

Remote-Controlled Robotic Platform for Electrochemical Determination of Water Contaminated by Heavy Metal Ions

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The aim of our study was to equip a remote-controlled robotic platform (ORPHEUS-HOPE) with electrochemical system for fast detection of heavy metal ions in water. The platform contains two cameras – one pan/tilt color camera with both manual and automatic parameter settings, and one rigid high resolution color camera for precise vision and zooms to screen printed electrodes at the end of the manipulator. The maximum payload at the end of the manipulator is 0.85 kg. Screen printed electrodes consist with working electrode (WE), reference electrode (RE) and auxiliary electrode (AE). WE electrode (carbon paste) was designed to be as large as possible (in this case geometrically comparable with the diameter of the 3 mm glassy carbon electrode with working area of 7.1 mm²), RE (Ag/AgCl paste) 1.3 mm² and AE (platinum paste) 6.2 mm². The analytical parameters of differential pulse voltammetry for remote heavy metals detection (conditional time, step potential, deposition time and temperature) were optimized in this work. Application of robotic platform ORPHEUS-HOPE allowed us to analyze water samples spiked with heavy metal ions in linear ranges as follows: 0.8 - 50 µg.mL⁻¹ in case of Pb(II), 0.04 - 13 µg.mL⁻¹ in case of Cu(II), 0.2 - 50 µg.mL⁻¹ Zn(II) and 0.02 - 25 µg.mL⁻¹ Cd(II). ORPHEUS-HOPE might be helpful for *in situ* analyzes in environment, possessing conditions incompatible with human presence, such as these after environmental catastrophes.

Keywords: electrochemistry; environmental analyzes; heavy metals; ORPHEUS-HOPE; remote-control

1. INTRODUCTION

Heavy metal pollution as a global problem includes contamination of air and surface waters as a consequence of traffic, heavy industry and mining [1]. Developing countries, who lack the

infrastructure for ecological mining, belong to the biggest mining-related environmental polluters [2]. Accidents in mining industry are generally of huge extent and leave a long-lasting impact on the surrounding environment. Especially in gold mining, the toxic mercury is used, which is released during the processing of gold into the air and water [3]. The breach in the dam of a tailing pond in the gold mine processing plant in Baia Mare (NW Romania) in January 2000 led to an ecological disaster in the rivers Szamos and Tisza [4]. The rupture of an alumina sludging reservoir in north-west Hungary (municipality Kolontár) caused the spilling red sludge with heavy metals [5]. Furthermore, it was shown that in the vicinity of recycling stations of car batteries, the leakage of heavy metals into the environment may occur [6]. Cadmium can be released into the environment during the incomplete cleaning of air pollution in metallurgy [7]. Due to these environmental problems, it is necessary to find appropriate analytical tools that would be able to determine the pollutants in the place of occurrence (*in situ*) [8]. Over the last two decades, the systems called „lab on a chip“ (LOC) or „micro total analysis systems“ (μ TAS) have been developed [9-11]. These analytical tools are able to perform all the steps required for sample analysis. Above all, it is the pretreatment of the sample reagents distribution, mixing, separation and detection [12]. For environmental applications, because of their ability to analyze turbid samples, the most suitable are miniaturized electrochemical detection systems [13,14], which have low energy requirements [13], and can be variably modified to achieve greater selectivity and sensitivity [15]. A suitable solution for these applications are printed electrodes, which allow to perform standard electrochemical analyzes [16-19] with potentials ranging from -1.6 to $+1.1$ V [11]. The advantage of printed electrodes is their low price [20]. Nowadays LOC systems are widely used in pharmaceutical, biochemical and military analyses [21]. Due to their low weight and small size, it is possible to perform a point-of-care testing, i.e., by conducting clinical (diagnostic tests) in the patient or anywhere where there is a lack of technical infrastructure. Another possible option is implementation of the LOC on remote-controlled mobile platforms (lab on a robot) [22-24]. This technical solution allows to perform remote control surveys, analysis and sampling in locations that are dangerous for man, much too remote or inaccessible. There are many ways in which robotic devices can move. Some of them are able to mimic crawling [25], the others are moved by belts [26,27], wheels [28,29], feet [30-32], they are able to fly [33,34] or swim [35].

