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EXCHANGE OF MERCURY BETWEEN WATER AND THE WALL OF A VESSEL AND ITS EFFECT ON THE RESULTS OF DETERMINATIONS

Contents: 1. Introduction, 2. Experimental, 3. Conclusions; 4. Streszczenie; References.

1. INTRODUCTION

Extremely high biological activity of mercury necessitates the assaying of low levels of the element in the natural environment. Assaying very low levels of mercury in water is of particular importance. There are, however, various processes which contribute to the vitiation of the results of mercury determinations in aqueous solutions [2, 4, 5]. In particular, migration of mercury from water to the walls of vessels used for sampling and storage of samples as well as the reverse process — the release of mercury from the walls have a marked effect on the results of mercury determinations in water [1, 6].

This paper presents the results of investigations (in phenomenological form) of the kinetics of exchange of mercury between the wall of a vessel and its aqueous solution caused by the physical sorption of mercury on the wall, and the kinetics of the reverse process — desorption of mercury from the wall, for various surface densities of solution. These processes were studied by using the previously described [7, 8] atomic emission spectrometry with a low-pressure ring discharge.

2. EXPERIMENTAL

The kinetics of the sorption of mercury from an aqueous solution on the wall of a vessel was studied indirectly by analysing variations in the mercury concentration in a sample of water placed in a proper vessel. For this purpose, a method described in [6] and the equipment reported in [7] were applied.

The investigations were carried out using vessels made from various materials, for various surface densities, the surface density, d_p being defined by $d_p = V_r / P_z$, where V_r is the volume of the aqueous solution of mercury and P_z is the surface area of the vessel moistened by the solution.

Curves shown in Fig. 1 illustrate the losses of mercury in time, from distilled water to which given quantities of mercury were added (without preservatives) due to sorption of mercury on the wall of the vessel. The initial concentration of mercury, C, was 1 ng dm^{-3} and the experiment was carried out at a temperature of 20°C. With various surface densities, the highest diurnal losses due to this phenomenon, reaching 40 per cent of the initial mercury content, occurred at $d_p = 0.12$ cm^3 cm^{-2}.

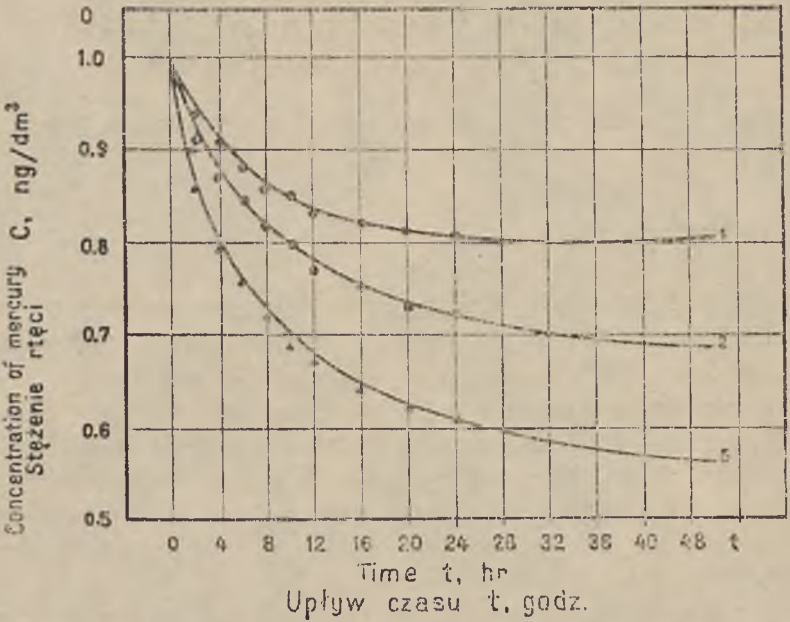

Fig. 1. Variations in the mercury level due to physical sorption in sodium glass vessels, in distilled water (without preservatives, at concentration $C = 1$ ng dm^{-3} at 20°) for: 1 — $d_p = 1.66$ cm^3 cm^{-2}; 2 — $d_p = 0.34$ cm^{3}cm^{-2}; 3 — $d_p = 0.12$ cm^3 cm^{-2}

