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Development of Method for Discontinuing Mercury-Containing Waste Including the Method of Analysis of Residual Concentrations

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Abstract

Environmental safety is one of the most important international and national tasks when using chemicals such as mercury, its compounds and mercury containing waste. Mercury (Hg) is a global pollutant. Constant anthropogenic mercury emissions and its presence in food chains affects human and ecosystem health and cause serious concerns. When released into the atmosphere with various emissions, mercury is deposited on the ground or water surface. Due to the global transport of mercury in the environment, its release is possible near sources of pollution, as well as at a remote distance.

Keywords: mercury–containing wastes, Minamata Convention, immobilization

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1. Introduction

At industrial enterprises, research institutes, medical and other institutions stored from ten to twelve tons of mercury [1]. The results of the 2012 inventory conducted in the Russian Federation showed that through the use of mercury-containing goods and devices (thermometers, light sources, batteries, etc.), 49.7 tons of mercury will enter the environment, of which 4.8 tons will go into the air, 4.9 tons - into the water, 11 tons–into the soil and 29 tons - into the waste (Table 1).

Tables 2 and 3 provide information on the generation and disposal of mercury-containing waste (MCW) in various industries and major regions of Russia. In accordance with the data presented in Table 2, the main volumes of MCW are formed in the chemical industry, mechanical engineering and non-ferrous metallurgy. The leaders in terms of the volume of MCW are Siberian, Ural, Volga and Central districts. The reason for this is the operation in these districts of a large number of enterprises from the above industries.

Table 1: Mercury release to the environment as a result of production and use of mercury-containing consumer goods, tons [4].

Source subcategory name	Air	Water	Soil	Ordinary waste	Special Processing / Disposal Sector
Mercury thermometers	0,312	0,910	0,054	1,785	0,065
Electric switches and relays with mercury	1,864	0,0	1,864	7,458	7,458
Mercury-containing light sources	0,485	0,026	0,790	3,899	0,312
Mercury batteries	0,113	0,008	0,272	1,714	0,351
Mercury-containing biocides and pesticides	2,000	4,000	8,000	6,000	0,0
Total	4,774	4,944	10,980	20,856	8,186

Table 2: Accumulation, formation and decontamination of MCW in 2002 in various industries of the Russian Federation [5].

Industry Name	MCW accumulated at the end of 2001		MCW formed in 2002		MCW neutralized in 2002	
	tons	%	tons	%	tons	%
Industry, including:	2874	83,1	7214	85,9	1655	65,8
chemical	1159	33,5	1200	14,3	536	21,3
engineering	801	23,5	3342	39,8	1158	46,0
non-ferrous metallurgy	691	20,0	2075	24,7	1,9	0,08
pulp and paper	20	0,58	45	0,53	-	-
electric power	41	1,19	126	1,5	16	0,64
fuel	30	0,87	85	1,0	-	-
Building Materials Industry	108	3,1	145	1,7	-	-
Housing and Utilities	332	9,6	62	0,07	185	7,4
Total in Russia	3458	100	8396	100	2517	100

In 2013, governments adopted the Minamata Convention, which was signed by 128 countries, including the Russian Federation [2]. The objective of the Convention is to protect human health and the environment from releases of mercury and its compounds. Under this Convention, participating Governments must take a number of measures, including to prevent the release of mercury into the atmosphere and the removal from production of certain mercury–containing products. In accordance with the Minamata Convention, a number of products containing mercury should be excluded from circulation by 2020 [3]. Another important provision of the Convention is the rejection of secondary mercury.

To reduce the level of environmental pollution, in particular aquatic ecosystems, and to comply with the provisions of the Convention, it is necessary to convert the

Table 3: Distribution of MCW by federal districts of the Russian Federation [5].