This work deals with the development of robotic platform ORPHEUS-HOPE and application in detection of heavy metals in the aquatic environment. Heavy metals Pb(II), Cu(II), Zn(II) and Cd(II) were analyzed by using a portable potentiostat and printed electrodes (classical three-electrode circuit), which were placed on a movable robot arm (ORPHEUS-HOPE).

2. EXPERIMENTAL PART

2.1 Chemicals and material

All metal standards including copper(II) nitrate trihydrate, lead(II) nitrate, zinc nitrate hexahydrate and cadmium sulfate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions were prepared in ACS water immediately prior to use. As electrolyte acetate buffer (0.2 M,

pH 5) was utilized. The pH values were measured by using an inoLab Level 3 instrument (Wissenschaftlich-Technische Werkstätten GmbH; Weilheim, Germany).

2.2 Screen printed electrodes' system

2.2.1 Electrode system design

Electrode system was designed and fabricated as a disposable planar three-electrode sensor in LabSensNano laboratories (University of Technology, Brno, Czech Republic). The dimensions of 0.625 μm alumina (25.4 \times 7.2 mm) were given by a dividing of standard 2 \times 2" alumina substrate. The shape and theoretical working area of electrodes were designed according to the previous optimization [36]. In accordance with the results of the optimization, the working electrode (WE) was designed to be as large as possible (in this case geometrically comparable with the diameter of the 3 mm GCE with working area of 7.1 mm²), reference electrode (RE) 1.3 mm² and auxiliary electrode (AE) 6.2 mm².

2.2.2 Electrode system fabrication

Screen-printed sensor was fabricated using a semiautomatic screen-printer Aurel C880 (Aurel Automation, Modigliana, Italy) and fired using BTU fast fire furnace for the thick-film processing (BTU, Billerica, MA, USA). The conductive layer was fabricated from AgPdPt-based paste (ESL 9562-G). AE was fabricated from Pt-based paste (ESL 5545-G). Both cermet pastes were obtained from ESL ElectroScience Europe (Berkshire, UK) and fired at 850 °C, according to the recommended values in the products datasheets. WE was a screen-printed electrode fabricated using a special polymer carbon paste for electrodes of electrochemical sensors (DuPont BQ221) from DuPont Company (DuPont, Wilmington, DE, USA) and cured at 130 °C for 10 minutes according to datasheet. RE was screen-printed using a special polymer Ag/AgCl paste (DuPont 5874, Ag:AgCl ratio 65:35) and dried at 120 °C for 5 minutes. The protective layer was fabricated from polymer dielectric paste (ESL 243-S) and cured at 150 °C for 10 minutes.

2.2.3 Electrochemical measurements

Differential pulse voltammetry was measured in the range of potentials -1.6 to 0.2 V. Changes in reduction signals were recorded with a potentiostat PGSTAT 101 (Metrohm, Herisau, Switzerland) and the results were evaluated by the Software NOVA 1.8 (Metrohm, Herisau, Switzerland). The individual parameters (conditional time, scan rate, deposition time and temperature) were optimized in this study for electrochemical detection of Pb(II), Cu(II), Zn(II) and Cd(II).

2.3 Descriptive statistics

Analysis of the data and their graphical interpretation were made using Microsoft Excel®, Microsoft Word® and Microsoft PowerPoint®. Results are expressed as mean ± standard deviation (S.D.) unless noted otherwise.