Rys. 1. Zmiany zawartości rtęci spowodowane sorpcją fizyczną, w naczyniach ze szkła sodowego, dla wody destylowanej (bez środków stabilizujących, przy stężeniu $C = 1$ ng/dm^3, temperatura $t = 20$°C) dla: 1 — $d_p = 1{,}66$ cm^3/cm^2; 2 — $d_p = 0{,}34$ cm^3/cm^2; 3 — $d_p = 0{,}12$ cm^3/cm^2

It was found that with submicro trace levels of mercury in water a decrease in the mercury level by one or even two orders of magnitude may occur within a relatively short period. This was illustrated in the experimental curves shown in Fig. 2 obtained for distilled water

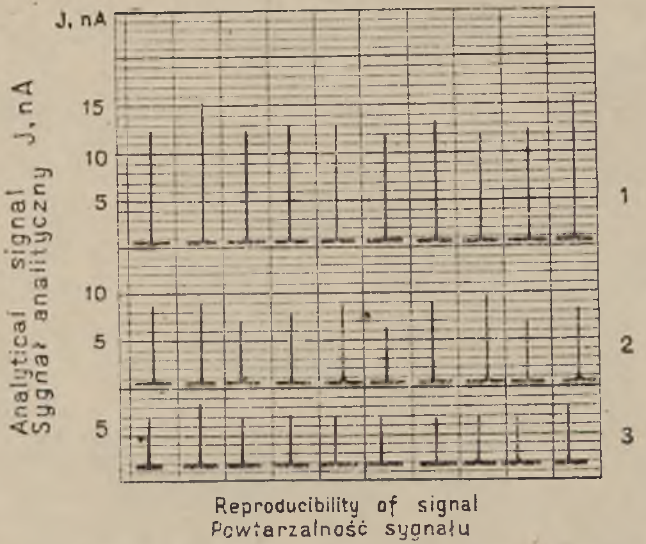

Fig. 2. Signal for a mercury solution in distilled water (without preservatives) stored in a sodium glass vessel at $C = 0.1$ ng dm^{-3}; $d_p = 0.34$ cm^3 cm^{-2}; $t = 20$°C: 1 — in freshly prepared solution; *2* — after 24-hr storage; *3* — after 1-week storage.

Rys 2. Sygnał otrzymany dla roztworu rtęci w wodzie destylowanej (bez środków stabilizujących, przechowywanej w naczyniu ze szkła sodowego, przy $C = 0{,}1$ ng/dm^3, $d_p = 0{,}34$ cm^3/cm^2 oraz $t = 20$°C: 1 — w roztworze świeżym, *2* — po dobowym przechowywaniu, *3* — po tygodniowym przechowywaniu.

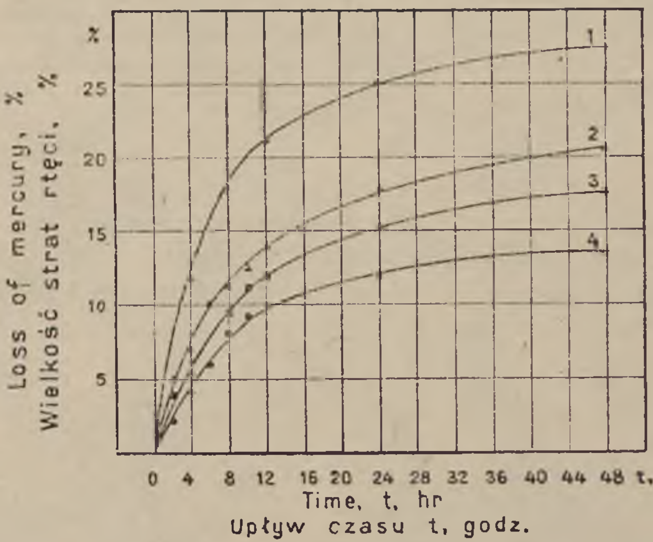

Fig. 3. Losses of mercury due to sorption on the walls of the vessels for $C = 1$ ng dm^{-3}, $d_p = 0.34$ cm^3 cm^{-2} and $t = 20$° in: 1 — sodium glass vessels; *2* — polyethylene vessels; *3* — siliconized vessels; *4* — quartz vessels.

Rys. 3 Wielkość strat rtęci spowodowanych sorpcją w ściance naczynia, dla $C = 1$ ng/dm^3, $d_p = 0{,}34$ cm^3/cm^2 oraz $t = 20$° powstające w: 1 — naczyniach ze szkła sodowego, *2* — naczyniach polietylenowych, *3* — naczyniach szklanych silikonowanych, *4* — naczyniach ze szkła kwarcowego.

