Liquid-Liquid Extraction and Spectrophotometric Determination of Mercury(II) with 2, 6-Dithiolphenol and its Derivatives in The Presence of Hydrophobic Amines

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***Abstract*— The purpose of this work is to systematically study the conditions for the interaction of Hg (II) with dithiolphenols (DP) {2,6-dithiolphenol (DTP), 2,6-dithiol-4-methylphenol (DTMP), 2,6-dithiol-4-ethylphenol (DTEP), 2,6-dithiol-4-propylphenol (DTPP) and 2,6-dithiol-4-tert-butylphenol (DTBP)} and hydrophobic amines (Am). Of the hydrophobic amines, aniline (An), N-methylaniline (mAn) and N, N-dimethylaniline (dAn) were used. Mercury begins to interact with DP at pH ~ 1.5. The optimum pH value is 2.9-4.4. Chloroform, dichloroethane, chlorobenzene and CCl_4 are the best extractants for dithiolphenolate-amine mercury complexes. With a single extraction with chloroform and dichloroethane, 98.3-99.2% mercury is isolated as MLC. MLC chloroform extracts have a maximum light absorption at 458-470 nm. The linearity range of the calibration dependence for chloroform extracts of the complexes is maintained in the range of mercury concentrations of 0.04-3.6 μg/ml. MLC Mercury (II) with DP and Am are stable in aqueous and organic solvents and do not decompose within 48 hours, and after extraction - more than a month. Extraction equilibrium occurs 5 minutes after one minute of shaking. Regardless of the base and nature of the amines, the optimum V_{aq}/V_{org} is 5/5-80/5. The molar ratios between the components of the complex were found by several methods: the method of the relative yield of the Staric - Barbanel, the method of direct and the method of equilibrium shift. The results show that the interaction of Hg (II) with DP and Am forms complexes with the composition of Hg(II):DP:Am = 1:2:2. The molar absorption coefficients of the dithiolphenolate-amine complexes were calculated by the saturation and mosquito methods, similarly to the calculation of ε for mercury complexes with DP and amines ε = (2.82 - 3.80) × 10^4. Acid-base properties of hydrophobic amines to a lesser extent affect the formation and extraction of complexes. In the dAn-mAn-An series, the pH of the reaction decreases. The study and comparison of the acid-base properties of the complexing agents FAG and complexation pH50 made it possible to determine the effect of the acidic properties of the –SH group on the pH of the complexation. The decrease in the acidic properties (ΔpK_1) of the reagent leads to a shift in the pH (ΔpH_{50}) of the complexation towards the weaker acidic region. It was found that a large amount of alkaline, alkaline earth elements, REE, F^-, Cl^- and Br^- does not affect the determination of mercury. Citrate, tartrate, J^-, CN^-, SCN-, $S_2O_3^{2-}$, NO_2^-, thiourea, are used for determination. The selectivity of Hg (II) determination is significantly**

increased in the presence of reagents that mask these elements. The proposed extraction-spectrophotometric methods for the determination of mercury with DP and Am were tested when determining it at various sites. The correctness of the determination of Hg (II) by the addition method and the dithizone method was evaluated.

Keywords—mercury; 2,6-dithiolphenol; hydrophobic amines; extraction-photometric method; determination

I. Introduction

Mercury is the most toxic element in natural ecosystems. Along with cadmium and lead, it belongs to superecotoxicants, because it exhibits high toxicity in trace amounts and is able to concentrate in living organisms [1]. The main anthropogenic sources of mercury release to the environment are non-ferrous metallurgy, fuel combustion, and the chemical industry. The lifetime of mercury in the atmosphere is estimated at 70 days [2]. The MPC of mercury in the soil is 2.1 mg/kg (gross content) [3]. The use of mercury and its compounds as catalysts, components of explosives, antiseptics of various surfaces, seed disinfectants, leads to the expansion of the range of used mercury-containing substrates.

Mercury can be recovered as intracomplex, as well as halide and thiocyanate complexes with basic reagents [4]. Many organic reagents, in particular containing heteroatoms sulfur and nitrogen, form with Hg (II) ions insoluble or intensely colored compounds that are widely used in analytical chemistry. Mainly organic reagents react with mercury, in the molecule of which the following functional-analytical groups are present [5]:

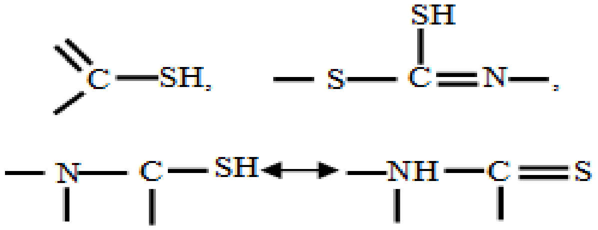
For the photometric determination of Hg (II), sulfur containing chelate forming reagents are mainly used, which in most cases have nitrogen as the second additional atom. Reagents containing N and O as donor atoms play a smaller role in the analytical chemistry of mercury [6]. For Hg (II), a large number of complex compounds with a coordination number of 2 (linear complexes) and 4 (tetrahedral complexes) are known. The mercury-ligand bond in all complexes is covalent [5].

B. General Procedure

- **General Procedure for the Determination of mercury (II)**

0.1-0.8 ml were injected into the graduated tubes with ground stoppers, with an interval of 0.1 ml of the initial Hg(II) solution, 2.2 ml of the 0.01 M DPh solution and 2.5 ml of Am. The required pH was adjusted by adding 1M HCl solution. The volume of the organic phase was adjusted to 5 ml with chloroform, and the aqueous phase to 20 ml with distilled water. After 10 minutes, the organic layer was separated and its optical density was measured at room temperature on CFC-2 at 490 nm.

Methods have been developed for the determination of mercury (II) in the form of mixed-ligand complexes with 2,6-dithiol-4-alkyl-thiophenols and 2-hydroxytiophenol and its derivatives [2,5-dihydroxythiophenol, 2-hydroxy-5-xlorthiophenol, 2-hydroxy –5-bromthiophenol, 2-hydroxy-5-yodthiophenol] in the presence of hydrophobic amines [7,8]. The purpose of this work is to systematically study the conditions for the interaction of Hg (II) with dithiolphenols (DP) {2,6-dithiolphenol (DTP), 2,6-dithiol-4-methylphenol (DTMP), 2,6-dithiol-4-ethyphenol (DTEP), 2,6-dithiol-4-propylphenol (DTPP) and 2,6-dithiol-4-*tert*-butylphenol (DTBP)} and hydrophobic amines (Am). Of the hydrophobic amines, aniline (An), N-methylaniline (mAn) and N, N- dimethylaniline (dAn) were used.