District	MCW accumulated at the end of 2001		MCW formed in 2002		MCW neutralized in 2002	
	tons	%	tons	%	tons	%
Central	376,9	10	2.184	26	950	38
North-West	88,4	2,6	145,2	1,7	44	1,8
South	1029,9	30	559	7	210	8
Volga	287,1	8	936	11	747,4	30
Ural	213,3	6	2422	29	54,8	2,1
Siberian	1407,9	41	2129,8	25	510,1	20
Far Eastern	54,6	1,6	19,4	0,2	0,135	0,0
Total in Russia	3458	100	8.396	100	2517	100

residual mercury compounds in the waste into the most stable form–mercury sulfide. In the Russian Federation, almost all existing technologies for the disposal of waste are focused on the production of secondary mercury. Ways of neutralizing mercury-containing waste with the conversion of metallic mercury and its compounds (including organic mercury) into the most safe forms for humans and the environment, provided there is a guaranteed absence of mercury–containing emissions into the atmosphere and wastewater discharges, including emergency and emergency situations, are currently absent and / or underdeveloped.

2. Methods

The main of the first tasks in the creation of technology for processing mercury-containing waste was the development of analytical methods for assessing the amounts of mobile compounds of mercury against its sulfide. In the development of this technique, the resistance of the latter, in contrast to metallic mercury and its oxides, to concentrated nitric acid was used. The process of developing the technique included: the study of the rate of dissolution of the metal mercury suspension in nitric acid of different concentrations; conducting a series of experiments of reverse titration with potassium iodide, sodium chloride and direct titration with ammonium thiocyanate; assessment of the effect on the accuracy of the glass and bentonite method.

To determine the recommended concentration of nitric acid, which will be further used to determine the content of metallic mercury in the samples, an experiment was carried out, including weighing samples of mercury close in weight to those used in further studies and dissolving in nitric acid of various concentrations. The reaction of

metallic mercury with nitric acid of various concentrations can occur in the following reactions:

$$3Hg + 8HNO_3 \rightarrow 3Hg(NO_3)_2 + 2NO + 4H_2O, \quad (1)$$

$$Hg + 4HNO_{3(\,onc.)} \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O. \quad (2)$$

According to the results of this experiment, it can be concluded that with a decrease in the concentration of nitric acid, the dissolution rate of mercury decreases exponentially and an acid with a concentration of at least 40% can be considered acceptable for an analytical experiment (dissolution time up to 20 minutes).

To determine the concentration of mercury ions, 3 methods were studied. The first is to treat $Hg(NO_3)_2$ with potassium iodide:

$$4KI + Hg(NO_3)_2 \rightarrow K2[HgI_4] + 2KNO_3, \quad (3)$$

$$K_2[HgI_4] + Hg(NO_3)_2 \rightarrow 2HgI_2\downarrow + 2KNO_3. \quad (4)$$

Back titration of a specific volume of potassium iodide solution of known concentration with mercury nitrate was used. A 2% solution of defenylcarbazone in ethanol was used as an indicator, which forms a complex with mercury ions, which gives the solution a bright blue color. In addition, it should be noted that since the dissolution of mercury occurs in concentrated nitric acid, when determining using KI or NaCl, it is necessary to reduce the acidity of the titrant (mercury nitrate with the addition of definylcarbazone as an indicator) to the content of nitric acid in the solution equal to 0.1 n, since otherwise diphenylcarbazone reacts with nitric acid, which significantly reduces the accuracy of determination.

The second method involves the treatment of $Hg(NO_3)_2$ with sodium chloride:

$$Hg^{2+} + 2\ NaCl \rightarrow HgCl_2\downarrow + 2Cl^{-}. \quad (5)$$

Titration was carried out similarly to titration using potassium iodide.

According to the third method, the reaction of $Hg(NO_3)_2$ with NH_4SCN was realized:

$$Hg^{2+} + 2\ NH_4NCS \rightarrow Hg(NCS)_2\downarrow + 2NH_4^{-}. \quad (6)$$

In this case, direct titration of a certain volume of a solution of mercury nitrate with a solution of ammonium thiocyanate of known concentration was used. As an indicator, a solution of iron nitrate was used, which forms brightly colored iron rhodonite with thiocyanates. The method is sensitive to the presence of chlorine ions in the system.

3. Results and Discussion

The graph (Fig. 1) shows that it is preferable to determine the concentration of mercury by a method that realizes the reaction of $Hg(NO_3)_2$ with NH_4SCN, since it gives the smallest measurement error.