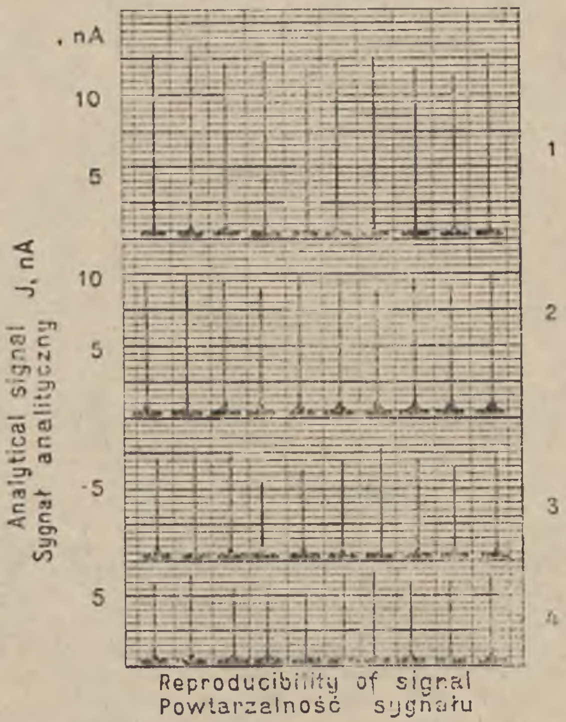

Fig. 4. Curvies of a signal after repetition of the measurements with samples of freshly prepared solution (*1*), that stored for 24 hrs. in a quartz vessel (*2*), in a polyethylene vessel (*3*), in a sodium glass vessel (*4*).

Rys 4. Krzywe sygnału otrzymane przy powtórzeniu pomiarów na próbkach sporządzonych z roztworu świeżego (*1*) oraz z roztworu przechowywanego przez jedną dobę w naczyniach ze szkła kwarcowego (*2*), polietylenu (*3*) i szkła sodowego (*4*).

with an initial mercury concentration of 0.1 ng dm^{-3} in freshly prepared solution, after 24 hrs and after keeping the solution in a sodium glass vessel for one week, respectively. The signal obtained after one-week storage corresponds to a decrease of its content by approximately two orders of magnitude.

The sorption kinetics of mercury on the walls of vessels was studied by using vessels made from sodium glass, glass siliconized with chlorosilanes, polyethylene vessels, and quartz vessels at $d_p = 0.34$ cm^3 cm^{-2}. The highest losses of mercury from solution, due to sorption on the walls, took place with sodium glass vessels and the lowest with quartz vessels (Fig. 3).

Variations in mercury concentrations in water due to its sorption on the walls of the vessels are particularly large in the submicro trace levels (0.01—1 ng dm^{-3}) of mercury. The largest variation of a signal for distilled water, free of preservatives, occurs with water samples

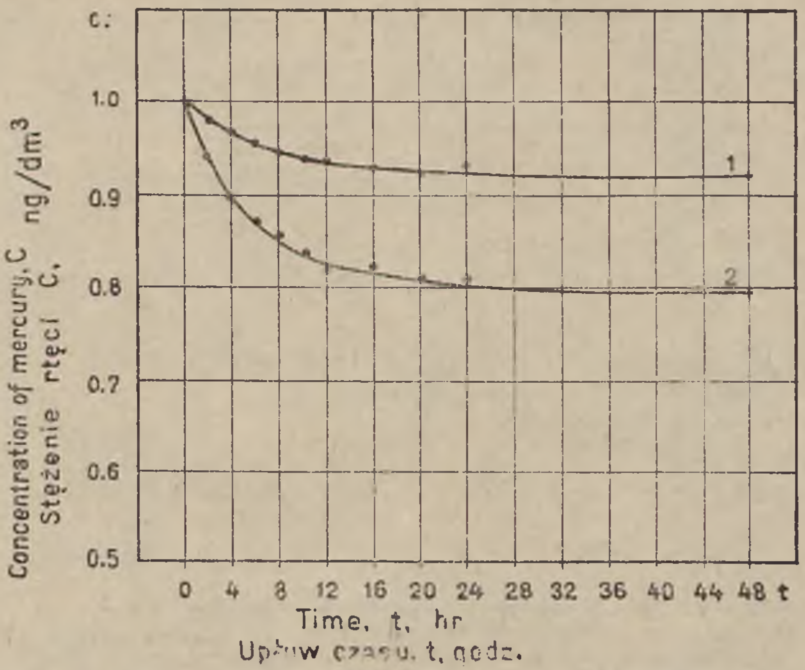

Fig. 5. The effect of the addition of 0 1 g dm^{-3} of potassium iodide on the stabilization of a solution of mercury in distilled water in a glass vessel at $C = 1$ ng dm^{-3}, $t = 20°C$, $d_p = 1.66$ cm^3 cm^{-2}

