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DETERMINATION OF TRACE AMOUNTS OF MERCURY IN WATER BY GRAPHITE-SPARK SPECTROSCOPY

C o n t e n t s: 1. Introduction, 2. Experimental, 3. Discussion of results, 4. Conclusions; Streszczenie; References

1. INTRODUCTION

Mercury compounds are common in nature, but they are highly dispersed, however [3, 6, 16]. The problem of pollution of the natural environment with mercury emerged dramatically (acute poisonings with mercury compounds) in various regions of the world in recent years. Rapidly growing pollution of the aquatic environment with mercury, as side effects of the economic activity of man, constitutes an increasing threat to life on the Earth [2, 5, 15]. In view of the highly effective bioconcentration of mercury in aquatic food chains, assaying low levels of the element in water is becoming increasingly important [13, 17, 22, 26].

The problem of assaying low mercury levels in the aquatic environment has been dealt with in many articles. Those of Stock and Zimermann, who developed the micrometric method of assaying mercury, and that of Hatch and Ott, who employed flameless atomic absorption spectrometry to assay mercury in water [7, 8], provide milestones. However, work is still continued in the search for new and effective methods [4, 18, 20, 27, 28].

In this paper an attempt was made to use graphite-spark atomic emission spectroscopy (AES) to assay trace amounts of mercury in water. Preliminary studies and experiments with isolation and partial electrolytic separation of mercury on the graphite electrode suggested that the combination of this method with that of AES should considerably improve the lower detection limit of mercury as compared with the electrogravimetric method [12, 14, 19, 24]. This paper inclu-

des the determination of the conditions of electrolysis, a study of the shape of electrodes on the stability of the plasmoid, the construction of a calibration curve and provides respective analytical relationship. The measurements were carried out with samples of polluted distilled water and artificial Baltic Sea water.

2. EXPERIMENTAL

In the method of mercury assay in water, the intensity of the 253.65-nm mercury line was measured, which was well excitable in the spark plasmoid [20, 29]. Mercury from a water sample to be analysed was deposited electrolytically onto the specially profiled conical part of a spectral graphite electrode. The electrode was then placed in the spark gap of the spark generator. The image of the spark plasmoid was projected by means of a quartz lens into the inlet slit of the spectrograph and the mercury content of the sample was determined on the basis of the blackening of the spectrographic plate.

The following devices were used in the measurements:

(i) an electrolyzer, schematic diagram of which is shown in Fig. 1. It consisted of a cylindrical glass vessel (60 mm i.d. × 95 mm in height). The upper lid of the electrolyzer was made from a 20-mm
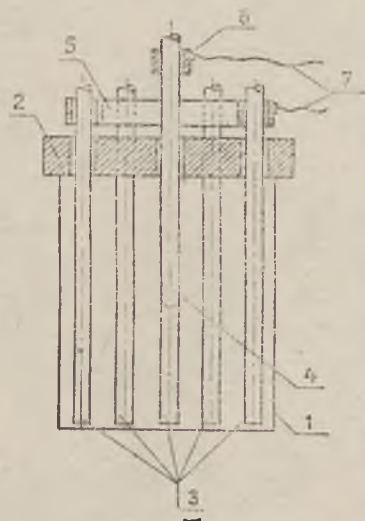

Fig. 1. Construction of the electrolyzer: *1* cylindrical vessel; *2* — bakelite lid; *3* — a set of electrodes providing anode; *4* — cathode; *5* — ring supplying voltage to anodes; *6* — cathode stiffening ring; *7* — connecting leads

Rys. 1. Budowa elektrolizera: *1* — naczynie cylindryczne, *2* — bakelitowa pokrywa, *3* — zespół elektrod stanowiący anodę, *6* — pierścień zaciskowy katody, *7* — przewody doprowadzające

bakelite plate. Graphite electrodes connected to each other with a metallic ring supplying voltage, were mounted in the lid on the periphery of the vessel 3 mm from the wall. The graphite cathode was fixed on the symmetry axis of the electrolyzer. The whole system was connected to a stabilized d.c. feeder (stabilization accuracy of 0.1

per cent) with continuous control of the output voltage;

(ii) spectrographic system (Fig. 2) including a Q-24 (Carl Zeiss, Jena) spectrograph, high-voltage spark generator HFO-1 (Carl Zeiss, Jena) and a FS 11 spark gap (Carl Zeiss, Jena);
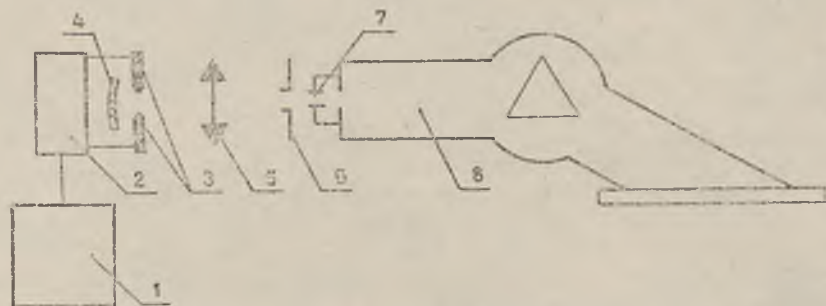

