6. Mellors, G. W. and Senderoff, S., *U.S.* 3444058 (1969).
7. McCawley, F. X., Wyche, Ch., and Schlein, D., *J. Electrochem. Soc. 116,* 1028 (1969).
8. Popov, B. N. and Laitinen, H. A., *J. Electrochem. Soc. 120,* 1346 (1973).
9. Koyama, K., Hashimoto, Y., Omori, S., and Terawaki, K., *Trans. Jpn. Inst. Met. 25,* 265 (1984).
10. Koyama, K., Hashimoto, Y., Omori, S., and Terawaki, K., *Trans. Jpn. Inst. Met. 25,* 804 (1984).
11. Terawaki, K., *Trans. Jpn. Inst. Met. 26,* 198 (1985).
12. Koyama, K., Hashimoto, Y., Omori, S., and Terawaki, K., *J. Less-Common Met. 132,* 57 (1987).
13. Baraboshkin, A. N., Shunailov, A. F., and Martinov, V. A., *Tr. Inst. Elektrokhimii, Akad. Nauk USSR 15,* 44 (1970).
14. Silný, A., *Sdel. Tech. 32,* 175 (1984).
15. Rawson, H., *Inorganic Glass-Forming Systems.* P. 207—208. Academic Press, London, 1967.

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Mercury Traces Determination by Voltammetry on Gold Fibre Microelectrode in Some Food Samples

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Gold fibre microelectrode was applied for mercury traces determination by differential pulse anodic stripping voltammetry in mushrooms. The food sample decomposition procedure with concentrated HNO_3 under elevated pressure and temperature in a digestion device is described. The method was tested on synthetic samples spiked with $Hg(ClO_4)_2$. Sufficient decomposition of the organic matrix was reached during the sample pretreatment and no significant loss of mercury was observed.

Differential pulse anodic stripping voltammetry (DPASV) is a powerful electroanalytical technique for trace analysis of many toxic metals [1—3]. Three types of working electrodes are generally used for mercury determination by DPASV: platinum, glassy carbon, and gold. Multiple anodic peaks assigned to intermetallic compounds formation [4] are considered as main disadvantage of Pt electrodes. Glassy carbon is considered to be more advantageous material because the formation of mercury intermetallic compounds with electrode is excluded [5]. On the other hand, droplets of mercury can be lost especially in the case when the method of exchanged solution is applied [6]. Improving of accumulation of mercury on glassy carbon requires addition of another codepositing metal, *e.g.* Cu(II) or Cd(II) which represents further complication of analysis [7]. This also holds for preplating or *in situ* deposition of Au films on a glassy carbon electrode [8]. The lowest detection limit was reported for rotating compact gold disk electrode [9].

The combination of unique microelectrode properties (especially the possibility of deposition in a quiescent solution) with the most advantageous electrode material – pure gold, led us to propose the application of gold fibre microelectrode [10]. This electrode besides the possibility to omit stirring during accumulation from low-volume sample also enables a considerable reduction of Au consumption for working electrode construction (to less than 0.1 g) thus lowering its cost which can be of importance in practical application.

Mercury is a pollutant the occurrence of which represents a considerable health hazard even in trace amounts. One of the food products through which mercury can be brought to human body are mushrooms. These are often raised in deserted ore mine premises, where the probability of mercury uptake from the ore dust is much higher in comparison with the mushrooms growing in forests. Mushroom producers are therefore required to certify that Hg amount does not exceed legal

limiting value of the state regulation [11]. This paper is an attempt to apply the Au-fibre microelectrode for an advantageous monitoring of the Hg amount in mushrooms.

EXPERIMENTAL

All chemicals were of anal. grade purity and were used without any further purification with the exception of HNO_3 which was purified by isothermic distillation. Stock 0.001 M solution of $Hg(ClO_4)_2$ was prepared by dissolution of the corresponding amount of HgO in the concentrated $HClO_4$ and dilution to exact volume with triply distilled water and as standard solution it was used in the dilution 5×10^{-7} mol dm^{-3} (prepared daily).

