IDA Microelectrode – a Suitable Sensor for Ultra-Trace Analysis of Mercury in Water

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Application of interdigitated array IDA microelectrode in trace analysis of Hg in tap and environmental water was investigated. The method was tested together with two other electroanalytical techniques applying different working electrodes ("convention size" rotating disc electrode and single fibre microelectrode). The testing was done using synthetic samples spiked with known amounts of Hg(II) in inorganic Hg(ClO₄)₂ and organic Hg(C₂H₅)₂ forms in the range of its legal limiting value by the state regulations for tap and environmental water. All three tested methods proved to be suitable for Hg ultra-trace analysis on the concentration level required by the state regulations. Nevertheless, the method applying gold IDA microelectrode provided the most reliable results.

Only few spectral and electroanalytical methods can be used for trace determination of Hg which is one of the toxic elements representing a considerable risk for human health [1] even in trace amounts in environment. Because of its high sensitivity anodic stripping voltammetry is usually the method of choice for Hg trace determination. Different types of electrode materials (platinum, glassy carbon, gold) were tested. The best results in trace analysis of Hg by anodic stripping voltammetry were reported by *Goto et al.* [2] for the compact gold rotating disc electrode (AuRDE) but as the authors stated much effort was needed to yield reliable results.

Application of microelectrodes brought some improvement in stripping voltammetry analysis [3]. In the previous work [4] we successfully applied a single Au fibre microelectrode (AuFME) in trace analysis of Hg in the ultrapure gallium arsenide. Recent trends in development of voltammetric sensors were focussed on application of interdigitated (IDA) microelectrodes. We obtained good results with application of such electrode in ultra-trace analysis of Fe in ultrapure spectral carbon [5].

In this paper the results of application of this sensor for Hg trace determination are reported comparing its efficiency to "conventional size" AuRDE and a single AuFME. Testing was done on synthetic samples with known Hg(II) amounts on the level of Hg legal limiting value by corresponding state regulations 1 μ g dm⁻³ for the tap [6] and the first class purity river water [7]. Five synthetic samples with Hg content 0.2 μ g dm⁻³, 0.4 μ g dm⁻³, 0.5 μ g dm⁻³, 1.0 μ g dm⁻³, and 2.0 μ g dm⁻³ were prepared. Hg content in the first sample was 5 times lower and in the last sample 2 times higher than were the corresponding legal limiting values. Hg^{2+} concentrations in the analyzed sample solutions were then in the range from 1×10^{-9} mol dm⁻³ to 1×10^{-8} mol dm⁻³.

EXPERIMENTAL

All chemicals were of anal. grade used without any further purification with the exception of isothermally distilled HNO₃. Stock 1×10^{-3} mol dm⁻³ Hg(ClO₄)₂ solution was prepared by dissolution of the equivalent quantity of HgO in concentrated HClO₄ and dilution to exact volume with triply distilled water. Stock 1×10^{-3} mol dm⁻³ Hg(C₂H₅)₂ solution was prepared by dissolution of the commercially available Hg(C₂H₅)₂ (Aldrich) of anal. grade in triply distilled water. Standard 2×10^{-7} mol dm⁻³ Hg(ClO₄)₂ and Hg(C₂H₅)₂ solutions used for spiking of the synthetic samples were prepared by dilution of the stock solutions daily.

The real sample of tap water was taken from the tap in our laboratory and the sample of the environmental water was collected from the river Danube. Samples were taken and stabilized by the procedures according to the state regulation [8].

AuRDE of the conventional size was made by inserting a gold wire (1 mm in diameter *ca.* 3 mm long) into a teflon carrier which was then screwed on a rotary adapter. AuFME was made using a gold fibre (20 μ m in diameter, *ca.* 2.5 cm long). The fibre was attached to subsidiary copper wire (*ca.* 10 cm long, diameter *ca.* 0.5 mm) by means of conductive silver epoxide (AI Technology). Wire was inserted into a glass tube (*ca.* 8 cm long, diameter *ca.* 0.5 cm) so that



Fig. 1. Schematic depiction of the vertically arranged IDA microelectrode. Au film deposited on a glass carrier is separated by 0.3 μ m thick insulation layer from an upper Au layer forming two pairs of interdigitated arrays each consisting of 26 segments 400 μ m long and 5 μ m wide separated by 5 μ m gap.

ca. 2 cm of gold fibre protruded out of the tube which was then filled with epoxide resin. AuIDA microelectrode was made at the Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology. The vertically arranged IDA microelectrode with bottom continuous Au-film and middle insulation layer was fabricated by using resist film sputtering, chemical vapour deposition, ion sputter/plasma etching, and UV photolitography with lift-off technique. Its construction is depicted in Fig. 1.

