

## SELECTIVE EXTRACTION OF MERCURY AND ITS PHOTOMETRIC DETERMINATION WITH DITHIONE IN THE ORGANIC PHASE

<sup>1</sup>Abdullaeva D.K., <sup>2</sup>Turabjanov S.M., <sup>3</sup>Giyasov A.Sh., <sup>4</sup>Egamberdiev E.A., <sup>5</sup>Rakhimjonova D.A., <sup>6</sup>Ziyadayeva A.E.

<sup>1,2,3,4,5,6</sup>Tashkent State Technical University named after Islam Karimov

<https://doi.org/10.5281/zenodo.11527632>

**Abstract.** A methodology has been proposed for highly selective and highly sensitive extraction photometric determination of mercury with dithione.

Mercury (II) from a highly acidic environment in the presence of iodide ions and dimethylformamide (DMF) has been found to be quickly and selectively extracted by chloroform and benzene. When chloroform or benzene solution of dithione and buffer solution with pH 2.5-14 is added to the extract and the aqueous-organic phases are shaken during 5-10 seconds, a painted complex compound is formed. The apparent molar repayment rate at a maximum light absorption of 610 nm is  $7.1 \cdot 10^4$ . The determination of mercury (II) is not prevented by 10,000 to 60,000 foreign ions within an error range of 2-5%.

The developed method has been applied to the analysis of industrial wastewater. The analysis time is 2-3 minutes, relative to the standard deviation of 0.02. The correctness and reproducibility of the method has been verified by the methods of additives in waste water. The method can be used to determine micro-containing mercury in air, biological materials, ores, rocks and other chemically complex materials without prior separation of accompanying elements.

The paper investigates conditions of selective extraction of a colorless halogenic complex of mercury (II) by inert organic solvents and its complexation with dithione directly in an organic phase, with the purpose of development of a highly selective, simple and accelerated method of extraction-photometric definition of mercury without preliminary separation of accompanying elements.

As a result of the research, a new highly selective, accelerated and simple extraction-photometric method for determining mercury directly in the organic phase has been developed.

Therefore, the developed method of extraction-photometric determination of mercury is recommended for the analysis of mercury in industrial wastewater, ores, rocks, concentrates, industrial waste and other chemically complex materials.

**Keywords:** extraction, extract, inert organic solvents, extraction-photometric, dimethylformamide, water-organic phase, hydro-solvate mechanism, complex formation.

**INTRODUCTION.** Mercury and its compounds can be used in chemical technology, metallurgy, medicine, instrumentation, the electrical industry, agriculture, dyestuff production, mining and other fields of modern technology.

There has been increased attention recently to the problem of micromercurarism - the manifestation of exposure to low mercury concentrations. According to GOST 1324-47, the maximum permissible concentration of mercury in the air of industrial premises is 0.01 mg/m<sup>3</sup>. However, recent research has identified 0.002-0.003 mg/m<sup>3</sup> as the new maximum permissible concentration of mercury in the air of the working area. Due to volatility and toxicity of mercury, certain safety measures must be observed when working with it.

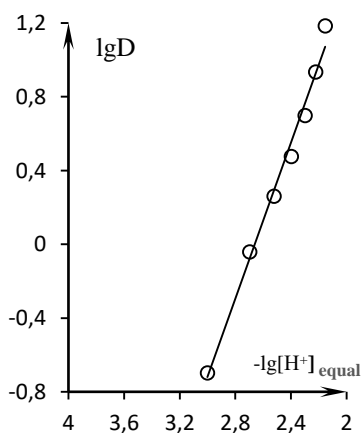
It is known that in many natural and industrial samples, mercury is found in ultra-small amounts. Therefore, most of the known methods of determination involve rather complex methods of separation from related elements. Various methods are used for this purpose, including sorption, cohabitation, and liquid-liquid and solid-phase extraction. These methods can be used in combination with subsequent determination of mercury by spectroscopic methods. The most common method for determining microquantities of mercury is atomic absorption spectrometry.