Polarographic analyzer PA4 (Laboratorní přístroje, Prague) for DPASV measurements with the following parameters was used: deposition potential + 0.2 V *vs.* SCE, deposition time varied according to Hg^{2+} concentration from 2 to 30 min, anodic stripping scan rate 50 mV s^{-1}, pulse height 50 mV, pulse frequency 5 Hz.

The base for the construction of the working fibre gold microelectrode was the gold fibre about 2.5 cm long, diameter 22 μm. It was attached to supporting Cu-wire (*ca.* 10 cm long, diameter *ca.* 0.5 mm) with silver epoxy resin or by a seal with Pb—Sn alloy and inserted into the glass tube (about 8 cm long, 0.5 cm inner diameter), so that about 2 cm of the gold fibre stuck out of the glass tube. The tube was then filled with epoxy resin. The electrode was conditioned by polarization at + 0.2 V *vs.* SCE for 10 s and subsequently at + 1.8 V *vs.* SCE for 30 s five times before the first use and after taking each curve by holding at + 1.8 V *vs.* SCE for 60 s.

Sample Preparation

For the pretreatment of mushrooms samples a pressure digestion device ZA-1 was applied. It is suitable for decomposition of a variety of biological materials containing easily evaporating pollutants such as Hg, As, Se. In a typical experiment 1 g of mushrooms was placed into the poly(tetrafluoroethylene) (PTFE) vessel together with 2 cm^3 of concentrated HNO_3. It was air-tightly closed with PTFE cap and sealed in a steal covering. It was placed in a hot air sterilizer for two hours to raise the rate of digestion by elevating the temperature to 160 °C. After cooling the clear solution (without any solid residues) was quantitatively removed and adjusted to 50 cm^3 with triply distilled water.

RESULTS AND DISCUSSION

Preliminary Testing

The legal limiting value of mercury content in mushrooms is 0.05 ppm [11]. It corresponds to the concentration 5×10^{-9} mol dm^{-3} of Hg^{2+} in the sample solution if procedure of sample digestion described in Experimental is used.

Preliminary testing of the proposed method of Hg^{2+} determination was done with synthetic Hg^{2+} samples. A series of such samples with the concentration of Hg^{2+} ranging from 1×10^{-9} to 5×10^{-8} mol dm^{-3} was prepared by addition of $Hg(ClO_4)_2$ standard solution to 2 cm^3 of concentrated HNO_3 and adjustment to 50 cm^3 with distilled water (the same media as arise after the sample decomposition). Potential + 0.2 V *vs.* SCE was used for Hg accumulation at which dissolved oxygen is not reduced and time-consuming deaeration of the analyzed solution can be omitted. No influence of dissolved oxygen on the pre-electrolysis yield was observed. The stirring of the analyzed solution during accumulation on a microelectrode was unnecessary. The method of exchanged solution was applied to optimize the signal formation during anodic stripping. The sample solution was exchanged for solution containing 0.1 mol dm^{-3} of $HClO_4$, 0.003 mol dm^{-3} of HCl, and 200 mg dm^{-3} of NaF. The stripping peak of Hg was observed at the potential + 0.6 V *vs.* SCE. Linear dependence of DPASV signal on Hg^{2+} concentration in the sample solution was observed all over the above-mentioned concentration range. Height of signal also linearly depends on the deposition time from 2 to 20 min. Described preliminary experiments proved that Hg accumulation can be done in media which arise after the sample digestion and also at the Hg^{2+} concentration level expected in sample solutions.

To verify Hg recovery and to exclude possible loss of mercury the digestion method described in Experimental was tested by means of mercury-spiked samples. Calculated amounts of $Hg(ClO_4)_2$ in the form of standard solution were added to samples of mushrooms (*Agaricus hortensis*) with low Hg content. This was determined by independent AAS method to be less than 1/10 of corresponding legal limiting value [11]. The mercury-spiked mushrooms samples were processed by procedure described in Experimental. The series in Table 1 corresponds to Hg^{2+} concentrations in the analyzed solution in the range from 1×10^{-9} mol dm^{-3} to 2.5×10^{-8} mol dm^{-3}. The multiple standard addition was used for the evaluation of Hg content. Different amounts of Hg(II) were added to parallelly determined samples before their diges-