Electrochemical measurements with working Au-RDE and single AuFME were carried out by means of the polarographic analyzer PA4 (Laboratorní přístroje, Prague, Czech Republic) set in a differential pulse mode. Bipotentiostat EG & G PAR (Princeton Applied Research) model 366 A was used for measurements with IDA microelectrode. Saturated calomel electrode (SCE) was used as a reference electrode and a platinum wire as a counter electrode.

Sample Digestion Procedure

All forms of mercury must be turned to Hg^{2+} in the process of the sample preparation not to escape electrochemical determination. Two different procedures were applied:

1. Commonly used "wet" procedure [2]. To 50 cm³ water sample 0.5 cm³ of $(m(\text{HCl}):m(\text{HNO}_3) = 3)$ and 0.1 cm³ of H₂O₂ were added and UV irradiation for 2 h followed in a silica cup with 100 W mercury lamp (distance 20 cm).

2. Procedure of "Fentons reagent" [9]. To 50 cm³ water sample a "Fentons reagent" (50 mm³ of fresh sat. Fe(NH₄)₂(SO₄)₂ and 100 mm³ of H₂O₂) was added and kept on a water bath for 30 min.

RESULTS AND DISCUSSION

Because all three working electrodes were made of equal electrode material the same procedure was used for their surface conditioning. Prior to a series of Hg voltammetric determinations they were conditioned by the five times repeated anodic and cathodic polarization scanning at a potential range from 0.2 V to 1.8 V vs. SCE in solution of 0.1 mol dm⁻³ HClO₄ + 0.003 mol dm⁻³ HCl. One minute polarization at the potential 1.8 V vs. SCE was satisfactory to keep the electrode active between consecutive measurements.

Experimental conditions used in Hg determination on AuRDE (mainly the deposition potential 0.05 V vs. SCE) were selected on the basis of the DPASV signal optimization. At this potential the limiting value of Hg²⁺ rate transport was reached and yet no time-consuming sample deaeration was needed since dissolved oxygen is electroinactive at that potential. Moreover, very few possibly interfering analytes are reduced at this positive potential. Deposition of Hg on the rotating working electrode (1600 min^{-1}) was done at this potential usually from 480 s to 1200 s (depending on the Hg^{2+} concentration). 30 s after the electrode rotation was stopped the potential was scanned from +0.05 V to +0.8 V vs. SCE at a 20 mV s⁻¹ rate. A stripping voltammogram was recorded in the differential pulse mode using a pulse amplitude of 25 mV; a pulse duration 50 ms and a pulse repetition time 100 ms. Hg anodic stripping peak at the potential about +0.55 V vs. SCE was used for evaluation.

Experimental conditions used in Hg determination on single AuFME were similar to the case of Au-RDE. The significant difference in performing analysis is that the deposition on a microelectrode is done in a quiescent solution. It is a consequence of prevailing of the spherical component of overall flux to a microsize working electrode. Due to this it is possible to omit stirring during accumulation. The results of the determination are not influenced by irregularities in the rotation of AuRDE. Some improvement was observed in results of analysis when a single AuFME instead of a common AuRDE was used [3] because the signal registered at AuFME was more suitable for evaluation.

Experimental conditions when IDA microelectrode was used for Hg determination were different. IDA microelectrode with preconditioned arrays was inserted into the analyzed solution. In the vertical arrangement both upper electrodes formed one array and the bottom Au-film the second array. One of its pair arrays was polarized by the potential +0.05 V vs. SCE at which Hg²⁺ from sample is deposited (the time interval was similar to those as in case of AuRDE or AuFME working electrodes). Next the potential of this array was switched by step to +0.8 V vs. SCE at which all deposited Hg is stripped. Simultaneously the second array of the IDA microelectrode started

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Sample	given	found	Standard deviation Limits at 0.95 confidence level $10^6 \sigma(w(Hg))$ (% of found amount)	
1	0.20	0.14 ^a	0.05	70 ± 31
		0.19 ^b	0.04	95 ± 25
		0.17 ^c	0.04	85 ± 25
2	0.40	0.31 ^a	0.09	77 ± 28
		0.35 ^b	0.06	88 ± 19
		0.43 ^c	0.06	107 ± 19
3	0.50	0.54 ^a	0.07	108 ± 17
		0.42 ^b	0.07	84 ± 17
		0.53 ^c	0.06	106 ± 15
3^d	0.50	0.48 ^a	0.05	96 ± 12
		0.44^{b}	0.07	88 ± 17
		0.52 ^c	0.06	104 ± 15
4	1.00	1.11 ^a	0.18	110 ± 22
		1.06 ^b	0.16	106 ± 20
		0.96 ^c	0.14	96 ± 17
5	2.00	2.15 ^a	0.26	107 ± 17
		1.64^{b}	0.29	82 ± 18
		2.11 ^c	0.21	106 ± 13

 Table 1. Results of Hg Analysis in Synthetic Samples. Standard Additions of Inorganic and Organic Hg Compounds Added to Triply Distilled Water. Values are Average of 5 Determinations

a) AuRDE, b) AuFME, c) IDA microelectrode; d) "Fentons reagent" digestion procedure.

