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## THE DETERMINATION OF MERCURY AT ULTRAMICROTRACE LEVELS IN WATER USING THE LOW-PRESSURE RING DISCHARGE

Contents: 1. Introduction, 2. Method, 3. Measuring point, 4. Application limits of the method, 5. Effect of water components on the results, 6. Determination of mercury in the Baltic Sea waters, 7. Conclusions; Streszczenie; References.

### 1. INTRODUCTION

The ability of mercury to bind with plant and animal proteins favours accumulation of the element in living organisms. The bioconcentration of mercury occurs particularly efficiently in the marine food chains. In fish tissue the concentration of mercury by accumulation can be by 3—5 orders of magnitude higher than that in sea water. The mercury content in marine predatory fishes can be estimated from the following relationship [8] provided that the mercury level in sea water is known:

$$C_F = 0.013 C_w - 0.179,$$

where  $C_F$  is the concentration of mercury in fish, in  $\text{mg kg}^{-1}$ , and  $C_w$  is the concentration of mercury in water, in  $\text{mg dm}^{-3}$ .

The mercury content in marine predatory fishes can attain high values (Fig. 1), even in waters with relatively low concentration of mercury. The bioconcentration of mercury in fish is markedly more efficient at higher levels of the element in water. Many papers have been confined to the problem of assaying low levels of mercury in water. Those which constituted the turning point were those by Stock and Zimermann [16], who developed the micrometric method for assaying mercury, and by Hatch and Ott [11] who applied flameless atomic absorption spectrometry for the determination of mercury in water. This method, together with various modifications of the procedure, has found widespread application to assay mercury in water at ultramicrotrace levels ( $10^{-8} \leq C_j \leq 10^{-6} \text{ g dm}^{-3}$ ) [2, 5, 19]. However, recently intensive studies have been carried out to assay mercury in water at submicro-

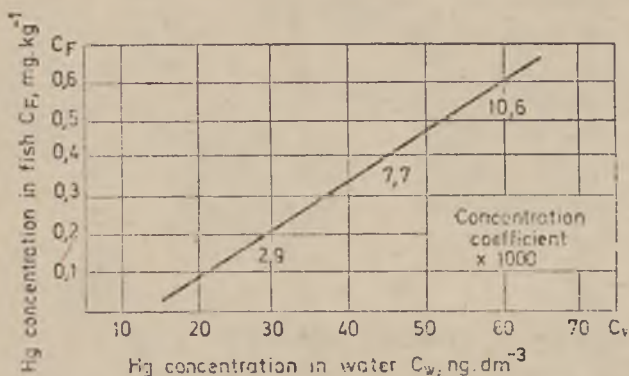


Fig. 1. Mercury content in marine fishes vs. concentration of mercury in sea water (after [8]).

Rys. 1. Zawartość rtęci w rybach morskich w zależności od stężenia rtęci w morzu (według [8])

trace levels ( $10^{-11} \leq C_j \leq 10^{-9} \text{ g dm}^{-3}$ ) by other methods [1, 12, 13]. At these levels the method of flameless atomic absorption spectrometry has found only limited application [2, 14].

This paper shows the possibility of using the atomic emission spectrometry of a low-pressure ring discharge for assaying mercury in water. The ring discharge utilized in this work occurred over the pressure range 13 — 1 333 Pa (0.1 — 10 Tr), hence under the term „ring discharge”, this particular kind of discharge is meant. The restriction of this term appears to be permissible, since the high-pressure kind of ring discharge has commonly been termed „inductively-coupled plasma” [7, 9, 18]. Owing to improvement of the method and exchange of some accessories, the sensitivity of the method increased and the detection limit of mercury in water changed as compared with earlier results [20, 21].

## 2. THE METHOD

Mercury was assayed in water by measuring the intensity of the HgI lines of mercury selected from the emission spectrum of the low-pressure plasmoid of the ring discharge.