Table 1. Results of Hg Analysis of Mercury-Spiked Mushrooms Samples (Values are Average of Five Determinations)

Sample	w_{Hg}(given)/ppm w_{Hg}(found)/ppm	Standard deviation s/ppm	Limits of confidence for 95 % probability %
1	0.010		
	0.008	0.005	80 ± 36
2	0.020		
	0.017	0.004	85 ± 30
3	0.050		
	0.044	0.006	88 ± 17
4	0.100		
	0.093	0.014	93 ± 15
5	0.200		
	0.182	0.018	92 ± 13
6	0.500		
	0.461	0.043	92 ± 9

tion. For the background correction only 2 cm^3 of concentrated HNO_3 were proposed in the digestion device under the same conditions as were used for samples with mushrooms. Linear dependence of DPASV signal on the amount of Hg(II) added to the sample was observed. Signal corresponding to 2×10^{-10} mol dm^{-3} of Hg^{2+} (deposition time 30 min) can still be resolved from background signals. This concentration can be considered to be an estimation of determination limit of Hg content by DPASV with gold fibre microelectrode. Results of analysis are given in Table 1.

Statistical evaluation of experiments with mercury-spiked samples shows that arithmetic mean of parallel determinations does not differ statistically from the given value in any of the spiked samples. The interval of reliability is well acceptable taking into account the low concentration level of the determined metal.

Sample pretreatment method was found suitable for the preparation of the sample solution. No significant loss of mercury was observed by the sample digestion procedure.

Real Samples Analysis

Real samples of mushrooms raised in a deserted ore mine premises were analyzed using procedure as applied for mercury-spiked samples. Results of measurement are given in Table 2 and those of Hg analysis of four mushrooms samples growing in forest are also included for comparison. As seen from the given results the Hg content in ore mine produced mushrooms in any of the samples does not exceed the legal limiting value [11], but it is generally higher than the Hg content in forest-growing mushrooms.

Table 2. Results of Hg Analysis of Some Real Mushrooms Samples Produced in Deserted Ore Mine Premises (Values are Average of Five Determinations)

Sample	w(Hg)/ppm	Sample	w(Hg)/ppm
1	0.015 ± 0.007	*8*	0.018 ± 0.009
2	0.020 ± 0.005	*9*	0.020 ± 0.012
3	0.023 ± 0.010	*10*	0.032 ± 0.016
4	0.025 ± 0.008	*11*[a]	0.010 ± 0.007
5	0.020 ± 0.009	*12*[a]	0.012 ± 0.008
6	0.021 ± 0.015	*13*[b]	0.010 ± 0.008
7	0.028 ± 0.010	*14*[b]	0.008 ± 0.005

a) Forest-growing mushrooms from Eastern and *b*) Western Slovakia.

REFERENCES

1. Wang, J., *Stripping Analysis: Principles, Instrumentation and Application*. VCH Publishers, Deerfield Beach, Florida, 1985.
2. Florence, T. M., *J. Electroanal. Chem. Interfacial Electrochem. 168*, 207 (1984).
3. Golimowski, J., Valenta, P., and Nürnberg, H. W., *Z. Lebensm.-Unters. Forsch. 168*, 353 (1979).
4. Hassan, M. Z., Untereker, D. F., and Bruckenstein, S., *J. Electroanal. Chem. Interfacial Electrochem. 42*, 161 (1973).
5. Yanga, S., Prasada Rao, T., and Prabhakara Rao, G., *Analyst* (London) *110*, 1361 (1985).
6. Sottery, J. P. and Anderson, G. W., *Anal. Chem. 59*, 140 (1987).
7. Kiekens, P., Mertens, M., Laire, Ch., and Temmerman, E., *Analyst* (London) *108*, 1082 (1983).
8. Svoboda, G. P., Sottery, J. P., and Anderson, G. W., *Anal. Chim. Acta 116*, 297 (1984).
9. Gustavsson, I., *J. Electroanal. Chem. Interfacial Electrochem. 214*, 31 (1986).
10. Rievaj, M. and Bustin, D., *Analyst* (London) *117*, 1471 (1992).
11. Regulations on pollutant content in CSFR, p. 98. Ministry of Health of the Slovak Republic, 31 July, 1986.

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