Other methods of analysis, including spectrophotometry, have not lost their significance. It is in this method that it is possible to use various organic reagents capable of combining separation, concentration and determination of mercury in one stage. The most commonly used methods for extractational photometric determination of the microquantities of mercury are dithione, rhodamine 6g, phthalensone, cresolphthaloin complex, 4-(2-pyridylase)-resorcin and others. [1,2]. However, at relatively high sensitivities, color reactions involving these reagents are low-elective. The determination of mercury is generally hindered by copper, lead, bismuth, cadmium, iron, zinc, gold, silver, aluminium and other elements that must be separated by extraction or sorption on anion exchangers [3-5]. More rapid methods are needed to control mercury content in natural and industrial facilities [6,7]. Therefore, finding new selective methods for determining microquantities of mercury is an important and urgent task.

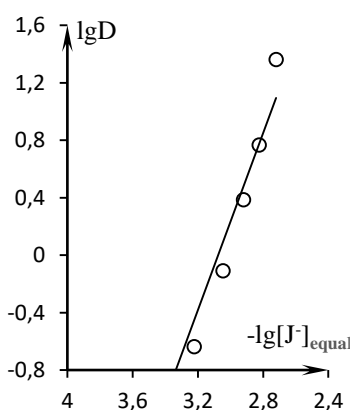
The paper investigates conditions of selective extraction of a colorless halogenic complex of mercury (II) by inert organic solvents and its complexation with dithione directly in an organic phase, with the purpose of development of a highly selective, simple and accelerated method of extraction-photometric definition of mercury without preliminary separation of accompanying elements.

**EXPERIMENTAL PART.** The study found that mercury (II) from a solution containing  $H_2SO_4$ , iodide ions and dimethylformamide (DMF) is well extracted by chloroform (benzene). Chloroform (II) has been found to be the optimal conditions for extracting mercury: 0.01-2.0 M  $H_2SO_4$ , 0.002 - 0.25 M  $NaI$ . 10-30 vol. % (by volume) DMF and shaking phases 5-10.

Having equal volumes of aqueous and organic phases, the extraction of mercury (II) at single extraction is 99.9 % and does not change to a 20:1 ratio of phase volumes. The composition of the extractable mercury iodide complex (II) is determined by the equilibrium shift method [8], where, in Fig. I, (Table I. 1) show that in the bilogarithmic coordinates  $lgD_{Hg} - lgC_{H^+}$ ,  $lgD_{Hg} - lgJ^-$  and  $lgD_{Hg} - lgC_{DMF}$  (where D - partition coefficient, C - concentration) there is a straight-line relationship with tangent angles of straight lines equal to 2,4,3. (Figures 1,2,3.), (Table 1).



**Fig.1.**



**Fig.2.**

**Fig.1,2. Determination of molar ratios of Hg:H<sup>+</sup> (Fig.1.), Hg: J<sup>-</sup> (Fig.2), in the extract by the equilibrium shift method  $C_{Hg}=0,997 \cdot 10^{-5}M$ ,  $C_{Hg}=0,995 \cdot 10^{-5}M$ ;  $A_l=048$   $V_w=V_o=10$  ml;  $l=1sm$ .**

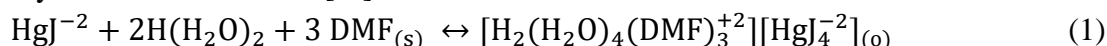
**Table 1.**

**Determination of molar ratios of Hg:H<sup>+</sup>, Hg: J<sub>4</sub><sup>-</sup>, Hg: DMF by the method of equilibrium shifts upon extraction with chloroform. (C<sub>Hg</sub> = 0.997·10<sup>-5</sup> M A<sub>I</sub> = 0.48)**

