Application of Voltammetric Microelectrodes for Mercury Trace Analysis in Food Products – Fruit Juices and Beer

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A method applying a gold fibre microelectrode is proposed for differential pulse anodic stripping voltammetry determination of traces of mercury in food products – fruit juices and beer. The method was tested using synthetic samples containing Hg at the trace level well below the state regulation limiting mass fraction value 10×10^{-9} for mercury content in food products. It was applied to Hg analysis in some real samples of fruit juices Fruiko and beer distributed to market.

An increased interest in human health leads to monitoring of some pollutants content in food products before they are allowed to be distributed to market. Mercury due to its toxicity and possible cancerogenity [1] belongs to pollutants the level of which in foods has to be monitored in order not to exceed the legal limiting mass fraction value 10×10^{-9} given by the state regulation [2]. Differential pulse anodic stripping voltammetry (DPASV) is one of the analytical methods providing sufficient sensitivity and accuracy to obtain data at that required level [3].

Application of microelectrodes in DPASV increased efficiency of this method and enabled to yield more reliable results than those obtained at conventional size electrodes. This is a consequence of better reproducibility of mass transport during the deposition step which can be performed in a quiescent solution [4]. Moreover, the microelectrodes are less susceptible to the main types of interferences commonly observed at macroelectrodes [5].

In this paper the method using microelectrode made of pure gold is described for the determination of mercury at the trace level in food products – fruit juices and beer.

EXPERIMENTAL

All chemicals were of anal. grade used without any further purification. None of used chemicals contained mercury at the level to provide a detectable DPASV signal. Stock 1×10^{-4} mol dm^{-3} mercury solution was prepared by dissolving the calculated amount of HgO in concentrated perchloric acid and dilution to exact volume with triply distilled water. Standard 2×10^{-6} mol dm^{-3} Hg^{2+} solution was prepared by dilution of the stock solution daily.

DPASV measurements were performed using PAR Model 273 A (Princeton Applied Research, USA) on line with computer PC-AT 80 386. Electrochemical software ECHEM (PAR EG & G) enabled data acquisition and processing thus ensuring automation, flexibility, and convenience of performing analysis. The instrument was set to DPASV mode with following parameters: deposition potential 0.2 V *vs.* SCE, deposition time varied according to mercury concentration from 2 to 20 min. Anodic stripping scan rate was 20 mV s^{-1}, pulse amplitude 50 mV and pulse frequency 5 Hz. Applied parameters were chosen on the basis of the experimental DPASV signal optimization. Attention was focused especially on the deposition potential selection. No difference in the height of DPASV signal was observed if the deposition potential varied in the range from −0.3 V to 0.3 V *vs.* SCE. At the potential 0.4 V *vs.* SCE lower signal was observed probably due to the fact that the limiting value of Hg^{2+} rate transport was not reached. At more negative potentials further electroactive species can be reduced and interfere with the mercury determination. The potential 0.2 V *vs.* SCE seems to be the most suitable because the Hg^{2+} reduction limiting current is certainly reached and very few possibly interfering analytes are reduced at such positive potential. Since also dissolved oxygen is electroinactive at that potential the time-consuming sample deaeration can be omitted. Two-electrode configuration was used. The reference saturated calomel electrode (SCE) connected to the sample solution by a salt bridge containing 1 mol dm^{-3} $NaNO_3$ solution was applied.

Construction of the gold fibre microelectrode was described in our previous report [6]. The base for its construction was a gold fibre (20 μm in diameter) attached to supporting copper wire with Ag-epoxy resin and sealed in a glass tube so that only *ca.* 2 cm of gold fibre protruded out of the tube. Prior to a series

of measurements it was 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} $HClO_4$ + 0.003 mol dm^{-3} HCl + 0.5 g dm^{-3} NaF. This solution was later used as an exchanged solution since it was found to be the most suitable for developing Hg^{2+} DPASV signal. One minute polarization at the potential 1.8 V *vs.* SCE was satisfactory to keep the electrode active between consecutive measurements. An individual microelectrode could be kept in good condition for several weeks.

