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DETERMINATION OF MERCURY CONTENT IN NATURAL BRINES BY ADSORPTION OF COLD VAPOR

Abstract: *The processes of reduction of various forms of mercury up to the atomic state have been studied. The use of ultrasound and the simultaneous action of ultrahigh-frequency and low-frequency ultrasound for the destruction of organic extracts of mercury have been investigated. The main factors of the action of ultrasound on the processes of reduction of mercury and on the processes of destruction of organic extracts of mercury have been experimentally proved, this are sound-chemical reactions with the participation of radicals. The advantage of the simultaneous action of ultrasound of different frequencies (high and low) relative to the degree of mercury extraction, which increases from 92.1 - 93.5 up to 96.1 - 98.5, has been experimentally shown. At the same time, the relative standard deviation increases significantly (Sr = 0.06 - 0.08).*

Key words: *mercury, cold vapor atomic absorption spectrometry, ultrasound, sample preparation, metrological characteristics.*

Language: *English*

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Introduction

The mercury content in kitchen salt varies from 4.5 · 10-5 to 1.2 · 10-2 mg / kg, in brine the mercury content can reach 5.3·10-2 mg / kg [1,p.51; 2,p.35; 3,p.11; 4,p.100]. Mercury belongs to highly toxic cumulative toxic substances [5,p.63; 6,p.722; 7,p.17; 8,p.155; 9,p.900; 10,p.90]. Nowadays a large number of works have been published that allow to determine of trace amounts of mercury [11,p.582; 12,p.118; 13,p.1433; 14, p.2185; 15, p.248].

One of the important directions in analytical chemistry for solving the problems of chemical expertise is the acceleration of the sample preparation process as a fundamental stage of analysis. The expressiveness of the sample preparation procedure is achieved by using different intensification methods. The use of ultrasound is universal and affordable.

It should be emphasized that the toxicity of mercury is determined by the form of its existence. The most toxic forms of mercury are - especially methylmercury. In salt lakes and salt pools there are conditions for the methylation of inorganic forms of mercury by biological and synthetic means, since they contain humic and other acids, the alga "Dunaliella

Salina". In works the determination of the total mercury content was carried out by cold vapor atomic absorption spectrometry.

The purpose of the work is to develop a method for atomic absorption determination of various forms of mercury by the cold vapor method in brines, various sodium chloride solutions using two-frequency ultrasound with improved metrological characteristics.

Experiment

An atomic absorption spectrometer "AAS-3" with an attachment "Julia-2", an ultrasonic disperser was used in the work. UZDN-1M with ultrasonic frequency variation 18-47 kHz and intensity 0.05 - 25 W / cm^2; US generator 24 - US GI - K - 1.2 with a set of magnetostrictive and piezoelectric emitters at frequencies of 66 kHz - 2.5 MHz; piezoelectric emitters TsTS - 19, which have good mechanical stability and stability of radiation at ultrasonic frequencies of 100 kHz - 2.5 MHz at an intensity of up to 12 W / cm^2.

To prepare the calibration solutions, we used the standard sample of the composition of mercury solutions 1 mg / ml GSO RR 3497-86, manufactured at the V.I. Bogatsky National Academy of Sciences of Ukraine (Odessa), chemical reagents of at least analytical grade. and bidistilled water.

Results and discussion

When determining mercury, sample preparation is carried out according to [12, p.120]. The content of organic forms of mercury was found as the difference between the content of total and inorganic forms of mercury. Table 1 shows the effect of the matrix on the determination of mercury.

Table 1 shows the average of the six studies. 1 - used the reduction of $SnCl_2$ in 1 M NaOH medium in the presence of 0.2 M $CuCl_2$; 2 - used the reduction of SnCl2 in 2M H_2SO_4; 3 - used the reduction of $SnCl_2$ in 2 M H_2SO_4 after oxidation with a bromide-bromate mixture for 2 min; 4 - used the reduction of $SnCl_2$ in an media of 2M H_2SO_4, after the influence of ultrasonic frequency 22 kHz, intensity 14 W / cm2 for 1 min; 5 - reduction of $SnCl_2$ in 2M H_2SO_4 medium was used after the influence of ultrasonic frequency 22 kHz, intensity 8 W / cm2 for 1 min. The content of HA and FA is given for every 10 g of sodium chloride.

Table 2 shows the effect of ultrasound in the presence of oxidants on the determination of mercury by atomic absorption spectrometry using the cold vapor method. Table 2 shows the average results of the six studies. Mercury was introduced in the form of Hg2 +; MMX, FMA at 5.00mkg / l. Frequency 22 kHz, duration 1 min. The correctness of the methodology was proved by analyzing the same samples by the standard method and the "injected-found out" method (Table 3).

