

Solvent Extraction of Mercury with Iodonitrotetrazolium Chloride

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The formation of an ion-associate complex between triiodomercurate(II) and iodonitrotetrazolium cation and its 1,2-dichloroethane extraction was studied spectrophotometrically. The optimum conditions for the formation of the ion-associate were found. The developed method was applied for the determination of mercury in soils at the 10^{-5} % level with the relative standard deviation below 1 %. The agreement between the determination based on the developed procedure and standard dithizone and 1-(2-pyridylazo)-2-naphtol procedures is satisfactory. The process of ion-associate extraction is characterised by the distribution constant ($K_D = 14.97$), extraction constant ($K_{ex} = 1.41 \times 10^4$) and ion-association constant ($\beta = 9.43 \times 10^2$).

Spektrofotometrycznie badano powstawanie kompleksu jonowo-asocjacyjnego między jonem trijodortęci(II) i kationem jodonitrotetrazoliowym oraz jego ekstrakcję za pomocą 1,2-dichloroetanu. Określono optymalne warunki powstawania kompleksu. Opracowaną metodę zastosowano do oznaczania rtęci w glebach na poziomie 10^{-5} % z względnym odchyleniem standardowym poniżej 1 %. Zgodność otrzymanych wyników z wynikami otrzymanymi standardową metodą z ditionem lub 1-(2-pirydyloazo)-2-naftolem jest zadowalająca. Proces ekstrakcji asocjatu jonowego charakteryzuje się stałą podziału, $K_D = 14,97$, stałą ekstrakcji, $K_{ex} = 1,41 \times 10^4$, i stałą trwałości asocjatu jonowego, $\beta = 9,43 \times 10^2$.

New accurate and reliable methods for analysis of various objects containing traces of mercury should be searched for this element. The most commonly used reagents for colorimetric determination of mercury is dithizone [1]. The reagent as well as the mercury complex are extremely sensitive and susceptible to changes in the laboratory conditions. For this reason the dithizone method becomes less reliable. Also, dithizone forms coloured complexes with a great number of other metals, and that leads to a greater probability of interferences in the analysis.

In general, colorimetric methods are convenient for analysis of a great number of samples and therefore many such methods have been published based on various reagents [1-8].

In aqueous solutions Hg(II) produces four stable mononuclear iodide complexes HgI^+ , HgI_2 , HgI_3^- , HgI_4^{2-} . In acid medium in the presence of I^- Hg(II) reacts with iodinitrotetrazolium chloride and gives compounds insoluble in water. The formed compounds are soluble in some organic solvents. The monocharged anionic complex HgI_3^- appears to react with the tetrazolium salt.

The aim of this paper is to use iodinitrotetrazolium chloride as a reagent for determination of traces of mercury(II), to apply the extraction-photometric method for the determination of mercury in soils and pesticides and to study the extraction equilibrium.

EXPERIMENTAL

Reagents and apparatus

Iodonitrotetrazolium chloride (INT) (Fluka) $1 \times 10^{-4} \text{ mol l}^{-1}$; mercury(II) acetate, p.a. - $1 \times 10^{-5} \text{ mol l}^{-1}$; sulphuric acid, p.a. - 2 mol l^{-1} ; hydrochloric acid, p.a. - 1.2 mol l^{-1} ; nitric acid, p.a. - 1.55 mol l^{-1} ; potassium iodide, p.a. - $1 \times 10^{-3} \text{ mol l}^{-1}$; 1,2-dichloroethane, p.a.

Spectrophotometer VSU 2-P (Carl Zeiss, Jena), $l = 1 \text{ cm}$; Specord UV-VIS (Carl Zeiss, Jena).

Extraction procedure

Into a separatory funnel of 100 ml are introduced the following solutions: 1 ml H_2SO_4 , 1 ml KI, 1 ml INT and a sample solution containing mercury(II). Distilled water is added up to 10 ml and the solution is extracted with 3 ml of dichloroethane for 30 s. The organic layer is filtered into a 1 cm cuvette and absorbance is measured at $\lambda = 260 \text{ nm}$. A blank, containing the same solutions without mercury, is prepared in parallel.

RESULTS AND DISCUSSION

The absorption spectra for the dichloroethane solution are characterized with one maximum. The absorption spectra of equimolar solutions of iodinitrotetrazolium chloride and ion-association complex with Hg(II) in sulphuric acid show the absorption maximum in the region of about 260 nm (Fig.1). The absorbance additivity of both components, without a significant shift of the absorption maximum, indicates formation of an ion-association complex.