to be polarized by the constant potential +0.05 V vs. SCE which was negative enough so that Hg^{2+} (stripped into the diffusion layer of the IDA microelectrode after the anodic stripping) was reduced. The surface of this array is in good preconditioned state not influenced by electrode process on a pair array. Submicrometrically narrow gap between microbands enables the significant increase of the diffusion layers overlap in comparison with IDA microelectrodes with horizontally spaced arrays the bands and gaps of which are usually of the comparable size (5 μ m). This is advantageous because of a lower possible loss of the determined species by diffusion to the bulk of solution. The experimental curve - time dependence of the reduction current was registered. This current was free of the undesirable capacity component because it was registered at the constant potential. The method of multiple standard additions was used for evaluation. As an example, some experimental curves taken in analysis of a synthetic sample with standard Hg²⁺ additions are depicted in Fig. 2. The results of Hg determination in the synthetic samples 1-3 spiked with inorganic and organic Hg compound by all three methods are given in Table 1. As it can be seen from the data all three tested electroanalytical methods proved to be appropriate for the ultra-trace Hg analysis on the concentration level required by the state regulations. The value "found" does not differ statistically from the value "given" in any of synthetic samples. Relatively wide reliability interval is acceptable taking into account the low concentrations of determined species. The signal registered in the synthetic sample with the lowest Hg^{2+} concentration can be clearly resolved from background signals. The signal corre-



Fig. 2. Experimental dependences I_c vs. t registered in Hg²⁺ analysis in synthetic samples. 1. Blank; 2. synthetic sample containing 0.2 μ g dm⁻³ Hg²⁺; 3. standard addition corresponding to 0.1 μ g dm⁻³ Hg²⁺ to the analyzed sample; 4. second standard addition corresponding to 0.1 μ g dm⁻³ Hg²⁺ to the analyzed sample.

sponding to 5×10^{-10} mol dm⁻³ Hg²⁺ (deposition time 30 min) can be still resolved from the background signals and this concentration can be considered to be the detection limit of the method.

No loss of Hg was observed in process of the sample solution preparation. Both methods of sample digestion provided similar results within the experimental error of the electroanalytical determination.

As it can be seen from data in Table 1 the method applying AuIDA microelectrode provided the most reliable results. It can be explained by the fact that the

Sample	Sample specification	$10^6 \cdot w(\text{Hg})$
Tap water ¹ Tap water ² Environmental water ¹ Environmental water ²	Tap in laboratory Tap in laboratory River Danube River Danube	$\begin{array}{c} 0.24 \pm 0.11 \\ 0.18 \pm 0.09 \\ 0.43 \pm 0.17 \\ 0.37 \pm 0.21 \end{array}$

 Table 2. Results of Hg Analysis in Some Real Water Samples.

 Values are Average of 5 Determinations

Number in index indicates the applied sample pretreatment procedure described in Experimental.

signal is recorded on the preconditioned surface of the adjacent pair array of the IDA microelectrode. The surface of this array was not influenced by the previous electrode reaction (deposition process) and was left in good preconditioned state. Moreover, the IDA microelectrode with the vertical arrangement used for the determination has a favourable geometry.

The method was applied to analysis of some real water samples. The results of Hg determinations are given in Table 2.

The experiments with real water samples were in agreement with the results of Hg analysis in synthetic samples. No difference in results of analysis in dependence on the sample pretreatment procedure was observed. No interference of the other species present in the real water samples was observed. It was in agreement with the expectation because only very few analytes could be reduced at such positive potential which was used for Hg electrodeposition. It can be stated that the method using AuIDA microelectrode is an advantageous alternative for Hg determination in tap and environmental water to DPASV methods applying AuRDE or AuFME working electrodes. Because of very favourable reduction potential the method was applied for Hg^{2+} determination but it can be used also for the other toxic elements determinations when appropriate potentials are used to polarize IDA microelectrode arrays.

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REFERENCES

- Thayer, J. S., Environmental Chemistry of the Heavy Metals, p. 145. VCH Publishers, New York, 1995.
- Goto, M., Ikenoya, K., and Ishii, D., Bull. Chem. Soc. Jpn. 53, 3567 (1986).
- Niwa, O., Morita, M., and Tabei, H., *Electroanalysis 3*, 163 (1991).
- 4. Rievaj, M. and Bustin, D., Analyst 117, 1471 (1992).
- Bustin, D., Mesároš, Š., Tomčík, P., Rievaj, M., and Tvarožek, V., Anal. Chim. Acta 305, 121 (1995).
- 6. STN 75 7111 State regulation for pollutants content in tap water (1998).
- 7. STN 75 7221 State regulation for pollutants content in environmental water (1999).
- 8. STN 75 7051 State regulation for collection of tap and environmental water samples (1999).
- Ping, L. and Dasgupta, P. K., Anal. Chem. 61, 1230 (1989).