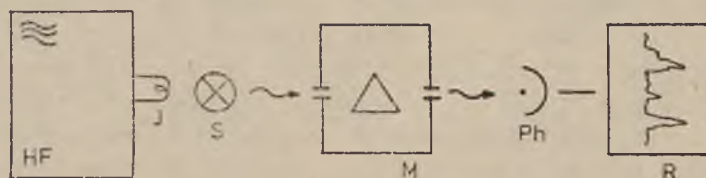


Fig. 2. Block diagram of the mercury concentration measuring point. HF — high-frequency generator; I — inductance coil (exciter); S — spectral lamp; M — monochromator; Ph — photomultiplier; R — recorder

Rys. 2. Schemat blokowy stanowiska pomiarowego służącego do oznaczania rtęci. HF — generator drgań elektromagnetycznych, I — cewka indukcyjna (wzbudnik), S — lampa spektralna, M — monochromator, Ph — fotopowielacz, R — rejestrator

To run the determination, a 1-cm<sup>3</sup> sample of the water to be analysed was vacuum-dried at 243 K (-30°C) in the discharge cell of the spectral lamp. After drying the sample, the lamp was evacuated to a pressure of 13 Pa (0.1 Tr) followed by switching on the generator of high-frequency electromagnetic field to cause ignition of the plasmoid of the ring discharge in the discharge cell of the spectral lamp. The radiation of the plasmoid was directed (Fig. 2) into the inlet slit of the monochromator. The mercury spectral line isolated from the radiation of the plasmoid was directed to a photomultiplier and the generated photocurrent to a recorder or electrometer through an amplifier. The mercury content of the sample was read out from the recorder or electrometer.

The low-pressure ring discharge, sometimes referred to as the H-type discharge, is generated when the discharge cell containing a rarefied gas is placed in the alternating magnetic field of an inductance coil (providing an exciter) coupled with a high-frequency generator. The spectrum of the plasmoid of the low-pressure ring discharge carried out in a spectral lamp filled with air at a lowered pressure of the order of 13 — 1 333 Pa (0.1 — 10 Tr) has a rich structure over the visible and near-ultraviolet regions [20, 21]. The structure is made up of the lines of atoms of the elements being the components of air and its impurities. In the ring discharge mercury is excited very strongly and in the spectrum of the plasmoid all ultimate lines of the element appear. When the air in the lamp is replaced by helium, the mercury lines are strongly amplified.

The content of mercury was determined photometrically based on the intensity of photocurrent generated in the photomultiplier. The measurements were run for the atomic lines of mercury, HgI of 253.62 and 435.83 nm. As the latter was better fitted to the region of the maximum sensitivity of the photomultiplier, it proved to be the most suitable for the determinations. This was particularly advantageous when using a spectral lamp filled with helium as a buffer gas. Apart from the measurements of the intensities of the 253.62 and 435.83-nm lines accomplished by means of the photomultiplier, visual control observations (by means of a spectroscope) were made of the 546.07-nm HgI line, which was very strongly excited in the spectral lamp employed.

### 3. MEASURING POINT

The measuring point (Fig. 3) was assembled by using generally accessible analytical and measuring instrumentation. A few specially — constructed devices provided the exceptions. The appliances consisted of the following:

- (i) Spectral lamp. A specially-constructed electrodeless spectral lamp

was used, the schematic of which is shown in Fig. 4. It consists of a discharge cell and a connector. The discharge cell was in the form of a quartz (Vitreosil) cylindrical cuvette (150 mm lang  $\times$  11.5 mm i.d.)

