CORRELATIONS OF ANALYTICAL PROPERTIES OF MERCURY COMPLEXES WITH 2-HYDROXYTHIOPHENOL AND PYRIDINE

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Abstract: *Five novel reagents were suggested for mercury (II) photometric determination: 2-hydroxythiophenol and its derivatives (HTDs), namely 2,5-dihydroxythiophenol, 2-hydroxy-5-fluorothiophenol, 2-hydroxy-5-chlorothiophenol, 2-hydroxy-5 - bromothiophenol, 2- hydroxy – 5-iodothiophenol. The molar absorptivity coefficient was (2.4-3.3)×10^4 (λ=450-480 nm). The optimal conditions for the complexation reaction correspond to pH range of 4.1 - 7.2. It has been proven that a compound with different ligands is formed in the ratio of Hg (II):HTDs:Py=1:2:2.*

Key words: *complexation, extraction, mercury, 2 - hydroxythiophenol, pyridin*
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Introductıon

To reduce the detection limit of trace amounts of elements by any method and to reduce the interfering effect of accompanying substances, preliminary concentration of metal ions from the analyzed objects is required. For this purpose, photometric methods are widely used, especially with the use of chelating organic reagents. The complexing properties of chelating organic reagents depend on the structure of functional analytical groups (FAG) [1].

The purpose of this study is to study the physicochemical and analytical properties of mercury complexes with 2-hydroxy-5-halogenthiophenol and pridine, the chemistry of complexation, and the establishment of regular relationships between the structure, and acid-base characteristics of the FAG of organic reagents and correlations of their analytical properties. Earlier, studies were conducted using other classes of complexing organic reagents as examples, which indicated the existence of a correlation dependence between the above properties. The study and comparison of the acid-base properties of organic reagents FAG and pH_{50} of mercury complexation with the production of 2-hydroxythiophenol and pridine allowed us to establish a quantitative correlation of the tyr ΔpK_{SH}–pH_{50} and $\sigma n-\Delta pK_{SH}$, that is, to determine the effect of the acidic properties of the sulfhydryl group of FAG on the parameters of complexation. Hg(II) ions form stable complex compounds with biomolecules that have a thiol group at the end of the molecule. Hg(II) is included in the category of thiol poisons. Therefore, the determination of mercury in a natural object is relevant [2-10]. The work [11] summarizes the methods of concentrating and separating small amounts of mercury in the analysis of environmental objects. *d*-elements with a filled d-orbital interact with donor atoms such as -O, -N, and -S, as well as polydentate ligands with π-bonds, which stabilize the complex.

In the photometric determination of mercury, sulfur-containing organic reagents with nitrogen as the second donor atom are mainly used. Reagents with a donor atom -O and -N are not of serious importance in the analytical chemistry of mercury [12-14].

The search for selective reagents for the photometric determination of mercury is currently relevant. In this regard, thio- and dithiophenols are in the center of attention of researchers [15-22].

The aim of this study is to determine the effect of mercury (II) ions on 2-hydroxythiophenol (HTP), and its derivatives (HTP, H_2L). Mixed ligand complexes (MLCs) of 2,5-dihydroxythiophenol (DHTP), 2-hydroxy-5-fluorothiophenol (HFTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), 2-hydroxy-5-iodothiophenol (HITP), and pyridine (Py) were studied.

Experımental part

Reagents and solutions. $Hg(NO_3)_2$ was used to prepare 1 mg/ml Hg(II) solution, and its concentration was determined by mercurimetric titration with NaCl solution using diphenylcarbazide as an indicator. The working solution was prepared using the starting $Hg(NO_3)_2$ solution [11]. A solution of 0.01 M HTDs and 0.01 M Py in chloroform was used in this work. HTDs was synthesized as part of the work [23], and its purity was determined by melting temperature and paper surface chromatography method. The ionic strength of the solution was kept constant (μ=0.1) by adding the calculated amount of KCl. The optimum acidity for the formation of mercury complexes was created using 0.1 M NaOH. Chloroform was used as an extractant.

Instrumentation. Concentration of hydrogen ion in water phase with glass electrode И.120.2. measured through the ionomer. The light absorption of the colored extracts was measured using a KFK-2 photocolorimeter (ℓ=0.5 cm) and an SF-26 spectrophotometer (ℓ=1.0 cm). The IR spectrum of MLKs and complexing reagents was performed on a UR-20 spectrophotometer in the range of 400-4000 cm^{-1}.

