

DETERMINATION OF THE MERCURY CONTENT IN NATURAL WATERS BY ACTIVATION ANALYSIS

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In view of increasing ecological efforts, the knowledge and determination of trace contaminants in natural waters is steadily gaining importance. Among trace elements, particularly selenium, arsenic, antimony and mercury have been objects for the development of analytical methods all based on activation, but utilizing different enrichment methods, depending on the character of the sample to be analyzed.

In the determination of trace elements in water by activation analysis, difficulties arise from the fact that usually only samples around some ml can be submitted to direct activation [1], and therefore concentration of the sample before irradiation is inevitable in most cases. This operation, however, involves the risk of contaminating the sample, particularly if the concentration of the trace element to be determined is of the p.p.b. order.

It is therefore preferable to use a minimum amount of reagents for this purpose, and to avoid the use of reagents in which the element to be determined is a typical contaminant.

In the present paper, a method for the enrichment and determination by activation analysis of trace amounts of certain metals will be reported. The method is based on the spontaneous deposition of metal traces on palladium black, joint activation of the palladium black with the metal traces, and separation of the radioisotope to be used for the determination from palladium black by isotope exchange. The method has the advantage that before irradiation, the water sample is not submitted to contact with any reagent except palladium black, and hence the risk of its being contaminated is reduced to a minimum.

The procedure will be demonstrated on the example of mercury determination in three water samples.

Mercury deposition on palladium black

The extent to which mercury present in the ionic form is deposited on palladium black preliminarily saturated with hydrogen is shown in Fig. 1. Plot 1 refers to a mercury nitrate concentration of 2 mg/l, plot 2 to 10 mg/l. The amount of palladium black was 100 mg in both experiments, the sample volume was 1000 ml. As demonstrated by plot 1, 100 mg palladium black is capable of binding 2 mg Hg quantitatively. This, in the case of a mercury concentration of 10 p.p.b. is equivalent to the mercury content in a 200 litre water sample.

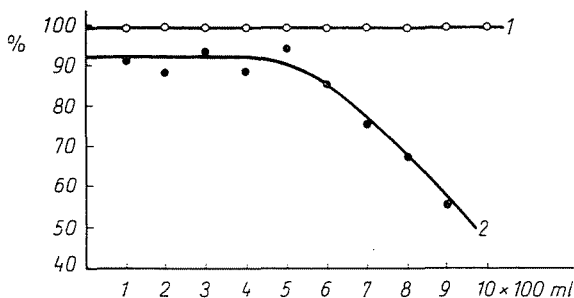


Fig. 1. Extent of Hg^{2+} deposition on 100 mg palladium black. Concentration of mercury nitrate in the solution: 1 : 2 mg/litre; 2 : 10 mg/litre

The thermal stability of mercury deposited on palladium black

Reckoning with the possibility that the temperature of the palladium black + trace element sample may reach 200 to 300 °C in the course of irradiation, we studied the thermal stability of the mercury deposited on palladium black. The results are presented in Fig. 2, demonstrating that up to 400 °C, no measurable amounts of mercury are evolved, so that no mercury losses must be considered during activation.

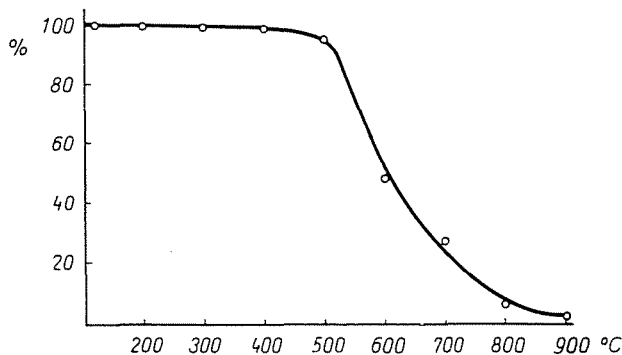
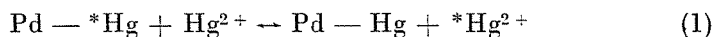


Fig. 2. Evaporation losses of mercury deposited on palladium black as a function of temperature (Y-axis: Residual mercury on palladium black, %)

Removal of ^{203}Hg and/or ^{197}Hg from palladium black by heterogeneous isotope exchange

In the course of activation, in addition to the radioisotopes ^{203}Hg and ^{197}Hg from the mercury deposited on the palladium black, several palladium radioisotopes (^{103}Pd , ^{107}Pd and ^{111}Pd) as well as ^{111}Ag will also be produced from the palladium black itself. Therefore, before measuring the gamma activity of the radioactive mercury isotopes, they must be separated from palladium black. For this purpose the irradiated sample was brought into contact with a mercury nitrate solution. As the result of the exchange reaction



a fraction (depending on exchange time) of the radiomercury on the palladium black passed into the solution in the form of mercury(II) ions, while radioactive palladium isotopes and ^{111}Ag remained in the solid phase.

