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## Solid-Phase Spectrophotometric Determination of Mercury(II) Ions Using Diphenylcarbazone

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### Abstract

A colorimetric sensor based on a transparent polymethacrylate matrix modified with diphenylcarbazone was developed with a view to spectrophotometric determination of Hg(II) in various objects. The effect of pH of a solution of diphenylcarbazone on its immobilization into a polymer matrix was studied. The maximum value of the analytical signal was reached near 520 nm and remained almost unchanged in the 3–11 pH range, as established. During the study of complexation of diphenylcarbazone immobilized into a matrix with mercury(II) ions, there were found optimum conditions for determination of Hg<sup>2+</sup>: pH 2.5–4 and duration of the interaction of mercury with diphenylcarbazone (with violet complex formation) of no more than 15 min. Mercury content was determined spectrophotometrically in the 1–25 µg/dm<sup>3</sup> range by measuring absorption of light near 540 nm. The developed procedure of express analysis of mercury(II) was tested during studying organomercury granosan pesticide by indirect electrooxidation..

**Keywords:** colorimetric sensor, solid-phase spectrophotometry, polymethacrylate matrix, mercury determination

### INTRODUCTION

Among numerous chemicals that pollute environmental objects, heavy metals, particularly Hg<sup>2+</sup>, are of special interest. Its content is rationed in water at MPC level of 0.01–0.5 µg/dm<sup>3</sup> (depending on water use purposes) [1, 2]. About 70 % of mercury circulating in the environment is of anthropogenic origin. Mercury finds large-scale uses in mineral extraction and chemical industry, for example, in the production of vinyl chloride, chlorine, or alkalis [3–5]. A part of mercury evaporates into the atmosphere, is present in water and soil as metal, poorly soluble complexes or Hg<sup>2+</sup> ion.

Among the known physicochemical methods of monitoring Hg<sup>2+</sup> in various objects at MPC

level, atomic absorption [6, 7], polarographic [8], voltammetric [9], potentiostatic [10], and other techniques [11] are most common. However, spectrophotometric methods [12–14] are most frequently used. Despite the simplicity of use and the presence of various procedures to determine Hg<sup>2+</sup>, they have some limitations related to the complexity of analysis of turbid and opaque solutions and the need for preliminary concentrating (when working with mercury microconcentrations). Furthermore, a number of complexants are not specific for Hg<sup>2+</sup>, which leads to overlapping of analytical signals [15]. Thus, broadening of opportunities of the spectrophotometric method of determination of Hg<sup>2+</sup> may be reached *via* carrying out complexation in a polymer

matrix, on which concentrating of analytes proceeds simultaneously [16]. This approach has demonstrated prospects during the analysis of muddy and multicomponent solutions of metals using, for example, a polymethacrylate matrix (PMM) [17, 18]. Transparent PMM retains its optical properties after reaction and therefore may be used for the purposes of spectrophotometric analysis.

The present work studied the solid-phase spectrophotometric determination of  $\text{Hg}^{2+}$  using diphenylcarbazone (DPC) immobilized into PMM.

## EXPERIMENTAL

To prepare an aqueous ethanol solution of DPC ( $1 \cdot 10^{-3}$  M), its initial solution with a concentration of  $5 \cdot 10^{-3}$  M was diluted with bidistillate in a day of the experiment. Initial solutions of  $\text{Hg}^{2+}$  were prepared in accordance with GOST 4520-78 [19]. The required pH value was reached using  $\text{HNO}_3$ ; pH control was carried out using pH-410 pH meter-millivoltmeter.

A polymethacrylate matrix generated by radical casting polymerization of methylmethacrylate and polyethylene glycol [20] represented a transparent plate with a size of  $6 \times 7$  mm and a mass of 0.03 g. Immobilization of DPC in PMM was carried out by sorption from a solution with a concentration of 0.001 M in static mode for 15 min. Mercury determination was performed by immersing the plate with DPC in a solution of mercury (II) in various concentrations and pH values and maintained for 1–30 min, and then absorption spectra were recorded or the optical density ( $A$ ) at the absorption band maximum was measured using Evolution 201 spectrophotometer.