1 — variations of the mercury concentration in a solution containing 0.1 g KI per dm^3

2 — variations of the mercury concentration in a solution without the addition of KI.

Rys. 5. Wpływ dodatku 0,1 g/dm^3 jodku potasowego na stabilizację roztworu rtęci w wodzie destylowanej w naczyniu szklanym przy $C = 1$ ng/dm^3, $t = 20°C$ $d_p = 1{,}66$ cm^3/cm^2;

1 — zmiany stężenia rtęci w roztworze z dodatkiem 0,1 g/dm^3 KJ,

2 — zmiany stężenia rtęci w roztworze bez dodatku KJ.

stored in sodium glass vessels. With the initial mercury concentration $C=0.1$ ng dm^{-3}, at $d_p = 0.34$ cm^3 cm^{-2}, at 20°C, the drop in the mercury concentration over 24 hrs. may be as high as 1—2 orders of magnitude. These variations have been shown in the form of analytical curves in Fig. 4, taken in a series of measurements of a freshly prepared solution of mercury in distilled water without preservatives, stored in vessels made from sodium glass, polyethylene and quartz glass.

The efficiency of the addition of potassium iodide to aqueous solution of mercury was also investigated. This salt has been known to prevent sorption on the wall. The addition of 0.1 g of potassium iodide to 1 dm^3 of a solution of mercury in distilled water reduced mercury losses due to sorption considerably, similar to [3]. Curves shown in Fig. 5 illustrate the losses of mercury in distilled water (initial mercury con-

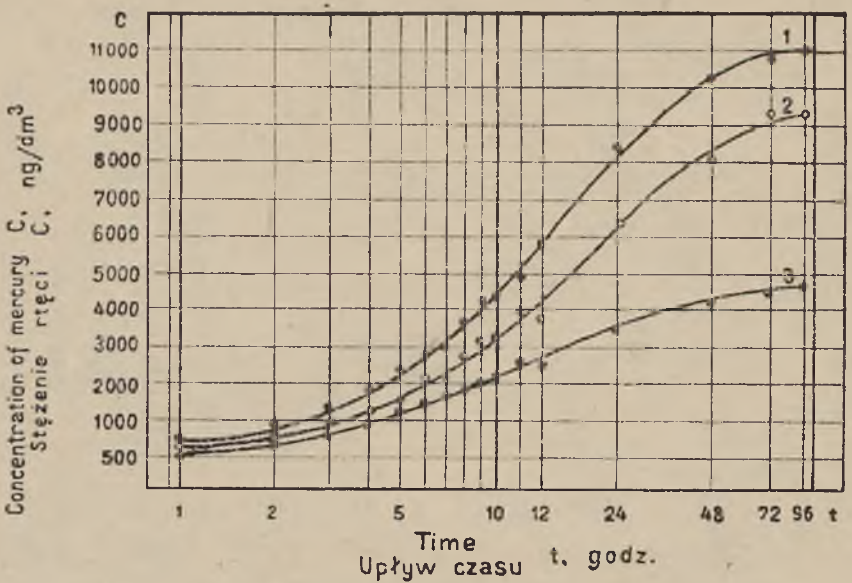

Fig. 6. Variations of the mercury concentration in distilled water (with preservatives added, at $d_p = 0.34$ cm^3 cm^{-2}, $t = 20°C$) caused by desorption of mercury from the walls of a vessel previously contaminated with mercury:
1 — in a sodium glass vessel,
2 — in a polyethylene vessel,
3 — in a quartz vessel.

Rys 6. Zmiana stężenia rtęci w wodzie destylowanej (z dodatkiem substancji stabilizujących, przy $d_p = 0{,}34$ cm^3/cm^2, $t = 20°C$) wskutek uwalniania rtęci ze ścianek naczynia skażonego uprzednio rtęcią
1 — w naczyniu ze szkła sodowgeo
2 — w naczyniu polietylenowym,
3 — w naczyniu ze szkła kwarcowego.

centration $C = 1$ ng dm^{-3}; $d_p = 1.66$ cm^3 cm^{-2}; $t = 20°C$) sabilized and not stabilized with potassium iodide, stored in a glass vessel.

