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ATOMIC EMISSION DETERMINATION OF CESIUM IN TABLE SALT AND BRINES

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Atomic emission spectrometry has been shown to be one of the most effective methods for determining cesium content in table salt and brines after preconcentration by coprecipitation. The most efficient collectors for cesium coprecipitation are ferrocyanides with the general formula $Me^{II}_2Fe(CN)_6$ (Me=Cu, Co, Ni). It was found that using copper ferrocyanide enables the extraction of up to 92% of cesium from solution. However, in water, brines, and salt solutions, cesium often exists in forms that cannot be coprecipitated (in more than 50% of cases). Therefore, organic cesium compounds (humic and fulvic acids) must be destroyed. The effect of ultrasound on highly mineralized waters, brines, and salt solutions to convert cesium compounds into coprecipitable forms was studied. It was established that the main factors contributing to the intensifying effect of ultrasound are the occurrence of sonochemical reactions, as well as the mixing and dispersing actions of ultrasound. An express method for determining cesium in table salt and brines was developed, involving the destruction of organic impurities and the coprecipitation of cesium with $Cu_2Fe(CN)_6$ under ultrasonic intensification. The detection limit for cesium is $2 \cdot 10^{-8}$ wt.%.

Keywords: atomic emission spectrometry, cesium, coprecipitation, highly mineralized waters, table salt, brines, ultrasound, metrological characteristics.

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Introduction

The development of analytical chemistry is one of the most important conditions for the creation of new technologies, improving product quality and environmental protection. Atomic emission spectrometry is referred to the most sensitive methods of analytical chemistry for the determination of alkali metals. It is characterized by high selectivity and expressiveness [1].

Table salt is the most important food product and raw material for industry [2]. In addition to the main substance, sodium chloride, it contains macroimpurities, such as salts of calcium, magnesium, potassium, sulfates, carbonates, hydrocarbonates, as well as microimpurities – cesium, copper, cadmium, lead, arsenic, mercury etc. [2]. In the light of the accident at the Chernobyl nuclear power plant, it is necessary to control the content of ^{137}Cs and total Cs in the environment [2]. According to sanitary and anti-epidemic rules and norms, the content of total Cs in table salt should be less than $2 \cdot 10^{-5}$ wt.%.

Table salt and brines are very difficult objects for analysis due to significant matrix influence that makes it impossible to obtain reliable results [1,2]. In this regard, extraction, coprecipitation and sorption are used for the separation of a matrix [2].

One of the promising means of increasing the selectivity and sensitivity of the atomic emission method is its combination with pre-concentration of the impurities by sorption or coprecipitation [1,3].

The use of sorption on synthetic ion exchangers requires a significant concentration of ion exchangers (about 7–10 g·dm^{-3}) and the degree of extraction of cesium does not exceed 80% [2]. Coprecipitation on ferrocyanides is considered to be more effective for the extraction of cesium from mineralized waters [4].

The direct determination of cesium in table salt using such a sensitive method of analysis as atomic emission spectrometry is not possible due to low contents and significant matrix effects; which necessitates the use of the concentrating. Among the most effective methods of concentrating cesium combined with atomic emission spectrometry are extraction, coprecipitation, sorption [2]. Methods based on chemical oxidation of organic substances are the most widespread for the destruction of organic compounds [5].

Thus, the Codex Standard for table salt commands the preliminary destruction of organic matter by boiling with ammonium persulfate in acidic medium for 30–40 min. The oxidation by chlorine, ozone, hydrogen peroxide, and boiling with mineral acids and with potassium permanganate in an acidic media are also used [6]. However, the chemical methods of destruction of organic substances are long-term (more than 6.5 h) and cause the contamination of the analyzed solutions with impurities from the used reagents. In this regard, physical methods of destruction of organic substances are also used: ultraviolet (UV) irradiation, photochemical oxidation, electrochemical oxidation, irradiation with a stream of ionizing radiation, etc. [7–9]. The applications of UV irradiation and photochemical oxidation have been most fully studied [8,9]. When water and brines are treated with UV radiation of a mercury lamp with a power of 250–500 W for 3–12 h, the almost complete (more than 95%) destruction of organic compounds is observed [9].