## RESULTS AND DISCUSSION

To determine  $\text{Hg}^{2+}$ , complexation reaction is widely used [11–13, 15, 21], as mercury is easy to identify by the spectrophotometry method as a coloured complex generated resulting from analyte interaction with an organic reagent (*e.g.*, with dithizon) including one immobilized into a polymer [22]. However, the reaction with dithizon occurs at pH 1–1.5 and is typical for many other metals. For this reason, to modify PPM, there were used aqueous ethanol solutions of DPC forming a complex with  $\text{Hg}^{2+}$  (Fig. 1) in a broad range of pH values.

An aqueous ethanol solution of DPC has absorption maxima near 290 и 340 nm; they are preserved in PMM. Initially, a colourless transparent PMM takes rose colour. The absorption spectrum contains a clearly defined intense maximum near 290 nm. The latter is diffuse in the visible spectrum range near 520 nm and corresponds to the enol form of the reagent owing to the basic nature of the matrix (Fig. 2, *a*).

The effect of the pH of DPC solution on its immobilization in PMM was studied (see Fig. 2, *b*). With an increase in pH of the analyzed solution, the value of analytical signal increases, reaches a maximum and remains practically unchanged in the 3–11 pH range. At all pH values the sorption time was 15 min.

After contacts with solutions of  $\text{Hg}^{2+}$  in various concentrations, PMM with sorbed DPC is painted in pink-purple colour in  $\text{HNO}_3$  medium. The violet colour of the matrix prevails in the analysed solution with increasing mercury concentration, which becomes apparent in spectra (Fig. 3, *a*) and attests to generating a strong and intensely painted keto complex of  $\text{Hg}^{2+}$  with DPC in the 1 : 2 ratio [14, 15].

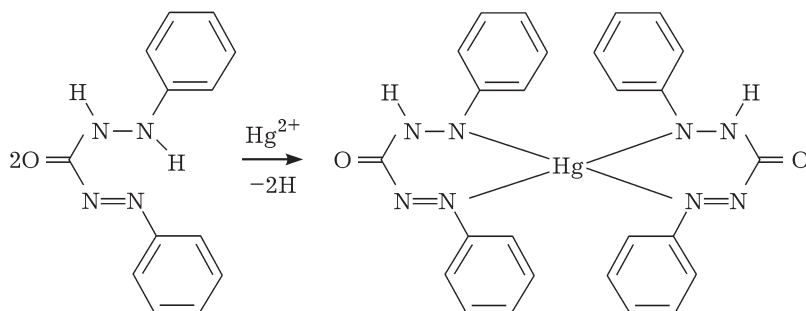


Fig. 1. Scheme for generating  $\text{Hg}^{2+}$ -DPC complex.

