23. Iyengar, R. R., Sathyanarayana, D. N., and Patel, C. C., *J. Inorg. Nucl. Chem. 34,* 1088 (1972).
24. Ray, A. and Sathyanarayana, D. N., *Bull. Chem. Soc. Jpn. 45,* 2712 (1972).
25. Murman, R. K. and Monzyk, B., *Inorg. Chem. 17,* 2461 (1978).
26. Barclay, G. A., Hoskins, B. F., and Kennard, C. H. L., *J. Chem. Soc. 1963,* 5691.
27. Anderson, O. P. and Packard, A. B., *Inorg. Chem. 18,* 3064 (1979).
28. Harrison, W. D. and Hathaway, B. J., *Acta Crystallogr., B 36,* 1069 (1980).
29. Anderson, O. P. and Packard, A. B., *Inorg. Chem. 19,* 2941 (1980).
30. Anderson, O. P., Perkins, C. M., and Brito, K. K., *Inorg. Chem. 22,* 1267 (1983).
31. Day, M. C. and Selbin, J., *Theoretical Inorganic Chemistry.* Reinhold, New York, 1963.
32. Ahrland, S. and Tagesson, B., *Acta Chem. Scand., A 31,* 615 (1977).
33. Schwing-Weill, M. J., *Bull. Soc. Chim. Fr. 1973,* 823.
34. Mironov, V. E., Makashev, Yu. A., Mavrina, I. Ya., and Krizhanovskii, M. M., *Zh. Neorg. Khim. 15,* 1301 (1970).
35. Kullberg, L., *Acta Chem. Scand., A 20,* 829 (1974).
36. Ahrland, S. and Rawsthorne, J., *Acta Chem. Scand. 24,* 157 (1970).
37. Fridman, J. D. and Sarbaev, D. S., *Zh. Neorg. Khim. 4,* 835 (1959).
38. Hancock, R. D., Finkelstein, N. P., and Evers, A., *J. Inorg. Nucl. Chem. 34,* 3747 (1972).
39. Milazzo, G. and Caroli, S., *Tables of Standard Electrode Potentials,* pp. 23, 279. J. Wiley, New York, 1978.
40. *Stability Constants of Metal-Ion Complexes.* Part A. *Inorganic Ligands,* pp. 10, 24, 25. Pergamon Press, Oxford, 1982.
41. Parker, A. J., *Chem. Rev. 69,* 1 (1969).
42. Heerman, L. F. and Rechnitz, G. A., *Anal. Chem. 44,* 1655 (1972).
43. Senne, J. K. and Kratochvil, B., *Anal. Chem. 43,* 79 (1971).
44. Manahan, S. E. and Iwamoto, R. T., *Inorg. Chem. 4,* 1409 (1965).
45. Misumi, S., Aihara, M., and Kinoshita, S., *Bull. Chem. Soc. Jpn. 47,* 127 (1974).
46. Ahrland, S., Bläuenstein, P., Tagesson, B., and Tuhtar, D., *Acta Chem. Scand., A 34,* 265 (1980).
47. Foll, A., Le Démézet, M., and Courtot-Coupez, J., *J. Electroanal. Chem. Interfacial Electrochem. 35,* 41 (1972).
48. Kordík, D., *Thesis.* P. 96. Faculty of Chemical Technology, Bratislava, 1982.
49. Monsted, O. and Bjerrum, J., *Acta Chem. Scand. 21,* 1116 (1967).

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Determination of Trace Lead in Human Urine Using Hanging Mercury Drop Semimicroelectrode Influence of Matrix Effect and Its Elimination

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Trace amounts of Pb were determined in human urine by anodic stripping voltammetry on hanging mercury drop electrode. Two types of electrodes were used: electrode of conventional dimension (r = 440 μm) and semimicroelectrode (r = 40 μm). Described is the possibility of simplification of the experiment and minimization of the sample volume and of time-consuming irradiation and deaeration by using the semimicroelectrode. Good precision and accuracy were obtained when using the simplified short procedure.

Determination of trace and ultratrace amount of metals in the human body and liquids is now assuming increasing importance in clinical analysis. In all of the analytical methods for metals determination it is necessary to consider the influence of matrix, which in the case of urine is formed largely by organic species. It can have a substantial influence on accuracy of determination. Some authors use mineralization with acids for decomposition of organic species in human urine samples which can lead to a contamination of the sample [1, 2]. A suitable procedure avoiding such a contamination is the method of *Batley* and *Farrar* [3] using low-energy UV or high-energy γ irradiations for decomposition of organic matter.