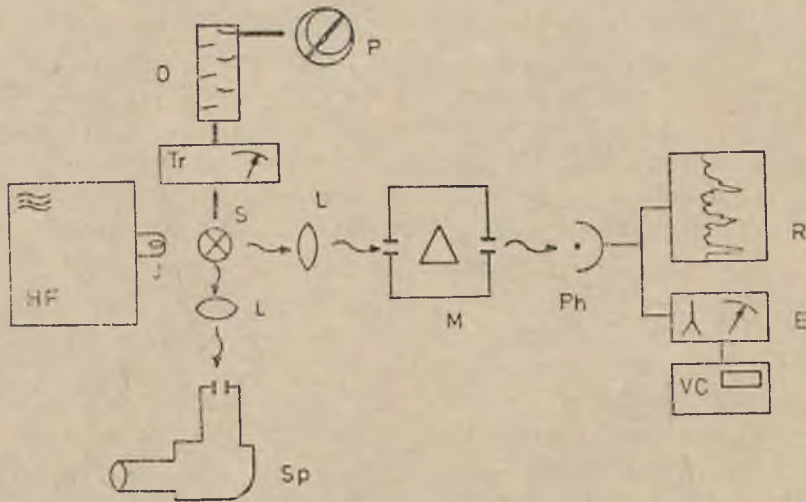


Fig. 3. Schematic diagram of the point used for measuring the concentration of mercury in sea water. *HF* — generator of electromagnetic vibrations; *I* — exciter; *O* — oil ejector; *P* — vacuum pump; *S* — spectral lamp; *Tr* — vacuum meter; *Sp* — spectroscop; *L* — quartz lens; *M* — monochromator; *Ph* — photomultiplier; *R* — tape recorder; *E* — electrometer; *VC* — digital voltmeter

Rys. 3. Schemat stanowiska pomiarowego użytego do oznaczania rtęci w wodzie morskiej. *HF* — generator drgań elektromagnetycznych, *I* — wzbudnik, *O* — odrzutnik oleju, *P* — pompa próżniowa, *S* — lampa spektralna, *Tr* — próżniomierz, *Sp* — spektroskop, *L* — soczewka kwarcowa, *M* — monochromator, *Ph* — fotopowielacz, *R* — rejestrator, *E* — elektrometr, *VC* — woltomierz cyfrowy

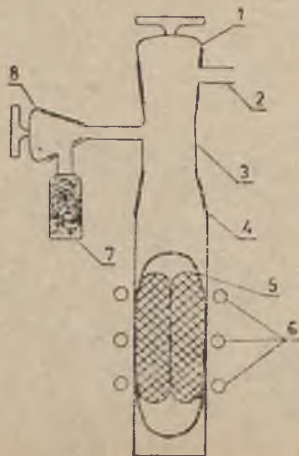


Fig. 4. Schematic diagram of the spectral lamp; 1 — valve cutting off the vacuum system; 2 — connection with the vacuum system; 3 — connector; 4 — vacuum joint; 5 — plasmoid of the ring discharge; 6 — inductance coil (exciter); 7 — filter; 8 — valve for filling the pump

Rys. 4. Schemat użytej lampy spektralnej; 1 — zawór odcinający układ próżniowy, 2 — połączenie z układem próżniowym, 3 — łącznik, 4 — szlif próżniowy, 5 — plazmoid wyładowania pierścieniowego, 6 — cewka indukcyjna (wzbudnik), 7 — filtr, 8 — zawór służący do napełniania pompy

The connector, equipped with a vacuum valve to cut off the lamp from the vacuum system and another valve to aerate the lamp, was made from Pyrex glass. The discharge cell was attached to the connector by means of a vacuum joint;

(ii) Spectrometric system. This consisted of a prismatic monochromator (SPM-2, Carl Zeiss in Jena), the spectroscopy (UM-2, Unimash) for visual observation of the 546.07-nm line and the photomultiplier (M 12 FQS 35, Werk für Fernsehelektronik);

(iii) The vacuum system. This consisted of a rotation vacuum pump (BL-32, UNITRA), oil ejector (of own construction), and a constant-resistance vacuum meter (PSO-69, ZOPAP);

(iv) The recording system, which included a tape recorder (K-201, Carl Zeiss, Jena), an electrometer (219A, UNITRA) and a digital multimeter (VC-10T, UNITRA);

(v) Feeding system of the spectral lamp. A specially-constructed high-frequency generator ( $f = 62$  MHz,  $P_{out} = 84$  W) was used. The generator was fed with an a.-c. 220-V voltage stabilized to within 0.01%.