II. Experimental

A. Reagents and Apparatus

A standard solution of mercury (1 mg / ml) was prepared by dissolving a portion of $Hg(NO_3)_2 \times 1/2H_2O$ in water with the addition of 1 ml of concentrated nitric acid and diluted with water in a volumetric flask to 1 l [9]. The titer was determined by the method of [10]. Lower concentrations of rastvors were obtained by diluting the initial solution with 0.01 M HNO_3.

Working 1×10^{-3} and 2×10^{-3}M solutions of DP and Am were prepared by dissolving the appropriate weights in chloroform.

The ionic strength of the solutions was kept constant (μ = 0.1) by introducing the calculated amount of KCl. To create the required acidity of the solutions, 1M solutions of HCl and H_2SO_4 were used.

The optical density of the organic phase was measured on a UFC-2, and a Shimadzu UV mini1240 spectrophotometer. The pH of the solutions was controlled with an I-130 ionomer with a glass electrode. IR spectra were recorded on a UR-20 spectrophotometer and a Bruker company.

- **Determination of mercury (II) in the water of the Caspian Sea**

A water sample was taken in the area of wastewater treatment of sewage treatment plants in the city of Khachmas, Siyazan and Lankaran of the Azerbaijan Republic. A sample of 5 l of filtered water filtered off from mechanical impurities is placed in a flat-bottomed flask, 200 ml of diluted (1:1) sulfuric acid and a few drops of $KMnO_4$ solution are poured in, added to the reverse chiller and boiled for 10 minutes. If at the same time the solution becomes colorless, add 2 - 3 drops of $KMnO_4$ solution. Pink color should persist for 15 minutes. A small excess of potassium permanganate interferes with the determination. After cooling, the reflux condenser is rinsed with a small amount of bidistilled water in the flask, disconnected, and a solution of hydroxylamine hydrochloride is added dropwise until the solution completely decolorizes. The solution is evaporated to dryness. The residue is dissolved in a mixture of concentrated acids HCl and H_2SO_4 (3:1). The excess acid is neutralized with a 10% ammonia solution to a pH of 3.0 - 3.5 and the mercury is determined according to the developed methods.

- **Determination of mercury (II) in soils**

A portion of the soil 20g decomposed in a conical flask equipped with a reflux condenser 5-7 ml conc. H_2SO_4 and an excess of fine-crystalline $KMnO_4$, which is added in small portions with stirring. The flask is heated until the SO_3 vapor is released. Cooled, poured through the refrigerator 25 ml of water. Excess $KMnO_4$ and manganese oxides are removed by adding 3% H_2O_2. Transfer the solution to a 50 ml volumetric flask, bring to the mark with water. An aliquot part (1 ml) was placed in a separatory funnel and the mercury was determined according to the developed methods. The developed methods for the determination of mercury were controlled by the method of additives.

- **Determination of mercury (II) in biological materials**

Mercury and its compounds are highly toxic. The need to identify small amounts of mercury in biological materials is mainly related to the determination of the degree of contamination of various foods with mercury. Determining small amounts of mercury in biological materials is a difficult analytical task.

Determination of mercury (II) in the blood. 1l blood of animals is dried and burned. The resulting ash is dissolved in water, added conc. HNO3. Add a small amount of KMnO4 and heat. After cooling, the excess acid is neutralized with a solution of NH4OH. Excess KMnO4 and manganese oxides are removed by adding 3% H2O2. Transfer the solution into a 50 ml volumetric flask, bring to the mark with water. An aliquot part (15 ml) was taken and mercury was determined according to the developed methods.

Determination of mercury in wheat. In a porcelain dish 50 q, wheat is susat at 105°C in an oven, then burned with asbestos in an open flame. The residue is calcined in a muffle furnace at 800°C. The mineralized residue of the sample is dissolved in 0.1 M solution, transferred to a volumetric flask with a capacity of 100 ml and diluted to the mark with distilled water. An aliquot part (1 ml) was placed in a separatory funnel and the mercury was determined according to the developed methods.

Determination of mercury in cheese. Dried 40 g of cheese, first at 70-80°C, and then at 120-130°C, in a porcelain dish. The dry residue is calcined in a muffle furnace at 600°C. The residue is dissolved in nitric acid (1: 1), transferred into a measuring funnel into a separating funnel and the mercury is determined by the developed methods.

Determination of mercury in beef liver. 50 q beef liver (in the case of meat 100g) is dried in a drying cabinet in a porcelain dish until cessation of vaporization stops. Then the dry residue is calcined in a muffle furnace at 570 ± 20°C. To speed up burning, the cup is removed from the muffle furnace and cooled to room temperature. It is treated with 3% H_2O_2 solution, dried in a drying cabinet and calcined again in a muffle furnace to gray ash. The resulting residue is dissolved in a solution of 2 M HNO_3, filtered into a separatory funnel and the excess acid is neutralized with a 0.1 M NaOH solution. The mercury content is determined by the extraction-photometric methods. Definition of mercury in fish (R. Rutilus caspius (vobla)). From the dorsal part of the body below the dorsal fin, 5 g of muscle tissue is separated and dried in a drying cabinet in a porcelain cup until the vapor release stops. Then dry the residue is calcined in a muffle furnace at 580 ± 20°C to gray ash. The resulting residue is dissolved in a solution of 2 M HNO_3 and filtered into a 100 ml volumetric flask. Excess acid is neutralized with 0.1 M NaOH solution. Aliquots were taken and the mercury content was determined with DP and Am. The developed methods for the determination of mercury were controlled by the method of additives and dithizone method.

III. Results and Discussion

DP with mercury (II) forms colored complexes that are insoluble in non-polar organic solvents. The charge of the complexes was established by anion exchange on the AB-17 anion exchange resin in the Cl-form. When determining the sign of charge of homogeneous ligand complexes by ion exchange chromatography, the anion exchange resin completely absorbs the colored part of the solution. With the introduction of hydrophobic amines into the system, extraction of the anionic complex into the organic phase is observed as a mixed ligand complex (MLC). Based on the data obtained, new selective and highly sensitive methods of photometric determination of trace amounts of mercury in various objects were developed.