C <sub>H<sub>2</sub>SO<sub>4</sub></sub> , M·10 <sup>-5</sup>	A	D	lgD	[H <sup>+</sup> ] <sub>equal</sub>	-lg[Dz]
0.001	0.08	0.200	-0.698	≈0.001	3.000
0.002	0.20	0.900	-0.041	≈0.002	2.698
0.003	0.31	1.823	0.261	≈0.003	2.523
0.004	0.35	3.000	0.477	≈0.004	2.397
0.005	0.40	5.000	0.698	≈0.005	2.300
0.006	0.43	8.600	0.934	≈0.006	2.222
0.007	0.46	15.330	1.185	≈0.007	2.155
0.008	0.48	5.714			
C <sub>NaI</sub> , M·10 <sup>4</sup>	A	D	lgD	[J <sup>-</sup> ] <sub>equal</sub> · M·10 <sup>4</sup>	-lg[J <sup>-</sup> ] <sub>equal</sub> .
3	0.03	0.06	-1.176	≈3	3.530
6	0.09	0.23	-0.636	≈6	3.222
9	0.21	0.77	-0.109	≈9	3.046
12	0.34	2.43	0.385	≈12	2.921
15	0.41	5.86	0.767	≈15	2.824
18	0.46	23.20	1.361	≈18	2.720
20	0.48			≈20	
C <sub>DMF</sub> , M	A	D	lgD	[DMF] <sub>equal</sub>	-lg[DMF] <sub>equal</sub> .
0,1299	0.03	0.066	-1.176	≈0,1299	0.886
0,2598	0.10	0.263	-0.579	≈0,2598	0.585
0,3897	0.21	0.777	-0.109	≈0,3897	0.409
0,5196	0.30	1.660	0.222	≈0,5196	0.284
0,6495	0.36	3.000	0.477	≈0,6495	0.187
0,7794	0.42	7.000	0.845	≈0,7794	0.041
0,9093	0.46	23.000	1.361	≈0,9093	-0.016
1,0392	0.48			≈1,0392	

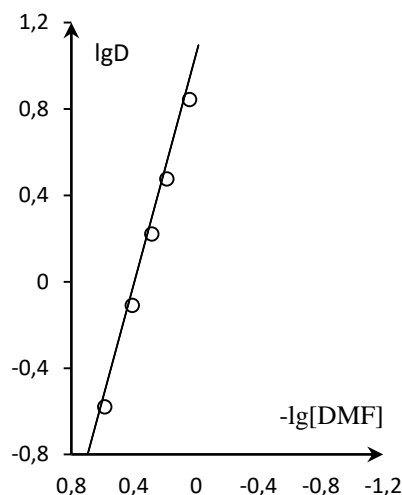
Consequently, mercury (II) is extracted by chloroform in the form of H<sub>2</sub> [HgJ<sub>4</sub>]; the solvated number of H<sub>2</sub>[HgJ<sub>4</sub>] in the extract is 3. The number of water molecules associated with H<sub>2</sub> [HgJ<sub>4</sub>] in the chloroform, determined by the spectrophotometric method using cobalt salts (II) [9] is 4.

Therefore, the mercury iodide complex (II) in the presence of DMF is extracted by chloroform through the hydro solvate mechanism [10].

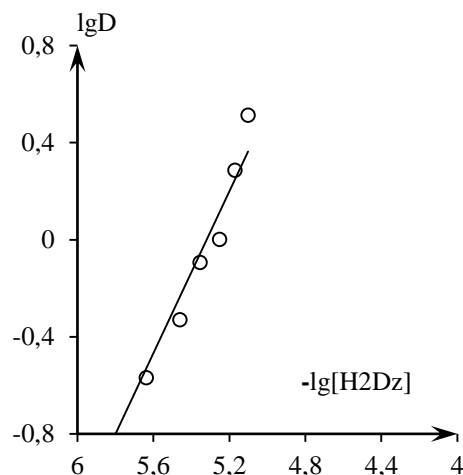


Once mercury (II) is extracted under optimal conditions, the aqueous phase is separated, dithione chloroform solution, acetate-ammonium buffer solution is added to the extract and the 10-15 s phases of mercury (II) are shaken. Judging by the dependence of optical density on pH, complete complex formation of mercury with dithione occurs in the pH range of 2.5-14.