UV irradiation with additional introduction of chemical oxidizing reagents gives the possibility to reduce the duration of organic substance destruction to 15–25 min and promotes the removal of dissolved oxygen from the analyzed samples that accelerates the voltammetric analysis [8]. However, the additional introduction of chemical reagents causes the contamination of the analyzed samples. Electrochemical oxidation is also used to destroy organic substances in the analyzed solutions [7], but in solutions containing a significant amount of chloride ions its use is impractical due to the saturation of the sample with chlorine [8]. The use of radiolysis for the destruction of organic matter has not become widespread due to the high potential for radiation damage to laboratory personnel; the absorbed dose of 10 Gy·s^{-1} is required for complete destruction of organic matter [10]. Microwave irradiation is used to intensify sample preparation: dissolution, destruction of organic compounds, and mineralization of food. The restraining factor is the rather significant price of the equipment [10]. It was shown that the use of ultrasound to intensify analytical processes has a number of advantages over the use of other physical methods of exposure [7]. Yurchenko et al. [11] first proposed to use the effect of ultrasonic vibrations for the destruction of organic compounds in the analysis of salt and brines. The appearance of cavitation bubbles in the ultrasound field, their growth, pulsation and collapse is an effective mechanism of local energy concentration leading to the formation of large amounts of radicals (10^4–10^6 at the rupture of each cavitation bubble), which have high reactivity [12].

The purpose of this work was to develop the method for the determination of cesium in table salt with ultrasound intensification of the process resulting in improved metrological characteristics.

Experimental

An atomic absorption spectrometer AAS-3 with the electrothermal atomizer EA-3 (Germany), analytical scales ONAUS RA 64 (65/0.0001 g), pH-meter rn-150 MI, the device for shaking of AIU 6s, standard aqueous solution of cesium of 10 mg·ml^{-1}, argon and helium of high purity, distilled water, measuring utensils were used. The high cesium contents were determined by the atomic emission method in an «acetylene-air» flame at a wavelength of 852 nm. ^{137}Cs was determined on a beta radiometer Rub-01P with a detector BDZHB-06P. Ultrasound treatment of solutions was performed using an upgraded ultrasound dispergator UZDN-1M with a set of magnetostrictive emitters that permits to treat the solutions by ultrasound of 15–47 kHz frequency and intensity from 0.5 to 25 W·cm^{-2}. A T-23 centrifuge (6000 rpm) was used to separate the precipitate from the solution. The experiments were performed in a reactor with a water jacket at the temperature of (20±1)^{0}C. Double-distilled water and reagents were of chemical grade. The intensity of ultrasound was determined by calculation and experimental methods.

Results and discussion

To establish the optimal concentration conditions, the concentration of NaCl, the duration of contact of the precipitate with the solution, the amount of collector (mmol·dm^{-3}), temperature, and the amount of Cs were changed by the precipitation. For this purpose, 1 dm^3 of NaCl solution (40–200 g·dm^{-3}) was placed in chemical beakers and certain amounts of $MgCl_2$, sulfates, $K_4Fe(CN)_6$, HNO_3, cesium solution, and copper, cobalt or nickel chloride were added to it.

The resulting mixture was stirred for selected time. The precipitate was separated from the solution by siphoning and centrifugation. Then the precipitate was dried, weighed and transferred to a cuvette of beta radiometer to determine the content of ^{137}Cs. To determine the high cesium contents, the precipitate was dissolved in 12 ml of diluted hydrochloric acid (1:1) under heating. Then 3.0 ml of sodium chloride solution (200 g·dm^{-3}) diluted with double-distilled water to 20 ml was added. Cesium was determined in the resulting concentrate with atomic emission method at a wavelength of 852 nm in «acetylene-air» flame. NaCl was administered to increase the sensitivity of cesium according to [13].

The experiments showed that NaCl does not affect the degree of coprecipitation of cesium to concentrations of 100, 75, and 60 g·dm^{-3}, respectively, at the use of $Me_2Fe(CN)_6$ collectors (Me=Cu, Co, and Ni) (Tables 1–3). The amount of a collector should be at least 6, 5 and 7 mmol·dm^{-3}, respectively. The time of contact of the precipitate with the solution should be at least 10, 12 and 12 min and the pH of the solution was within 3–8 for $Cu_2Fe(CN)_6$ and $Co_2Fe(CN)_6$ and 3–7 for $Ni_2Fe(CN)_6$. In the absence of mixing, the degree of coprecipitation of cesium rises with the increase of the solution temperature (Tables 1–3).