Tables 4 and 5 show the results of a study of the effect of low and high frequency ultrasound on the degree of extraction of mercury during the destruction of organomercury compounds. For additional control of the correctness of the results obtained, 0.050 μg / L of mercury (II) was introduced into the analyzed solutions. The results of the analysis are presented in Table 6. The destruction of mercury dithizonate extracts in carbon tetrachloride by two-frequency ultrasound was carried out.

Conclusions

The use of two-frequency ultrasound for the destruction of organic compounds of mercury, as well as for the destruction of organic extracts of mercury has been studied. It is shown that the use of dual-frequency ultrasound allows, in comparison with the use of single-frequency ultrasound, to increase the degree of mercury extraction from 93.0 to 98.3%. A technique has been developed for atomic absorption spectrometry by the cold vapor method to determine the total content of mercury, organic mercury, methyl and inorganic forms of mercury in brines and solutions of various sodium chloride compounds.

The correctness of the method for the determination of mercury was carried out by the "introduced-found" method. It is shown that the systematic error is insignificant. The detection limit for mercury is 0.001 μg / L with a sample volume of 3 ml and 0.0082 μg / L with a sample volume of 100 ml. When analyzing kitchen salt solutions with a concentration of 150 g / l, the detection limit can be reduced, but the precision is impaired. When determining the methyl forms of mercury, the detection limit is 0.003 and 0.0004 mg / kg, respectively.

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Table 1. The effect of the matrix on the determination of mercury at solutions analysis.

C $_{NaCl}$, g/l	Injected GK, mg/l	Injected FK, mg/l	Injected Hg, mkg/l			Found out Hg, mkg/l				
			Hg^{2+}	MMX	FMA	1)	2)	3)	4)	5)
1	2	3	4	5	6	7	8	9	10	11
NaCl solution										
50,00	0	0	0	0	0	—	—	—	—	—
50,00	0	0	5,00	5,00	5,00	14,91	4,91	14,84	14,84	10,04
100,00	0	0	0	0	0	—	—	—	—	—
100,00	0	0	5,00	5,00	5,00	14,82	4,81	14,44	14,81	9,92
120,00	0	0	0	0	0	—	—	—	—	—
120,00	0	0	5,00	5,00	5,00	14,63	4,44	13,46	13,56	9,34
130,00	0	0	0	0	0	—	—	—	—	—
130,00	0	0	5,00	5,00	5,00	13,13	4,19	12,45	13,04	8,94
150,00	0	0	0	0	0	—	—	—	—	—
150,00	0	0	5,00	5,00	5,00	12,00	3,70	10,82	11,82	7,75
Kitchen salt solution										
20,00	0,50	5,00	0	0	0	—	—	—	—	—
20,00	0,50	5,00	5,00	5,00	5,00	15,01	4,93	14,65	14,83	9,85
30,00	0,50	5,00	0	0	0	—	—	—	—	—
30,00	0,50	5,00	5,00	5,00	5,00	14,95	4,75	14,25	14,76	9,75
50,00	0,50	5,00	0	0	0	—	—	—	—	—
50,00	0,50	5,00	5,00	5,00	5,00	14,85	4,65	13,46	13,57	9,09
60,00	0,50	5,00	0	0	0	—	—	—	—	—
60,00	0,50	5,00	5,00	5,00	5,00	14,83	3,98	12,15	12,50	8,97
100,00	0,50	5,00	0	0	0	—	—	—	—	—
100,00	0,50	5,00	5,00	5,00	5,00	14,84	3,69	11,41	12,89	8,53
120,00	0,50	5,00	0	0	0	—	—	—	—	—
120,00	0,50	5,00	5,00	5,00	5,00	14,54	3,53	10,53	11,64	7,73
130,00	0,50	5,00	0	0	0	—	—	—	—	—
130,00	0,50	5,00	5,00	5,00	5,00	13,15	3,15	9,43	10,15	6,75
150,00	0,50	5,00	0	0	0	—	—	—	—	—
150,00	0,50	5,00	5,00	5,00	5,00	12,05	2,65	8,34	9,74	6,60
Barsa Kelmes lake brine										
20,00	0	0	0	0	0	1,09	0,33	1,06	1,08	0,49
20,00	0	0	5,00	5,00	5,00	16,03	4,87	14,64	14,74	10,37
30,00	0	0	0	0	0	1,62	0,46	1,55	1,58	0,78
30,00	0	0	5,00	5,00	5,00	16,38	5,38	15,51	15,75	10,56
50,00	0	0	0	0	0	2,64	0,62	2,22	2,32	1,07
50,00	0	0	5,00	5,00	5,00	17,39	4,42	15,60	15,66	9,98
60,00	0	0	0	0	0	3,15	0,74	2,35	2,37	1,20
60,00	0	0	5,00	5,00	5,00	17,76	4,47	14,07	14,17	9,86
100,00	0	0	0	0	0	5,32	1,11	3,13	3,25	1,88
100,00	0	0	5,00	5,00	5,00	19,84	4,47	12,94	13,17	9,16
120,00	0	0	0	0	0	6,25	1,22	4,42	4,52	1,83
120,00	0	0	5,00	5,00	5,00	20,45	4,68	13,51	14,08	8,01
130,00	0	0	0	0	0	5,58	1,24	4,06	4,22	1,90
130,00	0	0	5,00	5,00	5,00	18,54	3,74	11,62	12,14	7,36
150,00	0	0	0	0	0	5.52	1,25	3,65	4,03	1,41
150,00	0	0	5,00	5,00	5,00	16,14	3,33	8,91	10,35	7,64