Complexing agents (DTP, DTMP, DTEP, DTPP, and DTBP) are a tribasic weak acid (H_3R) and, depending on the pH of the medium, can exist in molecular and three anionic forms. Reagents were synthesized by a known method [11]. The synthesized compounds were characterized by physicochemical methods: IR and NMR spectroscopy [12-14] (Table I). In a strongly acidic medium (up to pH 3), the reagents exist only in molecular form H_3R (pK_1 = 6.30-6.98) and then slowly dissociate (pK_2 = 8.81-9.25, pK_3 = 11.26-11.35).

TABLE I. The results of studies of IR and NMR spectroscopy

DP	**İR (KBr)**	**^{1}H NMR (300,18 MHz, C_6D_6)**
DTP	3470 см$^{-1}$ v (OH), 3050 см$^{-1}$ v(CH), 2580 см$^{-1}$ v(SH), 1580 см$^{-1}$ v(C_6H_5).	δ 5.48 (s, 1H - OH), δ 3.47 (s, 2H - 2SH), δ 7.28 (s, 2H Ar-H), δ 6.95 (s, 1H - Ar-H).
DTMP	3460 см$^{-1}$ v (OH), 2570см$^{-1}$ v(SH), 2962 и 2872 см$^{-1}$ v(-CH_3), 1555см$^{-1}$ δ(C_6H_5), 1450 см$^{-1}$ δ_{as} (CH_3).	δ 5.24 (s, 1H- OH), δ 3.38(s, 2H - 2SH), δ 7.11 (s, 2H Ar-H), δ 2.38 (s, 3H –CH_3)
DTEP	3460 см$^{-1}$ v (OH), 2575см$^{-1}$ v(SH), 2965 и 2874 см$^{-1}$ v(-CH_3), 1555см$^{-1}$ δ(C_6H_5), 1460 см$^{-1}$ δ_{as} (-CH_2-CH_3).	δ 5.19 (s, 1H- OH), δ 3.32(s, 2H - 2SH), δ 7.11 (s, 2H Ar-H), δ 2.59 (s, 2H –CH_2-), δ 1.22 (s, 3H –CH_3)
DTPP	3465 см$^{-1}$ v (OH), 3050 см$^{-1}$ v(CH), 2572см$^{-1}$ v(SH), 2950 и 2874 см$^{-1}$ v(-CH_3), 1565см$^{-1}$ δ(C_6H_5), 1460 см$^{-1}$ δ_{as} (-CH_2-CH_3).	δ 5.39 (s, 1H- OH), δ 3.42(s, 2H - 2SH), δ 7.21 (s, 2H Ar-H), δ 2.59 (s, 2H –CH_2-), δ 1.22 (s, 3H –CH_3).
DTBP	3458 см$^{-1}$ v(OH), 2568см$^{-1}$ v(SH), 3040см$^{-1}$ v(CH), 1535см$^{-1}$ v(C_6H_5), 1395 δ (–C(CH_3)$_3$)	δ 5.2 (s, 1H- OH), δ 3.35(s, 2H- 2SH), δ 7.05 (s, 2H Ar-H), δ 1.42 (s, 9H- -C(CH_3)$_3$)

A. The influence of the pH of the aqueous phase on the degree of extraction

Mercury begins to interact with DP at pH ~ 1.5 (“Fig. 1”). Initially, with increasing acidity of the initial solution, extraction of Hg (II) increases, and with further increase it gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form of DP and most likely in solution they are in undissociated form. With an increase in the pH of the solution to 4.8 and above, the extraction of the complexes is practically not observed, which is apparently due to the hydrolysis of mercury (II) ions. The optimum pH value is 2.9-4.4.

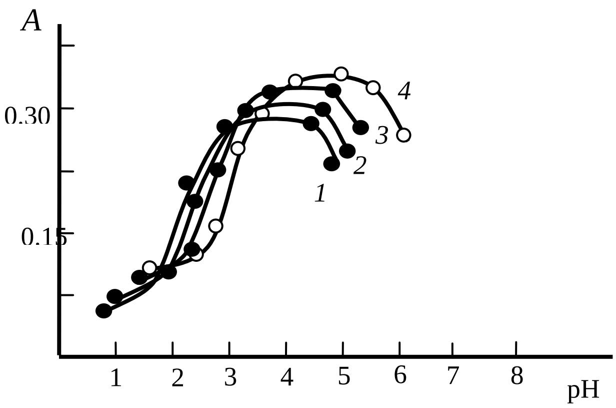


Fig. 1: Dependence of the degree of mercury (II) extraction in the form of a RLC on the pH of the aqueous phase.
1.Hg (II)-DTP-An, 2. Hg (II)-DTP-mAn,
3. Hg (II)-DTP-dAn 4.Hg (II)-DTBP-dAn.
$C_{Hg(II)}$ = 9.95×10^{-6}M, C_{DTP} = C_{AM} =0.96×10^{-3} M, КФК-2, λ = 440 nm, l = 0.5 cm.

B. Selection of organic solvents

For the extraction of Hg (II) complexes with DP and Am, chloroform, dichloroethane, chlorobenzene, carbon tetrachloride, toluene, *n*-butanol, ethyl acetate and mixtures of organic solvents were tested. Chloroform, dichloroethane, chlorobenzene and CCl_4 are the best extractants for dithiolphenolate-amine mercury complexes. With a single extraction with chloroform and dichloroethane, 98.3-99.2% mercury is isolated as MLC. The mercury concentrations in the organic phase were determined by dithizone [9], and in the aqueous phase - by difference. Further studies were conducted with chloroform and dichloroethane. The completeness of the transition of mercury to the organic phase was controlled by titration of $ZnSO_4$ [10], preliminary reextracting it with an excess of EDTA.

The introduction of a solvent, which decreases the dielectric constant of the solution, decreases the ionization constants of the acid of the reactants when the pH range of their reactive forms is changed, positively affects the stability of the formed complexes and increases the sensitivity of the complex formation reactions [15]

- **Absorption spectra**

Under optimal conditions, MLC mercury (II) chloroform extracts were obtained and their electronic absorption spectra were taken, which are shown in “Fig. 2”. Chloroform extracts of Hg (II) - DP-Am MLC have a maximum light absorption at 458-470 nm (Δλ = 188-190 nm). The colorings of the obtained complexes are close to each other, which also confirms the formation of an ionic associate.