Procedure. 0.3 ml of mercury solution, 2-2.5 ml of NaOH, and 2.5-3.0 ml of 0.01 M HTDs were added to the separating funnel, mixed well, and 2.0 - 2.5 ml of 0.01 M Py solution in chloroform was poured over it. The organic phase was diluted to 5 ml with chloroform, and the total volume was diluted to 25 ml with distilled water. After separating the phases, the optical density of the extract was measured in a КФК-2 photocolorimeter at a wavelength of 440-490 nm.

Results and dıscussıon

Selection of extractant and determination of distribution coefficient. Although Hg(II) ions form compounds with different compositions depending on the concentration of reagents with HTDs, when a pyridine is added to the system and the formed compound is extracted, stabilization of a specific composition occurs. In order to determine the distribution coefficient (D) of mercury, its HTP and its derivatives and MLC with Am were obtained and extracted with chloroform under optimal conditions. The amount of mercury in the organic phase was determined by the hydrogen peroxide method after re-extraction, and the concentration in the water phase was determined according to the difference.

The distribution coefficient (*D*) of MLCs between H_2O and $CHCl_3$ was calculated by the following formula [24]:

$$\boldsymbol{D} = \frac{[\boldsymbol{Hg}]_{\boldsymbol{org}}}{[\boldsymbol{Hg}]_{\boldsymbol{aq}}} \qquad (1)$$

Here, $[Hg]_{org}$ and $[Hg]_{aq}$ refer to the equilibrium concentrations of mercury in the organic and aqueous phases, respectively. The rapid establishment of equilibrium and the maximum extraction efficiency of Hg(II) ions in the form of a complex compound are observed when chloroform is used as the extractant. The percentage of single-stage extraction (R, %) is calculated using the following formula:

$$R = \frac{100 \cdot D}{D + \frac{V_{aq}}{V_{org}}} \qquad (2)$$

Here, V_{aq} and V_{org} are the volumes of the aqueous and organic phases.

When chloroform is used as the extractant, the single-stage extraction percentage is R = 98.4–98.8% (Table 1). Subsequent experiments were conducted using chloroform.

The effect of the pH of the aqueous phase on complex formation. In the complex formation reaction of mercury with HTDs and Py, the products are formed at a pH of 2.1, and the reaction completes at a pH of 8.5. The optimal conditions for the complex formation reaction correspond to a pH range of 4.1–7.2 (Table 1).

Absorption spectrum. Regardless of the nature of the hydrophobic amines used, all of the formed MLKs in the chloroform extract absorb light at wavelengths of 450–480 nm (Table 1). The molar absorption coefficient of the MLKs varies between $(3.3–2.4)\times10^4$.

Effect of reagent concentration and time on complex formation. The formation and extraction of Hg(II)–HTDs–Py MLCs require $(1–1.2)\times10^{-3}$ M HTDs and $(1.1-1.6)\times 10^{-3}$ M Py. The colored MLCs of mercury are formed immediately after mixing the reagents, and the optical density of the complexes does not change for 48 hours. For chloroform extracts of the complexes, the Lambert–Beer law holds for mercury in the concentration range of 0.04–25 µg/ml, enabling mercury determination. The parameters of the calibration curve, y = a + bx, were calculated using the least squares method, and the results are given in Table 1.

Molar ratio of components in the MLC. The molar ratio of components in the MLC was studied using straight-line, relative yield, and equilibrium shift methods [25]. The results from all three methods confirmed each other, establishing the molar ratio of Hg:HTDs:Am as 1:2:2.

Table 1. Formation conditions of Hg(II)-HTDs-Py with MLC, some physical-chemical, optical and analytical properties. ($C_{Hg(II)}=3.98\times10^{-5}$ M)

Compounds	pK of thiophenol derivatives		pH_{for}	pH_{op}	λ_{max}, nm	$\varepsilon\cdot10^{-4}$	lgk_{eq}	lgk_{ex}	$lg\beta_c$	$y = a + bx$
	pK_{SH}	pK_{OH}								
$[Hg(DHTP)_2](PyH)_2$	6.3	11.2	4.5-8.6	7.3-8.3	455	2.7	2.1	8.8	9.73	$0.012 + 0.0064x$
$[Hg(HTP)_2](PyH)_2$	5.8	10.9	3.6-8.5	6.1-7.2	450	3.06	2.3	9.2	8.95	$0.014 + 0.0059x$
$[Hg(HFTP)_2](PyH)_2$	5.15	10.8	3.5-8.2	5.6-6.7	460	2.7	2.0	8.7	7.28	$0.015 + 0.0057x$
$[Hg(HXTP)_2](PyH)_2$	5.1	10.6	3.4-8.1	5.6-6.7	460	2.6	1.9	8.5	7.24	$0.013 + 0.0059x$
$[Hg(HBTP)_2](PyH)_2$	5.05	10.4	2.4-7.5	4.5-6.6	464	2.6	1.8	7.8	6.72	$0.012 + 0.0060x$
$[Hg(HITP)_2](PyH)_2$	5.0	10.2	2.5-7.5	4.5-5.5	470	2.4	1.4	6.5	5.82	$0.014 + 0.0056x$