Sample Digestion Procedure

For the sample decomposition commonly used "wet" decomposition method [7] was adopted. A sample – 2 g of fruit juice or beer – was put into a teflon decomposition vessel together with 5 cm^3 of concentrated nitric acid and then it was airtightly closed with a cap and sealed in a steal covering. It was placed into a hot-air sterilizer at a temperature 160 °C for two hours. After cooling the sample solution was quantitatively removed and diluted to final 20 cm^3 volume with triply distilled water.

RESULTS AND DISCUSSION

The state regulation for pollutants contents in food products [2] allows the maximum value for mercury mass fraction in fruit juices and beer 10×10^{-9} If the procedure for sample decomposition described in Experimental is used, the content corresponds to the 2.5×10^{-9} mol dm^{-3} Hg^{2+} concentration in the analyzed solution. No problems were expected on this Hg^{2+} concentration level concerning sensitivity of DPASV

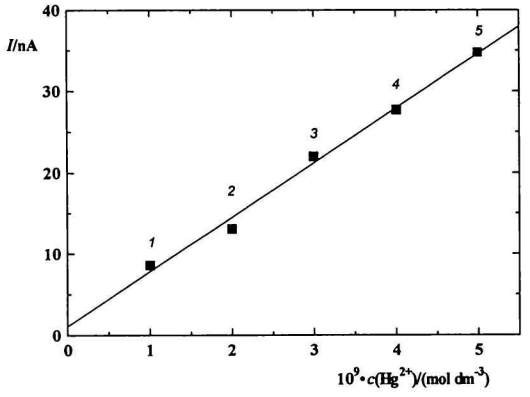

Fig. 1. DPASV signal dependence on Hg^{2+} concentration. The points of the plot are corresponding peak heights of the experimental voltammograms. DPASV settings as given in Experimental. Deposition time 10 min. *1.* 10 mm^3, *2.* 20 mm^3, *3.* 30 mm^3, *4.* 40 mm^3, *5.* 50 mm^3 of 2×10^{-6} mol dm^{-3} Hg^{2+} standard solution added to 20 cm^3 of 0.1 mol dm^{-3} $HClO_4$ + 0.003 mol dm^{-3} HCl + 0.5 g dm^{-3} NaF solution.

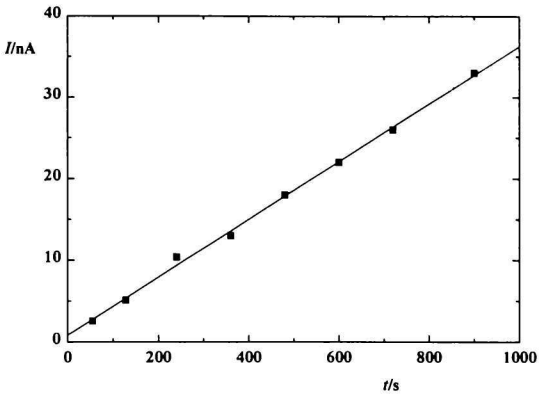

Fig. 2. DPASV signal dependence on the deposition time in the solution of 2×10^{-9} Hg^{2+} in the exchanged solution.

determination. The linearity of DPASV signal dependence on Hg^{2+} concentration was observed all over the investigated range from 1×10^{-9} to 5×10^{-9} mol dm^{-3} Hg^{2+} concentrations. The relationship between Hg^{2+} concentration and DPASV peak height remains strictly linear as shown in Fig. 1. A small positive intercept on current axis in Fig. 1 can be explained by the influence of the sample matrix or a residue on the working electrode. Its value is low in this case and does not substantially influence the mercury determination. Existence of the intercept is often reported in papers dealing with trace analysis. The linear dependence of DPASV signal on the deposition time in the range from 1 to 15 min was also observed (Fig. 2).

Respecting the above-mentioned concentration level a series of spiked samples with known amount of mercury were prepared. The spiking was done by pipetting appropriate amount of 2×10^{-6} mol dm^{-3} $Hg(ClO_4)_2$ standard solution directly to a solution with the composition similar to typical fruit juices (solution of glucose, fructose, citric and humic acids) not containing detectable amount of mercury (Hg mass fraction determined by independent AAS method less than 1×10^{-9}).