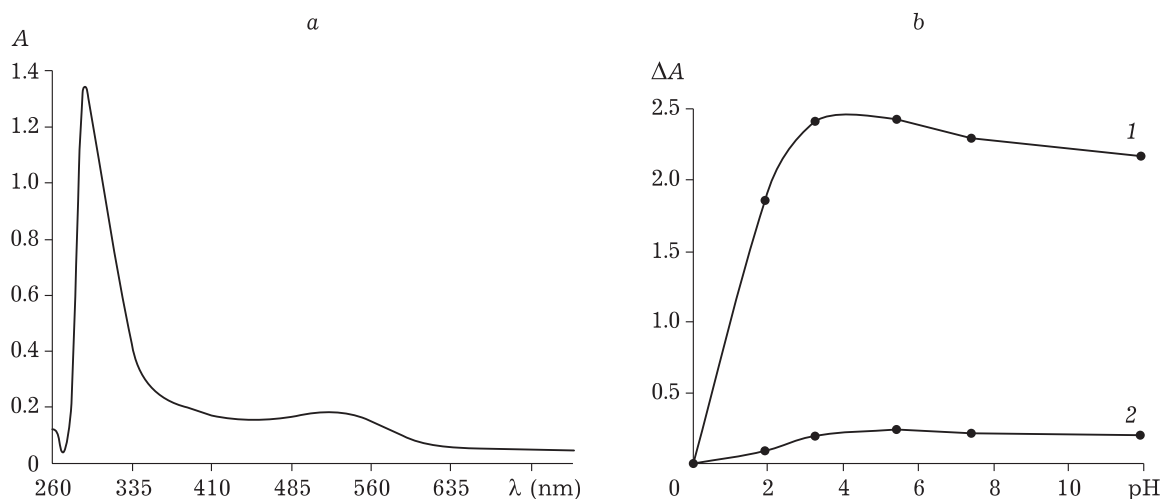


Fig. 2. Absorption spectrum of DPC in PMM after immobilization from an aqueous ethanol solution (a) and the effect of pH on  $\Delta A_{520}$  (1) and  $\Delta A_{290}$  (2) during immobilization of DPC in PPM (b).

The absorption spectrum of  $\text{Hg}^{2+}$ -DPC acquired resulting from the reaction of DPC with  $\text{Hg}^{2+}$  in PMM corresponds to its spectrum in an aqueous ethanol solution. That testifies to preserving the composition of the complex in PMM. Colour change is accompanied by the appearance of the absorption maximum near a wavelength of 540 nm, the optical density value of which was selected as the analytical signal. Absorption spectra for different concentrations of  $\text{Hg}^{2+}$ -DPC are overlapped in one isosbestic

point near 540 nm (see Fig. 3, b), which points out at the established equilibrium. Hence, DPC generates a complex with  $\text{Hg}^{2+}$  in PMM without the formation of intermediates.

The pH of  $\text{Hg}^{2+}$  affects a change in analytical signal value  $\Delta A_{540}$  (Table 1):

pH	1.2	2.0	2.5	3.5	4.0	5.0	7.5
$A_{540}$	0.01	0.02	0.15	0.18	0.17	0.06	0.05

Polymeric plates with DPC are decoloured at pH 0–2, therefore further mercury determination is impossible.