- **The effect of reagent concentration and shaking time**

The optimal concentration is necessary for the extraction of Hg (II) (0.72-0.92)×10^{-3} M concentration of DP. For maximum formation and extraction of the compound Hg (II)-DP-Am, it is necessary (0.72-1.0)× 10^{-3} M concentration of Am. A further increase in the concentration of DP and Am does not lead to a noticeable change in the optical density and release of the complexes.

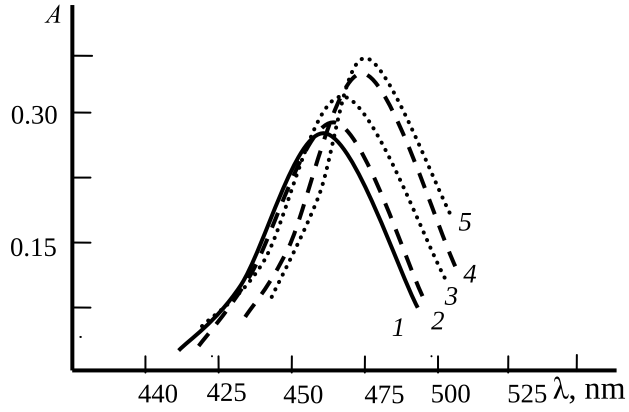


Fig. 2: Absorption of mixed-ligand complexes 1. Hg(II)-DTP-An, 2. Hg(II)-DTMP-An, 3. Hg(II)-DTEF-An, 4. Hg(II)-DTPF-An, 5. Hg(II)-DTBF-An $C_{Hg(II)}$ = 9.95×10^{-6}M, C_{DF} = 8.8×10^{-4} M, C_{Am} = 1.0×10^{-3} M; SF-26, l = 1 cm.

Mercury (II) MLC with DP and Am are stable in aqueous and organic solvents and do not decompose within 48 hours, and after extraction - more than a month. Extraction equilibrium occurs 5 minutes after one minute of shaking. Regardless of the base and nature of the amines, the optimum V_{aq}/ V_{org} is 5/5-80/5.

- **The composition of mixed-ligand complexes of mercury (II) with dithiolphenols and hydrophobic amines**

The molar ratios between the components of the complex were found by several methods: Starik–Barbanel relative yield method, straight line method and equilibrium shift method [16]. The results show that the interaction of Hg (II) with DP and Am forms complexes with the composition of Hg (II): DP: Am = 1: 2: 2

- **IR spectroscopic study of mercury (II) complexes with DP and amines**

In the IR spectra of the Hg (II)-DTEP-An complex in the region of 950–960 cm^{-1}, an intense absorption band appears, which is absent in the spectra of the reagent. This band is due to the valence vibration of the bond of the metallic ligand. The decrease in the intensity of the pronounced band at 2580 cm^{-1}, observed in the DTEP spectrum, and the appearance of two absorption bands in the spectra of the complex, one of which is shifted to lower frequencies, indicates that one of the - SH groups is involved in the formation of bonds. The disappearance of the absorption band in the region of 3200–3600 cm^{-1} with a maximum at 3460 cm^{-1} allows us to conclude that there are no free –OH groups in the synthesized complexes. The detection of absorption bands at 2270 cm^{-1} indicates the presence of protonated aniline [12–14].

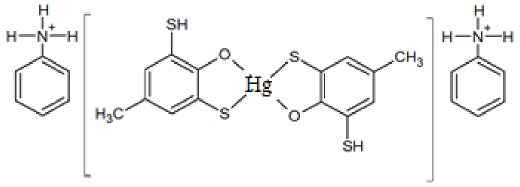
- **The chemistry of formation of mixed-ligand complexes of mercury (II) with DP and hydrophobic amines.**

To clarify the chemistry of the reaction for the formation of extractable complexes, the dependence of the degree of complexation of mercury (II) ions on the concentration of hydrogen ions was determined [17, 18]. The calculations were performed taking into account the ionization constant, hydrolysis of mercury (pK_{1h} = 3.5, pK_{2h} = 4.0) and the protonization constant of aniline. It was found that Hg^{2+} serves as a complexing ion, and the number of protons displaced from each DP molecule is 1.

The average value of γ calculated for the complexes turned out to be 1.05-1.18 [19]. Thus, Hg (II) MLC with DP and Am in the organic phase do not polymerize and are in monomeric form. Mercury hydroxide begins to precipitate at pH 2; complete precipitation occurs at pH 5-12 [20].

For the stripping of Hg (II) used aqueous solutions of ammonia. With an increase in the NH_3 concentration, the extraction of Hg (II) into the aqueous phase occurs rather quickly.

The mechanism of formation of the MLC can be represented as follows. When interacting with two DP molecules, mercury ions form doubly charged anionic complexes, which are extracted with two protonated Am molecules. Based on the ratio of components in the formed complexes, the number of protons being displaced and the ionic form of mercury, one can imagine the probable structure of the complex:



Hg (II) refers to mild acids and forms stable compounds with "soft bases", including those with ligands containing se ry as a donor atom.

- **Chemical and analytical characteristics of mercury (II) complexes with DP and hydrophobic amines**

Spectrophotometric methods have established molar absorption coefficients, two-phase stability constants, equilibrium constants, and complex extraction.

The molar absorption coefficients of dithiolphenolate-amine complexes were calculated by the methods of saturation and Komar, similarly to the calculation of ε to mercury complexes with DP and amines ε = $(2.82 - 3.80)\times10^{4}$.

The curve intersection method was used to calculate the two-phase stability constants. The calculation results are presented in Table III.

It can be assumed that the processes of complexation occur:

$$Hg^{2+} + 2H_2R^- \leftrightarrow [Hg(HR)_2]^{2-} + 2H^+ \quad (1)$$

$$[Hg(HR)_2]^{2-} + 2AmH^+ \leftrightarrow [Hg(HR)_2](AmH)_2 \quad (2)$$

According to the equation for the formation of an MLC, the equilibrium constant can be expressed by the equation

$$K_p = \frac{\{[Hg(HR)_2](AmH)_2\}_o}{\{[Hg(HR)^{2-}]\}_n\{[AmH^+]^2\}_n} \quad (3)$$

ransformation and logarithmization (3) we get:

$$lgK_p = lgD - 2lg[AmH^+] \quad (4)$$

Considering the state of Hg (II) and ligands in aqueous solutions, the extraction equation in this system can be represented as follows:

$$Hg^{2+} + 2HR^{2-} + 2AmH^+ \rightarrow [Hg(HR)_2](AmH)_2 \quad (5)$$

The extraction constants are calculated using the equation:

$$lgK_{ex} = lgD - 2lg[HR^{2-}] - 2lg[AmH^+] \quad (6)$$

The calculated values of lgK_{eq} and lgK_{ex} are presented in Table 3.