Chemistry of mixed-ligand complex formation. Considering the hydrolysis constants of HTDs and mercury, the state of the central ion at different pH levels was determined. It was found that under complex formation conditions (pH 2.5–8.5), the complex-forming ion of mercury is Hg^{2+}. The Py used exists in solution in the protonated form, PyH^+.

The state of mercury complexes with HTDs and pyridine in the chloroform extract was determined by calculating the degree of polymerization [16]:

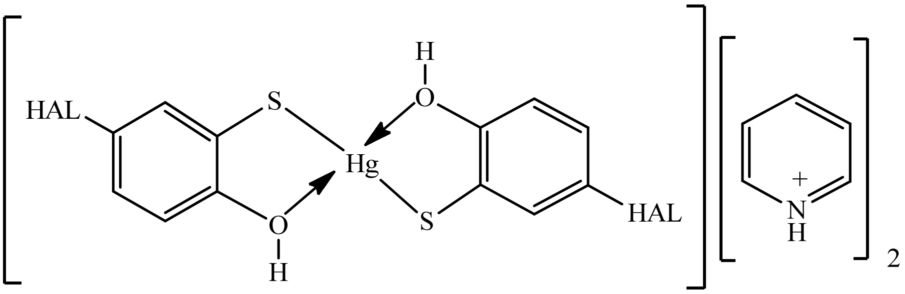
$$\gamma = \frac{\lg\frac{A_x}{A_{max}}}{(q+1)\lg\frac{C_i\varepsilon l - A_x}{C_k\varepsilon l - A_{max}}} \qquad (3)$$

Here, γ is the degree of polymerization; A_x and A_{max} are the optical densities of the extract; ε is the molar absorption coefficient; l is the thickness of the absorption layer in cm; q is the number of reagent molecules; C_i and C_c are the concentrations of mercury ions. It has been stablished that the complex compounds are monomers in the chloroform extract.

Taking this into account, the formation of the mercury complex with HTDs and Py can be represented by the following reaction equation:

$$Hg^{2+} + qH_2L + pPyH^+ \rightarrow [Hg(H_{2-n}L)_q](PyH)_p + pnH^+ \qquad (4)$$

Taking into account the coordination number and the ionic state of mercury in aqueous solution, it can be assumed that under the optimal conditions in which the complexes are formed, it forms MLCs with outer spheres in the following composition with HTDs and Py:



HAL=F, Cl, Br, J

The IR spectrum of the HTDs molecule [16, 19] and the complex it forms with mercury and Py have been compared as confirmation of the proposed structure of the MLCs. In the IR spectrum of the free ligand, a strong band in the range of 2580–2600 cm^{-1} can be attributed to ν_{SH}. A broad and intense absorption band in the range of 3200–3600 cm^{-1}, with a maximum near 3450 cm^{-1}, corresponds to ν_{OH}. The intense absorption band located in the frequency range corresponding to the valence frequency of the SH group disappears. This indicates that the sulfur atom is chemically bonded to the metal atom in the complex molecule [26].

Stability constant. When the composition of the formed MLK is known and the hydrolysis and dissociation constants of the central atom are determined, the stability constant can be calculated [15]. Based on the obtained results, the complex formation reaction can be written as follows:

$$Hg^{2+} + 2HL^- + 2PyH^+ \rightarrow [HgL_2](PyH)_2 + 2H^+ \qquad (5)$$

The stability constant (β_c) based on reaction (5) can be expressed as follows:

$$\beta_c = \frac{[HgL_2](PyH)_2}{[Hg^{2+}][HL^-]^2[PyH^+]^2} \qquad (6)$$

In the solution, various mercury ions such as Hg^{2+}, $Hg(OH)^+$, and $Hg(OH)_3^-$ are present. The concentration of mercury that is not included in the colored complex can be expressed in a general equation as follows:

$$C_{Hg} - C_c = [Hg^{2+}] + [Hg(OH)^+] + [Hg(OH)_2] + [Hg(OH)_3]^- \qquad (7)$$

In the optimal conditions under which the complex is formed, Hg^{2+} is involved as the complexing central ion. The equilibrium concentration of Hg^{2+} ions is calculated by the formula (8):

$$\mathrm{C_c} = \frac{A_x C_{\mathrm{Hg}}}{A_{max}} \tag{8}$$

$$[\mathrm{Hg}^{2+}] = \frac{\mathrm{C_{Hg\,total}} - \mathrm{C_{complex}}}{\left(1 + \frac{\mathrm{K_{h1}}}{[\mathrm{H}^+]} + \frac{\mathrm{K_{h1}K_{h2}}}{[\mathrm{H}^+]^2} + \frac{\mathrm{K_{h1}K_{h2}K_{h3}}}{[\mathrm{H}^+]^3}\right)} = \frac{\mathrm{C_{Hg\,total}} - \mathrm{C_{complex}}}{\Delta} \tag{9}$$

$pK_{h1} = 3.5$, $pK_{h2} = 4.0$, $pK_{h3} = 14.8 – 14.8$ is the hydrolysis constant of mercury [15]. The equilibrium concentration of HTDs was calculated considering the dissociation constant of the reagent:

$$[\mathrm{H_2L}] = \frac{C_{H_2L\,total} - 2C_{complex}}{\left(1 + \frac{K_{h1}}{[H^+]} + \frac{K_{h1}K_{h2}}{[H^+]^2}\right)} \tag{10}$$

The concentration of the amine can be calculated considering its protonation:

$$[\mathrm{Py}] = \frac{C_{Am\,total} - 2C_{complex}}{\left(1 + \frac{K_{h1}}{[H^+]} + \frac{K_{h1}K_{h2}}{[H^+]^2}\right)} \tag{11}$$

If we substitute the equilibrium concentrations of the central atom and ligands into equation (6), we obtain the value of the stability constant of MLC complexes. As an example, the data for calculating the stability constant of the $\mathrm{Hg[(HXTP)_2](PyH)_2}$ complex is provided in Table 2.

Table 2. Data for calculating the stability constant of the $\mathrm{[Hg(HXTP)_2](PyH)_2}$ complex (μ =0.1; pH =4.0-7.5; A_{max}= 0.53; $C_{Hg(II)}$= 3.98 ×10^{-5} M).

$[\mathrm{H_2L}]\cdot10^{-3}$	0.95	0.97	0.99	1.01	1.03	1.04
$[\mathrm{Py}]\cdot10^{-3}$	1.3	1.4	1.5	1.6	1.7	1.8
A_x	0.35	0.37	0.40	0.44	0.48	0.5
$\varepsilon_x\cdot10^{-4}$	2.1	2.2	2.3	2.4	2.5	2.6
$(A_x/\varepsilon_x)\times10^5$	1.67	1.68	1.74	1.83	1.92	1.94
$(C_{Hg} - A_x/\varepsilon_x)\times10^5$	2.31	2.30	2.24	2.15	2.06	2.04
$(C_{H2L} - 2A_x/\varepsilon_x)\times10^3$	0.0095	0.0097	0.0099	0.0100	0.0102	0.0103
$(C_{Py} - 2A_x/\varepsilon_x)\times10^3$	0.0103	0.0104	0.0105	0.0105	0.0106	0.0020
lgβ	7.18	7.19	7.23	7.25	7.28	7.30 lgβ =7.24±0.33

Equilibrium constant. According to equation (5), the equilibrium constant of the reaction is equal to:

$$\mathrm{K_{eq}} = \frac{\{[\mathrm{HgL_2}](\mathrm{PyH})_2\}_{\mathrm{org}}}{[\mathrm{HgL_2}]^{2-}_{\mathrm{aq}}[\mathrm{PyH}^+]^2_{\mathrm{aq}}} \tag{12}$$

Given that the distribution coefficient is equal to:

$$D = \frac{A_x}{A_{max} - A_x} = \frac{\{[\mathrm{HgL_2}](\mathrm{PyH})_2\}_{\mathrm{org}}}{[\mathrm{HgL_2}]^{2-}_{\mathrm{aq}}[\mathrm{PyH}^+]^2_{\mathrm{aq}}} \tag{13}$$

Here, A_x is the optical density in the given experiment, A_{max} is the optical density under the conditions in which the complex is fully formed.

