# PHTHALOCYANINE MODIFIED ELECTRODES BASED ON REDUCED GRAPHENE OXIDE FOR DETERMINATION OF LEAD IN DIFFERENT TYPES OF WATER

Georgiana-Luiza ARNOLD TATU and Jacobus Frederick VAN STADEN*

Laboratory of Electrochemistry and PATLAB Bucharest,
National Institute of Research for Electrochemistry and Condensed Matter, Bucharest 060021, Romania

In this study, modified electrodes based on reduced graphene oxide modified with iron (II) phthalocyanine or nickel (II) phthalocyanine were used for determination of lead in different types of water samples using differential pulse anodic stripping voltammetry. The lowest limits of quantification obtained, were 0.001035 µg L^{-1} for the modified electrodes, and 0.00207 µg L^{-1} for unmodified electrodes, with a correlation coefficient (R^2) between 0.996 and 0.997. The results obtained for the different sensors on real water samples were compared with the standard ISO method (SR EN ISO 11885:2009) using inductively coupled plasma optical emission spectrometry (ICP-OES) and it can be seen that all the sensors compared very well for the determination of Pb^{2+} ions in different types of water.
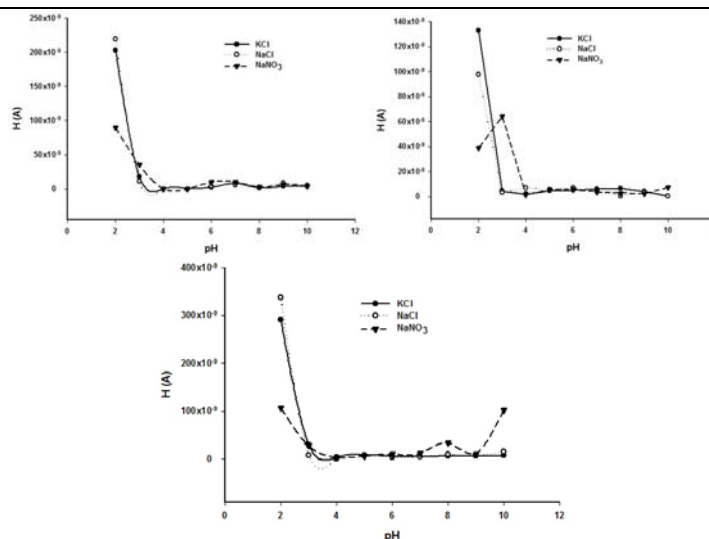
INTRODUCTION

There is currently a great concern in Europe (at the European Commission) about some "toxic" substances that are regularly detected in food coming from a number of food sources.[1–4] Retrieval data studies revealed that the consumption of contaminated commodities is related to several acute chronic diseases in humans and animals.[5–7]

Lead from lead batteries, corrosion of lead (housing and other lead plumbing systems) from lead and iron pipes (example Flint river, USA), contamination of lead from the environment and leaching of lead from these sources into fresh water rivers and lakes (even into food commodities) can eventually become harmful to humans.[8–15]

A reliable, sustainable and convenient analytical method therefore becomes needed for the determination of lead ions in water. Lead concentrations in drinking water should be below the **EPA** action level of 0.015 mg L^{-1} (parts per billion).[16,17]

We, therefore, developed a simple, sensitive and selective electrochemical method for the determination of lead ions in water. The method is based on reduced graphene oxide modified

---

* Corresponding author: koosvanstaden2012@yahoo.com, koosvanstaden@patlab.ro

electrodes with phthalocyanine for the detection of lead from different types of water samples (*e.g.*, fresh water, underground water, geothermal waste water) using differential pulse anodic stripping voltammetry (DPASV). The results compared favourably with standard iso-certified methods.

EXPERIMENTAL

1. Reagents and instrumentation

All chemicals were of analytical reagent grade, and $Pb(NO_3)_2$, KCl, NaCl, $NaNO_3$, $NaH_2PO_4 \cdot H_2O$, Na_2HPO_4 for the different solutions were purchased from Sigma-Aldrich. Reduced graphene oxide (RGox) was supplied by Sigma Aldrich, and paraffin oil by Fluka (Buchs, Sweden). Iron(II) phthalocyanine (Fe(II)Pc) and nickel(II) phthalocyanine (Ni(II)Pc) were from Aldrich.