In table 3 shows the main spectrophotometric characteristics of MLC.

Acid-base properties of hydrophobic amines to a lesser extent affect the formation and extraction of complexes. In the dAn-mAn-An series, the reaction pH_{50} is reduced. The color of the Hg-DTBP-dAn complex is more intense and does not fade for a long time. Studying and comparing the acid-base properties of FAG of complexing agents and pH_{50} of complex formation allowed us to determine the effect of the acidic properties of the –SH group on the complexation pH. Graphically, the correlations ΔpK_1-ΔpH_{50} are presented in “Fig. 4”. As can be seen from the figures, a decrease in the acidic properties (ΔpK_1) of the reagent leads to a shift in the pH (ΔpH_{50}) of the complexation towards the weaker acid region. The resulting correlation dependence:

$$\Delta pH_{50} = 0{,}702 \times \Delta pK_1 - 0{,}104 \quad \text{or}$$

$$\Delta pK_1 = \frac{\Delta pH_{50} + 0{,}104}{0{,}702}$$

TABLE II. Some chemical and analytical characteristics of mercury (II) complexes with DP and Am

H_3R	**pK_{SH}**	**ΔpK_{SH}**	**pH_{50}**	**ΔpH_{50}**	***lgβ***	**$\varepsilon \times 10^{-4}$**	**σ_n**
H	6.30	0.0	2.32	0.00	6.91	2.82	0
$-C_3H_7$	6.72	-0.42	2.71	-0.39	9.08	3.24	-0.126
$-C_2H_5$	6.84	-0.54	2.80	-0.48	9.70	3.14	-0.151
$-CH_3$	6.92	-0.62	2.86	-0.54	10.10	3.08	-0.170
$-C(CH_3)_3$	6.98	-0.68	2.91	-0.59	10.41	3.68	-0.197

The correlation dependences between the stability constants (lgβ) and the dissociation constants (pK_1) of the reagents are graphically presented in “Fig. 3”. The following correlation dependencies are obtained:

$$pK_{SH} = 4{,}96 + 0{,}194lg\beta \quad \text{or}$$

$$lg\beta = \frac{pK_{SH} - 4.96}{0.194}$$

The correlation dependences of pK_1 - lgβк show that with decreasing acidic properties of reagents, the strength of the complex compounds formed by them with the studied metal ions increases linearly. It is established that with an increase in the molar mass of the substituent, the molar absorption coefficient increases (“Fig. 3”). Correlation dependence is: $\varepsilon = 2.82 + 0.015M(X)$ $R^2 = 0.9835$

We found that the pH_{50} values of complex formation correlate with Hammett constants. Correlation dependence is:

$$pH_{50} = 2.52 - 3.15\sigma_n \quad (r = 0.98)$$

Thus, the properties of the resulting complexes depend on the nature of the metal ions and the acid-base properties of the 2-mercapto group of FAG reagents. Moreover, with the introduction of electron-donating substituents into the structures, that is, with a decrease in the acidic properties of the FAG reagent, the strength of the complexes increases, while pHopt and pH_{50} shift to a weaker acidic region.

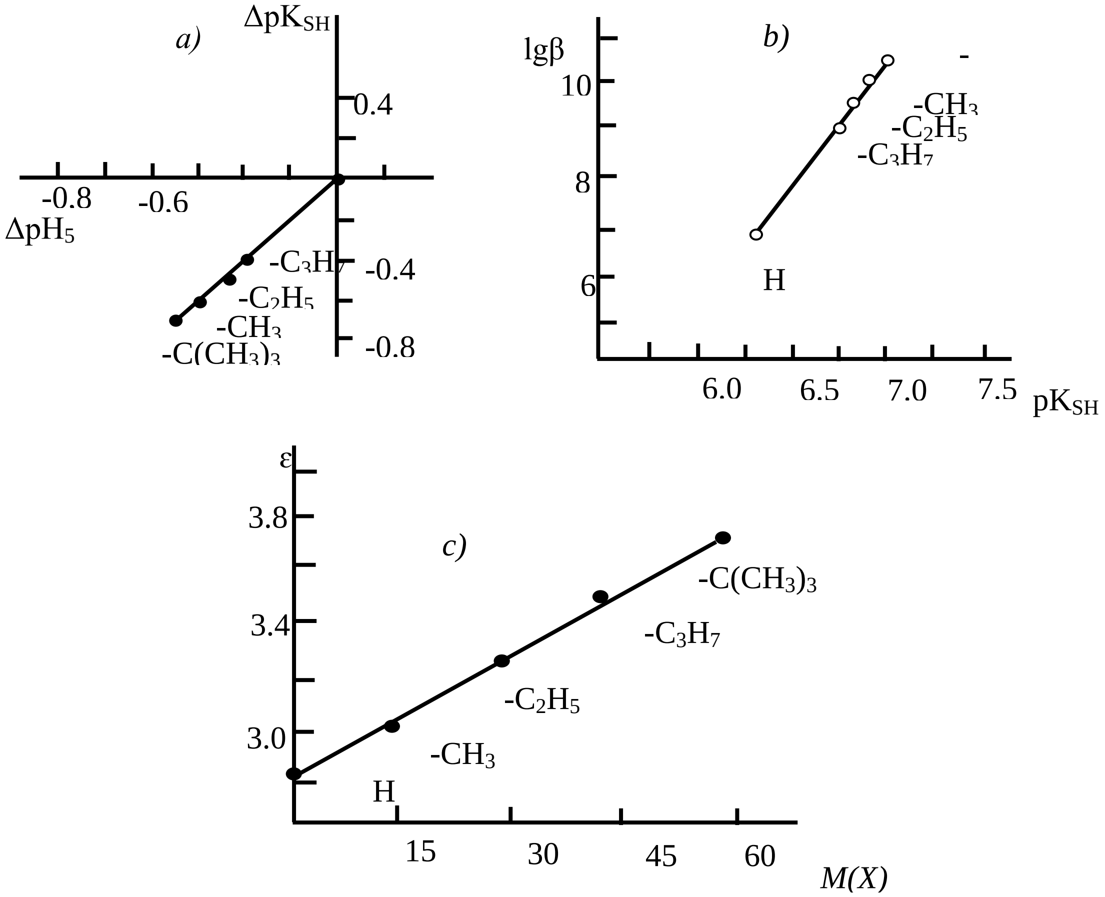


Fig. 3: *a)* Correlation between (ΔpKSH) and ΔpH50 for the Hg (**II**) -DF-An complex, *b)* Correlation between lgβ and (pKSH) for the Hg (II) -DF-An complex, *c)* Correlation between the molar mass of the substituent (M (X) molar absorption coefficient for the complex Hg (II) -DF-An