If we substitute the value D in equation (13), we get:

$$K_{eq} = \frac{D}{[PyH^+]_{aq}^2} \tag{14}$$

If we logarithmize the last expression, we get

$$K_{eq} = \lg D - 2\lg[PyH^+] \tag{15}$$

The value of $\lg K_{eq}$ is given in table 1.

Extraction constant. We can solve the equation (16) by transformation and calculate the extraction constant

$$K_{ex} = \lg D - 2\lg[L^{2-}] + 2\lg[PyH^+] \tag{16}$$

The results are also given in Table 1.

Dependence between the properties of reagents and complexes. A correlation has been identified between the pK_{SH} and $\lg\beta_{c.c.}$ of two-phase complexes of Hg (II) and HTDs. For this purpose, the first dissociation constant of HTDs has been compared with the conditional stability constants ($\lg\beta_{c.c.}$) of their MLC (Fig. 1).

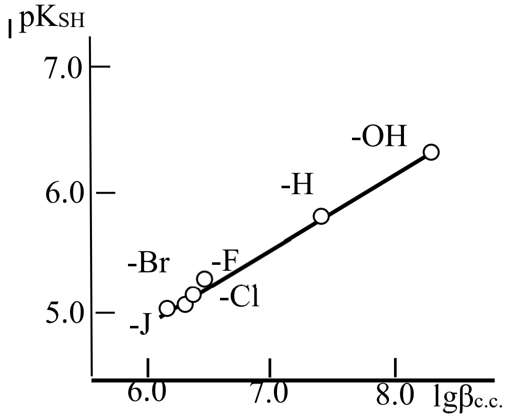


Fig. 1. Correlation between pK_{SH} and $\lg\beta_{c.c.}$ for complexes of Hg(II)-HTDs-Py.

This comparison can be assumed to be accurate, as all complex-forming reagents possess the same functional groups (–OH, –SH) and in all cases, they form a complex compound with mercury in the same composition (Hg:HTDs=1:2). The correlation identified by us allows for the prediction of the stability of complexes formed with mercury and other thiophenols containing similar functional groups.

The pK_{SH}, representing the acid-base property of the sulfhydryl group in the functional group of the reagents, and pH_{50} of mercury's analytical reactions were compared to determine the dependency between (pK_{SH}) and pH_{50}. The value of pH_{50} for the half-reaction was determined from the *A*=f(pH) graph. The quantity (ΔpK_{SH}) represents the difference between the pK_{SH} of the substituted reagent and the pK_{SH} of the unsubstituted reagent. As seen from Table 3 and Fig. 2, as the acidity property of the reagent increases, the pH_{50} of the complex formation reaction shifts to a more acidic environment. The linear dependence found in $\Delta pK_{SH} - \Delta pH_{50}$ coordinates is expressed by the following correlation equation (17):

$$\Delta pK_{SH} = 1.0072 \cdot (\Delta pH_{50})^{1.257} \text{ or } \Delta pH_{50} = \left(\frac{\Delta pK_{SH}}{6.274}\right)^{0.856} \tag{17}$$

Equation (17) can be used to predict the pH_{50} values of analytical reactions based on the acidity (pK_{SH}) of the complex-forming group in the reagents. The position and nature of substituents in the benzene ring influence the functional group acidity (pK_{SH}) and (pK_{OH}) values of complex-forming reagents [27].

Table 3. Correlation between the physicochemical characteristics of the MLCs formed by mercury with HTDs and Py.

H_2L	pK_{SH}	ΔpK_{SH}	pH_{50}	ΔpH_{50}	$\lg\beta_{c.c.}$
OH	6.33	-0.53	5.9	-0.6	9.73
H	5.80	-	5.3	-	8.95
F	5.15	0.65	4.7	0.6	8.31
Cl	5.10	0.70	4.6	0.7	7.24
Br	5.05	0.75	4.5	0.9	6.53
J	5.00	0.80	4.4	0.95	5.82

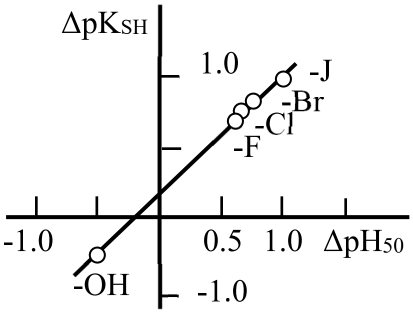


Fig. 2. Correlation between the acidity property of HTDs (ΔpK_{SH}) and the ΔpH_{50} of its complex formation reaction with mercury.