3. RESULTS AND DISCUSSION

3.1 Robotic platform (ORPHEUS-HOPE)

ORPHEUS-HOPE is a robotic platform constructed at the Brno University of Technology described in detail in [37]. It is a rugged robotic system made to operate in environmental unfavorable conditions to measure water contamination. It is able to work also in highly dangerous areas with chemical and nuclear risks, and can be easily equipped with additional devices, such as radiation sensors, biological sensors, etc. The robot is made to be highly reliable, and it fulfils various military standards. The robot is built on top of Orpheus-A platform that was made for military robot ORPHEUS-AC for chemical and nuclear contamination measurements [37]. The robot is equipped with two cameras – one pan/tilt color camera with both manual and automatic parameter settings (Fig. 1Aa), and one rigid high resolution color camera for precise analyte placement and measurement, Fig 1Ab. The robot has one degree of freedom manipulator with holder of screen printed electrodes (Fig 1Ac), while the other sensors can be either rigidly connected to the robot body or also placed on the manipulator. The maximum payload on the end of the manipulator is 0.85 kg. The robot base is rigid, has a low profile with high clearance because of big wheels. The robot may be operated wirelessly or by wire – both with digital protocol with military-grade encryption. The robot may be controlled by remote control or by using the virtual telepresence (Fig. 1Ad), as was described previously [37,38]. The basic parameters are summarized in Table and Figure 1A.

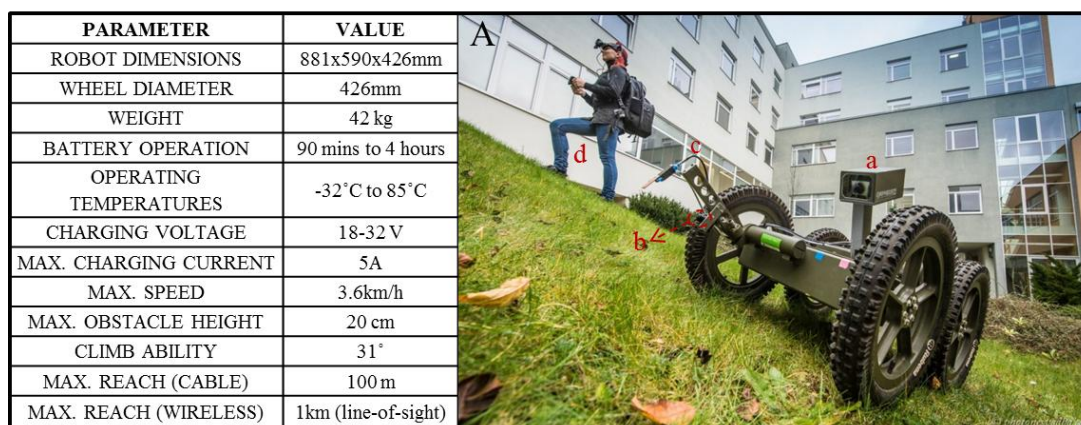


Figure 1. (A) Photography of robotic platform ORPHEUS-HOPE with operator, **a** = pan/tilt color camera, **b** = high resolution color camera, **c** = one degree of freedom manipulator with holder on screen printed electrodes, **d** = operator controlling the robot using visual telepresence.

3.2 Optimization of electrochemical detection of Pb(II), Cu(II), Zn(II) and Cd(II)

The electrochemical equipment consisted of a portable potentiostat PGSTAT 101, which was connected to a holder on the printed electrodes and a computer. Samples (3 μL) were dropped onto the printed electrode. Response of electrochemical signal of Pb(II), Cu(II), Zn(II) and Cd(II) ions, caused by a change in scan rate, step potential, deposition time and temperature was observed. The optimal response, for all metal ions, has been found and is marked with red point, Fig. 2 A5-D5.