The measurements were performed at a slitwidth of 0.025 mm and slit height of 20 mm.

#### 4. APPLICATION LIMITS OF THE METHOD

Calibration graphs for the measuring system were constructed separately for distilled water, artificial Baltic Sea water and artificial sea water. Artificial Baltic Sea water ( $B_2$ ) was prepared by employing the procedures reported in [10, 17], whereas artificial sea water ( $S_2$ ) was prepared according to the Polish Standard *Artificial sea water* [23]. In both kinds of sea water the suppression of some mercury lines was observed. The suppression was relatively strong for the 253.62-nm line. This was mostly due to the interaction of radiation with some atoms of the salts dissolved in the water, mainly with chlorine (Cl) and partly with chlorine molecules ( $Cl_2$ ). The filling of the spectral lamp with helium resulted in a very strong intensification of the atomic lines of mercury. In the presence of helium the intensity of the 435.82-nm line increased considerably. In Fig. 5 a calibration graph is shown for samples of distilled water polluted with mercury, constructed for the 253.62-nm line.

The calibration graph of the measuring system obeyed the following relationship for the measuring point and the method employed:

$$J_j = a C_j^{b/c} e^{-kC_j},$$

where  $J_j$  is the photocurrent,  $C_j = 10^{-j}$  g dm<sup>-3</sup> is the concentration of mercury in water, and  $a$ ,  $b$  and  $k$  are experimental constants. The

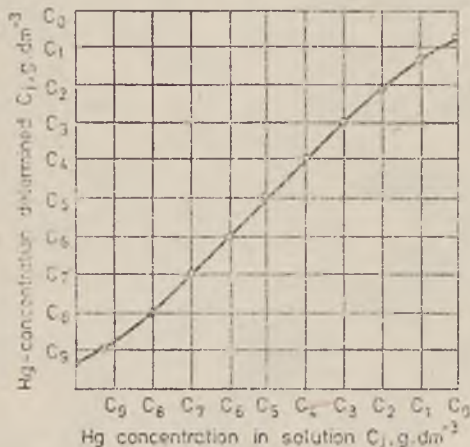


Fig. 5. Calibration graph of the measuring system for distilled water

Rys. 5 Krzywa cechowania układu pomiarowego dla wody destylowanej

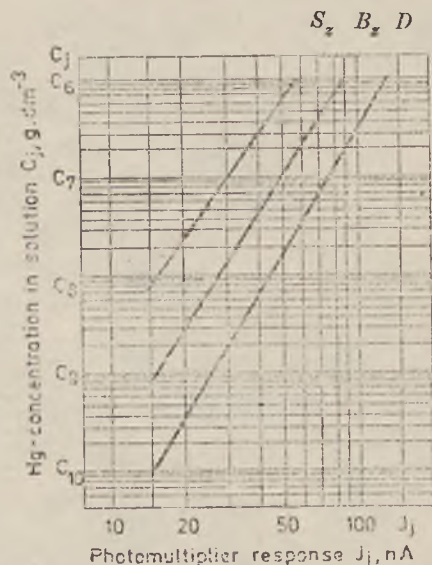


Fig. 6. Calibration graphs of the measuring system for the ranges of ultramicro and submicrotrace concentrations of mercury: *D* — in distilled water, *B<sup>z</sup>* — in artificial Baltic Sea water, *S<sub>z</sub>* — in artificial sea water.