A reverse process, i.e. desorption of mercury from the wall of the vessel and its migration into the bulk of the solution, was also studied. By analogy to the sorption, the desorption process was studied by monitoring variations in the mercury level in water. To contaminate the vessels with mercury, they were filled with a solution of mercury ($C = 1$ g dm^{-3}) in distilled water for 24 hrs. The solution was free of preservatives. Subsequently the vessels were filled with distilled water with the addition of concentrated nitric acid (p.a.) at a ratio of 1 : 9 and 0.1 g dm^{-3} of potassium iodide. In Fig. 6 the corresponding variations in mercury concentration in water due to desorption have been shown.

It was found that upon prolonged storage of water containing ultramicro traces of mercury (10—1000 ng dm^{-3}) a gradual decrease in mercury concentration occurred even in the presence of preservatives. A certain anomaly was observed in polyethylene vessels. With mercury levels of the order of 10 ng dm^{-3} in water stored in these vessels, a distinct drop occurred in the mercury level during first days followed by a gradual increase. With a solution of the initial mercury level of 20 ng dm^{-3} kept in polyethylene vessels, the mercury content increased twice within two months, whereas in the glass and quartz vessels the content decreased during this period (Fig. 7). The reason for this was probably leaching by nitric acid of mercury left after washing in deeper layers of the wall. However, the diffusion of mercury through the wall from the surrounding air cannot be ruled out.

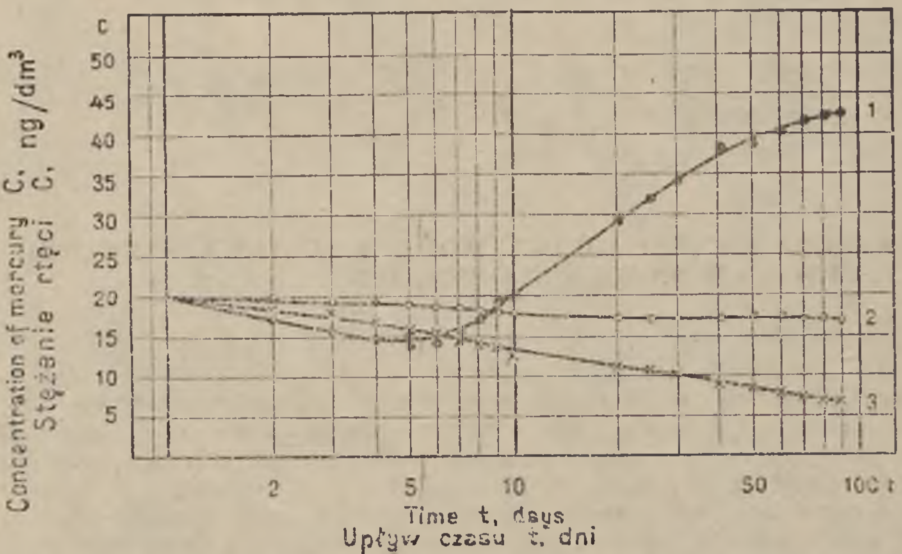

Fig. 7. Variations of the mercury concentration in aqueous solution with preservatives added, at an initial mercury concentraton of $C = 20$ ng dm^{-3} during prolonged storage of water in
1 — polyethylene vessels,
2 — quartz vessels,
3 — sodium glass vessels.

Rys. 7. Zmiany stężenia rtęci w roztworze wodnym z dodatkiem środków stabilizujących, przy początkowej zawartości rtęci $C = 20$ ng/dm^3 przy długotrwałym przechowywaniu wody w
1 — pojemnikach polietylenowych,
2 — naczyniu ze szkła kwarcowego,
3 — naczyniu ze szkła sodowego

3. CONCLUSIONS

The results of this study reveal the possibility of large errors of determination of ultramicro- and particularly submicro trace amounts of mercury in water due to migration of the metal between the wall

of the vessel. Of the vessels tested, the largest errors were observed in the case of the polyethylene vessels. In these vessels, under favourable conditions, the diurnal losses of mercury may amount to 50 per cent and even more over the range of ultramicro trace amounts. The kinetics of the exchange of mercury between the solution and the wall of the vessel depends largely on the surface density of the solution and the material which the vessel is made. Quartz vessels proved the most suitable for prolonged storage of water containing mercury, whereas the polyethylene vessels contributed most to errors in the measurements.