Phosphate buffer solutions (PBS, 0.1 mol L^{-1}) with pH = 2–10 were prepared by using different ratios between NaH_2PO_4 and Na_2HPO_4. Hydrogen chloride (HCl, 0.1 mol L^{-1}) and sodium hydroxide (NaOH, 0.1 mol L^{-1}) solutions were used for pH adjustment.

The standard solutions for differential pulse voltammetry (DPV) were prepared using 10^{-3} mol L^{-1} (207000 µg L^{-1}) of Pb^{2+} as stock solutions. All standard solutions of Pb^{2+} in the range 10^{-4} – 10^{-12} mol L^{-1} (20700–0.000207 µg L^{-1}) were prepared from the stock solution by serial dilution, with phosphate buffer solution (PBS) of different pHs containing KCl, NaCl or $NaNO_3$ (0.1 mol L^{-1}) as supporting electrolytes.

All solutions were prepared using deionized water obtained from a Direct-Q 3 Water Purification system (Millipore Corporation, France).

All measurements were recorded using a PGSTAT 100 potentiostat/galvanostat connected to a three electrode cell, and linked to a computer via an Eco Chemie (Utretch, The Netherlands) software version 4.9. An Ag/AgCl electrode served as reference electrode and a platinum electrode served as auxiliary electrode, new developed sensors served as working electrodes in the electrochemical cell. The pH measurements were performed using a CyberScan PCD 6500 Multiparameter.

DPV curves have been recorded at 0.01 V s^{-1}, with a pulse height of 0.025 V and step potential of 0.05 V. All measurements were performed at 25°C.

2. Design of the microsensors RGox, Fe(II)Pc/RGox, Ni(II)Pc/RGox

Reduced graphene oxide (RGox) pastes were modified with iron(II) phthalocyanine (Fe(II)Pc) or nickel(II) phthalocyanine (Ni(II)Pc). The modified reduced graphene oxide pastes were prepared as follows: 100 mg of reduced graphene oxide powder were mixed with 30 µL paraffin oil to form the reduced graphene oxide pastes. 25 µL from the solution of Fe(II)Pc (10^{-3} mol L^{-1}, prepared in dimethyl sulfoxide) or Ni(II)Pc (10^{-3} mol L^{-1}, prepared in N,N

dimethylformamide) was added to the reduced graphene oxide pastes mixed with 25 µL paraffin oil. The modified paste was placed into a very small plastic tube. Electrical contact was obtained with an Ag wire inserted into the paste. The surface of the electrode can be renewed by polishing with alumina paper. When not in use, the sensors were stored in a dry state, away from day light and at room temperature.

RESULTS AND DISCUSSION

1. Optimization of working conditions

Various DPV curves (0.01 V s^{-1}) were recorded in order to optimized the working conditions for RGox, Fe(II)Pc/RGox, Ni(II)Pc/RGox sensors, using a 10^{-6} mol L^{-1} (207 µg L^{-1}) solution of Pb^{2+} ions. Three different supporting electrolytes were tested (0.1 mol L^{-1} NaCl, 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} KNO_3) in PBS pH = 2 – 10. Figure 1 show the effect of pH and supporting electrolyte on the peak height for each sensor, using a solution of 10^{-6} mol L^{-1} (207 µg L^{-1}) Pb^{2+} ions. The sensor sensitivity increases in lower pH solutions. The supporting electrolyte with 0.1 mol L^{-1} KCl, PBS pH = 2 gave the best results for the Fe(II)Pc/RGox sensor. For RGox and Ni(II)Pc/RGox sensors we observed that the following two supporting electrolytes have a good response: 0.1 mol L^{-1} KCl, PBS pH = 2 or 0.1 mol L^{-1} NaCl, PBS pH = 2.

