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## ASSAYING THE MERCURY LEVEL IN WATER BY THE LUMINESCENCE METHOD

Contents: 1. Introduction, 2. Experimental, 3. Results and discussion; Streszczenie; References

### 1. INTRODUCTION

The mechanism of photoluminescence, i.e. the shining of substances after removal of the source of excitation radiation, is explained on the basis of a diagram of energy levels of a molecule, suggested by Jab-

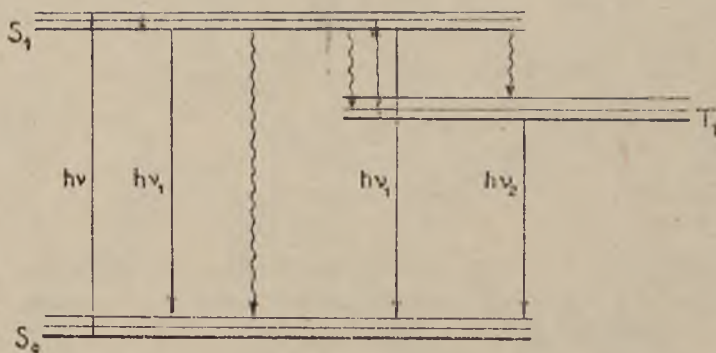


Fig. 1. Schematic diagram of energy levels of a molecule  
 Rys. 1. Schemat poziomów energetycznych molekuly

łoński [4] (Fig. 1). By absorbing light of energy  $h\nu$ , the molecule passes from the ground state  $S_0$  to an excited state  $S_1$  or to higher states. The life time of the excited state is relatively short (of the order of  $10^{-8}$ s) and, after thermal relaxation to the zero oscillation level, its deactivation is observed. From the state  $S_1$  the molecule may return to the ground state by a variety of ways, e.g.:

(i) by radiation transition with emission of fluorescent light of energy  $h\nu_1$ ;

(ii) by radiationless transition to the  $S_0$  state;

(iii) by radiationless transitions to the unstable triplet state  $T_1$ , which may subsequently produce retarded fluorescence [1] or fluorescence with emission of a quantum with energy  $h\nu_2$ .

Energy losses of a molecule during thermal relaxation in the excited state shift the fluorescence spectrum towards longer waves in respect of the absorption spectrum (Stokes' rule). Radiation transitions  $T_1 \rightarrow S_0$  are employed in the luminescence analysis. Quantitative analysis of the content of a fluorescent substance in a sample can be performed after taking into account all processes accompanying irradiation of the sample with light of intensity  $I_0$ . The amount of energy absorbed by the solution depends on the properties of the molecules, such as the molar absorptivity,  $\epsilon$ , their concentration,  $c$ , and path length,  $d$ , over which light is absorbed. Taking into account the Lambert-Beer law leads to the following equation for intensity of the absorbed radiation,  $I_a$ :

$$I_a = I_0 (1 - e^{-\epsilon cd}) \quad (1)$$

The component of the intensity used for the analysis is given by:

$$I_f = \varphi_f I_a \quad (2)$$

where  $\varphi_f$  is the absolute quantum yield of the fluorescence. For low concentration eq. (2) assumes the form

$$I_f = I_0 \varphi_f \epsilon d c = A c \quad (3)$$

Eq. (3), providing the basis of quantitative luminescence analysis, holds for solutions obeying the Lambert-Beer law. This feature rules out specific interactions of the molecules with the solvent and intermolecular interactions. These conditions provide limitation of the applicability of eq. (3) for the determination of concentration of a luminescent substance based on the measurement of its luminescence intensity. In the fluorimetric analysis, selection of the wavelength exciting the solution is also important. From eq. (3) it follows that the highest sensitivity of determination is when

$$\frac{dI_f}{cd} = I_0 \varphi_f \epsilon d = \max \quad (4)$$

This shows that the excitation should be accomplished with a wave of a length for which the extinction coefficient has a maximum value (assuming that the absorption spectrum superimposes the excitation spectrum).