The equilibrium shift method [8] has shown that mercury (II) with dithione in the organic phase interacts in a 1:2 molar ratio in the chloroform for more than 24 hours. (Fig. 4), (Table 2).



**Fig.3. Determination of molar ratios of Hg:DMF in the extract by the equilibrium shift method**  $C_{Hg}=0,997 \cdot 10^{-5} M$ ,  $C_{Hg}=0,995 \cdot 10^{-5} M$ ;  $A_I=048$   $V_w=V_o=10$  ml;  $l=1sm$ .



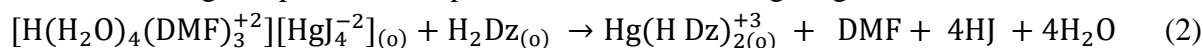
**Fig.4. Determination of molar ratios of Hg:H<sub>2</sub>Dz in the extract by the equilibrium shift method**  $C_{Hg}=7,48 \cdot 10^{-6} M$ ;  $A_I=047$ ;  $V_w=V_o=10$  ml;  $l=1$  cm.

**Table 2.**

**Determination of the composition of the mercury complex with dithione**  
**( $C_{Hg} = 7,48 \cdot 10^{-6} M$   $A_I = 0,47$ ) by the balance shift method**

$C_{H_2Dz}, M \cdot 10^{-5}$	A	D	lgD	$[H_2Dz]_{equal} \cdot M \cdot 10^6$	$-lg[Dz] \cdot$
0.195	0.05	0.119	-0.924	1.155	5.93
0.390	0.10	0.270	-0.568	2.303	5.637
0.585	0.15	0.468	-0.329	3.463	5.461
0.780	0.21	0.807	-0.093	4.458	5.354
1.170	0.31	1.238	0.002	5.613	5.251
1.365	0.36	1.937	0.287	6.764	5.170
1.560	0.40	3.272	0.514	7.921	5.102
	0.43	5.714	0.756		

Considering the mechanism of extraction of the mercury iodide complex (II) and the composition of complex compounds, the reaction of complex formation of mercury (II) with dithione in the organic phase can be presented in the following diagram:



The maximum light absorption of the mercury iodide complex (II) with dithione is at 490 nm. The molar light absorption coefficient of the complex is  $7.1 \cdot 10^4$ . The Bera Law is observed in the range of 0.5-70  $\mu g$  mercury in 10 ml of the extract. The reproducibility of the definitions is in the range of 2-5 %.

Methodology for determining mercury (II) in pure solutions. In a measuring cylinder with a 25 ml capacity, 0.5-70  $\mu g$  of mercury (II) is added with a worn-out cap, 1 ml 5 m  $H_2SO_4$  is added, diluted with water to 7 ml, 1 ml 1M  $NaJ$  containing 2% ascorbic acid (to prevent oxidation of

iodide ions) is added, 2 ml DMF, 5 ml chloroform and 5-10s is shaken. The mixture is transferred to a dividing funnel and the extract is poured into another dividing funnel. Pour 5 ml of 0.01% dithione chloroform solution and 10 ml of 25%  $NH_4OH$  solution into the extract and shake for 10-15 seconds. The resulting-colored mercury complex with dithione is filtered into a cuvette and photometrised on a KFK-2 photocolormeter relative to the idle solution.

In optimum mercury (II) extraction conditions, bismuth, copper, silver, cadmium, palladium and platinum ions are co-extruded. At the same time, when the extract is shaken with a 25%  $NH_4OH$  solution, the dithione complexes of copper, palladium bismuth and platinum are destroyed, the dithione beaten and the extract is re-extracted, while the mercury, silver and cadmium complexes remain in the extract. In the presence of large amounts of cadmium and silver and their dithione complexes in the extract are destroyed by 5M  $H_2SO_4$  solution. The results of the determination of mercury in the presence of foreign ions (with an ultimate error of no more than 2-5 %) are given in Table 3.