2. Optimization the parameters for the condition parameters

Influence of various parameters deposition potential, deposition time for RGox, for Fe(II)Pc/ RGox and for Ni(II)Pc/RGox sensors were determinate using different supporting electrolytes in 10^{-6} mol L^{-1} (207 µg L^{-1}) Pb^{2+} ions. Figure 2 shows the results for deposition potential and deposition time using different supporting electrolytes. RGox or Ni(II)Pc/RGox sensors used two supporting electrolytes: 0.1 mol L^{-1} KCl, PBS pH = 2 or 0.1 mol L^{-1} NaCl, PBS pH = 2. For Fe(II)Pc/RGox sensor only one supporting electrolyte was used: 0.1 mol L^{-1} KCl, PBS pH = 2. For all sensors the optimal response was using 0.1 mol L^{-1} KCl, PBS pH = 2 as supporting electrolyte and with a deposition potential for -1.2 V and with a deposition time of 150 s.

3. Response characteristic for Pb^{2+} ions

The response characteristic for Pb^{2+} ions is presented in Table 1 and in Figure 3. All three sensors have the proper high correlation coefficients (R^2) above 0.997. The highest sensitivity (3.8×10^{-7} A μg L^{-1}) was obtained for the unmodified sensor with a different linear concentration domain (0.00207-0.1035 μg L^{-1}), in comparison with the modified electrodes based on reduced graphene oxide. However, the lowest limit of quantification was obtained for the reduced graphene oxide electrodes modified with Fe(II)Pc and Ni(II)Pc (0.001035 μg L^{-1}).

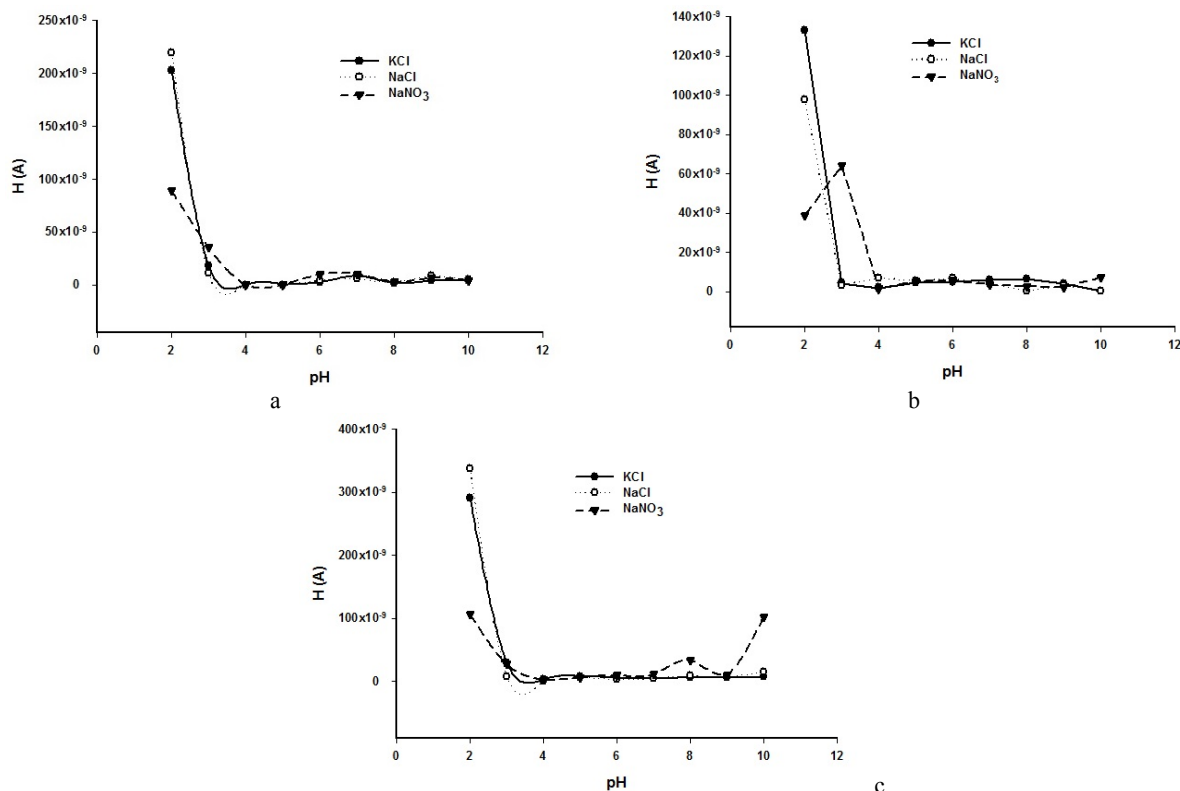Fig. 1 – The effect of electrolyte and pH on the peak height for a concentration of Pb^{2+} solution of 10^{-6} mol L^{-1} (207 μg L^{-1}): (a) RGox, (b) Fe(II)Pc/RGox, (c) Ni(II)Pc/RGox where H is the peak height (A).