Table 2. The effect of ultrasound in the presence of oxidants on the determination of mercury by atomic absorption spectrometry using the cold vapor method

C NaCI, g/l	US intensity W/sm^2	Found out Hg, mkg/l				
		H_2O_2	HNO_3	Mixture of HNO_3 and H_2O_2	Mixture of HNO_3 and HCl	Bromate mixture
50,00	1,4	14,21	14,10	14,54	14,17	14,60
100,00		13,91	13,71	14,11	14,05	14,14
120,00		13,08	12,86	13,13	13,06	14,52
130,00		12,31	12,02	12,61	12,00	13,35
140,00		10,63	10,75	11,03	10,81	12,42
50,00	1,5	14,86	14,75	14,92	14,83	14,92
100,00		14,70	14,64	14,84	14,77	14,74
120,00		14,60	14,02	14,70	14,46	14,62
130,00		13,35	13,15	13,65	13,24	13,64
140,00		12,00	12,11	12,31	12,13	12,53
50,00	2,0	14,89	14,81	14,90	14,83	14,92
100,00		14,63	14,70	14,85	14,81	14,72
120,00		14,64	14,04	14,73	14,43	14,65
130,00		13,25	13,16	13,63	13,24	13,67
140,00		12,07	12,07	12,34	12,07	12,37

Table 3. The correctness of the methodology of mercury determination.

Sample	Injected Hg, mkg/l			Found out Hg, mkg/l					
				The method					
	Hg^{2+}	MMX	FMA	Hg^{2+}	S_r	MMX	S_r	FMA	S_r
Barsa-Kelmez lake brine	0	0	0	1,62	0,035	0,44	0,057	0,30	0,070
	1,52	0,51	0,26	3,13	0,034	0,92	0,055	0,55	0,073
Slavyanck salt factory brine	0	0	0	0,43	0,044	0,12	0,057	0,06	0,080
	0,21	0,16	0,11	0,62	0,038	0,32	0,055	0,16	0,079
				The method					
Barsa-Kelmez lake brine	Hg^{2+}	MMX	FMA	Hg^{2+}	S_r	MMX	S_r	FMA	S_r
	0	0	0	1,62	0,040	0,44	0,062	0,31	0,078
	1,51	0,51	0,23	3,03	0,042	0,90	0,060	0,52	0,077
Slavyanck salt factory brine	0	0	0	0,40	0,045	0,14	0,061	0,06	0,080
	0,21	0,14	0,09	0,61	0,040	0,32	0,065	0,13	0,080

Table 4. Degree of extraction of mercury during the destruction of organomercury compounds under US.

Sample	Degree of extraction of mercury (%) under US (κHz)							
	17,5	18,5	44,5	50,5	60,5	80,5	101	111
Slavyanck salt mine brine	87	97	96	96	95	95	94	88
“Artemsalt” salt mine No 1 brine	86	96	97	96	96	95	94	87
Baskunchak lake brine	85	97	97	97	96	96	96	89
Bahmut river	88	98	98	97	97	97	95	92

Table 5. Degree of extraction of mercury during the destruction of organomercury compounds under high frequency US.

Sample	Degree of extraction of mercury (%) under high frequency US (кHz)							
Slavyanck salt mine brine	0,91	1,01	1,51	2,01	2,51	3,01	4,01	5,01
“Artemsalt” salt mine No 1 brine	90	96	96	95	95	90	65	38
Baskunchak lake brine	91	97	97	96	96	91	67	39
Bahmut river	92	97	96	96	96	90	69	41

Table 6. The results of mercury determination (n=6; p=0,95).

Sample	Injected Hg, mkg/l	The method		Standard method	
		Found out Hg, mkg/l	S_r	Found out Hg, mkg/l	S_r
Slavyanck salt mine brine	–	0,046	0,081	0,038	0,161
	0,050	0,093	0,071	0,080	0,152
“Artemsalt” salt mine No 1 brine	–	0,025	0,092	0,020	0,172
	0,050	0,073	0,081	0,064	0,161
Baskunchak lake brine	–	0,018	0,091	0,016	0,171
	0,050	0,067	0,082	0,059	0,152
Bahmut river	–	0,034	0,081	0,029	0,161
	0,050	0,082	0,082	0,072	0,152

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