A number of different solvents were tested: hydrocarbons, alcohols, chloroform, dichloroethane, tetrachloroethane, ketones, ethers and the most promising solvent for the ion-associate is dichloroethane.

The extraction equilibrium was reached in 15 s. The absorbance of the ion-associate was stable for 6 days. Beer's law was obeyed in the Hg(II) concentration range from 0.1 to $1.2 \mu\text{g ml}^{-1}$. The molar absorptivity of the associate, calculated by the method of Komar-Tolmatchov [9], was $\epsilon_{260} = (1.00 \pm 0.09) \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$.

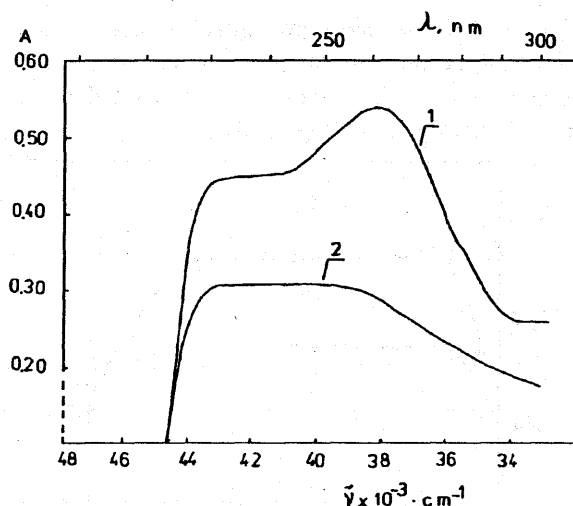


Figure 1. Absorption spectra in dichloroethane of iodinitrotetrazolium chloride (INT) in the presence (1) and absence of Hg(II) (2); concentrations recalculated for the organic phase: $C_{\text{Hg(II)}} = 1.33 \times 10^{-5} \text{ mol l}^{-1}$, $C_{\text{INT}} = 1.66 \times 10^{-5} \text{ mol l}^{-1}$

The stoichiometric coefficients of the ion-associate were established by various methods [9]: the method of isomolar series, the method of Asmus, the method of Bent-French and the method of molar ratios. The results show that in the ion-associate the reagent ratio is INT:Hg:I = 1:1:3.

To optimize the reaction conditions the effect of the type of the mineral acid and its concentration upon the interaction of INT and mercury(II) was studied. The effect of the hydrochloric, sulphuric, nitric acids on the extraction equilibrium was studied. The change of the absorbance of the ion-associate in the pH range 1–9 was also studied. The maximum absorbance for the ion-association complexes was obtained using sulphuric acid in the range 0.2–5.5 mol l⁻¹ (Fig. 2).

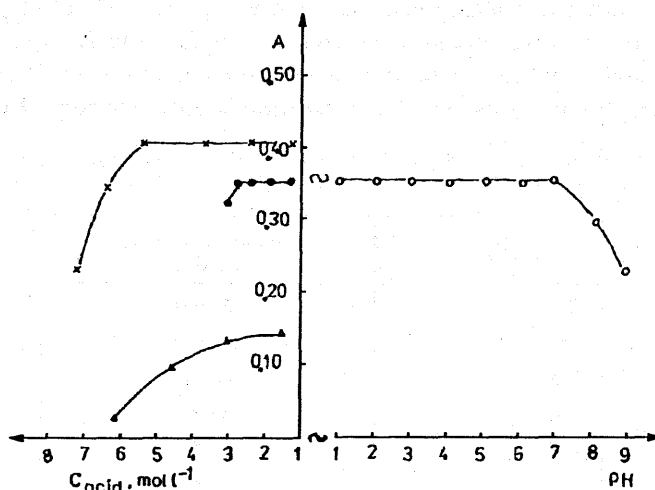


Figure 2. Effect of acidity on the extraction of Hg(II) in the presence of INT: \times H₂SO₄, \bullet HCl, Δ HNO₃; $C_{\text{Hg(II)}} = 4 \times 10^{-6} \text{ mol l}^{-1}$, $C_{\text{KI}} = 1 \times 10^{-4} \text{ mol l}^{-1}$, $C_{\text{INT}} = 5 \times 10^{-6} \text{ mol l}^{-1}$

The influence of idonitrotetrazolium chloride concentration on the ion-associate absorbance was studied. At an aqueous phase acidity 0.2 mol l^{-1} of sulphuric acid, the maximum extraction of the ion-associate was reached at a concentration of INT in the range 0.5×10^{-5} – $3 \times 10^{-5} \text{ mol l}^{-1}$ (Fig. 3).