Table 1

Effect of NaCl concentration, amount of collector (AC), solution pH, contact time (CT) of the collector with the solution, and temperature (t) on the degree of Cs coprecipitation (CC) using $Cu_2Fe(CN)_6$ as the collector

Concentration of NaCl, g·dm^{-3}	AC, mmol·dm^{-3}	pH	CT, min	t, ^{0}C	CC, %
40	6	3	10	20	92
50					92
70					92
100					92
110					90
120					88
150					85
100	2				55
	3				69
	4				78
	5				85
	6				92
	7				92
	10				92
	6	2			85
		3			92
		4			92
		5			91
		6			91
		8			92
		10			87
		3	2		70
			4		75
			6		84
			8		88
			10		92
			12		92
			14		92
			3	40	41
				50	59
				60	65
				70	75
				80	85
				90	88
				100	92

Thus, the best collector is $Cu_2Fe(CN)_6$ under the following conditions: the amount of NaCl is less than 100 g·dm^{-3}, the amount of collector is not less than 6 mmol·dm^{-3}, the solution pH is 3–8, and the contact time of the precipitate with the solution is not less than 10 min.

It should be noted that the order of mixing and the ratio of reagents significantly influence the degree of coprecipitation. The maximum possible degree of coprecipitation is achieved by introducing a small excess of $K_4Fe(CN)_6$ added to the $CuCl_2$ solution. These conditions correspond to those described in ref. [14]. As follows from Table 4, change in Cs concentration to 150 μg·dm^{-3} does not affect the degree of coprecipitation. With a further increase of the amount of cesium over 150 μg·dm^{-3}, the degree of coprecipitation decreases. This indicates the adsorption nature of the coprecipitation process. Thus, the possibility of quantitative (more than 90%) concentration of cesium from highly mineralized waters, brines and table salt on $Cu_2Fe(CN)_6$ collector is shown.

Table 2

Effect of NaCl concentration, amount of collector (AC), solution pH, contact time (CT) of the collector with the solution, and temperature (t) on the degree of Cs coprecipitation (CC) using $Co_2Fe(CN)_6$ as the collector

Concentration of NaCl, g·dm^{-3}	AC, mmol·dm^{-3}	pH	CT, min	t, ^{0}C	CC, %
40	5	4	12	20	92
50					92
75					91
80					88
100					85
120					82
150					60
75	2				62
	3				75
	4				85
	5				91
	6				91
	7				91
	10				91
	5	2			88
		3			90
		4			91
		5			91
		6			91
		8			90
		10			89
		4	2		68
			4		74
			6		80
			8		88
			10		90
			12		91
			14		91
			20	40	37
				50	55
				60	68
				70	74
				80	83
				90	87
				100	91

In solutions of table salt, brines and highly mineralized waters cesium is bounded with humic and fulvic acids, which complicates its quantitative concentration by coprecipitation (Table 5) [1].

To convert metals into ionic forms, boiling of sample solutions for 40 min with strong oxidants (H_2SO_4+$(NH_4)_2S_2O_8$, HNO_3, H_2SO_4+$KMnO_4$) is used that prolongs and complicates the analysis, increases the risk of contamination of sample solutions with Cs impurities. As can be seen from Table 5, the positive effect was observed for the process performed in the presence of all the above oxidants. It is established that the optimal parameters of ultrasound are as follows: frequency of 18–44 kHz, intensity of more than 7 W·cm^{-2}, and time of more than 3 min (Table 6).

However, in the analysis of table salt with a radioprotector (the content of $Fe_4[Fe(CN)_6]_3$ is 1 wt.%), the transfer of Cs to forms coprecipitated by ultrasound alone could not be achieved even with an intensity of 15 W·cm^{-2} (Table 5). In this regard, the process in the presence of oxidants has been studied. The effects of nitric acid, hydrogen peroxide (30%), a mixture of hydrogen peroxide and nitric acid (1:1) and a mixture of nitric and hydrochloric acids (1:3), recommended

Table 3

Effect of NaCl concentration, amount of collector (AC), solution pH, contact time (CT) of the collector with the solution, and temperature (t) on the degree of Cs coprecipitation (CC) using $Ni_2Fe(CN)_6$ as the collector

Concentration of NaCl, g·dm^{-3}	AC, mmol·dm^{-3}	pH	CT, min	t, ^{0}C	CC, %
40	7	4	12	20	91
50					90
60					90
70					85
100					75
120					64
150					42
60	2				42
	3				51
	4				70
	5				79
	6				88
	7				90
	10				90
	7	2			86
		3			89
		4			90
		5			90
		6			90
		8			88
		10			84
		4	2		64
			4		71
			6		78
			8		85
			10		89
			12		90
			14		90
			3	40	36
				50	53
				60	63
				70	72
				80	84
				90	87
				100	90

for the intensification of sample preparation by microwave irradiation, were studied as oxidants [13].