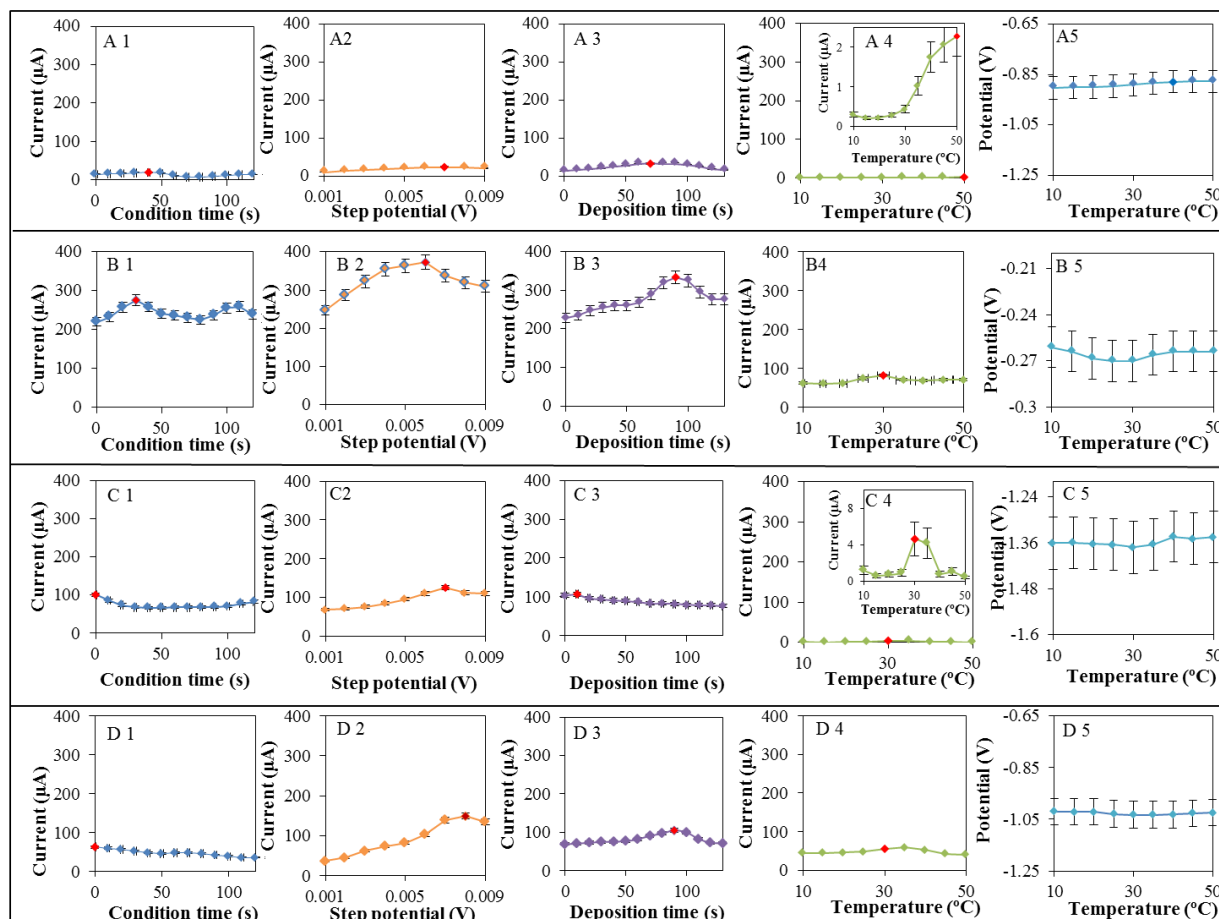


Figure 2. Optimization of the heavy metals detection (Pb(II) - A1-A5, Cu(II) – B1-B5, Zn(II) – C1-C5 a Cd(II) - D1-D5) in 0.2 M acetate buffer pH 5. The effect of condition time (A1-D1) on the change of electrochemical signal was observed in the time interval 0 – 120 s, scan rate (A2-D2) in the range 0.001 - 0.009 V, deposition time (A3-D3) in the time interval 0 – 120 s, the influence of temperature 0 - 50 $^{\circ}\text{C}$ (A4-D4) on the height of the electrochemical signal and the influence of temperature 0 - 50 $^{\circ}\text{C}$ on the potential change, A5-D5. The optimal value for each parameter is indicated as a red dot. For all measurements $\text{RSD} \leq 9\%$, $n = 3$.

3.3 Remote-controlled analysis of Pb(II), Cu(II), Zn(II) and Cd(II)

Remote-controlled analysis was carried out by robotic platform ORPHEUS-HOPE at room temperature (25 $^{\circ}\text{C}$). Other parameters (condition time, scan rate, deposition time) were set according

to the previous optimizations. Printed electrode was placed on the mobile robot arm. Using the remote control, the electrode was in a controlled manner immersed into a tested solution of 50 mL. The entire analysis was carried out using one electrode from lowest to highest concentration of an analyte in the concentration range from 0 – 100 $\mu\text{g}\cdot\text{mL}^{-1}$, by the method of standard addition.