Hg-Spiked samples were digested by the procedure described above. The method of exchanged solution was applied to avoid the unfavourable influence of matrix. The working gold fibre microelectrode was immersed into the sample solution. After the electrochemical accumulation of mercury at the potential 0.2 V *vs.* SCE the sample solution was exchanged for 0.1 mol dm^{-3} $HClO_4$ + 0.003 mol dm^{-3} HCl + 0.5 g dm^{-3} NaF solution without circuitry disconnection. The results of Hg analysis in spiked samples are given in Table 1.

Statistical evaluation of experiments shows that arithmetic mean of 5 parallel determinations does not differ statistically from the given value in any of the spiked samples. The reliability interval is well acceptable taking into account the low concentration level of determined species. The signal corresponding to $2 \times$

Table 1. The Results of Analysis of Mercury-Spiked Synthetic Samples. The Values Are Average of Five Determinations

Sample	$10^9 \cdot w$(Hg) given	$10^9 \cdot w$(Hg) found	Standard deviation/ $10^9 \cdot w$(Hg)	Limits of confidence for 95 % probability/%
1	4.00	4.26	0.77	106 ± 22
2	8.00	7.81	0.90	98 ± 14
3	12.00	11.47	1.16	96 ± 10
4	16.00	16.62	1.55	104 ± 9
5	20.00	19.38	1.81	97 ± 9

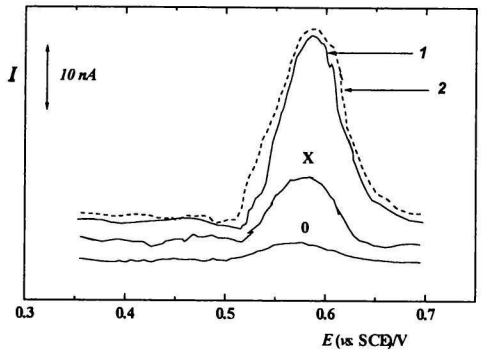

Fig. 3. DPASV voltammograms registered in trace analysis of mercury in the sample of fruit juice Exotic. Settings as described in Experimental. Deposition time 15 min. 0 blank; X mineralized sample. *1.* Standard of Hg(II) equivalent to the legal limiting value added to the sample before its decomposition; *2.* corresponding Hg^{2+} addition to the sample solution in the electrolytic vessel.

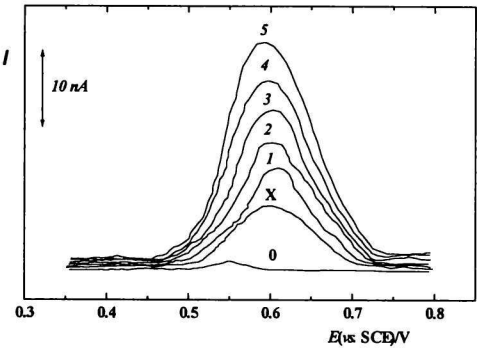

Fig. 4. Experimental DPASV voltammograms registered in trace analysis of Hg in beer. DPASV settings as given in Experimental. Deposition time 10 min. *1.* 10 mm^3, *2.* 20 mm^3, *3.* 30 mm^3, *4.* 40 mm^3, *5.* 50 mm^3 of 2×10^{-6} mol dm^{-3} Hg^{2+} standard solution added to 20 cm^3 of the decomposed beer sample in a polarographic cell.

10^{-10} mol dm^{-3} Hg^{2+} in the analyzed solution (deposition time 20 min) can still be resolved from background signals. This concentration corresponding to Hg mass fraction 0.8×10^{-9} can be considered to be an estimate of the detection limit.

The experiments with synthetic samples allowed to exclude possible loss of mercury during the sample decomposition procedure. The loss is not significant and can be neglected as follows from experiments in which corresponding amounts of mercury were added once to the analyzed sample before its digestion and secondly directly to the analyzed solution in the electrolytic cell. Experimental curves registered in these investigations are depicted in Fig. 3. Curve *1* was taken in the synthetic sample solution to which an amount of mercury in the form of Hg^{2+} standard equivalent to the legal limiting value 10×10^{-9} was added directly to the digestion vessel before its decomposition. Curve *2* was registered when the same amount of Hg^{2+} standard was added to the sample solution in the electrolytic cell. Both DPASV signals are practically the same, which confirms the above-mentioned conclusion that the loss of mercury in the sample digestion procedure is negligible. It also justifies the evaluation of mercury content in the sample just by a simple addition of Hg^{2+} standard to the sample in the electrolytic cell.