**Table 3**

**Determination of mercury in the presence of foreign ions  
(10 micrograms of mercury taken)**

M	M/Hg	M	M/Hg	M	M/Hg
Ag(I)	1000 <sup>1</sup>	Bi(III)	10000	V (V)	500
Tl (I)	1000	Al(III)	10000	Mo (VI)	10000
Zn(II)	60000	Br (III)	20000	W(VI)	100
Pb(II)	10000	Sb (III)	5000	W(VI)	5000 <sup>4</sup>
Ca(II)	20000	Jn(III)	40000	U(VI)	5000
Ba (II)	20000	As (III)	4000	Te (VI)	1000
Cu (II)	500	Au (III)	1000	Os(VIII)	200
Cu (II)	5000 <sup>1</sup>	Ga (III)	2000	Cl <sup>-</sup>	10000
Ni (II)	20000	La (III)	20000	Br <sup>-</sup>	10000
Fe (II)	60000	Rh (III)	1000	NO <sub>3</sub> <sup>-</sup>	20000
Be(II)	10000	Zr (IV)	20000	CH <sub>3</sub> COO <sup>-</sup>	8000
Mg(II)	40000	Ge (IV)	10000	C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	2000
Co (II)	10000	Ti (IV)	10000	CNS <sup>-</sup>	10000
Sn(II)	20000	Th (IV)	20000	NaF	10000
Pd (II)	100	Sn(IV)	20000	CS(NH <sub>2</sub> ) <sub>2</sub>	10000
Pd (II)	1000 <sup>2</sup>	Se (IV)	300	C <sub>5</sub> H <sub>8</sub> O <sub>6</sub>	10000
Mn (II)	60000	Se (IV)	1000 <sup>2</sup>	C <sub>4</sub> H <sub>6</sub> O <sub>6</sub>	Not interfere
Cd (II)	10	Pt(IV)	1000		
Cd (II)	10000	Nb (V)	10000		

Where M - ion or compound;

M/Hg - acceptable mass ratio to mercury;

1 - after the destruction of silver and cadmium dithione complexes in the extraction of excess dithione by a 10 ml 25% solution of  $NH_4OH$ ;

2- in the presence of 100 mg thiourea;

3 - in the presence of 200 mg tartaric acid.

The developed method of extraction and photometric determination of mercury was tested in industrial wastewater analysis (Table 4). The correctness and reproducibility of the method has been verified by the additive method.

**Table 4**

**Results of the determination of mercury in the waste water of the gold recovery plant and electroplating plants ( $p=4$ ;  $P=0,95$ )**

Industrial waste water	Chemical composition of wastewater, mg/l.	$(\bar{x} \pm \Delta \bar{x})^*$ , mg/l.	Sr
Gold extraction factory (Angren) NPO	H <sub>2</sub> S-7.3; Cl <sup>-</sup> -62.4; SO <sub>4</sub> <sup>-2</sup> -243; CNS <sup>-</sup> -68; Fe <sub>com</sub> -0.2; Cu-17.5; Pb-17.2; Zn-21.8 ; As-0.8; Hg-9.40	9.44±0,14	0,009
"Signal" (Tashkent)	PO <sub>4</sub> <sup>-3</sup> -5400; Cl <sup>-</sup> -420; SO <sub>4</sub> <sup>-2</sup> -3000; Ca-130; Mg-10; HCO <sub>3</sub> <sup>-</sup> -11; Cr <sup>+6</sup> -3500; Cr <sup>+3</sup> -2.0 ; Fe <sub>com</sub> -5.0; Cu-2000; Zn-500; N: -2000; Cd -50; Hg-6.3	6,45±0,12	0,11
PO SEZ (Frunze)	PO <sub>4</sub> <sup>-3</sup> -3000; Cl <sup>-</sup> -1055; SO <sub>4</sub> <sup>-2</sup> -250; Ca -200; Zn-3; Ni-100; HCO <sub>3</sub> <sup>-</sup> -5 ; Cr <sup>+6</sup> -200; Cr <sup>+3</sup> -15; Fe <sub>com</sub> -12 ; Cu-10; Hg-1.2	1,12 ±0,03	0,019

Methodology for determining mercury in waste water. A measuring cylinder (25 ml) with a lapped cork is filled with several ml of analyzed water and determined using the above method, including a single washing of the colorless extract of 10 ml of solution containing 0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.02 M NaJ , 0.2% ascorbic acid, 20% DMF, shaking for 5-10 seconds.