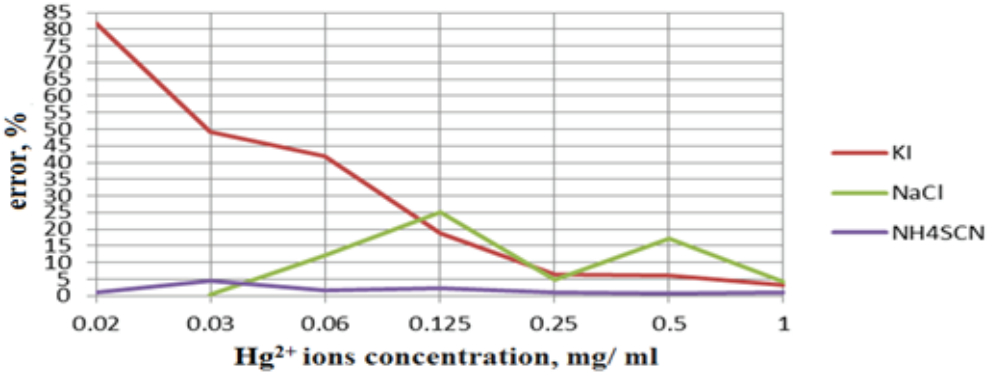

Figure 1: The accuracy estimation of various analytical methods

As a result of titrations, the limits for the detection of mercury were established:

- reaction by $Hg(NO_3)_2$ with KI constitutes 0,001 mg/cm^3;
- reaction by $Hg(NO_3)_2$ with NaCl – 0,03 mg/cm^3;
- reaction by $Hg(NO_3)_2$ with NH_4SCN – 0,02 mg/cm^3.

Based on the research of Hg^{2+} ions concentration, it was concluded that the mercury titration of KI and NaCl solutions presents certain difficulties, such as an inaccurate determination of the moment of solution color transition and, consequently, less accurate results. The titration of NH4SCN is an appropriate analytical method for determining the concentration of Hg2+, confirmed by the smaller error of the obtained results and a noticeable color change of the solution. However, this method is sensitive to the presence of chlorine ions in the system, and since it is supposed to use a mixture of pyrite and ferric chloride to reduce the residual amounts of metallic mercury to acceptable values, the titration method was also described for such systems.

4. Conclusion

The chosen method describes the recommended concentrations of titrant and titratable substances, compiles equations for determining the residual concentrations of mercury ions, and estimates the detection limits of mercury. The following formula is given for calculating the mercury concentration according to the developed method:

$$C_{Hg^{2+}} = \frac{H * V * 200}{2 * V_{Hg^{2+}}} = \frac{100 * H * V}{V_{Hg^{2+}}} \quad (7)$$

where: n is the normality of the selected titrant (units), V is the volume of the solution used in the titration (cm^3), $V(Hg^{2+})$ is the volume of the Hg^{2+} solution (cm^3).

It was also shown that the presence of glass in the system has practically no effect on the proposed analytical method, while bentonite significantly distorts the results due to the absorption of mercury ions: in some cases, from 50 to 90% of the ions in solution can be absorbed.

To immobilize mercury, the reactions in the mercury – sulfur – glass system were studied, and glass was taken as a substance present in a number of consumer goods. Studies have been carried out to determine the residual concentrations of mercury in the presence of glass in a 1:9 ratio, which is typical for thermometers manufactured according to State All-Union standard and sulfur. A series of experiments has shown that in the first 30 minutes, mercury does not completely disperse in the system (this is evidenced by differences in concentrations in the samples taken), but after this time dispersion still occurs, which is confirmed by the results of titration. It was also found that the greatest immobilization of mercury is achieved in the absence of water or its small presence (2-3 cm^3), as well as with a ratio of mercury to sulfur (1:1.5 by weight).

Thus, with selected mass ratios, the proportion of reacted mercury is 97-98%, which indicates the advisability of using this technique for industrial purposes for the disposal of mercury-containing wastes.

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