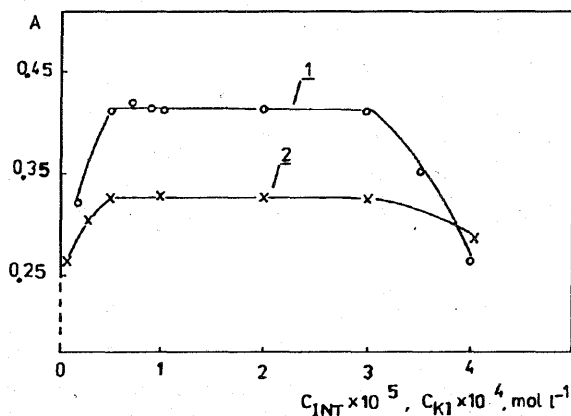


Figure 3. Dependence of the absorbance of the ion-associate on the concentration of: INT (1) and KI (2): 1 – $C_{\text{Hg(II)}} = 4 \times 10^{-6} \text{ mol l}^{-1}$, $C_{\text{H}_2\text{SO}_4} = 0.2 \text{ mol l}^{-1}$, $C_{\text{KI}} = 1 \times 10^{-4} \text{ mol l}^{-1}$; 2 – $C_{\text{Hg(II)}} = 4 \times 10^{-6} \text{ mol l}^{-1}$, $C_{\text{HCl}} = 0.12 \text{ mol l}^{-1}$, $C_{\text{INT}} = 5 \times 10^{-6} \text{ mol l}^{-1}$

An excess of potassium iodide is needed for the formation and extraction of the ion-associate of mercury(II) with idonitrotetrazolium chloride. The relation absorbance–iodide concentration is given in Fig. 3. The maximum absorbance of the complex is reached at iodide concentration of $0.5 \times 10^{-4} \text{ mol l}^{-1}$ in aqueous solution and does not change in the range from 0.5×10^{-4} to $3 \times 10^{-4} \text{ mol l}^{-1}$.

The effect of some ions on the extraction–photometric determination of mercury(II) under optimum conditions was studied. Most of the ions studied do not interfere even at high concentrations. No masking reagents were used. The ratios of the accompanying ions at which the bias was above 3 % are given in Table 1. The experimental data show that the determination of mercury is possible without its preliminary isolation from the accompanying ions. The determination is only interfered by Ag(I).

Table 1. Effect of accompanying ions ($C_{\text{Hg}} = 0.6 \mu\text{g ml}^{-1}$, $C_{\text{KI}} = 1 \times 10^{-4} \text{ mol l}^{-1}$, $C_{\text{INT}} = 1 \times 10^{-5} \text{ mol l}^{-1}$)

Foreign ion	Limiting mass ratio C_x/C_{Hg}
K	16666:1
Sr	11666:1
Mn	8333:1
Mg	6666:1
Pb, Ni	5000:1
Cu	1666:1
Mo(VI)	1000:1
Zn	833:1

Cd	166:1
W(VI)	83:1
Fe(III)	33:1
Al, Co	17:1
Ag	interfere
BO_3^{3-}	10000:1
PO_4^{3-}	8333:1
Cl^-	1666:1
Br^-	166:1
CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$	83:1
NO_3^-	17:1

The sensitivity of the method by Sandell [10] is $W_s = 2 \times 10^{-3} \mu\text{g cm}^{-2}$.

Investigation of the extraction equilibrium

The investigation was carried out to determine some extraction parameters. The distribution coefficient D_{INT} was calculated as a function of the concentration of Hg(II). To determine the distribution coefficient of tetrazolium salts INT, the absorbances obtained in the standard procedure were compared with those obtained after 3-fold extraction of the aqueous layer. The graphical representation of the experimental data is given in coordinates $\log D_{\text{INT}}/\log C_{\text{Hg}}$ (Fig. 4). The extrapolation of the curve to the intersection with the ordinate gave the value of the extraction constant

