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O.I. Yurchenko [a], T.V. Chernozhuk [a], A.N. Baklanov [a], M.V. Nikolenko [b], V.L. Cherginets [c], A.L. Rebrov [c]

DETERMINATION OF POTASSIUM AND LITHIUM IN BRINES BY SONOLUMINESCENCE SPECTROSCOPY METHOD

[a] V.N. Karazin Kharkiv National University, Kharkiv, Ukraine
[b] Ukrainian State University of Science and Technologies, Dnipro, Ukraine
[c] Institute for Scintillation Materials of the National Academy of Sciences of Ukraine, Kharkiv, Ukraine

The results of the development of a method for the sonoluminescence spectroscopic determination of K and Li in highly concentrated synthetic and natural brines with the simultaneous use of ultra-high (10–25 MHz) and low (18–23 kHz) frequency ultrasound of different intensities for sonoluminescence initiation are presented. The newly developed method also possesses considerably better metrological characteristics. A comparison of the proposed method with the flame atomic-absorption spectrometry method shows that the latter possesses better metrological characteristics than the proposed one; however, it cannot be used for the quantitative determination of the main substance in brines. The developed method makes it possible to decrease the lower detection limits of potassium and lithium chlorides in brines by 12 times (down to 0.1 $g \cdot dm^{-3}$) as compared with the simultaneous use of ultrasound of high and low frequencies. The optimal conditions are found to be high-frequency ultrasound with a frequency within 20–22 MHz and an intensity within 20 $W \cdot cm^{-2}$ plus low-frequency ultrasound with a frequency within 19–22 kHz and an intensity within 1.3–1.5 $W \cdot cm^{-2}$.

Keywords: natural brines, sonoluminescence spectroscopy, ultrasound, potassium, lithium.

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Introduction

Natural brines serve as raw material for the production of both dietary salt and sodium chloride of chemical quality for various purposes [1,2]. In the latter case, the information about both the main saline component – sodium chloride and admixtures of potassium and lithium chloride – is urgent since K^+ and Li^+ ions are isomorphic to Na^+ and the corresponding admixtures are hardly removable. The knowing these data gives possibility to determine not only the direction of the following use of the particular brine but also to provide the most effective work of vacuum pans (thermophysical characteristics) at the brine evaporation [3].

As to analysis of the brines, the used method should provide the express determination of the main substance (NaCl) and macroimpurities (Ca, K, Li, and Mg) immediately at the borehole before the supply of the brine in the vacuum pan [3,4]. In addition, the relative standard deviation (S_r) of the analysis results should not exceed 0.03 for the main component and 0.0 for the impurities [3].

Commonly, the content of NaCl in natural brines lies within 250–400 $g \cdot dm^{-3}$ and those for KCl and LiCl lie within 0.1–2 $g \cdot dm^{-3}$ and 0.1–3 $g \cdot dm^{-3}$, respectively [3].

Sonoluminescence spectroscopy is considered as one of the most available methods for the determination of the main substance NaCl in highly concentrated solutions [5–8].

Earlier, we proposed the routine for the determination of NaCl in brines by sonoluminescent method with the use of ultra-high frequency (UHF) ultrasound (*us*) of 20–22 MHz and intensity of 20 W·cm^{-2} and $S_r \leq 0.020$ [9].

The flame photometry method is considered as the best for K and Li determination in brines. However, the use of two analytical methods considerably complicates the brine analysis and make practically impossible the analysis immediately at borehole [3]. The sonoluminescence spectroscopy method with the use of *us* for the sonoluminescence initiation permits to determine ≥5 g·dm^{-3} of K and ≥10 g·dm^{-3} of Li that is not available for the analysis of real brines.

The simultaneous use of *us* of high (2–5 MHz) and low frequencies (LF, 20–100 kHz) leads to the increase of sonoluminescence flashes and changes the nature of the formation and collapse of cavitation bubbles and increase of amount of the latter in the solution [8]. Recently, we made an assumption that the use of simultaneous action of *us* of high and low frequencies for sonoluminescence initiation resulted in the increase of sensitivity of impurity determination [3].