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WYMIANA RTĘCI MIĘDZY WODĄ A ŚCIANKĄ NACZYNIA I JEJ WPŁYW NA WYNIKI OZNACZEŃ

Streszczenie

Na wyniki oznaczeń rtęci w wodzie w zakresie ultramikrośladów poważny wpływ wywiera sorpcja i desorpcja fizyczna rtęci w ściankach naczynia. Wykonano badania tego zjawiska dla naczyń szklanych, polietylenowych i kwarcowych, przy różnych gęstościach powierzchniowych roztworów rtęci, w wodzie destylowanej. Przy długotrwałym przechowywaniu wodnego roztworu rtęci w naczyniach z odpowiednich materiałów obserwuje się dość znaczne zmiany stężenia rtęci w roztworze, spowodowane zarówno przez sorpcję, jak i desorpcję rtęci w ściankach naczynia. Badania świadczą o możliwości powstawania w zakresie ultramikrośladowych, a zwłaszcza submikrośladowych stężeń rtęci w wodzie nawet bardzo dużych błędów oznaczeń, spowodowanych migracją rtęci między roztworem, a ścianką naczynia użytego do pobierania i przechowywania próbki. Stwierdzono, że największe możliwości powstawania błędów oznaczeń spowodowanych przez te zjawiska występują przy użyciu naczyń polietylenu. W naczyniach sporządzonych z tego materiału, w sprzyjających warunkach dobowe zmiany zawartości rtęci w zakresie ultramikrośladów mogą wynosić 50% i więcej stanu pierwotnego.

Kinetyka wymiany rtęci między roztworem a ściankami naczynia wykazuje przy tym dużą zależność od gęstości powierzchniowej roztworu, temperatury materiału z którego sporządzono naczynie itd.

Spośród badanych naczyń użytych do długotrwałego przechowywania wody zawierającej rtęć najkorzystniejsze okazały się naczynia ze szkła kwarcowego. Użycie do tego celu naczyń polietylenowych znacznie zwiększa ryzyko powstania przypadkowych błędów, spowodowanych stratami rtęci w wyniku jej migracji z roztworu do ścianki lub też procesu przeciwnego, mianowicie wzrostu stężenia rtęci wskutek procesów desorpcji rtęci ze ścianek naczynia do roztworu.

REFERENCES

1. Bothner M. H., *Mercury Contamination of Sea Water Samples Stored in Polyethylene Containers*, Analytical Chemistry, 47 (3), 1975, p. 592-595.
2. Dybczyński R., Tugsavul A., Suschny S., *Problems of Accuracy and Precision in the Determination of Trace Elements in Water as Shown by Recent International Atomic Energy Agency Intercomparison Tests*, Analyst, 1978, 103, p. 733-741.
3. Kaiser G. (et al.), *Emissionsspektrometrische Elementbestimmung in Nano- und Picogram-Bereich nach Verflüchtigung der Elemente in mit Mikrowellen induzierte Gasplasmen*, Talanta, 1975, 22, p. 889-899.
4. Maienthal E. J., Becker D. A., *A Survey of Current Literature on Sampling, Sample Handling and Long Term Storage for Environmental Materials*, Natl. Bureau Stand. Washington, Tech. Note 926, 1976.
5. Moody J. R., Lindstrom R. M., *Selection and Cleaning of Plastic Containers for Storage of Trace Element Samples*, Analytical Chemistry, 1977, 49 (14), p. 2264-2267.
6. Stoeppler M., Matthes W., *Storage Behaviour of Inorganic Mercury and Methylmercury Chloride in Sea Water*, Analytica Chimica Acta, 1978, 98, p. 389-392.
7. Wrembel H. Z., *Zastosowanie emisyjnej analizy do wykrywania śladowych ilości rtęci w wodzie*, Studia i Materiały Oceanologiczne, 1977, 17, p. 415-438.
8. Wrembel H. Z., *Zastosowanie optycznej analizy emisyjnej do wykrywania śladowych ilości rtęci w wodzie*, Studia i Materiały Oceanologiczne, 1977, 19, p. 128-135.