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AN ANALYSIS OF BRINES FOR CHROMIUM CONTENT BY SPECTROPHOTOMETRIC METHOD USING CO-PRECIPI-TATION CONCENTRATION

Abstract: Coprecipitation of chromium on magnesium hydroxide was studied. Coprecipitation mechanism was proposed. The use of high-frequency ultrasound (US) and simultaneous action of ultrahigh-frequency and low-frequency US for intensification of chromium coprecipitation was investigated. It has been found that dispersing and mixing effects are the determining factors of the US action on co-precipitation concentration. The method of spectrophotometric determination of chromium in brines has been developed. The content of chromium in the natural brines of Ukraine was determined. It was shown that the use of double-frequent US allows us to increase the degree of chromium determination from 92-93% up to 96-98% and also to improve metrological characteristics.

Key words: Chromium, brines, ultrasound, coprecipitation, spectrophotometry, metrologic characteristics.

Language: English

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Introduction

Chromium is toxic trace elements having cancerogenic effects. Its content is regulated in drinking water and food products [1,p.24; 2,p.662;

3,p.124], the maximum possible content of chromium is 0.1-0.5 mg/dm³. Brines are a raw material for production of various types of kitchen salt [4,p.158;5,p.576;6,p.763;7,p.45]. The content of

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chromium in kitchen salt should not be more than 0.1 mg/kg. However, the presence of chromium in natural brines leads to its appearance in kitchen salt [8,p.247;9,p.37;10,p.11]. We have previously developed the methodic for electrothermal atomic absorption determination of chromium in brines and kitchen salt. But not all laboratories have atomic absorption spectrometers. Therefore, it became necessary to develop the methodics of spectrophotometric determination of chromium in brines. Direct spectrophotometric determination is not possible due to significant matrix effects and insufficient sensitivity. Therefore, it is necessary to use preconcentration by co-precipitation, which is practically independent of the mineralization of the solution and does not require the use of toxic substances.

The purpose of this work is to develop an environmentally safe methodics for spectrophotometric determination of chromium in brines using coprecipitation concentration with improved metrological characteristics.

Experimental

We used spectrophotometer SF-46, electronic scales OHAUS PA 64 (65/0.0001 g), ultrasound disperser UZDN, centrifuge T23, measuring laboratory flasks, according to DSTU 1770-74, electron ionomer Rn-673, bidistilled water.

To prepare standard chromium solutions, standard samples of composition of MSO solutions with a chromium concentration of 1 mg/l were used. Sodium chloride, phr., was further purified by recrystallization. HCl, phr., was further purified by isotopic distillation.

A sample of kitchen salt with mass of 2.00 g is dissolved in 10 cm³ of bidistilled water, added with 0.05 cm³ of hydrochloric acid (1:1) and 10 cm³ of mixture of acetylacetone and chloroform (1:1), the mixture was shaken for 1 min, organic phase was separated. The water was transferred to a tube, pH was raised up to 6 with ammonia, and 10 cm³ of acetylacetone was added. The tube was placed in a magnetostrictive radiator and affected by a 44 kHz US system with an intensity of 2 W/cm² for 20 seconds. Then 0.5 cm³ of hydrochloric acid, 10 cm³ of acetylacetone were added to the tube and shaken for 1 minute. Chromium (III) detection limit - 0.01 mg/kg. For analysis, 10 g of brine with a sodium chloride content of not more than 200 g/cm³ was taken and brine was diluted with bydistilled water. 2 g of kitchen salt was dissolved in 10 cm³ of bidistilled water, 0.5 cm³ of hydrogen peroxide, was treated by ultrasound with frequency of 44 kHz, intensity of 2.0 W/cm² for 1 min. Then content of total chromium was determine.

Results and discussions

Figure 1 shows the dependence of the degree of destruction of organic compounds in the natural brines of the Geroyskoye source on the frequency of the US at the maximal possible intensity for modern piezoceramic emitters - 12 W/cm². From the experimental data, presented in Figure 1, it can be seen that with an increase in the frequency of US, the degree of chromium destruction decreases significantly. The decrease in the degree of ROP destruction is obviously explained by the fact that with an increase in the frequency of the US, an increase in the intensity of the US is also necessary to raise to the corresponding level of cavitation activity. It should also be noted that for solutions of kitchen salt and sea water, the similar dependencies of ROP destruction degree on the frequency of MW were obtained.

However, as the content of organic substances (humic and fulvic acids) in brine samples and sea water decreased, the dependence on frequency is less important; that can be explained by the fact that with a lower content of organic substances, a lower level of cavitation activity is needed for their destruction, which depends on the frequency of the US.

