanotubes (MWNTs) with PMMA as a vehicle is shown in the Fig. 1. The diameter of the electrode is 0.7 mm. The SEM image of fabricated electrode is shown in the Fig. 2. From the Fig. 2 is clear that the surface of the electrode is covered with high amount of MWNTs which are partially hidden under binding polymer vehicle. This problem is caused by the binding material of the electrode, which probably reduce the electrode active area leading to output current response suppression.



Figure 1: Example of screen-printed electrode with nanostructured surface

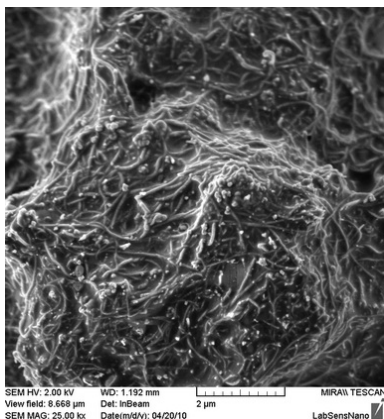


Figure 2: SEM image of the electrode surface structure

### Heavy metals analysis example

Lead ions detection using the MWNTs based working electrode in a three-electrode system employing differential pulse voltammetry (DPV) is shown in the figure 3. The measured sample was a real sample of the four lead painting differently poisoned aasvogel's eggs extract (from 100 to 1000  $\mu\text{mol/L}$ ). The results shown in the Fig. 3 represents voltammetric responses of the electrode to four different concentrations of lead poisoning of aasvogel's eggs. It could be concluded that MWNTs nanocomposition based working electrode is able to detect lead ions on real sample satisfactorily from 100  $\mu\text{mol/L}$ .

Although the obtained results are satisfactory for this application it was expected that the detection limit could be better. Therefore other experiments of the laboratory sample solution containing lead were done. It was found that the detection limit of this electrode is in the scale of units of  $\mu\text{mol/L}$ . This result is very good considering the surface of the electrode covered with polymer binding material which probably causes reduction of electrode active area. The result is also comparable to other standard electrodes. It could be concluded that after little optimization of the binding material, this electrode could be used as a working electrode of electrochemical voltammetric sensors for detection of species dissolved in aqueous solutions.

### Conclusion

The possibilities of standard electrodes miniaturization into the small hand held systems using nanostructured microelectrodes were shown and discussed in this paper. An example of the screen-

printed electrode, its surface structure and the current DPV response to real biological sample of the lead painting poisoned aasvogel's

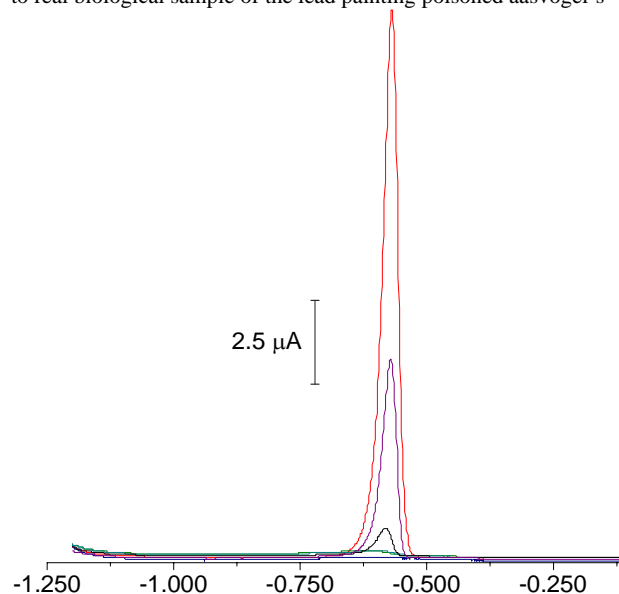


Figure 3: Example of electrode with nanostructured surface response to lead contained in the lead painting poisoned aasvogel's eggs extract.

eggs extract with satisfactorily results is shown here too. Using the standard laboratory sample, it was found that the detection limit of fabricated electrode is in the scale of units of  $\mu\text{mol/L}$  which is comparable to the results obtained with standard solid electrodes. This confirms our presumption about the suitability of MWNTs based screen-printable nanocomposition to be used as the working electrode of electrochemical sensors.

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