Table 1

Response characteristics of the electrodes used for determination of Pb^{2+}

Parameter \ Sensors	Equation of calibration*	r	Sensitivity (A μg L^{-1})	Linear conc. range (μg L^{-1})	Limit of quantification (μg L^{-1})
RGox	$H = 2.3 \times 10^{-9} + 3.8 \times 10^{-7} \times C$	0.99847	3.8×10^{-7}	0.00207– 0.1035	0.00207
Fe(II)Pc/RGox	$H = 2.0 \times 10^{-9} + 5.7 \times 10^{-8} \times C$	0.99812	5.7×10^{-8}	0.001035 – 1.035	0.001035
Ni(II)Pc/RGox	$H = -6.8 \times 10^{-10} + 1.5 \times 10^{-7} \times C$	0.99871	1.5×10^{-7}	0.001035 – 1.035	0.001035

* H is the peak height (A); C is the concentration (μg L^{-1})

4. Real samples

Different types of waters (wasterwater, surface water, drinking water from spring, groundwater) were used for analytical determination of Pb^{2+} ions. Buffered water samples (1:1, v/v) were screened using the proposed sensors before and after the addition of certain amounts of Pb^{2+} ions. The results obtained using anodic stripping voltammetry compared with the standard ISO-method (SR EN ISO 11885:2009) using inductively