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## ULTRA-HIGH FREQUENCY ULTRASOUND AND SIMULTANEOUS INFLUENCE OF ULTRA-HIGH AND LOW FREQUENCY ULTRASOUND IN SONOLUMINESCENT SPECTROSCOPY

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The use of ultra-high frequency (UHF) ultrasound (10–25 MHz) in sonoluminescence spectroscopy was studied. Methods for determining impurities in highly concentrated solutions were developed and used to determine the main substance content in natural brines and solutions of CsCl (400 and 600 g/dm<sup>3</sup>) and LiCl (400 g/dm<sup>3</sup>). The simultaneous use of UHF and low-frequency (LF) ultrasound (18–23 kHz) for the sonoluminescence determination of potassium, lithium, calcium, and magnesium in NaCl brines was studied. When using the simultaneous action of UHF and LF ultrasound, the lower limit of determination of KCl, LiCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> in brines decreases fivefold (0.10 g/dm<sup>3</sup>) compared with the separate use of UHF or LF ultrasound. The optimal parameters are as follows: UHF: frequency of 20–22 MHz and intensity of 20 W/cm<sup>2</sup>; LF: frequency of 19–22 kHz and intensity of 1.3–1.5 W/cm<sup>2</sup>.

**Keywords:** chlorides, highly concentrated solutions, sonoluminescence spectroscopy, relative standard deviation, potassium, lithium, calcium, magnesium.

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### Introduction

The sonoluminescence spectroscopy is an important method of analysis used in some branches of industry such as the salt industry and nuclear power industry [1–13]. For the salt industry, an information on the content of sodium chloride in natural brines (280–450 g/dm<sup>3</sup>) is required in order to maintain the effective thermophysical characteristics of vacuum evaporators. As for the cooling systems of nuclear reactors, it is important to determine the content of the main substance in salt coolants on the basis of cesium and lithium chlorides [1,2,14].

The initial stage of the development of sonoluminescence spectroscopy as a method of analysis was connected with the influence of low-frequency (LF) ultrasound (18–100 kHz) on the determination of the basic substance in highly concentrated solutions (200–300 g/dm<sup>3</sup>) with  $S_r=0.050-0.067$  [1,2].

Then the high-frequency (HF) ultrasound (0.5–5.0 MHz) was used to initiate sonoluminescence, which permitted to determine the basic substance in highly concentrated solutions of alkaline element salts (300–600 g/dm<sup>3</sup>) [2,3].

The use of HF ultrasound (3–5 MHz) to initiate

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sonoluminescence for the determination of main substance content in highly concentrated technological solutions was described on the examples of salt coolants of nuclear power plants on the basis of CsCl (400 and 600 g/dm<sup>3</sup>) and LiCl (400 g/dm<sup>3</sup>) and  $S_r$  of the obtained results was within 0.037–0.049 range [3,10].

Ultrasound with a frequency of up to 3–5 MHz was also to determine the content of the basic substance in sodium chloride brines [14]. It was found that the value of the relative standard deviation decreased with the increase of the ultrasound frequency that could be explained by a decrease in the number and total volume of cavitation vesicle that decreased the sensitivity of the analysis [14].

The simultaneous use of ultrasound of two different frequencies to initialize sonoluminescence led to the increase in the sensitivity of the determination of elements in salts due to change in the nature of the formation and collapse of cavitation bubbles [6].

The proposed work is devoted to the further study of sonoluminescence spectroscopy, in particular, the possibility of initiating sonoluminescence by ultra-high-frequency (UHF) ultrasound for determination of the main substance content in highly concentrated technological solutions and the simultaneous action of UHF and LF ultrasound for the determination of the macro-impurity (Ca, Mg, K, and Li) content in natural brines.

#### **Experimental**

The sonoluminescence spectrometer was constructed by replacing a burner of the AAS-3 atomic absorption spectrometer (Germany) with a reactor including piezoelectric and magnetostrictive ultrasound emitters [13].

Ultrasonic oscillations were initiated by standard magnetostrictive emitters with ultrasonic operating frequencies of 18, 20, 22 and 24 kHz and piezoelectric emitters with ultrasonic operating frequencies of 10, 15, 18, 22 and 25 MHz, connected to a 24-UZGI-K-1.6 M lamp generator permitting to vary ultrasound frequencies from 18 kHz to 25 MHz [6].

Certified piezoelectric emitters manufactured by the Experimental Machine-Building Plant of the Ukrainian Research Institute of the Salt Industry were used.

The solutions were saturated with extra pure argon. Extra pure NaCl was used for spectral analysis, other reagents were of the analytical grade of purity.

Synthetic sodium chloride brines containing 400 g of NaCl per dm<sup>3</sup> (the concentration is equal to that in Slavyansk brine), natural brines of the Slavyansk or Drohobych sources and solutions of CsCl (400 and 600 g/dm<sup>3</sup>) and LiCl (400 g/dm<sup>3</sup>), according to procedures described in [5,11].