TABLE III. Characteristics of MLC mercury (II) with DP and Am

Compound	**The pH range of formation and extraction**	**The pH range of maximum extraction**	**λ, nm**	**Δλ, nm**	**$\varepsilon\times10^{-4}$**	**lgβ**	**lgK_{eq}**	**lgK_{ex}**	**R,%**
$[Hg(DTP)_2](An)_2$	2.3-5.6	2.9-3.8	458	188	2.82	6.95	4.91	9.45	98.3
$[Hg(DTP)_2](mAn)_2$	2.3-5.8	2.9-3.9	462	192	3.05	6.98	5.09	9.53	98.4
$[Hg(DTP)_2](dAn)_2$	2.5-5.9	3.0-4.0	465	195	3.20	7.05	5.28	9.61	98.4
$[Hg(DTMP)_2](An)_2$	2.8-6.9	3.1-4.1	460	186	3.05	10.10	6.06	10.05	98.6
$[Hg(DTMP)_2](mAnH)_2$	2.9-7.1	3.2-4.2	464	190	3.20	10.21	6.19	10.14	98.7
$[Hg(DTEP)_2](AnH)_2$	2.7-5.8	3.1-4.0	462	186	3.14	9.70	5.83	9.96	98.5
$[Hg(DTEP)_2](mAnH)_2$	2.7-6.0	3.3-4.1	465	189	3.24	9.75	5.95	10.05	98.6
$[Hg(DTEP)_2](dAn\ H)_2$	2.8-6.5	3.4-4.2	470	194	3.50	9.80	6.12	10.24	98.7
$[Hg(DTBP)_2](AnH)_2$	2.5-5.5	2.9-3.9	463	185	3.24	9.08	5.24	9.82	98.4
$[Hg(DTBP)_2](AnH)_2$	2.6-6.6	3.3-4.3	465	185	3.68	10.41	6.16	10.28	98.7
$[Hg(DTBP)_2](mAnH)_2$	2.7-6.8	3.4-4.3	466	186	3.75	10.55	6.23	10.33	98.9
$[Hg(DTBP)_2](dAnH)_2$	2.9-6.9	3.4-4.4	470	190	3.80	10.64	6.32	10.38	99.2

- **Spectrophotometric determination of mercury (II)**

Mercury is a toxic poison of cumulative action and is widespread in the environment. Mercury compounds are absorbed, deposited in the muscles, kidneys, nervous system and brain, have a direct effect on embryogenesis.

The main sources of additional mercury inputs are the burning of fossil fuels and emissions from soils during deforestation and agricultural land use. A specific feature of its geochemistry is the predominant migration in the gaseous state both in the earth's crust and in the atmosphere. It is believed that mercury enters the water basins and, accordingly, mercury in their bottom sediments mainly from the atmosphere. In this regard, it is necessary to control the content of mercury in food, raw materials, water, feed [21].

Graduated graphs of Hg (II) determination with DP and amines are presented in "Fig. 4".

The linearity range of the calibration dependence for chloroform extracts of the complexes is maintained in the range of concentrations of mercury 0.04-3.6 µg/ml (Table IV). The equation of the calibration dependence for the spectrophotometric signal indication is given in Table. 4. Based on the equations of the calibration curves, the limit of photometric detection and the limit of quantitative determination of mercury in the form of ionic associates were calculated [22].

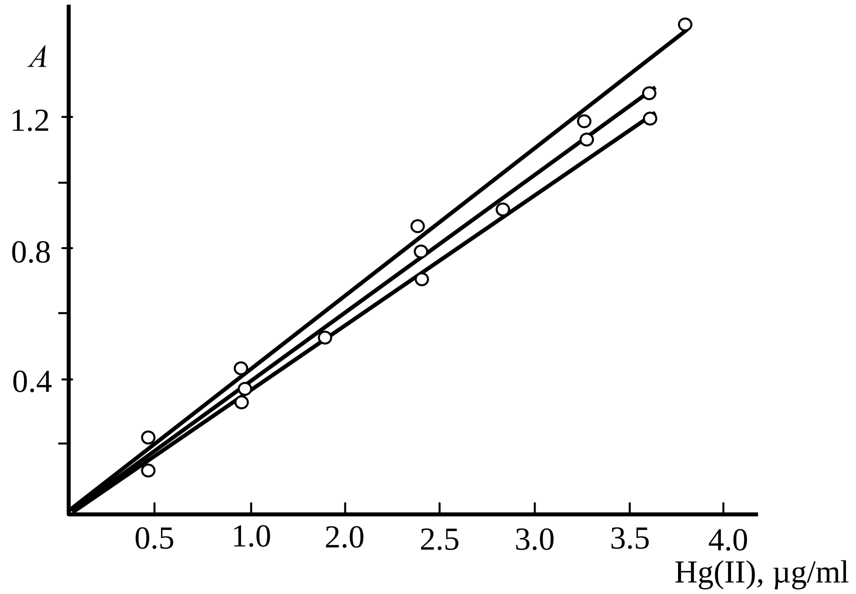


Fig. 4: The dependence of the optical density of the extracts of MLC on the concentration of mercury
1 - Hg (II) -DTMP -An, 2 - Hg (II) -DTMP-mA, 3-Hg (II) -DTMP-dAn.
C $_{Hg(II)}$ = 3.57 · 10-5 M, C_{DTMF} = CAm = 8.0 10^{-4} M, SF-26, *l* = 1.0 cm