coupled plasma optical emission spectrometry (ICP-OES) are presented in Table 2. It can be seen that all sensors have good results for the determination of Pb^{2+} ions in different types of water, and the relative standard deviation (RSD%) was less than 0.19% (n = 5).
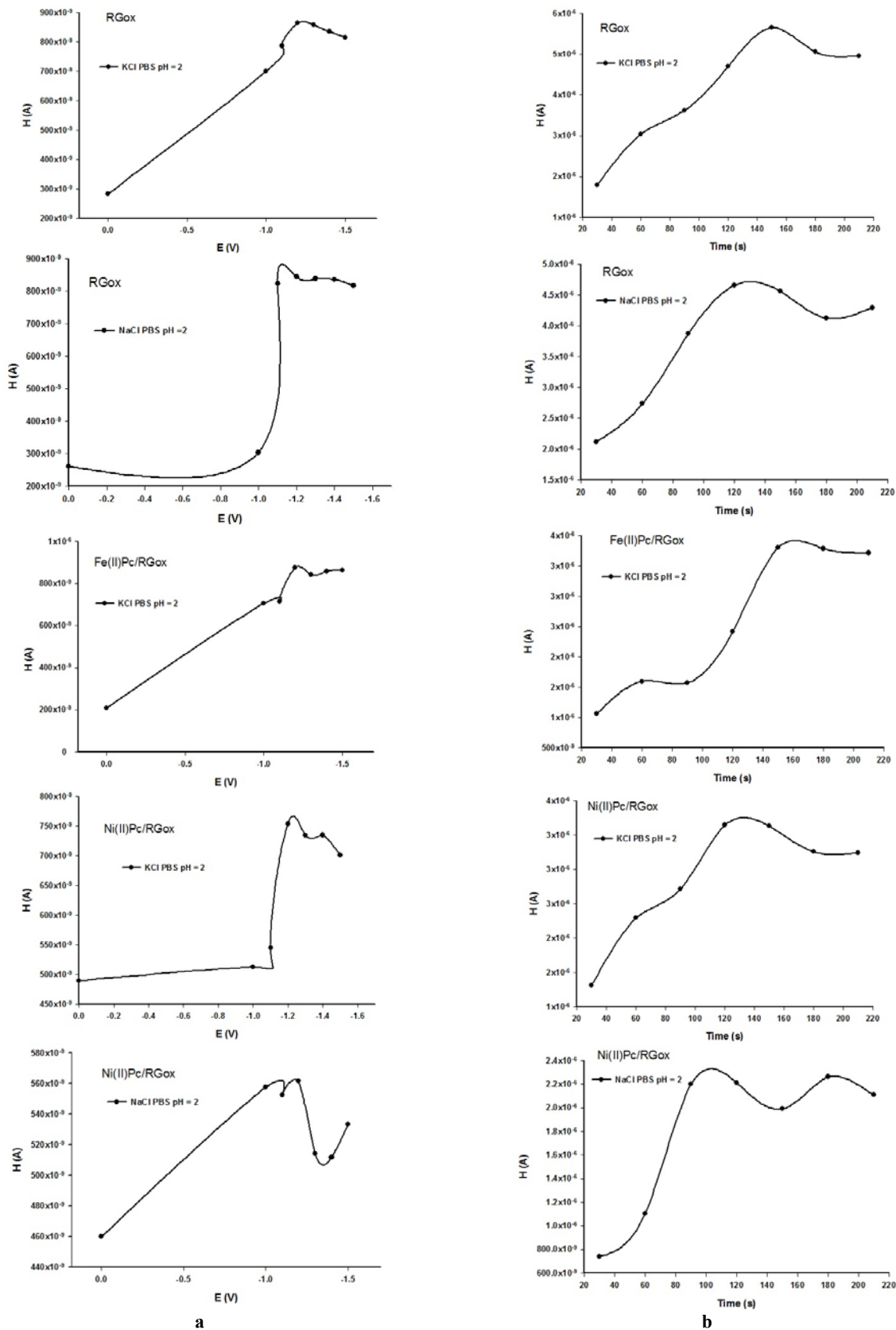
Fig. 2 – Influence of various parameters: a) deposition potential, b) deposition time for RGox with 0.1 mol L^{-1} KCl, PBS pH = 2 as supporting electrolyte, RGox with 0.1 mol L^{-1} NaCl, PBS pH = 2 as supporting electrolyte, Fe(II)Pc/RGox with 0.1 mol L^{-1} KCl, PBS pH = 2 as supporting electrolyte, Ni(II)Pc/RGox with 0.1 mol L^{-1} KCl, PBS pH = 2 as supporting electrolyte, Ni(II)Pc/RGox with 0.1 mol L^{-1} NaCl, PBS pH = 2 as supporting electrolyte, for a concentration of Pb^{2+} solution of 10^{-6} mol L^{-1} (207 µg L^{-1}) where H is the peak height (A).
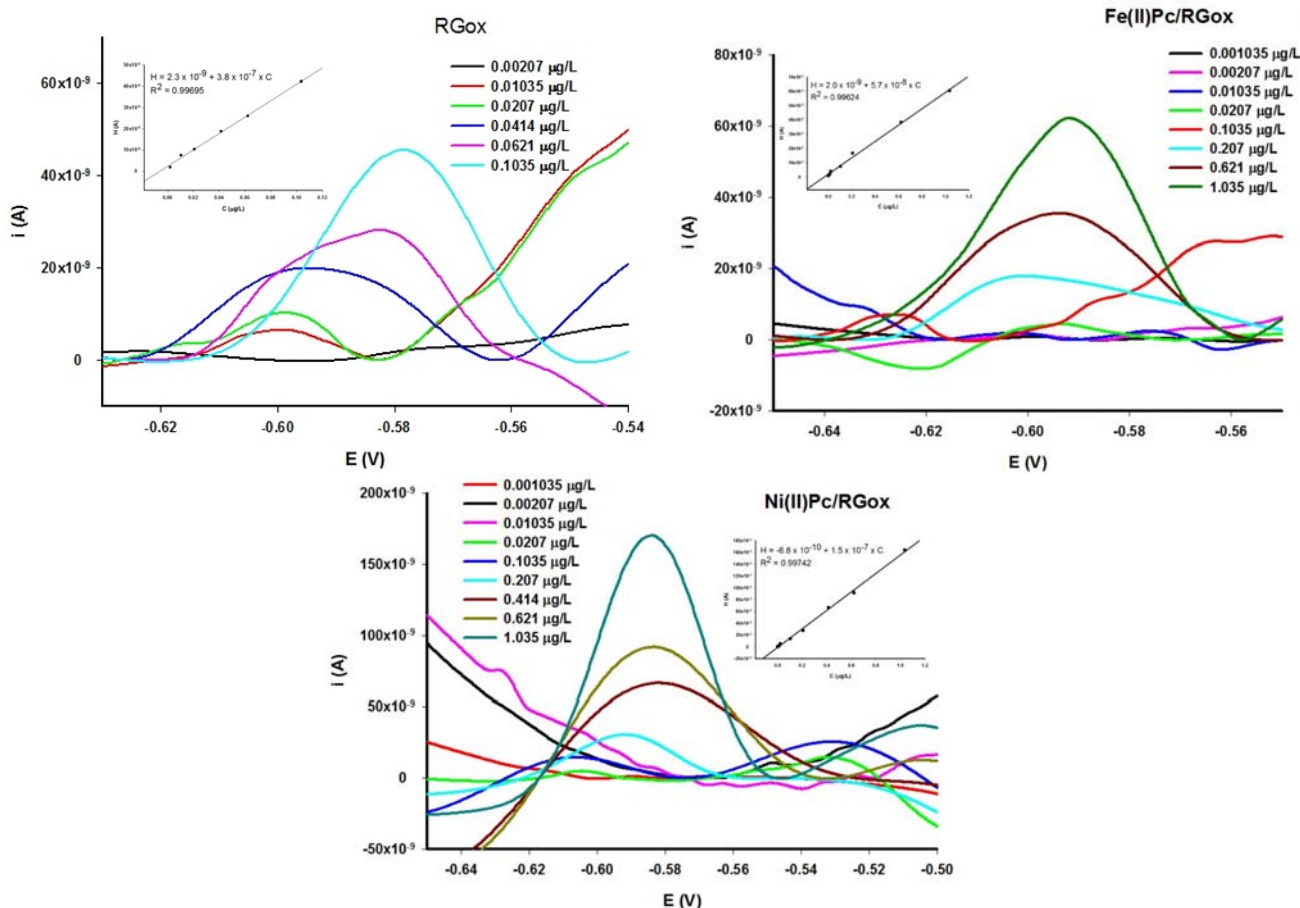
Fig. 3 – The anodic stripping voltamograms for the Pb^{2+} ions at different concentration; insert: the peak current vs. the concentration of Pb^{2+} ions.

