Gold Fibre Microelectrode — Application in Trace Analysis of Arsenic and Mercury in Water

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An efficient, reliable and rapid procedure for the routine arsenic and mercury traces determination in tap and environmental waters is proposed. It is based on the application of a gold fibre microelectrode as a working electrode of unique properties. Of these especially the possibility of electrodeposition in a quiescent solution is of special importance because it enables a substantial simplification of experimental procedure enabling thus a convenient performance of experiments. Detection limits and precision of differential pulse anodic stripping gold fibre microvoltammetry (DPASV) are comparable to those obtained by gold rotating disk electrode (RDE). Proposed procedures were tested using synthetic samples spiked with arsenic and mercury. They were found suitable for mentioned pollutants monitoring on the concentration level limited by the state regulation of their contents in drinking water.

Mercury and arsenic are poisons of cumulative character [1] directly attacking nervous system [1]. They can be brought to environment from different sources, most frequently as emissions from coal power stations. They are biologically nondegradable but undergo a biogeochemical cycle in the environment by which they can get to the drinking (tap) water [2].

Of numerous analytical techniques for As and Hg trace monitoring atomic absorption spectrometry (AAS) remains predominant and constitutes the basis of official reference method [3, 4]. Electroanalytical methods, especially those with the preconcentration of determined species on a working electrode also provide sufficient sensitivity and precision for such analysis. Moreover, the instrumentation is substantially less expensive. Different types of electrode materials, glassy carbon, platinum, and gold were applied in stripping analysis of arsenic [5—7] and mercury [8—10]. The lowest determination limits for arsenic [7] and also for mercury [10] were reported for gold.

An attractive feature of microelectrodes — a steady-state diffusion mass transport — eliminates the need of forcing the solution convection during the deposition step [11]. The use of quiescent solutions simplifies the instrumentation and operation of stripping analysis yielding results comparable (or even better) to those obtained at conventional size rotating disk electrodes [12].

Our proposal of reliable and rapid procedure for routine analytical monitoring As and Hg in tap water is based upon the application of a gold fibre working microelectrode. It combines the unique properties of microelectrode with the most advantageous material [7, 10] for arsenic and mercury determination.

EXPERIMENTAL

All chemicals were of anal. grade purity used without any further purification.

Stock arsenic solution of mass concentration ρ 1 mg cm^{-3} As(III) was prepared by dissolving 1.320 g of diarsenic trioxide in a minimum amount of 20 mass % potassium hydroxide solution. The solution was acidified to pH 1 with sulfuric acid and diluted to 1 dm^3. Stock mercury solution of mass concentration ρ 0.2 mg cm^{-3} Hg(II) was prepared by dissolution of 0.2166 g of mercury oxide in the concentrated $HClO_4$ and dilution to exact volume 1 dm^3. Triply distilled water was used to prepare all solutions. Standard solutions of desired arsenic and mercury concentrations were prepared by dilution with H_2O from the stock solutions daily.

A PA 4 polarographic analyzer (Laboratorní přístroje, Prague) was used for measurements. It was set to DPASV mode with 50 mV pulses of 5 Hz frequency. For arsenic determination the deposition potential – 0.3 V *vs.* SCE and scan rate 20 mV s^{-1} for anodic stripping was used while for mercury analysis the deposition potential 0.2 V *vs.* SCE and scan rate 50 mV s^{-1} for anodic stripping were found to be more suitable. Deposition time varied according to As(III) or Hg(II) concentrations from 1 min to 20 min. Two-electrode configuration was applied. The construction of the working microelectrode was described in detail in our previous paper [13]. It was stored

in the air when not in use. Prior to a set of determinations it was immersed into chromosulfuric acid for 10 min. After rinsing with distilled water the conditioning was carried out by polarization of the microelectrode (see below). The reference saturated calomel electrode (SCE) was connected to the sample solution *via* a salt bridge containing 1 M-H_2SO_4 solution (exchanged daily).