The simultaneous use of *us* of high and low frequencies described in refs. [7,9] gives possibility to decrease the lower detection limit of Ca and Mg determination in natural brines to 1–3 g·dm^{-3} whereas this limit lies within 5–6 g·dm^{-3} when using the *us* of only low frequency.

It should be noted that the possibility of the simultaneous use of *us* of ultrahigh and low frequencies for the sonoluminescence initiation at the brine analysis for K and Li determination was not described before.

The present work is devoted to the investigation of possibility of the sonoluminescence spectroscopy use with simultaneous action of ultrahigh and low frequencies for sonoluminescence initiation to determine of K and Li content in brines.

Experimental

The sonoluminescence spectrometer based on the atomic–absorption spectrometer AAS-3 was used for the measurements [8]. *Us* oscillations were initiated by standard magnetostriction emitters with working *us* frequencies of 18, 20, 22 and 24 KHz and piezoelectric emitters with working *us* frequencies of 10, 15, 18, 22 and 25 MHz attached to lamp generators for changing *us* frequencies. Such a setup gives possibility to change *us* frequency from 18 kHz to 25 MHz.

Sodium chloride of chemical grade, potassium chloride and lithium chloride of analytical grade and distilled water were used for the preparation of artificial brines. Before the analysis, the solutions were saturated with argon of high purity.

In the work, the following underground natural NaCl-based brines obtained from the depth of 350–400 m were analyzed: Slavyansk deposit, Drohobych deposit and Khodzhaikan deposit (Uzbekistan).

Sodium chloride of chemical quality and potassium and lithium chlorides of reagent quality were used for the preparation of artificial brine. The solutions were prepared with the use of distilled water. The solutions were saturated with argon of extra high purity. The content of NaCl in the artificial brine was constant 400 g·dm^{-3} whereas KCl and LiCl concentrations were 0.1 or 0.2 g·dm^{-3}. These solutions were prepared under the pressure of 2 atm.

All the brines were kept under the pressure to avoid the salt precipitation due to the salt solubility decrease when the brines are raised to the surface [3].

The solution for analysis (1000 ml) was placed in the chamber of 1200 ml volume using the pressure of 2 atm and cooled to temperature of 20±0.5^{0}C. Then cesium chloride was added to the solution up to the concentration of about 30 g·dm^{-3}. Then the solutions were saturated with argon bubbled with the rate of 20 ml·min^{-1} for 0.5 h. Then the *us* action was applied. The sonoluminescence spectrometer was adjusted to the corresponding analytical lines of Na, K, and Li according to ref. [3]. After adjusting, the contents of the main component and admixtures were determined.

The determination was performed with an argon flow through the chamber to avoid the solution degassing. The maximal *us* intensity did not exceed 20 W·cm^{-2} due to the equipment possibilities [3].

The results below are averaged values of 6 experiments. The sonoluminescence intensity was expressed in arbitrary units.

Results and discussions

We studied the sonoluminescence intensity of the sonoluminescence of NaCl solutions with KCl and LiCl admixtures at the varying different parameters (admixture concentrations, UHF and LF frequency, and intensity).

It can be seen that the simultaneous use of UHF and LF *us* gave possibility to decrease the lower detection limits the lower detections limit of KCl and LiCl in brines by 12 times (0.1 g·dm^{-3}) comparing with the use of *us* of high and LF [3] (Table 1). The best results were obtained at UHF *us* frequencies within 20–22 MHz at intensity of 20 W·cm^{-2} and LF *us* frequencies within 19–22 kHz at intensities within 1.3–1.5 W·cm^{-2} (Tables 1–4).

As a result, on the basis of the performed investigations, a routine for the determination of admixtures of K and Li in brines was developed. Its correctness was confirmed by the «added-found» method and by the analysis of the same samples by alternative methods: sonoluminescence spectroscopy with the use of LF *us* for the sonoluminescence initiation, the same with the use of HF *us* and the flame atomic-absorption spectrometry (AAS) (Table 5).

In follows from Table 5 that the sonoluminescence spectroscopy method with the use of simultaneous action of UHF and LF *us* provides the better results of K and Li determination in natural brines due to better metrological characteristics than that of the sonoluminescent methods with the use of only LF *us* or with the use of high-frequency and LF *us*.