An extraction and photometric method have been developed and the determination of mercury is recommended for the analysis of industrial wastewater, air, ores, rocks, biological and other materials without prior separation of the associated elements.

The initial solution of mercury (II) was prepared from a salt of mercury nitrate (II) of the "Chemically Pure (CP)" brand. The solution titer was set by potentiometric titration with rhodanide solution [6]. Dithione chloroform solution was used. The spectra of extracts from mercury complexes (II) were taken on the SF-26 spectrophotometer, l=1 cm. The optical density of the solution was also measured on the photoelectric colorimeter KFK-2.

**RESULTS.** Therefore, the research we have carried out concludes that the low selectivity of definitions of metals using basic dyes, as well as the use of other organic reagents in the complex formation in the water phase, is a major disadvantage of existing methods.

The research has focused on ways to increase the selectivity and sensitivity of photometric definitions, as these analytical characteristics play an important role in the practice of analytical chemistry. We investigated the conditions for the selective extraction of the mercury iodide complex in the presence of DMF inert organic solvents and its determination directly in the organic phase without separating the accompanying elements.

Researchers have shown that mercury (II) from a highly acidic environment in the presence of iodide ions and DMF is selectively extracted by chloroform (benzene). In 5-10 second phase shaking, mercury (II) is extracted by 99.9 % without changes up to a 20:1 ratio of phase volumes. Under these optimal conditions, bismuth, silver, cadmium, palladium and platinum ions are

extracted together with mercury. However, when the extract is shaken with a 25%  $NH_4OH$  solution, the dithione complexes of copper, bismuth, palladium and platinum are destroyed and the mercury, silver and cadmium complexes remain in the extract. In the presence of large quantities of cadmium and silver, their dithione complexes in the extract are destroyed by 5M  $H_2SO_4$  solution.

It has been established that the mercury iodide complex from a highly acidic environment is selectively extracted by the hydro-salt mechanism in the DMFA. The method is also valuable because after the extraction of mercury (II) in the organic phase, it is possible to form complexes with more sensitive organic reagents, which are not widely used due to their low selectivity.

**CONCLUSION.** As a result of the research, a new highly selective, accelerated and simple extraction-photometric method for determining mercury directly in the organic phase has been developed.

Therefore, the developed method of extraction-photometric determination of mercury is recommended for the analysis of mercury in industrial wastewater, ores, rocks, concentrates, industrial waste and other chemically complex materials.