## 2. EXPERIMENTAL

The choice of an organic molecule useful for a particular fluorimetric assay depends on its luminescent properties and the chemical method necessary to prepare the samples for measurement. In this method, rhodamine B ( $C_{28}H_{30}ClN_2O_3$ ) was used as a luminescent molecule. The authors of the articles [2—6] found that in the presence of mercury compounds rhodamine B formed rhodamine — mercuric (RB-Hg) complexes exhibiting photoluminescence over the visible range. The absorption spectrum of the RB-Hg complexes was measured on a SPECORD UV-VIS (C. Zeiss) spectrophotometer. Emission spectra were measured using the equipment shown in Fig. 2.

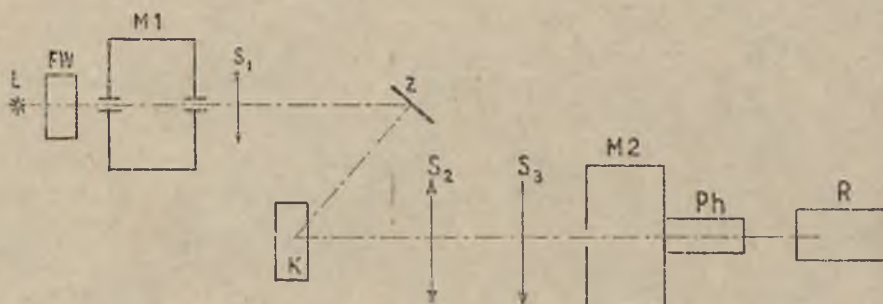


Fig. 2. Block diagram of the measuring appliances

Rys. 2. Schemat blokowy aparatury pomiarowej

The excitation wavelength,  $\lambda_{ex} = 545$  nm, was obtained by means of a xenon lamp L (XBO/101), water filter FW, monochromator M1 (SPM2 Zeiss) and lens  $S_1$ . The excitation radiation was directed by means of mirror Z on cuvette K in which the sample was placed. The fluorescence light of the RB-Hg complexes was passed by the lens system  $S_3$  and  $S_2$  into the slit of monochromator M2 (SPM2). Photocurrent from the photomultiplier Ph (M12 FC51 Werk für Feinschelelektronik) was read out by means of an electrometer (219A UNITRA) or recorded on recorder R (K-200 Zeiss). Samples were prepared as described in [7].



### 3. RESULTS AND DISCUSSION

A study of the time-response of the absorption spectra revealed that optical density of an extract containing the rhodamine-mercury com-

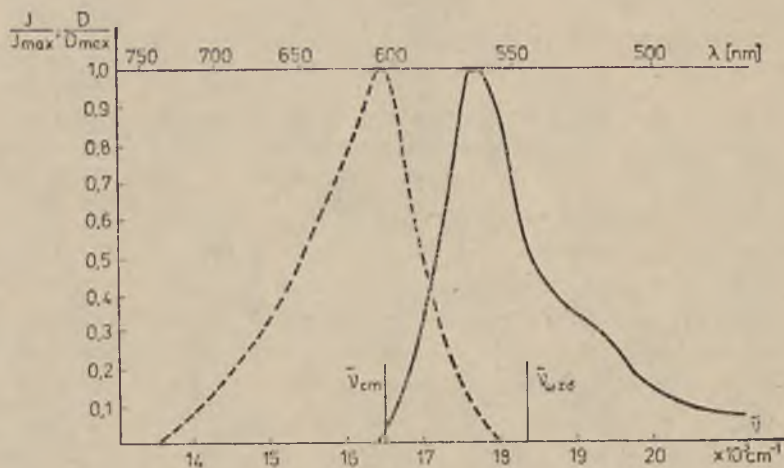


Fig. 3 Spectra of absorption (————) and fluorescence (-----) of the rhodamine-mercury complex

Rys. 3. Widma absorpcji (————) i fluorescencji (-----) kompleksu rodaminowo-rtęciowego

plexes stabilized itself within 2 hours after its preparation (Fig. 3). This feature does not impose time limitations for performing the luminescence analysis.