Model of robotic platform with an electrode immersed into analyzed solution is shown in Figure 3A. Real image taken with pan/tilt color camera is shown in Figure 3B. In this manner all samples of metal ions (Pb(II), Cu(II), Zn(II), Cd(II)) were analyzed. From the collected values the calibration curves were constructed. The linear electrochemical response of Pb(II) ions was observed in the concentration range 0.8 – 50 $\mu\text{g}\cdot\text{mL}^{-1}$ (Fig. 3C) with a coefficient of determination $R^2 = 0.9904$. For Cu(II) ions was electrochemical signal linear in the range 0.04 – 13 $\mu\text{g}\cdot\text{mL}^{-1}$ (Fig. 3F) with a coefficient of determination $R^2 = 0.9983$. For Zn(II) ions were obtained values linear in the concentration range 0.2 – 50 $\mu\text{g}\cdot\text{mL}^{-1}$ (Fig. 3D) with a coefficient of determination $R^2 = 0.9853$. Finally, by Cd(II) ions the values were linear in the concentration range 0.02 – 25 $\mu\text{g}\cdot\text{mL}^{-1}$ with a coefficient of determination $R^2 = 0.9983$.

Ultimately, slopes of calibration curves were compared, Fig. 3G. In this manner, it was found that the system responded exhibited the highest sensitivity to Cu(II) and Cd(II) ions. Limit of detection (LOD) for Cu(II) ions was determined as 0.01 $\mu\text{g}\cdot\text{mL}^{-1}$ and for Cd(II) ions as 0.006 $\mu\text{g}\cdot\text{mL}^{-1}$. On the other hand, the lowest sensitivity of electrochemical system was observed in case of Pb(II) and Zn (II) ions. LODs were determined to be 0.2 $\mu\text{g}\cdot\text{mL}^{-1}$ Pb(II) and 0.07 $\mu\text{g}\cdot\text{mL}^{-1}$ Zn(II) respectively.