### **REFERENCES**

1. Gladyshev V.P., Levitskaya S.A., Phillipova L.M. 1. Analytical chemistry of mercury. M.: Science. -1974 - Pages 228 – 93 (in Russian).
2. A.M. Lukin, K.A. Smirnova, Mercury Reagent Assortment. - Moscow: BIITECHEM Publishing House - 1967.- p - 40 (in Russian).
3. Eshwar M.C., Nagarkar S.G. Z. Anal.Chem.1972, V.260. p – 289 (in Russian).
4. T.V.Ramakrishna, G.Aravamudan , M. Vijarakumar . Anal.Chim. Acta, 1976. V 84, p – 369 (in Russian).
5. Kamatsu Sumno, Namura Tosnaku. J.Chem.Soc. Japan Pure Chem. Sec, 1967.V 88. P – 542.
6. D.K.Abdullayeva, S. M.Turabjanov, L. S.Raximova, A. Sh.Giyasov. Selective extraction of cadmium (II) and photometric determination of it with 1-(2-pyridylase)-2-naphthol (PAN) directly in the organic phase. Universe: Chemistry and Biology issue :4(82). April 2021. Moscow. P- 39-45.
7. D.K.Abdullayeva, A. Sh. Giyasov , M. A. Ziyayeva , U. I. Sharipova , N. I. Ibragimov 1 , R. E. Choriyeu , Sh. M. Shamuratova , and I. T. Usmonxodjayeva. Selective extraction-photometric determination of silver (I) with dithizone. International Scientific Conference "Fundamental and applied scientific research in the development of agriculture in the Far East" (AFE-2022). Tashkent, Uzbekistan, January 25-28, 2023. Set konferensiy E3STom 371 (2023) P-1-9.
8. Bulatov, M.I.; Kalichkin, I.P. Practical Manual on Photocolorimetric Methods of Analysis - 1986. Pages 244-251 (in Russian).
9. Mitchell J., Smith D. Aquametry. M.: Chemistry – 1980. - Pages 345- 354.
10. Zolotov, B.Z. Iofa, L.K. Chuchalin Extraction of Halogenide Complexes of Metals. Moscow: Science. 1973, p - 379 (in Russian).
11. Clhalik J.Potensimetri. Praha, CSAV, 1961.
12. Aston S.R., Riley I. P. chim.acta, 59 349 (1972).
13. D.K.Abdullayeva, A.Sh. Giyasov, R.Sh. Abdumatjitov, E.A. Egamberdiev. Selective extraction of silver (I) iodide complex and photometric determination of it with 1-(2-

- pyridylazo) -2-naphthol (PAN). Composite materials. Uzbek scientific, Technical and Production journal. No.3/2023. 6-9 pages.
14. D. Abdullaeva, A. Giyasov, O. Muratkulov, N. Rakhmatova, Sh. Mengliev, Sh. Zokirova, D. Tursunov, S. Turabjanov. Selective extraction of silver (I) and photometric determination of 1, 5 di-(2-naphthyl)-thiocarbazon (dinaftizone) in the organic phase. E3S Web of Conferences 497, 02037 (2024) ICECAE.
  15. V. Mironov, L. D. Tsvlodub. Electronic absorption spectra of thiourea complexes of monovalent copper, silver, and gold in an aqueous solution. 4, 1997, vol. 64, pp. 458-462.
  16. S.Sasic, A.Antic-Jovanovic, M.Jeremic . An investigation of the equilibrium of mercury(II) thiocyanate complexes in DMF solutions via Raman spectra and factor analysis. J. Chem. Soc. Faraday Trans. 21, 1998, vol.94, pp.3255-3260.
  17. Agarwal Arvind, A. N. Vishnoi. Chemical shifts of L[III] X-ray absorption edge of mercury and valence state of mercury ion in its compounds. Indian J. Phys. A N 2, 2000, vol.74, pp.127-129.
  18. V. L.Talrose, R. D.Jacob, A. L.Burlingame, M. A.Baldwin. Laser desorption-ionization mass spectrometry of complex salts of cesium, mercury, and iodine. Chem. Phys. N 4, 2002, vol. 21, pp. 6-17. Castro Miguel, Cruz Julian, Otazo-Sanchez Elena, Perez-Marin Leone l. Theoretical study of the Hg{2+} recognition by 1,3-diphenyl-thiourea. J. Phys. Chem. A N 42, 2003, vol.107, pp.9000-9007.
  19. Castro Miguel, Cruz Julian, Otazo-Sanchez Elena, Perez-Marin Leonel. Theoretical study of the Hg{2+} recognition by 1,3-diphenyl-thiourea. J. Phys. Chem. A N 42, 2003,vol.107,pp.9000-9007.
  20. Eland John H. D., Feifel Raimund, Edvardsson David .Single and double photoelectron spectroscopy of atomic mercury..J. Phys. Chem. A N 45, 2004, vol.108, pp.9721-9725.