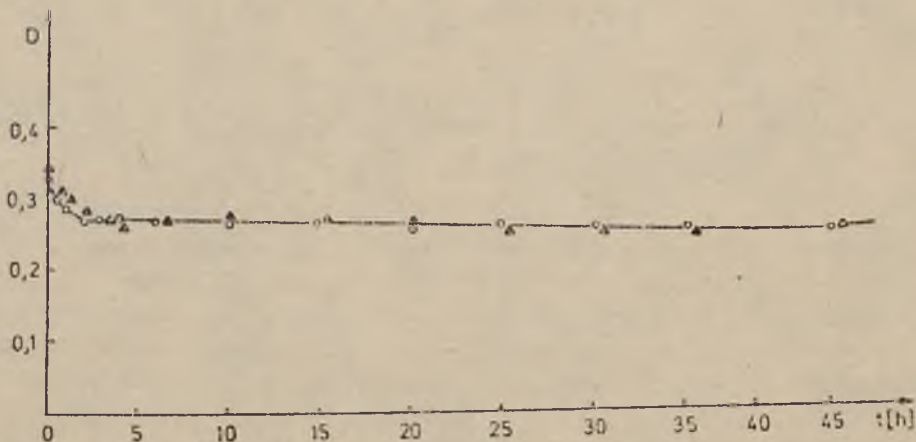


Fig. 4. Time response of the optical density of an extract containing the RB-Hg complexes

Rys. 4. Zależność gęstości optycznej ekstraktu zawierającego kompleksy RB-Hg od czasu

The measurements of the intensity of fluorescence of the RB-Hg complexes were accomplished at 600 nm in the type B artificial sea water prepared after the Polish Standard PN-66/C-06502 and in the artificial Baltic Sea water prepared by using a procedure developed by Trzosińska [8]. Normalized absorption and emission spectra are shown in Fig. 4. Table lists mean values of the intensity of fluorescence of the complex corresponding to definite amounts of mercury added to the solution, and mean standard deviations.

Concentration of mercury in water,  $c$ , and the intensities of photocurrent generated by light of fluorizing complex in artificial sea water ( $I_M$ ) and in artificial Baltic Sea water ( $I_B$ )

Stężenie rtęci w badanej wodzie ( $c$ ) oraz natężenie fotoprądu wywołanego przez światło fluoryzującego kompleksu w zastępczej wodzie morskiej ( $I^M$ ) i bałtyckiej ( $I^B$ )

$c$ [M]	$I^M \times 10^{-9}$ [A]	$I^B \times 10^{-9}$ [A]
$1 \times 10^{-8}$	$1.79 \pm 0.63$	—
$2 \times 10^{-8}$	$2.44 \pm 0.45$	—
$5 \times 10^{-8}$	$4.30 \pm 0.92$	$1.80 \pm 0.65$
$1 \times 10^{-7}$	$7.17 \pm 0.70$	$3.07 \pm 0.74$
$2 \times 10^{-7}$	$9.25 \pm 1.63$	$4.25 \pm 1.98$
$5 \times 10^{-7}$	$16.25 \pm 1.42$	$7.12 \pm 1.29$
$1 \times 10^{-6}$	$23.10 \pm 3.06$	$10.55 \pm 1.81$
$2 \times 10^{-6}$	$30.40 \pm 2.30$	$14.59 \pm 2.08$
$5 \times 10^{-6}$	$49.74 \pm 3.59$	$25.15 \pm 3.25$
$1 \times 10^{-5}$	$70.95 \pm 6.13$	$37.24 \pm 2.49$
$2 \times 10^{-5}$	$101.30 \pm 8.10$	$55.00 \pm 5.56$
$5 \times 10^{-5}$	$189.20 \pm 15.15$	$81.91 \pm 8.32$
$1 \times 10^{-4}$	$258.15 \pm 10.47$	$135.00 \pm 12.72$
$2 \times 10^{-4}$	$339.80 \pm 15.56$	$185.05 \pm 9.70$
$5 \times 10^{-4}$	$440.10 \pm 15.45$	$289.60 \pm 11.86$

Fig. 5 provides graphic illustration of the data in Table. The intensity of fluorescence of the complex for a given mercury concentration was found to be lower in the Baltic Sea water than in sea water. This was due to different concentrations of NaCl in the water examined according to the results reported in [7].