Figure 2 shows the dependence of degree of destruction of organic chromium compounds in brines on the intensity of US at its frequency of 400 kHz and the action time of 2 minutes. As follows from Figure 2, with the increase in US intensity, the degree of destruction of organic chromium compounds increases.

The effect of the time of US action on the degree of ROP destruction at different US frequencies was also investigated, while the intensity of the US was maximal possible - 12 W/cm². As follows from the results of the experiments given in Fig. 2, in order to achieve the ROP destruction rate 90%, the time of US action should be the longer the higher US frequency, since with an increase in the US frequency, it is necessary to raise the corresponding level of cavitation activity and increase the US intensity, which is limited by the mechanical strength of the piezoelectric power of US intensity not more than 12 W/cm². From the results of experiments, it also follows that it is possible to use ROP for destruction in brines of US action with frequency up to 200, 250 and 600 kHz, respectively, when the ROP destruction time increases up to 10 min [11,p.34].

However, with an increase of time of action of the US, the metrological characteristics of the Chromium determination results deteriorated in all samples. Moreover, with an increase in the frequency of US, for the destruction of organic compounds, a large intensity or duration of the US action was required. In the analyzed samples, characterized by a large content of organic substances, with an increase in the frequency of US, a significant deterioration in the metrological characteristics of the obtained results was observed. Therefore, the satisfactory metrological

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characteristics of the Chromium determination results in salt brines and solutions of kitchen salt were obtained with use of US with a frequency of up to 100 kHz. At the same time, compared with use of previously studied low-frequency range of US, the results of analysis, obtained using medium-frequency US had better reproducibility. It may be explained by higher level of stability of piezoelectric emitters operation compared to magnetostrictive ones [12,p.45].

Thus, for the destruction of organic substances in brines, US can be used in the frequency range from 18 to 100 kHz, and in sea water - from 18 to 200 kHz; the results can be obtained in the frequency range of 80-100 kHz, respectively.

The two types of bubbles are formed in the cavitation field: large deformed bubbles (VDB), which cause physicochemical effects: surface cleaning, mass exchange, erosion and small spherical bubbles (GSB), during the splitting of which sound chemical reactions and sonoluminescence occur. When using the combined action of high (1 MHz) and low frequencies (18-47 kHz), the total mass of the GSB prevails over the total mass of the airborne bubbles. In this regard, the use of compatible high and low frequency SLM for the destruction of organic compounds in salt solutions and brines has been studied. In this case, laboratory equipment was used, the same as in the study of the combined action of high and low frequencies in sonoluminescent spectroscopy.

The change in frequency of the low-frequency US from 18 up to 47 kHz by the value of the degree of ROP destruction in the brines was not affected, a comparison of the obtained results using high-frequency US with a frequency of 1 or 2 MHz show us that the best results were obtained in the first case (Table 2).

The optimal intensity of the high-frequency US and the low-frequency US depends on their relation, the type of the analyzed product and frequency of high-frequency US (Table 1). In this case, the optimal intensity is an intensity that ensured the achievement of the maximum possible degree of destruction of organic compounds. It should be noted that the optimum intensity when using only one low-frequency US that is significantly higher and ranged from 7.0 to 10 W/cm² [13,p.67; 14,p.77; 15,p.17].

The action time of the two frequency US should be not less than 0.5 minutes for sea and river water, and not less than 1.0 minutes for brines of Ukrainian sources, and for brines of Lake Jaksá-Archaeologist (Kazakhstan) - 2 minutes, since the last source is characterized by abnormally high content of organic

substances (Table 3). It should also be noted that even with a 3 times increase in time of US action, the degree of destruction of organic compounds does not change. The order of switching on low and high frequency US did not affect the results.

The proposed method provides the obtained results of analysis with better metrological characteristics than standard method, based on destruction of organic compounds in salt solutions and brines. An improvement of metrological characteristics is explained by the higher stability of ultrasonic emitters at low US intensities.

The most expressive method is the method based on the use of low-frequency US (10 W/cm²) and the method based on the use of low-frequency US with hydrogen peroxide addition, but the last method is hindered by the need to introduce additional reagents. The maximal possible degree of ROP destruction is provided by the method, based on the use of medium frequency US (80-100 kHz) and the method based on the use of simultaneous action of high and low frequency US. The first method does not require complex design and provides results with better metrological characteristics, and the second is more expressive.

Conclusions

1. Coprecipitation of chromium on magnesium hydroxide was studied. It has been shown that at optimal conditions degree of coprecipitation does not exceed 93%, respectively. To increase degree of coprecipitation, it is recommended to use US action.

2. We studied the use of US in determining chromium in brines: how to transfer chromium compounds to the forms undergoing, coprecipitation, as well as how to intensify concentration by coprecipitation on magnesium hydroxide.