In our earlier work [2, 3] we demonstrated that the kinetics of isotope exchange in systems consisting of metal monolayer on a noble metal and metal ion can be described by the relationship

$$\ln(1 - F) = - \frac{(A) + (B)}{(A) \cdot (B)} \cdot R_{\max} \cdot \ln t + \ln(1 - F)_{t=1} \quad (2)$$

where $(1 - F)$ is the exchange fraction, i.e. the radiomercury fraction not exchanged till the moment t , (A) and (B) mercury concentrations on the surface of the solid phase and in the solution, resp., and R_{\max} the exchange rate.

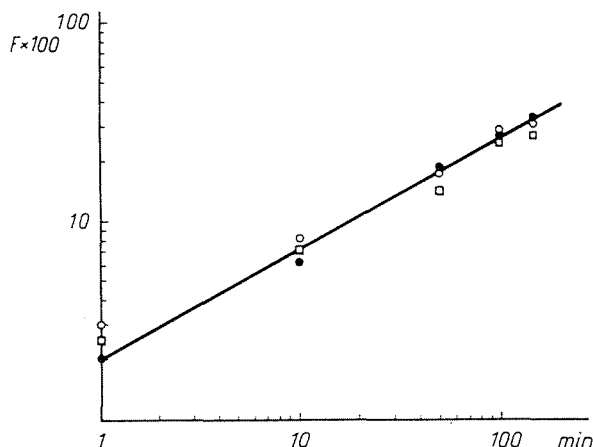


Fig. 3. Time dependence of exchange fraction. $\circ\circ\circ$ 50 μg mercury on 100 mg palladium black; $\square\square$ 10 μg mercury on 100 mg palladium black; $\bullet\bullet\bullet$ 1 μg mercury on 100 mg palladium black

Under the given experimental conditions, namely when the surface concentration of mercury (A) is much lower than mercury concentration in the solution (B), Eq. (2) assumes a simpler form:

$$\ln(1 - F) = -k_{\max} \cdot (B) \cdot \ln t + \ln(1 - F)_{t=1} \quad (3)$$

i.e. the time dependence of the exchange fraction is invariable with (A). In other words, under otherwise identical conditions, identical fractions of the mercury will pass into the solution by isotope exchange from palladium blacks containing different amounts of mercury. Some experimental data confirming this statement are presented in Fig. 3.

Determination of the mercury content in water samples

We analyzed water samples taken from the Budapest section of the Danube, from the river Tisza and from the lake Velence. Sample volumes as listed in Table 1 were admitted to a small chromatograph column filled with 100 mg palladium black previously saturated with hydrogen. The flow rate of the water samples was adjusted to ~ 200 ml/hr. Hydrogen was continuously led into the water in the column above the palladium black, to avoid an escape of the hydrogen sorbed by the palladium. The water samples were passed through the column without previous filtration, to avoid adsorption of mercury present in a non-ionic form on the filter, since this — presumably significant — effect could falsify results.

The mercury standard series was prepared by admitting mercury nitrate solutions containing 1, 10 and 50 μg Hg, resp., to columns containing 100 mg palladium black each, previously saturated with hydrogen. As demonstrated by Fig. 1, the mercury quantities applied for standards are quantitatively precipitated on the platinum black under the given experimental conditions.

The palladium blacks with the mercury contents of the water samples and with the mercury standards, resp., were activated in reactor with a neutron flux of $\sim 10^{17} \text{ m}^{-2}\text{s}^{-1}$ for 3 hours. After activation the samples were added to 5 ml each of a 0.1 M mercury nitrate solution, agitated for 30 minutes and separated by filtration. An aliquot of the solutions was used for activity measurement carried out with a NaI(Tl) scintillation detector coupled with a 256-channel amplitude analyzer. For the evaluation of the gamma spectra the 77 keV photopeaks of ^{197}Hg was used. The results are summarized in Table 1.

Table 1
Mercury concentrations found in natural waters

| Origin of water sample | Tested volume | Hg found, p.p.b. |
|------------------------|---------------|------------------|
| River Danube | 3000 ml | 1.0–1.7 |
| River Tisza | 2900 ml | <0.2 |
| Lake Velence | 2450 ml | <0.1 |

Discussion

The described method is little intended for routine tests, but primarily for solving tasks where — owing to the extremely low mercury content of the samples — very large volumes have to be concentrated before activation. The described procedure allows such concentration from samples having volumes of several 10 litres.

It appears that the procedure is successfully applicable for concentrating all trace elements which are spontaneously deposited on palladium black, viz. copper, selenium and tellurium. We intend to develop analytical procedures for the determination of these elements too.

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Summary

A method was developed for determining mercury traces in natural waters. The procedure is based on the spontaneous deposition of mercury on palladium black, activation of the palladium black together with the mercury deposited on it in a nuclear reactor, and separation of the radioactive mercury isotopes from palladium black and other isotopes formed in activation by means of isotope exchange.

References

1. BECKNELL, D. E.—MARSH, R. H.—ALLIE, E. JR.: *J. Anal. Chem.*, **43**, 1230 (1971).
2. TÓTH, G.: *Radiochim. Acta*, **17**, 12 (1972).
3. MILLER, J.—TÓTH, G.: *Magy. Kém. Foly.*, **78**, 265 (1972).

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