Rys. 6. Krzywe cechowania układu pomiarowego w zakresie ultramikro i submikrośladowych stężeń rtęci: *D* — w wodzie destylowanej, *B<sub>z</sub>* — w zastępczej wodzie bałtyckiej, *S<sub>z</sub>* — w wodzie morskiej

coefficient, *k*, describing self-absorption of the radiation in the plasmod, amounted to 0.037. For the ultra — and submicrotrace levels of mercury in water ( $10^{-8} \leq C_j \leq 10^{-6}$  and  $10^{-11} \leq C_j \leq 10^{-9}$  g dm<sup>-3</sup>, respectively), the attenuation of the signal due to self-absorption is negligible (Fig. 5) and consequently the expression for the calibration graph assumes the form:

$$J_j = a C_j^b$$

In the distilled water the values of  $a=2350$  and  $b=0.23$  were obtained over this concentration range of mercury for the 253.62-nm line.

Due to attenuation of the 253.62-nm line by some components of the sea water, the calibration graphs for particular kinds of the water differed. The sensitivity of the method was also lower for the two kinds of sea water than for distilled water.

In Fig. 6 calibration graphs of the system are shown over the ultramicro trace concentration range of mercury for the three kinds of water.

The detection limit, CL, was determined from the equation reported in [6]:

$$J_L = J_N + s \sqrt{\frac{2}{n}} (t_L + t_N)$$

where  $J_L$  and  $J_N$  are the signals corresponding to the detection limit and noises, respectively;  $s = \max. (s_L, s_N)$ , where  $s_L$  and  $s_N$  are standard deviations of the signal and noise, respectively;  $t_L$  and  $t_N$  are respective critical values of the  $t$  variable of the Student distribution.

The determination limit,  $C_D$ , of mercury in water was determined as a concentration at which the error of the method amounted to 25 per cent. It was calculated from the expression reported in [13]:

$$J_D = J_N + 6s$$

where  $J_D$  and  $J_N$  are signals corresponding to the detection limit and noise, respectively.

Table 1 lists numerical values obtained for the detection and determination limits for various kinds of water.

Table 1. Detection limit ( $C_L$ ) and determination limit ( $C_D$ ) of mercury in various kinds of water (D — distilled water;  $B_z$  — artificial Baltic Sea water;  $S_z$  — artificial sea water)

Tab. 1. Granica wykrywalności ( $C_L$ ) i oznaczalności ( $C_D$ ) rtęci w różnych odmianach wody (D — woda destylowana,  $B_z$  — zastępcza woda bałtycka,  $S_z$  — zastępcza woda morska)

Kind of water Odmiana wody	$C_L$ , ng dm <sup>-3</sup>	$C_D$ , ng dm <sup>-3</sup>
D	0.001	0.3
$B_z$	0.01	2.0
$S_z$	0.2	10.0

A series of control determinations confirmed the suitability of the developed method and technique for assaying ultramicro trace amounts of mercury in sea water and submicrotrace amounts of the element in distilled water. The results of these determinations are listed in Table 2.

The method and measuring technique developed in this work enabled to shift the determination limit of mercury in water at least

by one order of magnitude as compared with the flameless atomic absorption spectrometry. By using this method and technique it is possib-

Table 2. Results of control measurements in various kinds of water (D — distilled water; B<sub>z</sub> — artificial Baltic Sea water; S<sub>z</sub> — artificial sea water; S<sub>R</sub> — relative standard deviation; n = 20)

Tab. 2. Wyniki pomiarów kontrolnych w różnych odmianach wody (D — woda destylowana, B<sub>z</sub> — zastępcza woda bałtycka, S<sub>z</sub> — zastępcza woda morska, S<sub>R</sub> — względne odchylenie standardowe, n = 20)

Kind of water Odmiana wody	Hg added Dodano Hg ng dm <sup>-3</sup>	Hg found Wykryto Hg ng dm <sup>-3</sup>	S <sub>R</sub>
D	0.00	0.1	0.09
	100.00	97.6	
B <sub>z</sub>	0.0	0.4	0.12
	100.0	92.7	
S <sub>z</sub>	0.0	0.5	0.17
	100.0	89.4	

le to assay mercury in water over the range between ultramicro and submicro trace levels.