3. A project of an express method for determining chromium in brines has been developed, including ROP destruction, coprecipitation of chromium on magnesium hydroxide with US process intensification. In the resulting chromium concentrate, the SF was determined by the diphenylcarbazide method at 535 nm. Lower limit of chromium detection in brines is 0.001 mg/kg, relative standard deviation of analysis results does not exceed 0.08.

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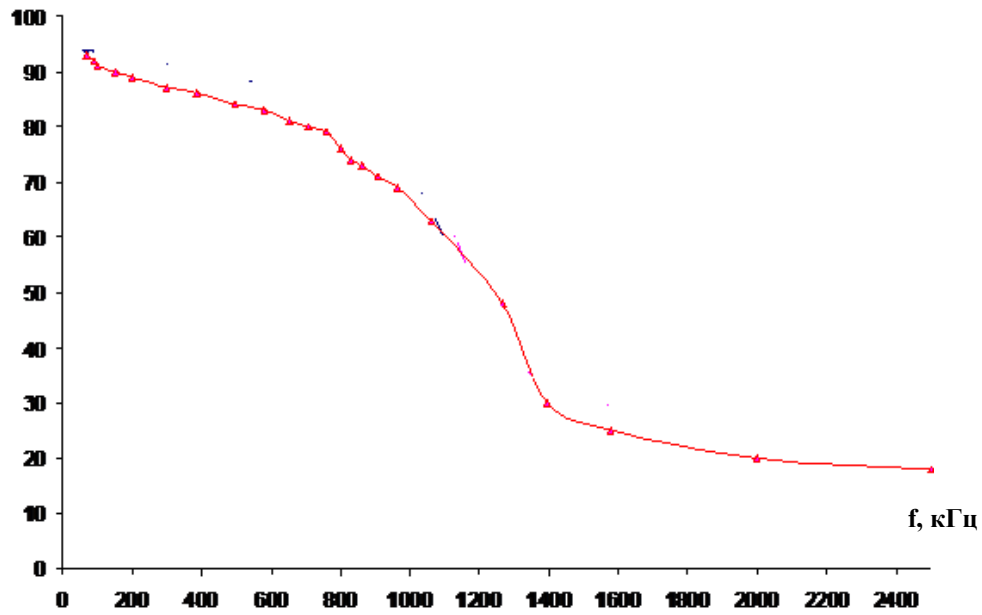


Fig.1 Ultrasound frequency dependence on the degree of destruction of organic compounds in the natural brines

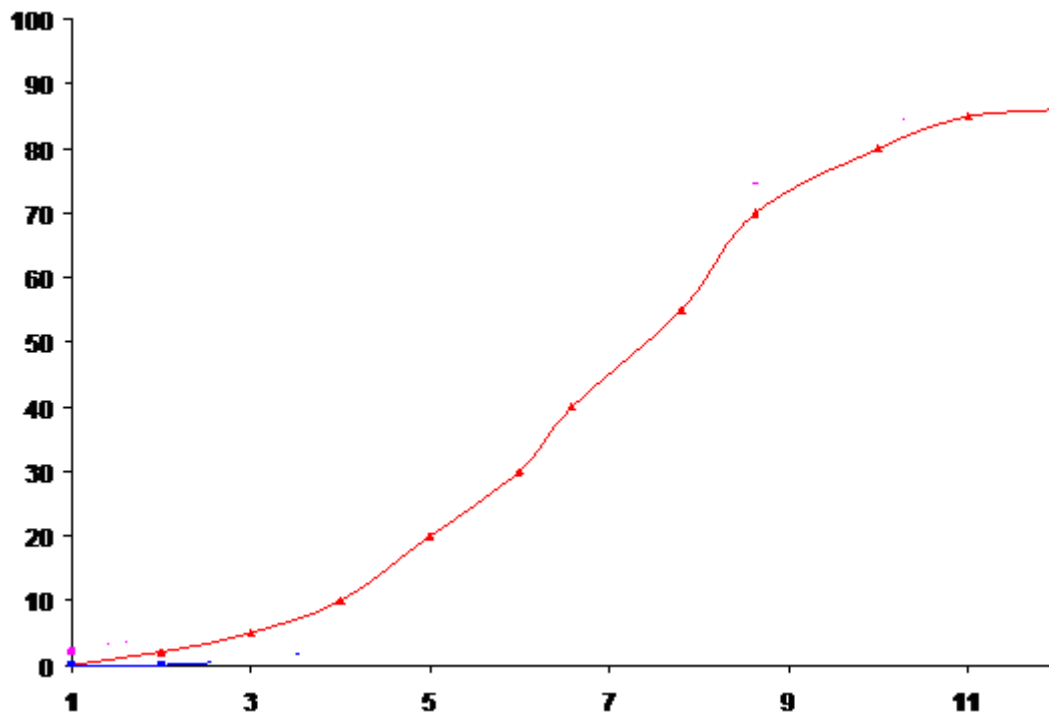


Fig.2 Ultrasound intensity dependence on the degree of destruction of organic compounds in the natural brines