In this case, the quantitative extraction of cesium requires 1 dm^3 of the sample solution and at least 10 ml of HNO_3 solution or 5 ml of H_2O_2 solution or the same amount of a mixture of H_2O_2 and HNO_3 or a mixture of HNO_3 and HCl. Thus, the introduction of hydrogen peroxide seems optimal. The use of ultrasound in the presence of hydrogen peroxide allows quantitatively converting cesium into molds. Coexisting and improving the metrological characteristics of the analysis, while the intensity of ultrasound can be reduced from 7 to 2 $W \cdot cm^{-2}$ (Table 5). Under the optimal conditions, the degree of coprecipitation of cesium reaches 92% and cannot be increased by increasing the amount of collector and the contact time of the precipitate with the solution. To increase the degree of coprecipitation, the influence of ultrasound was used. Ultrasound parameters (frequency of 20–44 kHz, intensity of 2 $W \cdot cm^{-2}$, and exposure time of 30 s) were determined experimentally (Table 7). At these conditions, the degree of coprecipitation increases to 98–99%. The number of collectors can be reduced by 5 times. The presented data show the importance of ultrasound action on the process in the impossibility of sound-chemical reactions (saturation of the sample with CO_2) at a constant temperature.

The main factors of intensifying action of ultrasound on transfer of Cs to the forms exposed to the coprecipitation in the course of sound-chemical reactions are summarized in Table 8.

Thus, the use of the ultrasound treatment of samples to determine cesium in highly mineralized water, brines and salt allows increasing the expressiveness, reducing the detection limit and improving the metrological characteristics of the analysis. The detection limit of cesium in highly mineralized waters, brines and table salt by the procedure developed in this work is $2 \cdot 10^{-8}$%.

Table 4

Dependence of the coprecipitation degree of Cs on $Cu_2Fe(CN)_6$ on the amount of microcomponent

Amount of cesium, $\mu g \cdot dm^{-3}$	Coprecipitation degree, %
5	92
25	92
50	92
150	92
155	90
170	82
200	66
250	52

Conclusions

Cesium coprecipitation with Cu^{II}, Co^{II} and Ni^{II} ferrocyanides was studied. It was shown that when the most efficient collector, $Cu_2Fe(CN)_6$, is used under optimal conditions, the degree of Cs deposition was 92%. It was established that more than 50% of Cs is found in waters, brines and salt solutions in forms that cannot be coprecipitated. The use of ultrasound in the determination of Cs for the conversion of its compounds into forms that can be coprecipitated, as well as for the intensification of concentration by

Table 5

Results of cesium determination in different natural brines[a] (P=0.95, n=6)

Object of analysis	Injected Cs, $\times 10^7$, %	Found out Cs, $\times 10^7$, $\%/S_r$					
		without treatment	with treatment				
			1	2	3	4	5
Artemsil table salt	0	–	–	–	–	–	–
	2.00	2.07/0.03	1.76/0.09	1.86/0.06	1.90/0.05	1.87/0.07	2.06/0.05
Heroic salt factory table salt	0	4.26/0.03	8.97/0.08	9.26/0.05	9.31/0.05	4.29/0.06	5.31/0.05
	2.00	6.11/0.04	10.45/0.09	11.19/0.06	11.26/0.06	6.19/0.06	7.27/0.06
Heroic salt factory table salt[b]	0	4.26/0.03	8.76/0.08	4.35/0.05	9.31/0.05	4.29/0.06	5.31/0.05
	2.00	6.11/0.04	10.58/0.09	6.29/0.06	11.29/0.06	6.19/0.06	7.27/0.06
Brine of Slavyansk salt factory	0	3.81/0.04	9.43/0.09	9.66/0.06	9.68/0.06	3.96/0.06	5.76/0.06
	2.00	5.75/0.03	11.55/0.08	11.70/0.07	11.73/0.07	6.01/0.07	7.88/0.07
Brine of Syvash	0	1.88/0.05	6.04/0.09	6.34/0.06	6.46/0.06	2.06/0.06	2.27/0.06
	2.00	4.01/0.04	7.85/0.09	8.43/0.07	8.59/0.07	3.09/0.07	4.81/0.07

Notes: [a] – the results of six experiments are averaged (n=6); [b] – the experiments were performed without stirring the solution with exposure for 12 min.

coprecipitation with $Cu_2Fe(CN)_6$ has been studied. The developed express method for the determination of cesium involves the destruction of organic impurities and coprecipitation of cesium with $Cu_2Fe(CN)_6$ under ultrasonic intensification of the process. The detection limit of cesium is $2 \cdot 10^{-8}$%.