Table 2

Sample results ($\mu g\ L^{-1}$) from different types of water samples for Pb^{2+}

Sample/ Method	Sensors	RGox	Fe(II)Pc/RGox	Ni(II)Pc/RGox
Sample 1 wastewater	ASV**	5.47±0.15	5.44±0.19	5.47±0.15
	ICP-OES***	5.5	5.5	5.5
Sample 2 surface water	ASV**	1.37±0.06	1.39±0.08	1.37±0.05
	ICP-OES***	1.40	1.40	1.40
Sample 3 drinking water from spring water	ASV**	1.01±0.04	1.08±0.02	0.88±0.05
	ICP-OES***	1.10	1.10	1.10
Sample 4 groundwater	ASV**	0.59±0.01	0.57±0.01	0.59±0.02
	ICP-OES***	0.6	0.6	0.6

* Relative standard deviation for 5 measurements (n=5)

** ASV = anodic stripping voltammetry

***ICP-OES = Inductively coupled plasma atomic emission spectroscopy.

CONCLUSION

Several sensors based on reduced graphene oxide modified with Fe(II)Pc or Ni(II)Pc were proposed for the determination of Pb^{2+} ions. It can be seen that all sensors have the same parameters (0.1 mol L^{-1} KCl, PBS pH = 2). The highest linear domain for the sensors was recorded for the modified electrodes. All sensors have good results for the determination of Pb^{2+} ions in different types of water.