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Table 1. Ultrasound frequency influence on the degree of destruction of Chromine ROP

Sample	The degree of destruction of organic compounds %	
	1 Mhz	2 Mhz
Brine from Sloviansk factory	99	98
Brine from Bascunchak lake, Russia	99	96
Brine from Barsa-Kelmez lake, Kazahstan	99	96
Brine from Henichesk factory	97	97
Sea water, Yalta village	99	97
River water, Bahmut river.	99	96

Table 2. Ultrasound intensity influence on the degree of destruction of organic compounds in the natural brines

US intensity, W/sm ²	degree of destruction of organic compounds % at US intensity, W/sm ²					
	1	2	3	4	5	6
<i>Brine from Heroiske factory</i>						
1	45	61	74	86	90	96
2	93	98	97	99	98	99
3	93	96	98	99	99	99
4	943	97	98	99	99	99
<i>Brine from Sloviansk factory</i>						
1	66	67	72	83	87	92
2	97	98	98	99	98	99
3	98	99	98	99	99	99
4	98	99	98	99	99	99
<i>Brine from Barsa-Kelmez lake, Kazahstan</i>						
1	47	57	65	743	75	80
2	90	93	98	98	98	99
3	93	96	98	99	99	99
4	96	976	98	99	99	99

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Table 3. Ultrasound time influence on the degree of destruction of ROP

<i>Sample</i>	<i>US time, min.</i>	<i>The degree of destruction of ROP, %</i>
<i>Brine from Sloviansk factory</i>	0,5	94
	1,0	98
	2,0	99
	3,0	99
	4,0	99
<i>Brine from Barsa-Kelmez lake, Kazakhstan</i>	0,5	83
	1,0	87
	2,0	98
	3,0	98
	4,0	99

Table 4. The results of chromine determination (n=5; p=0,95)

<i>Sample</i>	<i>Found out, mg/kg</i>
<i>Brine from Sloviansk factory</i>	0,033/0,092
<i>Brine from Barsa-Kelmez lake, Kazakhstan</i>	0,543/0,092
<i>Without organic compounds destruction</i>	
<i>Brine from Sloviansk factory</i>	-
<i>Brine from Barsa-Kelmez lake, Kazakhstan</i>	0,220/0,060

Table 5. Comparative characteristic of destruction methods of ROP in brines (n=5; p=0,95)

<i>Factor</i>	<i>Factors value</i>
<i>Destruction of ROP by the standard method– US of 22 kHz frequency</i>	
<i>Optimal US intensity</i>	10 W/sm ²
<i>Time of the process</i>	0,3–0,5 min.
<i>Standard deviation</i>	0,070–0,087
<i>Destruction of ROP by the method– with 100 kHz US frequency</i>	
<i>Optimal US intensity</i>	12 W/sm ²
<i>Time of the process</i>	2–4 min.
<i>Standard deviation</i>	0,062–0,071

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References:

- Lurie, Yu.Yu. (1984). *Analiticheskaya himiya stochnyh vod.* (p.448). Moscow: "Chemistry".
- Sato, A. (2019). *Bunseki kagaky.* V.24,(10), pp.663-667.
- Sato, A. (2020). *Bunseki kagaky.* V.34,(10), pp.123-127.
- Yurchenko, O.I. (2019). *Theoretical & Applied Science.* V. 33, pp.158-163.
- Baklanov, A.N. (2007). *Anal. Chem.,* V.62, pp.575-582.
- Chmilenko, F.A. (1993). *Ukrainian chemical journal,* V.59, pp.762-766.
- Kuzmin, N.M. (1996). *Anal. Chem.,* V.1, pp.44-48.
- Volkova, N.N. (1987). *Anal. Chem.,* V.42, pp.246-251.
- Chmilenko, F.A. (1991). *Ukrainian chemical journal,* V.57, pp.37-39.
- Avruhina, A.K. (1979). *Analytycheskaya himiya choma.* (p.222). Moscow: "Chemistry".
- Margulis, M.A. (1986). *Zvukohimicheskiye reakcii.* (p.228). Moscow: "Chemistry".
- Reznikov, A.A. (1970). *Metody analiza prirodnyh vod.* (p.480). Moscow: "Nauka".
- Furman, A.A. (2020). *Neorganicheskie chloridy.* (p.410). Moscow: "Chemistry".
- Furman, A.A. (2020). *Povarennaya sol.* (p.287). Moscow: "Chemistry".
- Petrov, O.V. (2020). *Metody analiza rassolov.* (p.176). Moscow: "Chemistry".