The linear relationship of  $I_f = I_f(c)$  demonstrates convincingly the possibility of employing this method for mercury assay in water. In spite of its low determination limit ( $2 \times 10^{-6}$  g dm<sup>-3</sup>), the method has many advantages. The analysis can be performed in a relatively short time and samples can be prepared at the sampling site, thus eliminating what is difficult to determine — the processes of penetration of mercury into the walls of the vessels. Fig. 5 suggests that the method

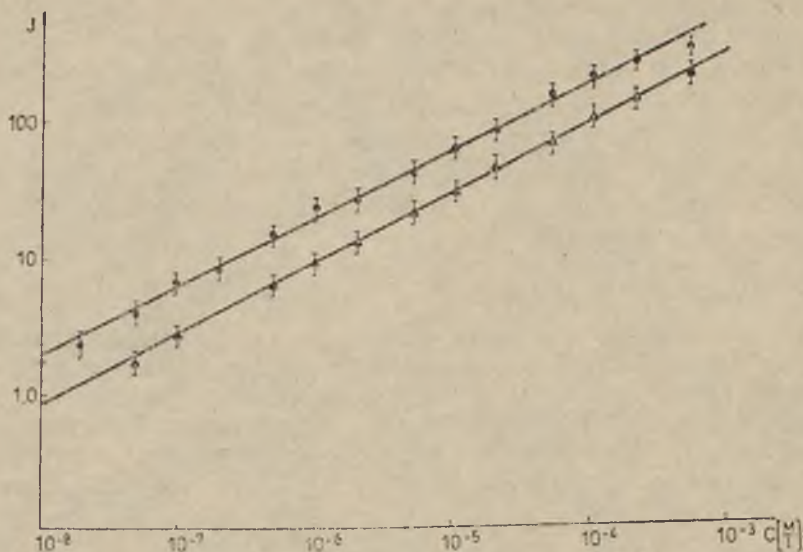


Fig. 5. Relationships between fluorescence intensity of complexes and concentration of mercury in artificial sea water (M) and artificial Baltic Sea water (B)

Rys. 5. Zależność natężenia fluorescencji kompleksów od koncentracji rtęci w zastępczej wodzie morskiej (M) i zastępczej wodzie bałtyckiej (B)

indicates good sensitivity. Small variations in the mercury concentration in solution produce large differences in the intensity of fluorescence of the rhodamine-mercury complexes.

To be able to assay lower mercury concentrations, the instrumentation should be modified. The determination limit of mercury could be markedly lowered by concentration of the rhodamine-mercury extract. Accordingly, the objectives of further studies will be to lower the determination limit and apply the method for analysis of natural waters.

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## OZNACZANIE ZAWARTOŚCI RTECI W WODZIE METODĄ LUMINESCENCYJNĄ

### Streszczenie

Praca dotyczy możliwości zastosowania metody luminescencyjnej do określania zawartości rtęci w wodzie. Podstawą analizy ilościowej jest tworzenie się w roztworach wodnych kompleksów rodaminowo-rtęciowych (RB-Hg), wykazujących



fluorescencję w zakresie długości fal światła widzialnego. Zmierzono widma absorpcji i fluorescencji kompleksów oraz wykonano pomiary ich trwałości w mieszaninie ekstrahującej (benzen + eter etylowy w stosunku objętościowych 2:1).

Stwierdzono liniową zależność natężenia fluorescencji kompleksów w zakresie  $10^{-8}\text{M}$  —  $5 \cdot 10^{-4}\text{M}$  rtęci w wodzie.

Pomiary wykonano dla przypadku zastępczej wody bałtyckiej i wody morskiej typu B. Wskazano na możliwość obniżenia granicy oznaczalności poprzez dokonanie załączenia ilości fluoryzujących kompleksów w luminezującej próbce.

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