REFERENCES

1. T. Heberer, M. Lahrssen-Wiederholt, H. Schafft, K. Abraham, H. Pzyrembel, K.J. Henning, M. Schauzu, J. Braeunig, M. Goetz, L. Niemanni, U. Gundert-Remy, A. Luch, B. Appel, U. Banasiak, G. Fleur Bol, A. Lampen, R. Wittkowski and A. Hensel, *Toxicol. Lett.,* **2007**, *175***, 118. (Doi: 10.1016/j.toxlet.2007.10.002).
2. P. Coppens, M. F. da Silva and S. Pettman, *Toxicology* , **2006**, *221***, 59. (DOI: 10.1016/j.tox.2005.12.022.)
3. T. Wenzl, R. Simon, E. Anklam and J. Kleiner, *Trends. Analyt. Chem.*, **2006**, *25***, 716. (DOI: 10.1016/ j.trac.2006.05.010).
4. K. Grob, M. Biedermann, E. Scherbaum, M. Roth and K. Rieger, *CRC. CR. Rev. Food Sci.*, **2006**, *46***, 529. (DOI: 10.1080/10408390500295490).
5. W. L. Bryden, *Asia Pac. J. Clin. Nutr.*, **2007**, *16***, 95.
6. J. Fink-Gremmels, *Vet. Quart.*, **1999**, *21*, 115. (DOI: 10.1080/01652176.1999.9695005).
7. M. E. Zain, *J. Saudi. Chem. Soc.*, **2011**, *15*, 129. (DOI: 10.1016/j.jscs.2010.06.006).
8. M. Torrice, *Chem. Eng. News.*, **2016**, *94*, 26.
9. T. H. Tulchinsky and E. A. Varavikova, "The New Public Health", Third Edition, 2014, p. 471. (DOI: 10.1016/B978-0-12-415766-8.00009-4).
10. World Health Organization International Agency for Research on Cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Inorganic and Organic Lead Compounds, Lyon, France, 2006, p. 87.
11. M. Dikilitas, S. Karakas and P. Ahmad, "Plant Metal Interaction Emerging Remediation Techniques", 2016, p. 41. (DOI: 10.1016/B978-0-12-803158-2.00003-5).
12. R. L. Canfield and T. A. Jusko, "Reference Module in Neuroscience and Biobehavioral Psychology Encyclopedia of Infant and Early Childhood Development", 2008, p. 200. (DOI: 10.1016/B978-012370877-9.00091-8).
13. K. Weizsaecker, *Primary Care Update for OB/GYNS*, **2003,** *10*, 304. (DOI: 10.1016/S1068-607X(03)00074-X).
14. A.-M. Georgescu, F. Nardou, V. Zichil and I. Denisa Nistor, *Appl. Clay. Sci.*, **2018**, *152*, 44. (DOI: 10.1016/j.clay.2017.10.031).
15. A. K. Juric, M. Batal, W. David, D. Sharp, H. Schwartz, A. Ing, K. Fediuk, A. Black, C. Tikhonov, H. M. Chan and L. Chan, *J. Hazard. Mater.*, **2018**, *344*, 55. (DOI: 10.1016/j.jhazmat.2017.09.035).
16. U. S. Environmental Protection Agency, Lead and copper rule revisions white paper, 2016.
17. E. Süren, S. Yilmaz, M. Türkoglu and S. Kaya, *Environ. Monit. Assess.,* **2007,** *125*, 91. (DOI: 10.1007/s10661-006-9242-5).