Sample Preparation

Sample digestion procedures commonly used for natural water decomposition involve a step in which metal-binding organic substances are decomposed by UV irradiation in acidic media and in the presence of oxidizing agent [11]. Omitting this step may cause that some Hg or As escape the electrode reduction in electrochemical accumulation. After this step the sample contains both Hg and As in their highest oxidation state. This is advantageous in mercury determination but electroinactive pentavalent arsenic has to be reduced in a part of sample to As(III). The sample preparation was done according to the following procedure: to 40 cm^3 of water sample 2 cm^3 of concentrated sulfuric acid was added followed by 0.5 cm^3 of 30 mass % H_2O_2. The sample was then irradiated in a 50 cm^3 quartz cell with a 100 W UV mercury lamp (distance 20 cm) for 2 h. Then the sample was divided into two parts. To one portion designed for arsenic determination 0.5 cm^3 of natrium sulfite saturated solution was added (to reduce electroinactive pentavalent arsenic to As(III)) and heated for *ca.* 30 min at the temperature close to the boiling point. Elevated temperature helps to complete the reduction of As(V) and to remove the excess of natrium sulfite. Part of the sample for mercury analysis was heated without any addition to get rid of excess H_2O_2.

RESULTS AND DISCUSSION

Spiked Samples

The legal limiting value of arsenic mass concentration ρ(As) in drinking water is 0.05 mg dm^{-3} [1]. The same state regulation allows the maximum ρ(Hg) 0.001 mg dm^{-3}. This corresponds approximately to 6.67×10^{-7} mol dm^{-3} As(III) and 5×10^{-9} mol dm^{-3} Hg(II) concentrations. In respect to this concentration level the proposed procedure was tested using synthetic samples spiked with arsenic and mercury in amounts ranging from one fifth to the double of the limiting value for both pollutants mass concentrations. The method of exchanged solution was used for As and Hg determination. This procedure although not necessary for tap water makes the analysis more universal, applicable also for waste water samples possibly containing components interfering with As or Hg electrolytical dissolution. For arsenic stripping analysis 1 M-sulfuric acid exchanged solution was found to be the most advantageous. For anodic dissolving of mercury the exchanged solution consisting of 0.1 M-$HClO_4$, 0.003 M-HCl and ρ(NaF) = 500 mg dm^{-3} was the most suitable. These media were also found convenient for conditioning of the working electrode before the first use and in between the determinations. The exchange of solutions was carried out without switching the instrument off. The working electrode was removed from the sample solution first. Both electrodes were then rinsed carefully with distilled water and submerged into the exchanged solution in a reversed order (the working electrode as the second one).

Determination of Arsenic. The working gold fibre microelectrode was conditioned prior to analysis in 1 M-sulfuric acid by applying a potential of 2.0 V *vs.* SCE for 20 s followed by a potential of 0 V *vs.* SCE for 7 s [7]. The potential – 0.3 V *vs.* SCE was applied for electrolytical deposition of arsenic in the deaerated sample solution (10 cm^3). Stirring of the analyzed solution during As accumulation on the microelectrode was unnecessary. After arsenic plating for 60—480 s (depending on its concentration) the sample solution was replaced by the exchanged solution (1 M-H_2SO_4) and anodic stripping started by polarizing the working electrode to more positive potentials (parameters for DPASV determination are given in Experimental). The peak of arsenic oxidation appears at the potential *ca.* 0.2 V *vs.* SCE. Polarization of the working electrode continued to 2.0 V *vs.* SCE for electrode conditioning prior to analysis of the next sample. Good reproducibilities are obtained with this electrode conditioning. For five parallel determinations in the same sample solution the peak heights were within 8 % reproducibility interval.

Determination of Mercury. Though Hg(II) concentration 5×10^{-9} mol dm^{-3} corresponding to the legal limiting value [1] is approximately 130 times lower than that of As(III) the determination of mercury at this concentration level causes no problems. This is because of very favourable matrix and also due to the advantageous electrode reaction (reversibility). Moreover at the potential applied for the Hg electrodeposition 0.2 V *vs.* SCE fewer interfering electroactive species are reduced. This is the reason why even time-consuming deaeration of the analyzed solution can be omitted.