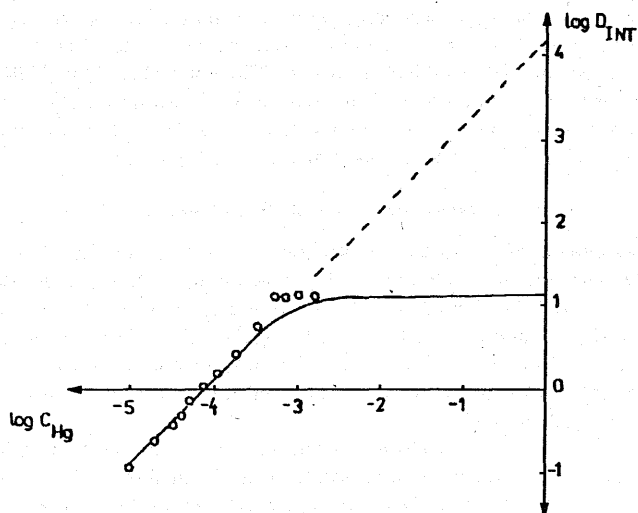


Figure 4. Logarithmic dependence of D_{INT} on the Hg(II) concentration

$K_{\text{ex}} = K_D \beta$ [11], and the horizontal part of the curve gave the distribution constant K_D of the ion-associate. Using the K_{ex} and K_D values the association constant β was calculated.

The reliability of the results obtained was checked up by fitting a theoretical curve (full line in Fig. 4) in the same coordinates. A good agreement is seen between the experimental data and the theoretical curve.

The tangent of the slope of the curve is 1. This confirms once again that the component ratio in the complex is $\text{INT}^+:\text{HgI}_3^- = 1:1$.

The values of the equilibrium constants obtained in a graphical way are as follows:

$$K_{\text{ex}} = \frac{\{\text{INT} [\text{HgI}_3]\}_o}{[\text{INT}^+][\text{HgI}_3]} = (1.41 \pm 0.01) \times 10^4$$

$$\beta = \frac{\{\text{INT} [\text{HgI}_3]\}}{[\text{INT}^+][\text{HgI}_3]} = (9.43 \pm 0.08) \times 10^2$$

$$K_D = \frac{\{\text{INT} [\text{HgI}_3]\}_o}{\{\text{INT} [\text{HgI}_3]\}} = 14.97 \pm 0.11$$

Determination of mercury in soils and pesticides

The method was applied for the determination of traces of mercury in various types of soils. The samples were collected from depth of 0–20 cm.

The extraction–photometric method was used for determination of mercury in pesticides: falizan and germizan.

Preparation of the soil sample

2 g of soil, 5–7 ml of conc. H_2SO_4 and excess of KMnO_4 are placed in a flask equipped with reflux condenser. The crystals of KMnO_4 are added slowly in small portions, on stirring. The flask is heated until fumes of SO_3 occur. After cooling, 10 ml of distilled water are added. The excess of KMnO_4 and manganese oxides is decomposed by adding H_2O_2 [12]. The obtained solution is alkalized with conc. NH_3 (pH 10) in order to precipitate iron as hydroxide. It is filtered through filter paper N 390. The solution is transferred into a 25 ml volumetric flask. Before diluting it up to the mark with water the solution is acidified to pH 3. Aliquots of this solution are taken for analysis.

Extraction and determination of mercury

The following solutions are transferred into separatory funnels: 1 ml H_2SO_4 , 1 ml KI, 1 ml INT and the soil sample solution or an appropriate amount of pesticide solution. The volume of the aqueous phase is brought to 20 ml (for soil) or 10 ml (for pesticide) with distilled water. For soil samples 5 ml of a saturated solution of NH_4F is added to mask the interfering ions. The aqueous solution is extracted with 3 ml of dichloroethane for 30 s. Then the absorbance of the organic phase is measured at 260 nm. A blank, containing the same solutions without the sample solution, is prepared. The concentration of mercury is determined using a standard graph.

The accuracy of the results was checked using the dithizone and 1-(2-pyridylazo)-2-naphtol methods. A good agreement of the results for mercury was obtained by the three methods (Table 2). Taking into consideration the high selectivity, sensitivity and rapidity, the method with iodinitrotetra-zolium chloride can be successfully used for the determination of traces of mercury.

Table 2. Content of mercury (%) in soil and pesticides samples ($n = 5$)

Soil samples, pesticides	Dithizone method	1-(2-Pyridylazo)-2-naphthol method	Iodonitrotetrazolium chloride method	RSD, %
Lessive cinnamonic	5.9×10^{-5}	6.2×10^{-5}	6.0×10^{-5}	0.9
Pseudopodzolic	2.3×10^{-5}	2.0×10^{-5}	2.1×10^{-5}	0.7
Alluvial	9.5×10^{-5}	9.4×10^{-5}	9.7×10^{-5}	0.8
Falizan	0.82		0.80	0.6
Germizan	1.39		1.40	0.80

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