Fig. 2. Block scheme of the spectrographic system: *1* — spark generator; *2* — spark gap; *3* — electrodes; *4* — spherical mirror; *5* — quartz convergent lens; *6* — shutter; *7* — inlet slit; *8* — spectrograph

Rys. 2. Schemat blokowy układu spektrograficznego: *1* — generator iskry, *2* — iskiernik, *3* — elektrody, *4* — zwierciadło sferyczne, *5* — kwarcowa soczewka skupiająca, *6* — migawka, *7* — szczelina wejściowa spektrografu, *8* — spektrograf

(iii) a set-up for reading and interpretation of spectra including an SP-2 spectrum projector (Carl Zeiss in Jena), a GII microphotometer (Carl Zeiss, Jena) and an Abbe comparator (Carl Zeiss);
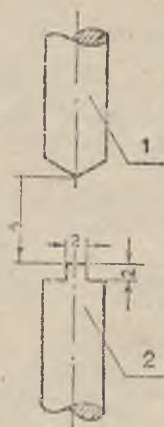
(iv) WU-1 spectrographic plates (ORWO, Wolfen) developed in an A-71 (ORWO) developer at 293 K up to a contrast coefficient of $\gamma = 0.93$.

The conditions of electrolysis were determined based on [12, 19, 24]. On the assumption that the deposition time of mercury from the solution should not exceed 1 hour and that the efficiency of the electrolyzer at a mercury concentration of 10^{-8} g dm^{-3} should not be lower than 25 per cent, the following conditions of the electrolysis were established: duration, $0.5 \leqslant t \leqslant 1$ h; temperature of the solution 293 K; current intensity in the electrolyte $I = 0.6$ A; electrode voltage, $3 \leqslant U \leqslant 9$ V. Under these conditions, from a 0.2-dm^3 sample of mercury concentration of 10^{-8} g dm^{-3}, a minimum amount of 0.5 ng of mercury deposited on the electrode, the amount being sufficient to obtain a signal strong enough to assess the detection limit of the method [20, 27].

Spatial distribution of the plasmoid of the spark discharge depends largely on the distribution of spark break-down channels [10, 11]. Electrodes with specially profiled tips proved particularly useful in the stabilization of the spatial configuration of the plasmoid. With a combination of electrodes in which the tip of the lower one was profiled in the shape of a cylindrical ridge (concentric with the electrode), 2 mm high, and the upper one conical with an apex angle of 120° (Fig. 3),

Fig. 3. The optimum position of electrodes in the spark gap: 1 — upper electrode with conically-profiled tip; 2 — lower electrode with cylinder-shaped tip

Rys. 3. Optymalny układ elektrod w iskierniku: 1 — elektroda (górna) z końcówką wyprofilowaną w kształcie stożka, 2 — elektroda (dolna) z końcówką wyprofilowaną w formie walca

a plasmoid with highly stable spatial distribution was obtained, embracing the maximum area of the upper electrode.

The mercury content in water sample was estimated from relative transmittance, T, corresponding to the blackening of the spectrographic plate with the 256.65-nm line of mercury. The CII 229.69-nm carbon line
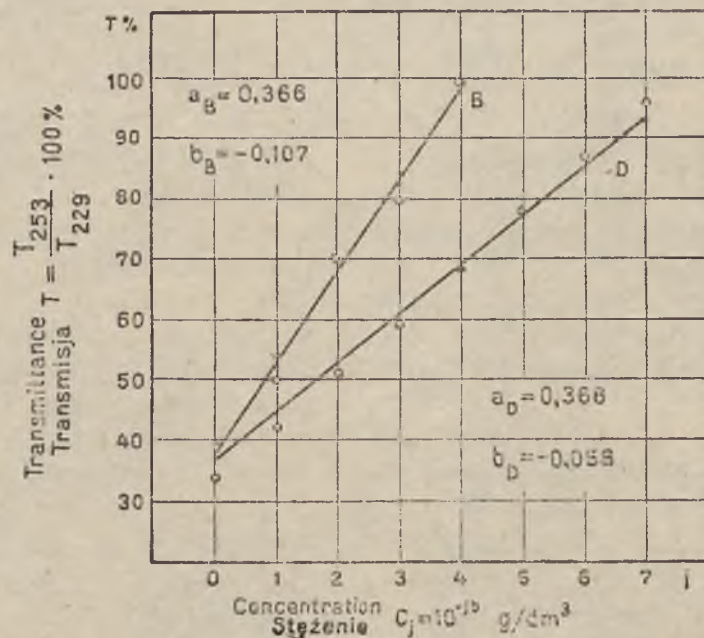

Fig. 4. Calibration curve or the system: B — for artificial Baltic Sea water; D — for distilled water