Anodic stripping voltammetry (ASV) belongs to the most suitable methods for determination of low concentrations of metals. *Copeland* and co-

workers determined Pb in urine in the concentration range 6.6 up to 27 ng cm^{-3} using ASV at thin mercury film electrode in the acetate buffer medium [2]. Recently electrodes with characteristic size of several micrometers became a useful tool for stripping voltammetric determination of metals [4—6]. Application of these electrodes is advantageous for several reasons.

Polarization *I—E* curves obtained at the microelectrodes are wave-shaped and mutually independent, which is due to the fact that the contribution of time-independent spherical diffusion to the mass transport is substantial already in a short time of polarization. This can be seen from eqn (*1*) – the Cottrell equation corrected for spherical diffusion

$$I = \underbrace{\frac{4zFD^{1/2}r^2c}{t^{1/2}}}_{\{a\}} + \underbrace{4zFD\pi rc}_{\{b\}} \qquad (1)$$

where *F* is Faraday constant, *z* number of exchanged electrons, *D* diffusion coefficient, *c* concentration, and *r* radius of the electrode. Term {*a*} depends on time *t* and term {*b*} is time-independent. Since the term {*a*} is proportional to r^2 and the term {*b*} to *r*, the contribution of term {*a*} can be neglected as the radius of electrode *r* becomes small (semimicro- and microelectrodes) [7].

Microelectrodes are mainly applied in the working procedures where constant substance flow is required, *e.g.* in stripping voltammetry. Advantage of using microelectrodes in stripping voltammetry, coming from the possibility to perform electrodeposition step in unstirred solutions, follows also from eqn (*1*) [8—10]. Another important property of microelectrodes is that the very low current results in the beneficial effect of very low ohmic potential loss with a resulting tolerance for samples of low ionic strength. For a small flowing current the reference electrode is not charged by current, which enables to measure with two-electrode measuring systems [6].

The possibility to simplify the electrode arrangement (two-electrode system) as well as the possibility to leave out the stirring, enables a considerable minimization of sample volume. Such an application of microelectrodes in microanalysis has been described by *Baranski* [11] who determined cadmium in a special cell of volume 5 mm^3

EXPERIMENTAL

All used chemicals were of anal. grade purity, water used for the preparation of solutions was deionized and redistilled.

Apparatus

The measurements using electrodes of conventional size and semimicroelectrodes were made using Polarographic analyzer PA-3 (Laboratorní přístroje, Prague).

Two types of working electrodes were used both applying commercial instrument SMDE 1 (Static Mercury Drop Electrode, Laboratorní přístroje, Prague): *A*) The mercury drop electrode with radius r = 440 μm (the macroelectrode), the inside radius of capillary was r_k = 123 μm. *B*) The mercury drop electrode with radius r = 40 μm (the semimicroelectrode), the inside radius of capillary was r_k = 20.3 μm.

The measurement with the macroelectrode was done in three-electrode system with auxiliary Pt electrode (Radelkis, Budapest) and reference saturated calomel electrode (SCE). The measurement with semimicroelectrode was done in two-electrode system. Two types of reference electrodes were used in the latter case. Saturated calomel electrode was used for measurements in large-volume samples. The determination in small volume needed miniaturization of reference electrode – Ag wire covered with AgCl was used as the reference electrode in this case.

Two types of electrolysis cell were used:

– the cell delivered commercially with the instrument PA-3 (volume approx. 100 cm^3);

– for the determination of small sample volumes the cell of soft glass was made with the volume of approximately 100 mm^3

Working Procedures

The samples of urine were UV-irradiated to decompose the organic matter in a quartz vessel. Time of irradiation depended on the thickness of urine layer. After this procedure matrix did not influence the determination of lead.

a) 10 cm^3 of adjusted (irradiated) sample mixed with 10 cm^3 of acids (0.08 M-HCl and 0.06 M-HNO_3) was deaerated in an electrolytic vessel by bubbling nitrogen during 10 min. The electrodeposition was done at the potential E_d = – 0.65 V measured *vs.* SCE during 10 min. Dissolution of accumulated species was followed by differential pulse voltammetry (DPV) with the scan rate 5 mV s^{-1} and the pulse amplitude 25 mV. The lead in the samples of urine was determined with the method of standard addition.

b) 50 mm^3 of adjusted (irradiated) sample solution was taken for stripping analysis. The measurement was done without deliberately added supporting electrolyte using semimicroelectrode. The