The quantitative effect of substituents can be characterized by the Hammett constant for para-substituents' inductive effects [28]. A linear correlation has been identified between σn and pK_{SH} for the investigated complex-forming reagents. The σ_n-ΔpK_{SH} correlation graph is depicted in Fig. 3.

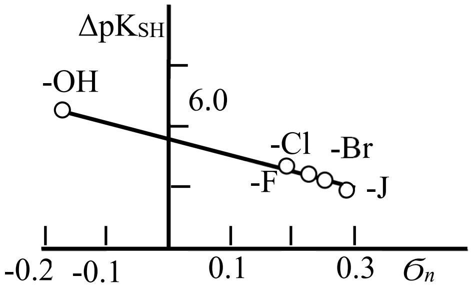


Fig. 3. Correlation in the σ_n-ΔpK_{SH} system

These correlations are expressed by the following equation (18):

$$pK_{SH} = pK_{SH}^{*} - \rho\sigma_n r \qquad (18)$$

Here, pK_{SH}^{*} is the dissociation constant of the unsubstituted thiophenol; ρ- is the characteristic reaction constant for HTDs; r- is the correlation constant. The calculations for the correlation (r) and the reaction constant (ρ) in the σ_n–ΔpK_{SH} system are provided in Table 4:

$$r = \frac{\sum(\sigma_n-\bar{\sigma}_n)(pK_{SH}-p\bar{K}_{SH})}{\sqrt{\sum(\sigma_n-\bar{\sigma}_n)^2(pK_{SH}-p\bar{K}_{SH})^2}} = \frac{0.116}{\sqrt{0.0078}} = 1.3137 \qquad (19)$$

$$\rho = \frac{pK_{SH}-p\bar{K}_{SH}}{\sigma_n^i} \qquad (20)$$

Table 4. Data for the calculation of correlation (r) and reaction constant (ρ) in the σ_n – pK_{SH} system.

Substituents	H	OH	F	Cl	Br	J	Average price
σ_n	0	-0.178	0.126	0.238	0.265	0.299	$\bar{\sigma}_n$=0.196

$\sigma_n - \bar{\sigma}_n$	0.196	0.018	0.029	0.042	0.0609	0.103	
$(\sigma_n - \bar{\sigma}_n)^2$	0.0384	0.0003	0.0009	0.0018	0.0048	0.0106	
pK_{SH}	5.8	6.33	6.12	5.1	5.05	5.0	$p\bar{K}_{SH}$=5.456
$pK_{SH} - p\bar{K}_{SH}$	0.344	0.874	0.537	0.356	0.406	0.456	
$(pK_{SH} - p\bar{K}_{SH})^2$	0.1183	0.7639	0.2612	0.1267	0.1648	0.2079	
$(\sigma_n - \bar{\sigma}_n)\ (pK_{SH} - p\bar{K}_{SH})$	0.0562	0.0044	0.0040	0.0036	0.0167	0.0356	$\sum$=0.116
$(\sigma_n - \bar{\sigma}_n)^2\ (pK_{SH} - p\bar{K}_{SH})^2$	0.0045	0.0002	0.0001	0.0001	0.0008	0.0022	$\sum$=0.0078
ρ	0	2.9775	2.9769	2.9412	2.8302	2.6756	$\bar{\rho}$=2.2853

Effect of interfering ions. Using the calibration curve graph, the interference effect of extraneous ions on the results of mercury determination with HTDs and Py was studied. Alkali and alkaline earth metals, Nb(V), Ta(V), Zr(IV), and small amounts of Fe(II) (40μg), Cu(II) (25μg), Ni(II) (30μg), and Co(II) (60μg) do not interfere with the determination. When these latter ions are present in excess, their interference can be eliminated by adjusting the pH of the medium, using masking agents, or by extraction.

Determination of mercury in air. The newly developed method was applied to determine the amount of mercury in the air. For this purpose, an absorbing liquid containing 5 ml of 0.1 N $KMnO_4$ and 5 ml of 10% H_2SO_4 was collected in a deflagmator [29]. Air was passed through the solution at a rate of 60 L/hour. Excess $KMnO_4$ was reduced with H_2O_2, and the H_2SO_4 was neutralized with 1 N NaOH. The amount of mercury was then determined using HXTP and An, as well as dithizone. When the mercury concentration in the air was re-measured, an amount of mercury was added to the absorbing mixture. The mercury concentration in the air was found to be 8±0.56 μg/m² (S_r = 0.07).

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