Rys. 4. Krzywa cechowania układu: B — dla zastępczej wody bałtyckiej, D — dla wody destylowanej

was used as an external reference. The relative transmission was calculated from the following expression:

$$T = \frac{T_{253}}{T_{229}} \tag{1}$$

where T_{253} is the transmission of the 253.65-nm analytical line of mercury and T_{229} the transmission of the CII 229.69-nm line. The calibration curve, $T = T(C)$ (Fig. 4), was constructed for distilled water (D) and for artificial Baltic Sea water (B). The latter was prepared according to [25]. The calibration curve was described by the Scheibe-Lomakin equation [10, 28, 30] written in the form:

$$T = a \, (10^{-j}) \, b \tag{2}$$

where a and b are parameters, and $C_j = 10^{-j}$ g dm^{-3} the mercury concentration in solution. For the two kinds of water, $a_D = 0.3656$, $b_D = -0.058$ and $a_B = 0.3657$, $b_B = -0.107$ were obtained. Limiting concentration corresponding to the detection limit c_w , and the determination limit, c_o , was calculated from the following relationships [9, 21]:

$$T_w = \sqrt{\frac{2}{n}} \; t_w \tag{3}$$

and

$$T_o = 0.92 \; s, \tag{4}$$

where s is the standard deviation and t_w is the critical variable of the Student distribution. The limiting values calculated from eqns. (2) — (4) for both konds of water are listed in Table.

Detection limits of mercury in water (D — distilled water; B — artificial Baltic Sea water)
Graniczne wartości wykrywalności rtęci w wodzie (D — woda destylowana, B — zastępcza bałtycka woda morska)

Kind of water Odmiana wody	s	Tw	Cw, g/dm³	To	Co, g/dm³
D	0.986	0.945	8×10^{-8}	0.908	2×10^{-7}
B	0.984	0.943	1×10^{-4}	0.905	3×10^{-4}

3. DISCUSSION OF RESULTS

Both the detection and determination limits obtained in this work are likley to be considerably elevated. Optimization of the analytical procedure would most probably shift these limits by 1—2 orders of magnitude.

At the present state of investigations the sensitivity of the method, described by the parameter b in eq. (2) is a matter for discussion. The parameter depends largely on the kinetics of desorption of mercury from the surface of the electrode and on the kinetics of its volatility outside the region of the plasmoid. Variations of the mercury concentration within the plasmoid, dC', caused by its liberation from the electrode (with consideration of chemical reactions occurring in the electrode) and those due to the removal of mercury outside the plasmoid region are described by the equation [1, 23]:

$$-\frac{dC'}{dt} = C^n [k_1 \exp(-k_1 tn) - k_2 \exp(-k_2 tn)] \tag{5}$$

where k_1 and k_2 are the coefficients of desorption and elimination, respectively, and n is the parameter describing the kinetics of chemical reactions occurring on the electrode. A solution of eq. (5) can be written in the form:

$$C' = C - BC^n = AC^{b'} \tag{6}$$

Eqn. (6) shows that $n \geqslant 1 \rightarrow b' \leqslant 1$ and vice versa, $n \leqslant 1 \rightarrow b' \geqslant 1$ Accordingly, the kinetics of reactions accompanying the desorption of mercury from the electrode and its volatilization outside the region of the plasmoid has a decisive effect on the course of the calibration graph.

4. CONCLUSIONS

The results of these investigations show that the method employed enables the detrmination limit to be shifted by apprcx. 4 orders of magnitude in relation to the electrogravimetric method. In relation to the conventional AES (with thermal excitation sources) the determination limit is at least one order of magnitude better. There are also some potential possibilities enabling the improvement of the determination and detection limits by at least one order of magnitude. The relatively low time consumption, the possibility of using simple analytical instruments and the carrying out of the analyses by technicians afford further advantages of the method.

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OZNACZANIE ŚLADÓW RTĘCI W WODZIE PRZY UŻYCIU SPEKTROSKOPII ISKRY GRAFITOWEJ

Streszczenie

W pracy przedstawiono wyniki wstępnych badań nad możliwością oznaczania śladów rtęci metodą emisyjnej spektroskopii atomowej z użyciem iskry grafitowej i elektrolitycznego, wstępnego wydzielania rtęci z roztworu na elektrodzie. Badaniami objęto próbki wody destylowanej i zastępczej wody morskiej skażone rtęcią. Osiągnięta granica oznaczalności rtęci w tych odmianach wody świadczy o możliwości użycia tej metody do oznaczania mikrośladowych zawartości rtęci w wodzie. W porównaniu z metodą elektrograwimetryczną uzyskano przesunięcie granicy oznaczalności rtęci w wodzie o ok. 4 rzędy wielkości, natomiast w porównaniu z klasyczną analizą emisyjną (przy zastosowaniu termicznych źródeł wzbudzenia) osiągnięto poprawę granicy oznaczalności o jeden rząd wielkości.

Stosunkowo mała czasochłonność analizy wykonywanej w tej metodzie, możliwość użycia dość prostej aparatury analitycznej, jak również możliwość wykonywania analiz przez średni personel techniczny — stanowią dodatkowe zalety opracowanej metody.

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