For this purpose, a chamber with a capacity of 1200 ml and the pressure of 2 atm was filled with 1000 ml of the analyzed solution which then was saturated with argon for 5 minutes and cooled to the room temperature. Cesium chloride was added to the NaCl and LiCl solutions to the concentration of approximately 30 g/dm<sup>3</sup> [14]. The analyzed solutions were further saturated with argon for 30 min with the flow rate of 20 ml/min.

For the analysis the solutions were treated with ultrasound of the appropriate parameters. The sonoluminescence spectrometer was tuned to the corresponding analytical lines of sodium, cesium and lithium according to ref. [2] and the content of the main component was determined. During the experiments, the supply of argon was not stopped in order to avoid degassing of the solution. Experiments to study the effect of ultrasound frequency on the intensity of sonoluminescence were carried out using the maximum possible ultrasound intensity of 20 W/cm<sup>2</sup>, limited by the capabilities of the equipment, including the mechanical strength of the ultrasonic emitter [14]. The results presented in Tables 1–8 are average of six determinations. The confidence level is 0.95.

#### **Results and discussion**

The frequency of ultrasound used to initiate sonoluminescence affected the sonoluminescence

Table 1  
Dependence of sonoluminescence intensity of sodium, lithium and cesium chlorides on the frequency of initiating ultrasound

Solution, concentration, g/dm <sup>3</sup> (origin)	Sonoluminescence intensity at different ultrasound frequency*					
	10 MHz	15 MHz	18 MHz	20 MHz	22 MHz	25 MHz
LiCl, 400	23.12	1.71	7.32	9.69	10.18	1.45
CsCl, 400	80.03	6.21	16.22	31.72	35.24	5.04
CsCl, 600	118.12	9.20	24.30	47.50	52.86	7.51
NaCl, 400	9.53	0.45	0.96	3.49	4.01	0.60
NaCl, 600	14.25	0.71	1.40	5.23	6.00	0.87
NaCl, 406 (Slavyansk)	9.53	0.49	1.00	3.91	4.25	0.57
NaCl, 387 Drohobych	11.03	0.57	1.06	3.35	3.39	0.64

Note: \* – The intensity of ultrasound is 20 W/cm<sup>2</sup>. The temperature of the solution is 20.0±0.5°C.

*Ultra-high frequency ultrasound and simultaneous influence of ultra-high and low frequency ultrasound in sonoluminescent spectroscopy*

intensity of cesium chloride, lithium chloride and sodium chloride (Table 1).

The intensity of sonoluminescence of cesium, lithium and sodium chlorides during the rise of the ultrasound frequency from 10 MHz to 25 MHz underwent the following changes: a sharp decrease in the 10–15 MHz range, an increase in the 15–22 MHz range followed by decrease up to 25 MHz. The intensity of sonoluminescence of all chlorides reached the maximum at 20–22 MHz and then sharply decreased.

It should also be noted that the intensity of NaCl sonoluminescence in the natural brines differs from that in the synthetic brine. This can be explained by the presence of impurities in the brines, mainly of organic nature affecting the intensity of the sonoluminescence. Thus, the intensity of sonoluminescence of NaCl in the Drohobych brine (mineralization is 387 g/dm<sup>3</sup>, the average content of humic acids is 0.037 mg/dm<sup>3</sup>, fulvic acids is 8.76 mg/dm<sup>3</sup>) is higher than that in the Slavyansk source (mineralization is 406 g/dm<sup>3</sup>, the average content of humic acids is 0.012 mg/dm<sup>3</sup>, fulvic acids are 1.06 mg/dm<sup>3</sup>) [11].

It should also be noted that the sonoluminescence intensity for all the studied chloride solutions was proportional to the salt concentration at the use of ultrasound of all studied frequencies (10–25 MHz) (Table 2).

The intensity of sonoluminescence of CsCl, LiCl and NaCl increased to the maximum possible intensity of 20 W/cm<sup>2</sup> the increase of ultrasound intensity [2] (Table 2).

Thus, the possibility of using UHF ultrasound in sonoluminescence spectroscopy to determine the base substance in brines is shown. Relative standard deviations of the analysis results are dependent on the frequency of ultrasound (Table 3). The minimal values are achieved at the ultrasound frequency of

20–22 MHz (Tables 1–3) [8,11].

The method to determine the main substance concentration in concentrated solutions of alkali metal chlorides and in natural sodium chloride brines was developed. The correctness of the method was checked by the analysis of the same samples by the gravimetric method (Table 3). The method of sonoluminescence spectroscopy using UHF ultrasound provides the better results (the lower relative standard deviations) of the determination of the main substance in highly concentrated solutions of alkali metal chlorides and in natural chlorides sonoluminescence spectroscopy comparing with the results obtained using LF and HF ultrasound.