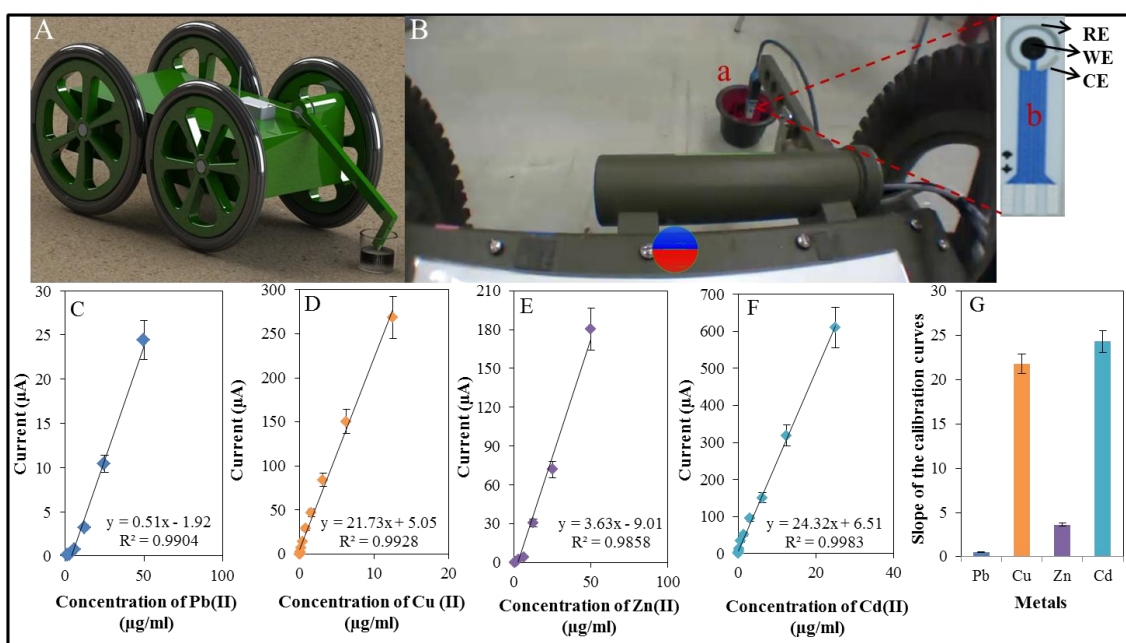


Figure 3. **A)** Illustrative model of robotic platform ORPHEUS-HOPE with an electrode immersed in the analyzed solution. **B)** Real image (analyzed sample) taken with pan/tilt color camera. **(a)** using printed electrode **(b)**. Calibration curves of **C)** Pb(II) with the coefficient of determination $R^2 = 0.9904$, **D)** Cu(II) with the coefficient of determination $R^2 = 0.9928$, **E)** Zn(II) with the coefficient of determination $R^2 = 0.9858$ and **F)** Cd(II) with the coefficient of determination $R^2 = 0.9983$. **G)** Comparison of slopes of the calibration curves. For all measurements $\text{RSD} \leq 9\%$, $n = 3$.

Table 1. Analytical parameters of electrochemical determination of metals

| Metal | Regression equation | Linear dynamic range ($\mu\text{g.mL}^{-1}$) | $R^{2\text{a)}$ | LOD ($\mu\text{g.mL}^{-1}$) ^{b)} | LOQ ($\mu\text{g.mL}^{-1}$) ^{c)} |
|---------|------------------------|--|-----------------|---|---|
| Zinc | $y = 3.635x - 9.0115$ | 0.2 – 50.0 | 0.9858 | 0.07 | 0.2 |
| Cadmium | $y = 24.322x + 6.5184$ | 0.02 – 25.0 | 0.9983 | 0.006 | 0.02 |
| Copper | $y = 21.773x + 5.0567$ | 0.04 - 13 | 0.9928 | 0.01 | 0.04 |
| Lead | $y = 0.5155x - 1.9276$ | 0.8 – 50.0 | 0.9904 | 0.2 | 0.8 |

a) Regression coefficients.

b) LODs of detector (S/N = 3).

c) Limits of quantification of detector (S/N = 10).

For example heavy metal concentration in sediments of the rivers Szamos and Tisza was determined as $\text{Cu(II)} = 612 \text{ mg.kg}^{-1}$, $\text{Cd(II)} = 23 \text{ mg.kg}^{-1}$, $\text{Pb(II)} = 374 \text{ mg.kg}^{-1}$ and $\text{Zn(II)} = 3095 \text{ mg.kg}^{-1}$ [4]. The techniques most widely used for the total form of heavy metals include inductively coupled plasma optical emission spectrometry (ICP-OES) [39], inductively coupled plasma mass spectrometry (ICP-MS) [40], atomic absorption spectrometry (AAS) of electrothermal or hydride generation [41]. These techniques are highly accurate and sensitive, but difficult to be applied in field conditions *in situ*. Detection limits established in this work are not comparable with ICP-MS (pg.mL^{-1}), ICP-OES (pg.mL^{-1}) and AAS (pg.mL^{-1}), but are sufficient for analyzing liquid samples at the site of accident, where the concentrations of these metals rapidly elevates [4,42], and therefore is easily detectable in the proposed manner.

Detection limit and sensitivity of printed electrode can be improved by modification of working carbon electrode with a suitable material which will increase active surface of the working electrode. For example carbon nanotubes and nanorods may be used as was shown by [43,44]. Creating of nanostructured electrode surfaces can be done by growth of carbon nanotubes directly on a substrate [43,45], or by preparing a paste containing nanopowder which is mixed with a suitable binder and applied to the prepared substrate by screen printing [46].

4. CONCLUSIONS

In this work, an electrochemical method using printed electrodes was optimized. Determined optimal parameters were implemented in the robotic platform ORPHEUS-HOPE. By using this particular platform, the solutions containing Pb(II) , Cu(II) , Zn(II) and Cd(II) were analyzed. Described robotic framework can be used as a mobile, remote-controlled analytical tool used for determination of heavy metals in the environment.

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Conflict of interest

The authors have declared no conflict of interest.

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