## 5. THE EFFECT OF WATER COMPONENTS ON RESULTS

To determine the effect of sea water components on the signal intensity, a series of measurements were run for the 253.62-nm line with populations of samples of nominally equal mercury concentrations, prepared by using solutions containing some components of the artificial sea water only.

Solution R<sub>1</sub> contained only sodium compounds which make up approx. 79.4 per cent by weight of all components of artificial sea water. Solution R<sub>2</sub> contained the remaining components of the water, with the exception of sodium compounds, which constitute about 20.6 per cent of all components. Solution R<sub>3</sub> comprised heavy metal nitrates which occur in artificial sea water at a level of 0.0005 per cent.

As regards samples prepared using distilled water, suppression of the signals was observed in these solutions (Fig. 7). In an extreme case, the attenuation of the signal in artificial sea water of full composition amounted to approx. 65 per cent. In the remaining solutions, the strongest attenuation was noted in solutions containing chlorine and sodium compounds. Other sea water components did not affect the signal intensity appreciably.



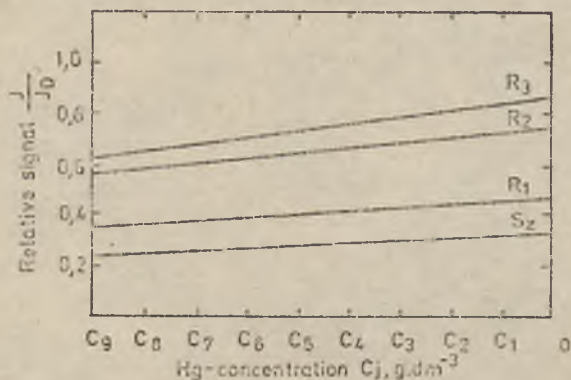


Fig. 7. Signal intensities for solutions of various contents of sea water components (normalized to signal in distilled water) at various concentrations of mercury in water.

Rys. 7. Wielkość sygnału dla roztworów o różnych zawartościach składników wody morskiej (unormowane do sygnału otrzymywanego dla wody destylowanej) przy różnych stężeniach rtęci w wodzie.

## 6. DETERMINATION OF MERCURY IN BALTIC SEA WATER

The concentration of mercury in Baltic Sea water was measured by this apparatus and method in 1976—1978. Water samples were taken in the coastal zones of Kołobrzeg and Ustka and in the region of the Słupsk Sandbank (Ławica Słupska). A few samples taken in the Gulf

Table 3. The content of mercury in some Baltic Sea regions (C = concentration of mercury in water;  $\bar{c}$  = mean concentration of mercury in water;  $S_R$  = relative standard deviation; n = number of measurements)

Tab. 3. Zawartość rtęci w niektórych obszarach Bałtyku (C — stężenie rtęci w wodzie,  $\bar{c}$  — średnie stężenie rtęci w wodzie,  $S_R$  — względne odchylenie standardowe, n — liczba pomiarów)

Region Rejon	C, ng dm <sup>-3</sup>	$\bar{c}$ , ng dm <sup>-3</sup>	$S_R$	n
Coastal waters (Ustka) Wody przybrzeżne	20—180	40	0.75	30
Coastal waters (Kołobrzeg) Wody przybrzeżne	30—190	45	0.82	30
Słupsk Sandbank Ławica Słupska	10—150	34	0.45	12
Gulf of Gdańsk (Sopot) Zatoka Gdańska	120—360	105	0.67	7

of Gdańsk were also analysed. They were stored in polyethylene containers and the analyses were run 24 hrs. after sampling. The samples were acidified with nitric acid to  $\text{pH} \leq 2$  and 0.1 g of potassium iodide was added per  $\text{dm}^3$ . Nitric acid was added to minimize losses of mercury due to sorption on the walls of the container, whereas potassium iodide decreased migration of mercury from the solution to the atmosphere. The results are shown in Table 3.