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Table 6

Effect of ultrasound parameters on the degree of destruction of organic cesium compounds

Ultrasonic intensity, $W \cdot cm^{-2}$	Degree of Cs organic compound destruction, %	Ultrasonic frequency, kHz	Degree of Cs organic compound destruction, %	Time of ultrasonic treatment, min	Degree of Cs organic compound destruction, %
4	67	15	95	0.5	84
5	85	18	98	1	93
6	94	20	98	2	96
7	98	44	98	3	99
8	98	45	96	4	99
9	98	47	94	5	99

Table 7

Influence of oxidizer on the degree of cesium extraction (P=0.95, n=6)

Sample	Found out Cs, $\times 10^7$ wt.%/S_r				
	HNO_3	H_2O_2	HNO_3+H_2O_2	HNO_3+HCl	without oxidizers
Table salt of the Heroic Saltworks	9.29/0.05	9.31/0.05	9.39/0.06	9.36/0.06	4.26/0.03
Salt of Slavic salt-boiling plant	9.71/0.06	9.68/0.06	9.74/0.07	9.70/0.07	3.81/0.04
Highly mineralized water, Genichesk saltworks	6.42/0.06	6.46/0.06	6.51/0.07	6.44/0.07	1.88/0.05
Table salt of the Heroic saltworks with the radioprotector	9.31/0.06	9.31/0.05	9.37/0.06	9.35/0.06	4.26/0.03

Table 8

Effect of ultrasound parameters on degree of cesium coprecipitation (n=6)

Ultrasound intensity, $W \cdot cm^{-2}$	Degree of Cs coprecipitation, %	Ultrasound frequency, kHz	Degree of Cs coprecipitation, %	Time of ultrasonic treatment, min	Degree of Cs coprecipitation, %
0.5	36	15	80	10	76
1	88	18	92	15	80
2	98	20	99	20	90
4	98	44	99	25	98
5	99	45	90	30	98
6	98	47	87	35	98

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АТОМНО-ЕМІСІЙНЕ ВИЗНАЧЕННЯ ЦЕЗІЮ У КУХОННІЙ СОЛІ ТА РОЗСОЛАХ

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В роботі показано, що атомно-емісійна спектроскопія відноситься до найкращих методів визначення вмісту цезію в кухонній солі та розсолах після попереднього співосадження. Найкращими колекторами для співосадження є фероціаніди загальної формули $Me^{II}_2Fe(CN)_6$ (Me=Cu, Co, Ni). Встановлено, що використання фероціаніду міді дає можливість екстрагувати до 92% цезію з розчину. Проте у воді, розсолах і розчинах солі цезій знаходиться у формах, з яких не може бути співосадженим (більше 50% випадків), тому ці органічні сполуки (гумінові і фільвові кислоти) повинні бути зруйновані. Було вивчено дію ультразвуку на високомінералізовані води, розсоли і розчини солі для перетворення сполук цезію у форми з яких він може бути співосаджений. Встановлено, що основними факторами, які обумовлюють інтенсифікуючу дію ультразвуку на переведення цезію у форми, з яких він може бути співосадженим, є сонохімічні реакції, перемішуюча і розмішуюча дія ультразвуку. Розроблено експрес-метод визначення цезію в кухонній солі і розсолах, який полягає в руйнуванні органічних домішок у розчинах і співосадженні цезію з $Cu_2Fe(CN)_6$ під дією ультразвуку. Нижня межа визначення цезію дорівнює $2 \cdot 10^{-8}$ мас.%.

Ключові слова: атомно-емісійна спектроскопія, цезій, співосадження, високомінералізовані води, кухонна сіль, розсоли, ультразвук, метрологічні характеристики.

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Atomic emission spectrometry has been shown to be one of the most effective methods for determining cesium content in table salt and brines after preconcentration by coprecipitation. The most efficient collectors for cesium coprecipitation are ferrocyanides with the general formula $Me^{II}_2Fe(CN)_6$ (Me=Cu, Co, Ni). It was found that using copper ferrocyanide enables the extraction of up to 92% of cesium from solution. However, in water, brines, and salt solutions, cesium often exists in forms that cannot be coprecipitated (in more than 50% of cases). Therefore, organic cesium compounds (humic and fulvic acids) must be destroyed. The effect of ultrasound on highly mineralized waters, brines, and salt solutions to convert cesium compounds into coprecipitable forms was studied. It was established that the main factors contributing to the intensifying effect of ultrasound are the occurrence of sonochemical reactions, as well as the mixing and dispersing actions of ultrasound. An express method for determining cesium in table salt and brines was developed, involving the destruction of organic impurities and the coprecipitation of cesium with $Cu_2Fe(CN)_6$ under ultrasonic intensification. The detection limit for cesium is $2 \cdot 10^{-8}$ wt.%.

Keywords: atomic emission spectrometry; cesium; coprecipitation; highly mineralized waters; table salt; brines; ultrasound; metrological characteristics.

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