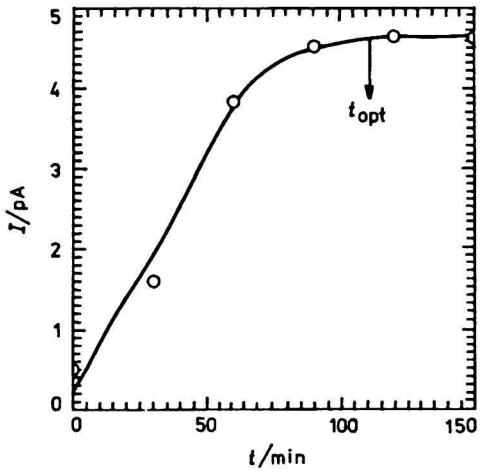

Fig. 1. Dependence of peak current on time of irradiation for thickness layer l = 5 cm.

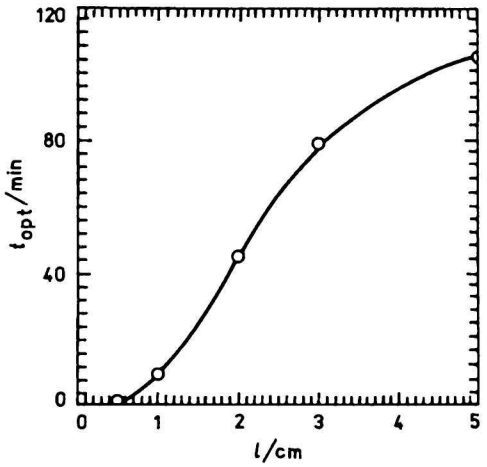

Fig. 2. Dependence of optimum time of irradiation of sample on the thickness of solution layer.

electrodeposition proceeded at the potential E_d = – 0.65 V measured *vs.* Ag/AgCl during 10 min. Dissolution was followed by DPV with the scan rate 5 mV s^{-1} and the pulse amplitude 25 mV.

RESULTS AND DISCUSSION

In the procedures for electrochemical determination of lead in urine described in the literature [1—3] the indicating electrode was always of conventional size (1 mm up to 1 cm). In this procedure the samples were adjusted by mineralization with acids [1, 2] and UV irradiation [3], respectively, before measurement. Supporting electrolyte was always added for determination of heavy metals and it was recommended to stirr the solution uniformly during electrodeposition and to deoxygenate it by bubbling nitrogen. A modified procedure for determination of lead in human urine is proposed in this paper using a semimicroelectrode.

As an optimum time of irradiation we considered the time after which there was no time change in peak hight of Pb and its dependence on Pb standard addition was linear (Fig. 1). As it can be seen in Fig. 2 the optimum time grows with growing thickness of sample layer. For the layer of about 3 cm the optimum time exceeds one hour. From this point of view it seems favourable to analyze low-volume samples since it enables to shorten the time of analysis.

We have found out that the concentration of supporting electrolyte is not critical for analytical signal generation in the case of semimicroelectrode (Fig. 3). The analysis can be done even without deliberately added electrolyte.

Another practically important fact is that the deoxygenation of solution sample by nitrogen has a little effect on the peak current when using semimicroelectrode. As it can be seen in Table 1 the time-consuming bubbling by nitrogen can be left out for the semimicroelectrode. It is necessary, however, for the macroelectrode.

The lead in the sample was identified and determined by the standard addition method. The results were calculated with correction on volume change by the standard addition.The results of parallel determinations of five human urine samples were evaluated statistically by the method of *Dean* and *Dixon* [12] and are presented in Table 2. The table demonstrates that the amount of Pb found in the corresponding urine sample does