The AAS methods possesses better metrological characteristics than the proposed one, however, it cannot be used for the determination of the main substance content in brines.

Conclusions

Thus, the use of simultaneous action of UHF (10–25 MHz) and LF (18–23 kHz) *us* for determination of K and Li in brines was investigated.

The results show that the simultaneous use of UHF and LF *us* gave possibility to decrease the lower detection limits the lower detections limit of KCl and LiCl in brines by 12 times (0.1 g·dm^{-3}) comparing with the use of *us* of high and LF [3] (Table 1). The best results were obtained at UHF *us* frequencies within 20–22 MHz at intensity of 20 W·cm^{-2} and LF *us* frequencies within 19–22 kHz at intensities within 1.3–1.5 W·cm^{-2}.

Table 1

Sonoluminescence intensity of KCl and LiCl admixtures in NaCl solutions with the concentration of 400 g·dm^{-3} at different UHF *us* frequencies (intensity 20 W·cm^{-2}) and admixture concentrations (LF frequency and intensity in all the experiments were 22 kHz and 1.5 W·cm^{-2}, respectively)

Component	Concentration, g·dm^{-3}	Sonoluminescence intensity at different *us* frequency				
		18 MHz	19 MHz	20 MHz	22 MHz	23 MHz
KCl	0.10	–	0.03	0.17	0.20	0.07
	0.20	–	0.06	0.32	0.39	0.15
	0.40	–	0.11	0.67	0.80	0.28
	1.00	0.20	0.30	1.71	2.04	0.70
	2.00	0.59	0.61	3.32	4.03	1.38
LiCl	0.10	–	–	0.12	0.11	–
	0.20	–	0.05	0.23	0.22	0.09
	0.40	–	0.11	0.41	0.45	0.15
	1.00	0.12	0.48	1.22	1.11	0.90
	2.00	0.21	0.72	2.32	2.20	1.16

Table 2

Sonoluminescence intensity of NaCl solutions with the concentration of 400 g·dm^{-3} with admixtures (KCl and LiCl concentrations are 0.4 g·dm^{-3}) at different LF *us* frequencies (intensity 1.5 W·cm^{-2}) (UHF frequency and intensity in all the experiments were 20 MHz and 20 W·cm^{-2}, respectively)

Determined component	Sonoluminescence intensity at different LF *us* frequency				
	18 kHz	19 kHz	20 kHz	22 kHz	23 kHz
KCl	0.45	0.61	0.67	0.61	0.17
LiCl	0.29	0.39	0.41	0.38	0.10

Table 3

Sonoluminescence intensity of NaCl solutions with the concentration of 400 g·dm^{-3} with admixtures (KCl and LiCl concentrations are 0.4 g·dm^{-3}) at different LF *us* intensities (frequency 22 kHz) (UHF frequency and were 20 MHz and 20 W·cm^{-2}, respectively)

Determined component	Sonoluminescence intensity at different LF *us* intensity				
	1.2 W·cm^{-2}	1.3 W·cm^{-2}	1.4 W·cm^{-2}	1.5 W·cm^{-2}	1.6 W·cm^{-2}
KCl	0.12	0.65	0.64	0.67	0.20
LiCl	0.08	0.41	0.40	0.41	0.10

Table 4

Sonoluminescence intensity of NaCl solutions with the concentration of 400 g·dm^{-3} with admixtures (KCl and LiCl concentrations are 0.4 g·dm^{-3}) at different UHF *us* intensities (frequency 20 MHz) (LF frequency and intensity in all the experiments were 22 kHz and 1.5 W·cm^{-2}, respectively)

Determined component	Sonoluminescence intensity at different UHF *us* intensity				
	16 W·cm^{-2}	17 W·cm^{-2}	18 W·cm^{-2}	19 W·cm^{-2}	20 W·cm^{-2}
KCl	0.52	0.54	0.56	0.59	0.67
LiCl	0.30	0.32	0.37	0.38	0.41