Real Samples Analysis

Samples of fruit juices (Fruiko) and beer were analyzed. Both types of samples are distributed on market and so obliged to fulfil the state regulation on Hg content in food products. The real samples were pretreated by the common "wet" decomposition procedure described in Experimental and then analyzed using the DPASV method. The method of multiple standard addition was used as exemplified in Fig. 4 for Hg analysis of beer. The DPASV signal at + 0.6 V *vs.* SCE increases proportionally to Hg^{2+} standard additions to the sample solution.

To avoid inconvenient and time-consuming decomposition procedure an attempt was made to determine Hg directly in the sample without any decomposition. Mercury was electrodeposited on the microelectrode from the sample solution using the same deposition potential as in the case of the decomposed sample. The use of the method of exchanged solution is strictly required in this case. Replacing the sample is moreover preceded by rinsing the microelectrode with distilled water. In case of fruit juice samples the results are very similar to those found for the corresponding decom-

Table 2. The Results of Hg Analysis in Some Real Samples of Fruit Juices and Beer. The Values Are Average of Five Determinations

Sample	Sample specification		$10^9 \cdot w$(Hg)
Beer	Stein – 10°	*1*	4.4 ± 1.0
	Stein – 10°	*2*	2.6 ± 1.6
	Topvar – 10°	*1*	3.8 ± 1.1
	Topvar – 10°	*2*	1.2 ± 1.1
Fruit juice	Fruiko – Jablko	*1*	2.7 ± 0.9
	Fruiko – Jablko	*2*	2.4 ± 0.8
	Fruiko – Exotic	*1*	3.1 ± 0.9
	Fruiko – Exotic	*2*	2.7 ± 1.0
	Fruiko – Multivitamin	*1*	2.4 ± 1.1
	Fruiko – Multivitamin	*2*	2.6 ± 1.4

1. Pretreated sample; *2.* sample without any pretreatment.

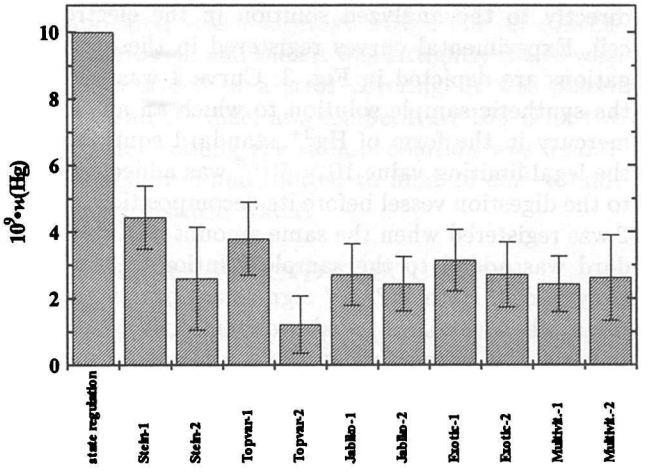

Fig. 5. Results of some real samples analysis of Hg. Error bars represent the standard deviations of the determinations. Numbers indicate decomposed (*1*) and nondecomposed (*2*) samples.

posed samples (Table 2). More complex beer matrix, however, disabled direct DPASV mercury determination probably due to the presence of the surface-active species adsorbing on the gold microelectrode surface. In this case the sample digestion cannot be avoided. All results of real samples analysis are summarized in Table 2 and Fig. 5. As it can be seen the Hg mass fraction does not exceed the legal limiting value 10×10^{-9} in any of the analyzed real samples. The method is suitable for mercury content determination in food samples on this required level and can be an alternative to the commonly used AAS method. In some cases (juices) it is even possible to determine Hg in sample without its decomposition. In other cases (beer) it can be used to yield at least a preliminary information about a mercury content. It is recommended, however, to confirm this result by analysis of the decomposed sample. In combination with the above-mentioned decomposition/digestion technique the DPASV analysis is suitable for mercury content determination in many kinds of food samples (vegetable, meat, flour).

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