There were considerable fluctuations in the concentration of mercury in the Baltic Sea waters. Similar results from other regions of the Baltic Sea were reported in [3]. Extremal concentrations of mercury in these regions differed by two orders of magnitude. A too short observation period excluded the possibility of revealing the cyclic nature of variations of the mercury concentration.

## 7. CONCLUSIONS

The measurements carried out in this paper confirmed the suitability of the method for assaying ultramicrotrace levels of mercury in sea water. The method is particularly useful in investigations of subtle processes of exchange of mercury between the solution and walls of vessels used in analytical procedures, as well as between the atmosphere and water surface. These processes provide the main sources of vitiation of the results in the analysis of ultramicrotrace amounts of mercury in water [22].

The results of the measurements of the concentration of mercury in the Baltic Sea water showed that in the regions studied the mercury content ranged from 30 to 60  $\text{ng dm}^{-3}$ , occasionally attaining levels of 10 and 100  $\text{ng dm}^{-3}$  (in extremal cases even more than 350  $\text{ng dm}^{-3}$ ). The concentration of mercury in the Baltic Sea exhibits seasonal variations.

It was also found that the sensitivity of the method was largely affected by proper fitting of the analytical line of the element to the maximum sensitivity range of the photomultiplier, as well as the use of proper bufferring gas for filling the lamp. The use of helium as the bufferring gas increases the sensitivity of the method in the case of mercury.

## OZNACZANIE MIKROŚLADÓW RTĘCI W WODZIE Z UŻYCIEM NISKOCIŚNIENIOWEGO WYŁADOWANIA PIERŚCIENIOWEGO

### Streszczenie

Zdolność rtęci do wiązania się z białkiem sprzyja akumulowaniu się jej w organizmach żywych i biokoncentracji rtęci w łańcuchach pokarmowych. Biokoncentracja rtęci przebiega szczególnie efektywnie w wodnych łańcuchach pokarmowych. W tkankach ryb może nastąpić zateżenie rtęci, spowodowane akumulacją, nawet o 3—5 rzędów wielkości w porównaniu z zawartością rtęci w wodzie. Powoduje to konieczność oznaczania nawet bardzo niskich zawartości rtęci w wodzie.

W pracy przedstawiono możliwość użycia emisyjnej spektrometrii niskociśnieniowego wyładowania pierścieniowego do oznaczania ultramikrośladów rtęci w wodzie. Osiągnięta granica oznaczalności wynosząca dla wody destylowanej ok.  $0,1 \text{ ng. dm}^{-3} \text{ Hg/H}_2\text{O}$ , kwalifikuje się metodę zwłaszcza do badania subtelných procesów wymiany rtęci między roztworem a otoczeniem, np. między roztworem a ściankami naczyń, stosowanych w technice analitycznej lub do badania procesów wymiany rtęci między atmosferą i powierzchnią wody. Zjawiska te są w zakresie ultramikrośladów głównymi źródłami błędów oznaczeń rtęci w roztworach wodnych.

Badania wykonane w wodach bałtyckich wykazały, że zawartość rtęci, w objętych badaniami obszarach morza, mieści się naogół w granicach od 30 do  $60 \text{ ng. dm}^{-3}$ , osiągając czasami wartości rzędu  $10 \text{ ng. dm}^{-3}$ , a niekiedy powyżej  $100 \text{ ng. dm}^{-3}$ , w skrajnych przypadkach nawet powyżej  $350 \text{ ng. dm}^{-3}$ .

Stwierdzono również, że dla czułości metody duże znaczenie ma dopasowanie linii analitycznej oznaczanego pierwiastka do zakresu maksymalnej czułości widmowej fotopowielacza użytego do detekcji promieniowania, jak również użycie odpowiedniego gazu buforowego służącego do napełnienia lampy spektralnej. Użycie helu jako buforu powoduje przy rtęci zwiększenie czułości metody.

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