Table 5

Results of K and Li admixture determination in artificial and natural brines

Determined component	Added, g·dm^{-3}	Found, g·dm^{-3}							
		Sonoluminescence methods						AAS [2]	
		us 22 kHz		*us* 22 kHz+4 MHz		*us* 22 kHz+22 MHz		$\overline{C}$	S_r
		$\overline{C}$	S_r	$\overline{C}$	S_r	$\overline{C}$	S_r		
Synthetic brine 400 g·dm^{-3} NaCl, 0.40 g·dm^{-3} KCl, and 0.40 g·dm^{-3} LiCl									
KCl	–	–	–	–	–	0.39	0.020	0.40	0.011
	0.10	–	–	0.49	0.051	1.40	0.021	1.39	0.010
LiCl	–	–	–	–	–	0.40	0.020	0.38	0.014
	0.10	–	–	0.50	0.050	1.36	0.021	1.38	0.015
Natural brine No. 1 (Slavyansk, Ukraine)									
KCl	–	–	–	0.07	0.070	0.08	0.022	0.09	0.011
	0.10	–	–	0.16	0.071	0.18	0.022	0.19	0.011
LiCl	–	–	–	0.14	0.071	0.14	0.023	0.14	0.010
	0.10	–	–	0.23	0.072	0.23	0.023	0.24	0.011
Natural brine No. 2 (Drohobych, Ukraine)									
KCl	–	–	–	2.14	0.074	2.34	0.021	2.23	0.017
	2.00	–	–	4.12	0.074	4.25	0.022	4.25	0.016
LiCl	–	–	–	1.56	0.074	1.80	0.023	1.80	0.017
	2.00	–	–	3.50	0.075	3.75	0.020	3.79	0.023
Natural brine No. 3 (Khodzhaikan, Uzbekistan)									
KCl	–	5.12	0.103	5.65	0.089	5.79	0.025	5.86	0.029
	3.00	7.44	0.099	8.49	0.081	8.76	0.022	8.79	0.027
LiCl	–	4.37	0.112	4.45	0.089	4.75	0.028	4.80	0.028
	3.00	6.71	0.108	6.99	0.087	7.64	0.025	7.76	0.025

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ВИЗНАЧЕННЯ КАЛІЮ ТА ЛІТІЮ В РОЗСОЛАХ МЕТОДОМ СОНОЛЮМІНЕСЦЕНТНОЇ СПЕКТРОСКОПІЇ

О.І. Юрченко, Т.В. Черножук, О.Н. Бакланов, М.В. Ніколенко, В.Л. Чергинець, О.Л. Ребров

Наведено результати розробки методики сонолюмінесцентного спектроскопічного визначення калію та літію у висококонцентрованих синтетичних та природних розсолах з одночасним використанням ультразвуку надвисокої (10–25 МГц) та низької (18–23 кГц) частоти для ініціювання сонолюмінесценції. Розроблена нова методика має значно кращі метрологічні характеристики. Порівняння запропонованого методу з методом полум'яної атомно-абсорбційної спектрометрії показує, що останній має кращі метрологічні характеристикиб але не може бути використаний для кількісного визначення основної речовини у розсолах. Запропонований підхід дозволяє знизити нижню межу виявлення KCl та LiCl у розсолах у 12 разів (до 0,1 г·дм$^{-3}$) порівняно з використанням ультразвуку високих та низьких частот. Оптимальними умовами є використання ультразвуку високої частоти в межах 20–22 МГц та інтенсивності в межах 20 Вт·см$^{-2}$ та низькочастотного ультразвуку з частотою в межах 19–22 кГц та інтенсивністю в межах 1,3–1,5 Вт·см$^{-2}$.

Ключові слова: природні розсоли, сонолюмінесцентна спектроскопія, ультразвук, калій, літій.

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O.I. Yurchenko [a, *], T.V. Chernozhuk [a], A.N. Baklanov [a], M.V. Nikolenko [b], V.L. Cherginets [c], A.L. Rebrov [c]

[a] V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

[b] Ukrainian State University of Science and Technologies, Dnipro, Ukraine

[c] Institute for Scintillation Materials of the National Academy of Sciences of Ukraine, Kharkiv, Ukraine

[*] e-mail: yurchenko@karazin.ua

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Keywords: natural brines; sonoluminescence spectroscopy; ultrasound; potassium; lithium.

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