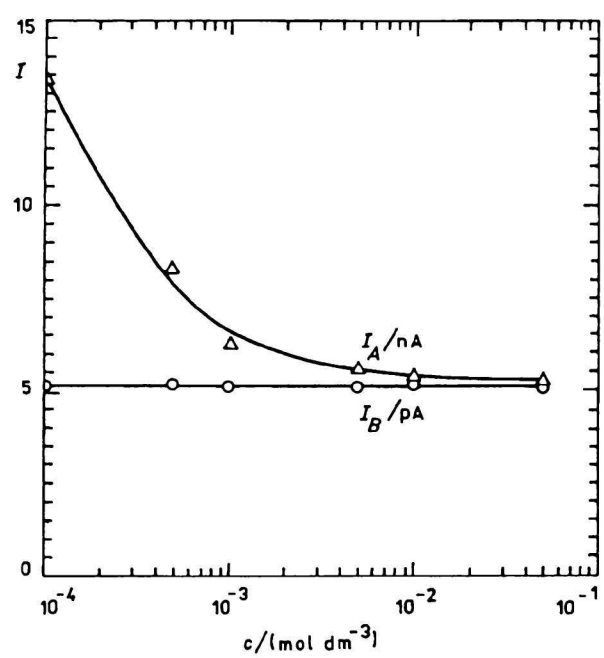

Fig. 3. Dependence of peak current at the use of macroelectrode (I_A) and semimicroelectrode (I_B) on concentration of supporting electrolyte.

Table 1. Dependence of Peak Current at Macroelectrode (*A*) and Semimicroelectrode (*B*) *vs.* Time of Sample Deoxygenation

t	I_A	I_B
min	nA	pA
0	6.5 ± 1.2	5.1 ± 0.5
1	6.3 ± 1.0	5.2 ± 0.4
2	6.1 ± 1.1	5.1 ± 0.7
3	5.8 ± 0.7	5.1 ± 0.3
5	5.5 ± 0.7	5.2 ± 0.2
10	5.6 ± 0.2	5.1 ± 0.4

not differ for the three procedures. Standard deviation of lead determination is also well comparable for all procedures including the procedure *B2* enabling a substantial reduction of time of analysis.

The comparison of described procedures allows to conclude that the use of semimicroelectrodes for determination of lead in urine is advantageous since it enables to analyze small-volume samples without adding supporting electrolyte, leaving out deoxygenation of solution and the stirring in the electrodeposition step. The application of two-electrode measuring system has also no influence on results which are comparable with the results obtained using described know-how of procedures. The method of determination of lead in human urine described in this work simplifies the experimental conditions of analysis, eliminates possible influence of contamination by supporting electrolyte and enables the minimization of sample volume. The volume minimization enables minimization of time for UV irradiation of sample.

REFERENCES

1. Lund, W. and Eriksen, R., *Anal. Chim. Acta 107*, 37 (1979).
2. Copeland, T. R., Christie, J. M., Osteryoung, R. A., and Skogerboe, R. K., *Anal. Chem. 45*, 2171 (1973).

Table 2. Results of Five Parallel Determinations of Lead in Human Urine

Method	Sample	ρ(Pb)	Standard deviation
		ng cm^{-3}	ng cm^{-3}
A1	*1*	14.5	1.9
	2	18.1	2.1
	3	13.6	1.3
	4	10.5	0.9
	5	16.7	1.2
B1	*1*	13.2	1.3
	2	18.2	1.9
	3	14.4	1.5
	4	10.1	1.3
	5	15.9	1.1
B2	*1*	15.8	2.1
	2	19.3	2.5
	3	14.1	1.4
	4	10.3	1.3
	5	16.2	1.5

A1 – the conventional size of electrode, large sample volume, HCl and HNO_3 added in concentrations 0.08 mol dm^{-3} and 0.06 mol dm^{-3}, respectively;

B1 – the semimicroelectrode, large sample volume, HCl and HNO_3 added in concentrations 0.08 mol dm^{-3} and 0.06 mol dm^{-3}, respectively;

B2 – the semimicroelectrode, microvolume, no deliberately added electrolyte.

3. Batley, G. E. and Farrar, Y. J., *Anal. Chim. Acta 99*, 283 (1978).
4. Wightman, R. M., *Anal. Chem. 53*, 1125A (1981).
5. Ewing, A., Dayton, M. A., and Wightman, R. M., *Anal. Chem. 53*, 1842 (1981).
6. Pons, S. and Fleischmann, M., *Anal. Chem. 59*, 1391A (1987).
7. Lin Sinru, Osteryoung, J., O'Dea, J. J., and Osteryoung, R. A., *Anal. Chem. 60*, 1135 (1988).
8. Dayton, M. A., Browns, J. C., Stutts, K. J., and Wightman, R. M., *Anal. Chem. 50*, 946 (1980).
9. Wehmeyer, K. R. and Wightman, R. M., *Anal. Chem. 57*, 1989 (1985).
10. Sottery, J. P. and Anderson, C. W., *Anal. Chem. 59*, 140 (1987).
11. Baranski, A. S. and Quon, M., *Anal. Chem. 58*, 407 (1986).
12. Dean, K. B. and Dixon, W. J., *Anal. Chem. 23*, 636 (1951).

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