Working electrode was conditioned in the exchanged solution by a 10 s polarization at 0.2 V *vs.* SCE followed by a 30 s polarization at 1.8 V *vs.* SCE. This was repeated five times before its first use. The same volume (10 cm^3) of the digested sample solu-

Table 1. Results of Analysis in Synthetic As and Hg Spiked Water Samples (Values Are Average of Five Determinations)

Spiked sample	Spiked amount ρ(given)/μg dm^{-3} ρ(found)/μg dm^{-3}		Standard deviation	Limits of confidence for 95 % probability
	As	Hg	s/μg dm^{-3}	%
1	10			
	7.8		2.4	78 ± 36
2	20			
	17.2		4.3	86 ± 30
3	50			
	44.1		6.5	88 ± 17
4	100			
	92.2		9.7	92 ± 12
5		0.20		
		0.16	0.03	80 ± 22
6		0.40		
		0.38	0.05	95 ± 16
7		1.00		
		0.95	0.12	95 ± 15
8		2.00		
		1.88	0.19	94 ± 12
9	20	1.00		
	14.3		5.5	72 ± 46
10	50	0.40		
	42.8		8.8	86 ± 24
11	20	1.00		
		0.96	0.11	96 ± 14
12	50	0.40		
		0.38	0.05	95 ± 16

tion for Hg analysis is placed in an electrolytic vessel. Stirring of the sample solution during Hg accumulation deposition for 2—20 min (in dependence on Hg(II) concentration) is not necessary. Anodic stripping in exchanged solution is started by polarization of the working electrode to more positive potentials (parameters are given in Experimental). The peak of mercury oxidation appears at the potential 0.6 V *vs.* SCE. Polarization continues to 1.8 V *vs.* SCE at which the electrode is conditioned for 60 s before analysis of successive sample.

The heights of the anodic stripping peaks of both determined pollutants depended linearly on their concentrations for all over the above-mentioned concentration range (1.33×10^{-7}—1.33×10^{-6} mol dm^{-3} for As(III) and 1×10^{-9}—1×10^{-8} mol dm^{-3} for Hg(II)). Their signals were also linearly dependent on the deposition time in the interval 2—20 min for 2.67×10^{-7} mol dm^{-3} As(III) and 4—20 min for 2×10^{-9} mol dm^{-3} Hg(II).

The results of As and Hg determination in the spiked samples are given in Table 1. Statistical evaluation of experiments shows that the arithmetic mean of parallel determinations does not differ statistically from the given As or Hg values in any of the spiked samples. The interval of reliability is well acceptable taking into account the concentration levels of determined metals. Slightly lower found values, especially in the case of arsenic, can be explained as a loss of determined species during digestion procedure and/or by insufficient arsenic reduction. Their influence on the results of analysis is negligible. No significant mutual interference of As and Hg was observed in the investigated range. As shown in Table 1 arsenic did not interfere with mercury determination even if present in more than 100-fold excess. It is in agreement with the expectation because As(III) is not reduced at the potential of mercury accumulation (0.2 V *vs.* SCE). At the potential – 0.3 V *vs.* SCE used for arsenic deposition both pollutants are accumulated. The interference of mercury in arsenic determination has not been found substantial (Table 1) if mercury was present in amounts typical for polluted river water [14].

The signals corresponding to 1.3×10^{-8} mol dm^{-3} As(III) and 1×10^{-10} mol dm^{-3} Hg(II) (deposition times 20 min) can still be resolved from background signals. These concentrations (corresponding approximately to 1/50 of legal limiting values) can be considered as estimates of the determination limits of arsenic and mercury.

Real Sample Analysis

Samples of tap water from east and west districts of Bratislava and natural water from the river Dan-

Table 2. Results of As and Hg Analysis in Some Tap and River Water Samples (Values Are Average of Five Determinations)

Sample	Specification	Determined species	ρ(Pollutant)/(μg dm^{-3})		
1	tap *a*	As	<1		
1	tap *a*	Hg	0.15 ± 0.07		
2	tap *b*	As	<1	<1	*c*
2	tap *b*	Hg	0.11 ± 0.06	<0.2	*c*
3	river Danube	As	2.8 ± 0.8	3.9 ± 0.7	*c*
3	river Danube	Hg	0.21 ± 0.10	<0.2	*c*

a) East and *b*) west district of Bratislava; *c*) determined by independent AAS method.

ube (samples were taken and stabilized according to usual procedure [14]) were analyzed. Multiple standard addition method was used for the evaluation of arsenic and mercury contents (the overall time required for both metals determination was around 2 h). Results are given in Table 2 together with values found by the independent AAS method. As shown in Table 2 no significant difference was observed. As it can be seen from these data arsenic and mercury contents in tap water are substantially lower than corresponding limiting values [1]. Both pollutants contents in the river Danube water though higher than those in the tap water also do not exceed these rather strict limits. The method was found well suitable for both pollutants control in water samples with respect to the corresponding state regulation for tap [1] and river [14] water.

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