TABLE IV. Analytical characteristics for the Hg-DF-Am triple complexes

Compound	**The formation of calibration curves (mg ml^{-1})**	**A=*a*C+*b***	**Limit of detection (LOD): ng ·mL**	**Limit of quantification (LOQ): ng ·m^{L-1}**	**Sandell's sensitivity (ng·cm^{-2})**
[Hg(DTP)$_2$](An)$_2$	0.05-2.6	0.019+0.131x	13	43	7.10
[Hg (DTP)$_2$](mAn)$_2$	0.05-2.6	0.016+0.142x	12	39	6.56
[Hg (DTP)$_2$](dAn)$_2$	0.05-2.6	0.025+0.138x	11	36	6.28
[Hg(DTMP)$_2$](An)$_2$	0,04-2.8	0.034+0.135x	12	39	6.56
[Hg (DTMP)$_2$](mAnH)$_2$	0,04-2.8	0.039+0.140x	11	36	7.05
[Hg (DTEP)$_2$](AnH)$_2$	0.05-2.9	0.021+0.130x	11	36	6.40
[Hg (DTEP)$_2$](mAnH)$_2$	0.05-2.8	0.018+0.143x	10	33	6.20
[Hg (DTEP)$_2$](dAn H)$_2$	0.04-2.9	0.031+0.139x	9	29	5.74
[Hg (DTBP)$_2$](AnH)$_2$	0.04-3.0	0.039+0.142x	11	36	6.20
[Hg(DTBP)$_2$](AnH)$_2$	0,05-3.2	0.029+0.168x	10	33	5.46
[Hg (DTBP)$_2$](mAnH)$_2$	0,04-3.4	0.043+0.165x	9	29	5.36
[Hg (DTBP)$_2$](dAnH)$_2$	0,04-3.6	0.042+0.168x	9	29	5.29

- **Influence of foreign ions**

To assess the applicability of the extracts of MLC for the separation and determination of mercury, the interfering influence of extraneous ions was studied. The experiments were carried out according to the recipe, according to which the calibration graphs were constructed, with the only difference that, in addition to Hg (II), a certain amount of the corresponding ions was injected into the solution.

The selectivity of the spectrophotometric determination of mercury in the form of the complexes studied is presented in Table V. It has been established that large quantities of alkaline, alkaline-earth elements, REE, F^-, Cl^- and Br^- do not interfere with the determination of mercury. Cytrates, tartrates, J^-, CN^-, SCN^-, $S_2O_3^{2-}$, NO_2^-, thiourea, are used for the definition. The selectivity of Hg (II) determinations is significantly increased in the presence of reagents masking the indicated elements.

In table VI shows the data allowing to compare the analytical characteristics of the methods for determining mercury (II) with some already known reagents.

TABLE V: Influence of interfering ions on the determination of Hg(II) with (30.0 μg Hg added) (*n*=3, P= 0.95)

Ion	Molar Excess of the Ion	Masking reagent	Found, μg (RSD (%))	
			DTP+An	DTMP+An
Co(II)	50		30.0(2)	30.0(2)
Ni(II)	50	Complexon III	29.8(2)	29.8(2)
Fe(II)	200	Sodium fluoride	29.8(3)	29.8(3)
Cd(II)	80		29.6(4)	29.6(4)
Al(III)	180		30.0(2)	30.0(2)
Fe(III)	80	Oxalic acid	30.2(4)	30.2(4)
Zn(II)		Complexon III		
Zr(IV)	50		29.8(3)	29.8(3)
W(VI)	25	Oxalic acid	29.6(5)	29.6(5)
Cu(II)	50		30.2(5)	30.2(5)
Ti(IV)	30	Tyrone	29.6(3)	29.6(3)
V(IV)	20	Tyrone	29.6(3)	29.6(3)
Mo(VI)	10	Sodium fluoride	30.4(4)	30.4(4)
Cr(III)	20		29.8(4)	29.8(4)
Nb(V)	50	Sodium fluoride	30.1(5)	30.1(5)
Ta(V)	50	Sodium fluoride	30.1(5)	30.1(5)
UO_2^{2+}	50		29.2(4)	29.2(4)
Pd(II)	13		29.8(2)	29.6(3)
Pt(II)	23		29.8(3)	29.6(3)
Mn(II)	1500		30.4(4)	30.4(4)
Thiourea	90		29.8(4)	29.8(4)
Citrate	345		30.1(5)	30.1(5)
Tartaric asid	196		30.4(4)	29.6(3)
Oxalic acid	25		29.8(4)	29.6(3)

TABLE VI. Comparative characteristics of mercury determination methods

Reagent	pH (solvent)	λ, nm	ε×10^{-4}	Beer's law range (μg·ml^{-1})	Ref.
Known methods					
Dithizone	CCl_4 (1-2)	485	3.84	0- 2	[6,9]
Sodium Diethyldithiocarbamate	CCl_4 (9.3-10.3)	278	3.3		[9]
Cresolphthalein	9.6-10.3	583	0.526	0.1-4.0	[6,9]
Methylthymol blue	Water (6.0)	630	0.101		[5,9]
Variamine blue B	2.9	600	4.03		[5,6,9]
Proposed method					
DTP + dAn	$CHCl_3$ (3.0-4.0)	465	3.20	0.05-2.6	
DTMP + dAn	$CHCl_3$ (3.0-4.0)	464	3.20	0.04-2.8	
DTEP + dAn	$CHCl_3$ (3.0-4.0)	470	3.50	0.04-2.9	
DTPP + dAn	$CHCl_3$ (3.0-4.0)	463	3.24	0.04-3.0	
DTBP + dAn	$CHCl_3$ (3.0-4.0)	470	3.80	0.04-3.6	

IV. Analytical applications

Determination of mercury (II) in natural and industrial materials

Many photometric methods [23, 24, 5] of mercury determination have been proposed, but the lack of these techniques is low sensitivity and selectivity, therefore, the development of simple highly sensitive methods for analytical control of mercury content in various objects is relevant, since mercury is one of the main and most toxic environmental pollutants

The proposed extraction-spectrophotometric methods for the determination of mercury with DP and Am were tested when determining it in various objects. The correctness of the determination of Hg (II) by the addition method and the dithizone method was evaluated.

A. Determination of mercury (II) in the water of the Caspian Sea

A water sample was taken in the area of wastewater treatment of sewage treatment plants in the city of Khachmas, Siyazan and Lankaran of the Azerbaijan Republic. Determine mercury by the developed methods. The results of the determination are presented in table VII.