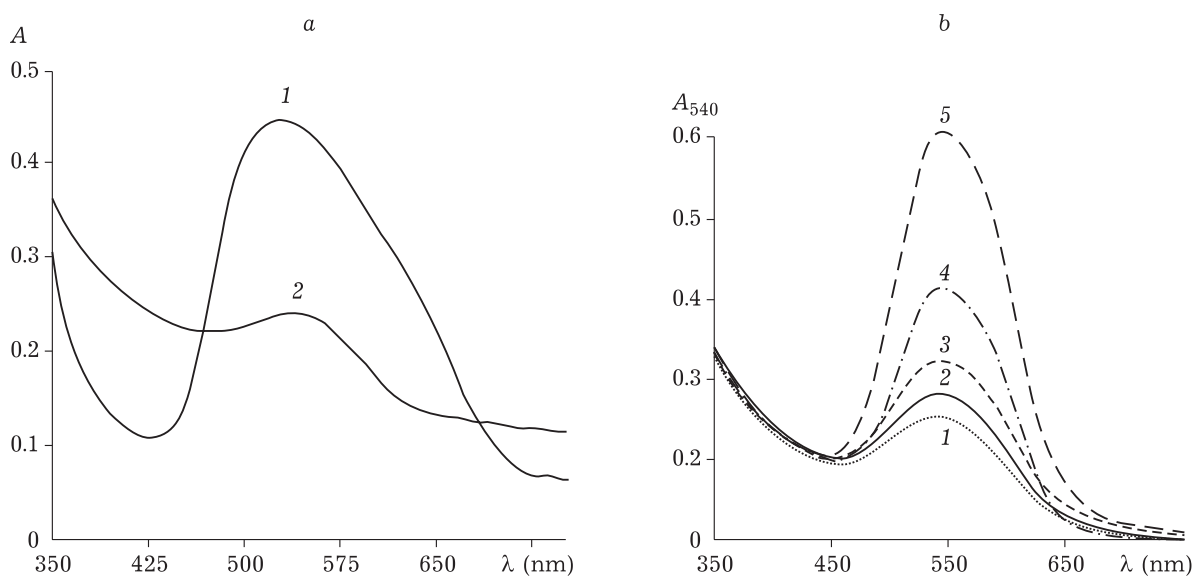


Fig. 3. Absorption spectra of  $\text{Hg}^{2+}$ -DPC (a) after analytical reaction of DPC and  $\text{Hg}^{2+}$  in PMM (1) in an aqueous ethanol solution (2) and of PMM modified with DPC after contacts with  $\text{Hg}^{2+}$  solutions in various concentrations (b),  $\mu\text{g}/\text{dm}^3$ : 5 (1), 10 (2), 15 (3), 20 (4), 25 (5).

TABLE 1

Metrological characteristics of determination of  $\text{Hg}^{2+}$  at different pH

pH	Calibration curve	Linearity range, $\mu\text{g}/\text{dm}^3$	$r$	$S_{\text{ad}}^2$	$C_{\text{min}}$ , $\mu\text{g}/\text{dm}^3$
2.5–4.0	$A_{540} = (0.039 \pm 0.004) + (0.07 \pm 0.01)C_{\text{Hg}^{2+}}$	1–25.0	0.998	0.0003	0.05
4.5–6.0	$A_{540} = (0.47 \pm 0.06) + (0.20 \pm 0.02)C_{\text{Hg}^{2+}}$	4–20.0	0.990	0.0006	0.4
6.5–7.5	$A_{540} = (3.8 \pm 0.8) + (0.7 \pm 0.2)C_{\text{Hg}^{2+}}$	–	0.982	0.07	5.6

Note.  $r$  – correlation coefficient;  $S_{\text{ad}}^2$  – variance of adequacy of calibration dependence.

The maximum absorption of light is observed at pH 2.5–4. In this case, the linearity range of the calibration curve is 1–25  $\mu\text{g}/\text{dm}^3$ ; the correlation coefficient is 0.998.

The solid-phase spectrophotometric method of determination of  $\text{Hg}(\text{II})$  has been developed resulting from the carried out research. The procedure has been tested during the analysis of samples selected during oxidative destruction of organomercury granosan pesticide. The active substance of this pesticide is ethylmercurchloride, *i.e.* I hazard class organomercury compound [23].

The determination was carried out as follows: 50 mL of the analysed solution was subjected to UV treatment for 30 min, then pH was brought to 3 and modified DPC was placed into the PMM sample. The plate was aged for 15 min, then was pulled out, dried with filter paper, and adsorption was measured near 540 nm. The content of  $\text{Hg}^{2+}$  was assessed according to the calibration graph constructed under similar conditions. The following results of  $\text{Hg}^{2+}$  determination on polymeric plates with DPC in the process of granosan destruction were obtained: initial content 141.55  $\mu\text{g}/\text{dm}^3$ , after 1.5 h of granosan oxidative destruction 2.52, 3 h – 0.56, after 4.5 h – 0.10  $\mu\text{g}/\text{dm}^3$ .

## CONCLUSION

A polymethacrylate matrix with immobilized DPC may be used as a disposable analytical sensor for solid-phase spectrophotometric determination of  $\text{Hg}^{2+}$  at MPC level in water and aqueous solutions. The developed procedure is cost-effective, easy to perform, and may be used for analysis of water bodies under both laboratory and field conditions.

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