TABLE VII. The results of the determination of Hg (II) in the waters of the Caspian Sea, μg / ml (*n* = 6, P = 0.95)

Water	Method	Is entered	Found	Content in sample	S_r
Khachmas	DTP+An	10	14,65	0.093±0.009	0.05
	DTMP+мAn	10	14,45	0.088±0.011	0.04
Siyazan	DTMP +An	20	25,60	0.112±0.007	0.06
	DTEP+мAn	20	25,35	0.104±0.011	0.03
Lankaran	DTEP+dAn	20	24,25	0.085±0.012	0.04
	DTBP+dAn	20	24,80	0.094±0.013	0.05

B. Determination of mercury (II) in soils

Mercury was determined by the developed methods. The developed methods for the determination of mercury were controlled by the method of additives. The soil mercury content is 13 μg/kg.

C. Determination of mercury (II) in biological materials

Determining small amounts of mercury in biological materials is a difficult analytical task.

Determination of mercury (II) in the blood. Mercury was determined by the developed methods. The results of the determination are presented in table VIII.

Determination of mercury in wheat. Mercury was determined by the developed methods. The results of the determination are presented in table VIII.

Determination of mercury in cheese. Determine mercury by the developed methods. The results of the determination are presented in table VIII.

Determination of mercury in beef liver. The mercury content of beef liver (in the case of meat 100g) is determined by extraction-photometric methods. The results of the determination are presented in table VIII.

The developed methods for the determination of mercury were controlled by the dithizone method and the method of additives.

Determination of mercury in fish (R. Rutilus caspius (vobla)). Determined the content of mercury with DP and Am. The developed methods for the determination of mercury were controlled by the method of additives and dithizone method. The correctness and reproducibility of the definition of mercury in fish are shown in Table VIII.

TABLE VIII. The results of the determination of mercury in biological materials (*n* = 6, P = 0.95)

Mercury is defined as the object being analyzed	Analyzed object	Is entered	Found	Contents in the sample	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
DTP + dAn	blood	20	22.05	6.85	0.05	6.85±0.27
DTMP + mAn	beef liver	20	20.29	5.70	0.04	5.70±0.25
Dithizone	beef liver	20	20.35	5.78	0.04	5.78±0.34
DTMP + mAn	wheat	20	20.32	6.4	0.05	6.40±0.43
DTBP + dAn	cheese	10	13.20	8.0	0.03	8.0±0.42
	a fish	20	24.45	89	0.04	89±1.43
Dithizone	a fish	20	24.50	90	0.05	90±1.25
DTEP + dAn	Beef meat	10	10.25	2.5	0.04	2.5±0.23
DTBP + dAn	blood	20	22.32	7.72	0.04	7.72±0.45
DTPP +An	cheese	10	10.30	7.5	0.05	7.5±0.37
DTEP + dAn	Beef meat	20	20.23	2.3	0.05	2.3±0.19

5. CONCLUSION

1. The purpose of this work is to systematically study the conditions for the interaction of Hg (II) with dithiolphenols (DP) {2,6-dithiolphenol (DTP), 2,6-dithiol-4-methylphenol (DTMP), 2,6-dithiol-4-ethylphenol (DTEP), 2,6-dithiol-4-propylphenol (DTPP) and 2,6-dithiol-4-tert-butylphenol (DTBP)} and hydrophobic amines (Am). Of the hydrophobic amines, aniline (An), N-methylaniline (mAn) and N, N-dimethylaniline (dAn) were used.

2. Mercury begins to interact with DP at pH ~ 1.5. The optimum pH value is 2.9-4.4. For the extraction of Hg (II) complexes with DP and Am, chloroform, dichloroethane, chlorobenzene, carbon tetrachloride, toluene, *n*-butanol, ethylacetate and mixtures of organic solvents were tested. Chloroform, dichloroethane, chlorobenzene and CCl_4 are the best extractants for dithiolphenolate-amine mercury complexes. With a single extraction with chloroform and dichloroethane, 98.3-99.2% mercury is isolated as MLC. Chloroform extracts of Hg (II) - DP - Am MLC have a maximum light absorption at 458-470 nm ($\Delta\lambda$ = 188-190 nm).

3. The optimal concentration is necessary for the extraction of Hg (II) (0.72-0.92)×10^{-3} M concentration of DP. For maximum formation and extraction of the compound Hg (II)-DP-Am, it is necessary (0.72-1.0)× 10^{-3} M concentration of Am. The linearity range of the calibration dependence for chloroform extracts of the complexes is maintained in the range of concentrations of mercury 0.04-3.6 µg/ml. Mercury (II) MLC with DP and Am are stable in aqueous and organic solvents and do not decompose within 48 hours, and after extraction - more than a month. Extraction equilibrium occurs 5 minutes after one minute of shaking. Regardless of the base and nature of the amines, the optimum V_{aq}/ V_{org} is 5/5-80/5.

4. The molar ratios between the components of the complex were found by several methods: Starik–Barbanel relative yield method, straight line method and equilibrium shift method. The results show that the interaction of Hg (II) with DP and Am forms complexes with the composition of Hg(II):DP:Am=1:2:2. The molar absorption coefficients of dithiolphenolate-amine complexes were calculated by the methods of saturation and Komar, similarly to the calculation of ε to mercury complexes with DP and amines ε = (2.82 - 3.80)×10^4.

5. Acid-base properties of hydrophobic amines to a lesser extent affect the formation and extraction of complexes. In the dAn-mAn-An series, the pH of the reaction decreases. Studying and comparing the acid-base properties of FAG complexing agents and pH50 complexation made it possible to determine the effect of the acidic properties of the –SH group on the pH of complexation. A decrease in the acidic properties (ΔpK1) of the reagent leads to a shift in the pH (ΔpH_{50}) of the complexation towards the weaker acid region.

6. It has been established that large amounts of alkaline, alkaline earth elements, REE, F^-, Cl^- and Br- do not interfere with the determination of mercury. Citrate, tartrate, J^-, CN^-, SCN^-, $S_2O_3^{2-}$, NO_2^-, thiourea, are used for determination. The selectivity of the determination of Hg (II) is significantly increased in the presence of reagents that mask these elements.

7. The proposed extraction-spectrophotometric methods for the determination of mercury with DP and Am were tested when determining it in various objects. The correctness of the determination of Hg (II) by the addition method and the dithizone method was evaluated.

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