The gravimetric method has almost the same metrological characteristics as the method of sonoluminescence spectroscopy with UHF ultrasound, but is inferior to it in expressiveness.

Table 4 presents the results of studying the effect of the frequency of UHF ultrasound, and concentration of NaCl on the intensity of sonoluminescence of admixtures (KCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>). It is seen that the intensity of KCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> sonoluminescence is directly proportional to their concentration in the range of 0.1–2.0 mg/dm<sup>3</sup> at the background of NaCl (400 g/dm<sup>3</sup>) that gives possibility to determine their content in NaCl solutions and the brines. The frequency of UHF ultrasound affects both the intensity of sonoluminescence of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> and its dependence on the admixture concentration.

The highest intensities of KCl and LiCl sonoluminescence are observed in the range of 20–22 MHz, and for CaCl<sub>2</sub> and MgCl<sub>2</sub> it is 22 MHz due to the nature of the formation and collapse of cavitation bubbles, as well as their number per unit volume of the solution [11]. The increase of the UHF ultrasound frequency over 22 MHz leads to a sharp decrease of the cavitation activity [5,8].

Table 2

**Dependence of sonoluminescence intensity of CsCl, LiCl and NaCl on the intensity of initiating ultrasound**

Solution, concentration, g/dm <sup>3</sup> (origin)	Intensity of sonoluminescence at different ultrasound intensity*			
	17 W/cm <sup>2</sup>	18 W/cm <sup>2</sup>	19 W/cm <sup>2</sup>	20 W/cm <sup>2</sup>
LiCl, 400	6.78	7.92	8.99	10.18
CsCl, 400	23.12	26.35	31.01	35.24
CsCl, 600	36.02	40.79	46.53	52.86
NaCl, 400	2.57	2.71	3.54	4.01
NaCl, 600	3.84	4.05	5.31	6.00
NaCl, 406 (Slavyansk)	2.56	3.07	4.04	4.25
NaCl, 387 Drohobych	2.78	3.20	3.21	3.39

Note: \* – The intensity of ultrasound is 20 W/cm<sup>2</sup>. The temperature of the solution is 20.0±0.5°C.

Table 3

Result of the main substance content determination in brines and highly saturated technological solutions at temperature of  $20.0 \pm 0.5^\circ\text{C}$

Solution, concentration, $\text{g}/\text{dm}^3$ (origin)	Additionally introduced determined component, $\text{g}/\text{dm}^3$	Concentration, $\text{g}/\text{dm}^3$							
		Sonoluminescence method (frequency)						Gravimetric method [14]	
		22 kHz		12000 kHz		22000 kHz			
		$\bar{C}$	$S_r$	$\bar{C}$	$S_r$	$\bar{C}$	$S_r$	$\bar{C}$	$S_r$
LiCl, 400	–	382	0.034	393	0.031	399	0.012	399	0.010
	50	410	0.036	429	0.032	442	0.013	445	0.011
CsCl, 600	–	380	0.032	390	0.027	396	0.012	399	0.010
	50	408	0.031	422	0.028	445	0.013	447	0.011
CsCl, 400	–	570	0.045	570	0.038	592	0.012	593	0.010
	100	648	0.048	689	0.039	694	0.014	674	0.010
NaCl, 406 (Slavyansk)	–	382	0.044	389	0.033	403	0.017	401	0.015
	50	414	0.045	425	0.034	449	0.018	447	0.015
NaCl, 406 (Slavyansk)	–	367	0.050	376	0.034	382	0.018	382	0.014
	50	403	0.051	419	0.033	430	0.016	430	0.015
NaCl, 400	–	373	0.052	384	0.032	390	0.015	392	0.013
	50	401	0.051	420	0.033	441	0.016	443	0.014
NaCl, 400	–	559	0.055	570	0.038	588	0.017	590	0.012
	100	619	0.054	679	0.038	682	0.018	648	0.012

Table 4

Dependence of sonoluminescence intensity of KCl, LiCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  on the frequency of UHF ultrasound and solutions concentrations\*

Admixture	Concentration, $\text{g}/\text{dm}^3$	Sonoluminescence intensity at different ultrasound frequency				
		18 MHz	19 MHz	20 MHz	22 MHz	23 MHz
KCl	0.10	–	0.05	0.24	0.21	0.07
	0.20	–	0.10	0.47	0.39	0.15
	0.40	–	0.19	0.99	0.82	0.28
	1.00	0.26	0.48	2.49	2.01	0.70
	2.00	0.52	1.01	5.02	4.02	1.38
LiCl	0.10	–	–	0.19	0.18	0.05
	0.20	–	0.06	0.37	0.37	0.09
	0.40	–	0.12	0.81	0.80	0.14
	1.00	0.19	0.30	2.02	1.85	0.89
	2.00	0.38	0.60	4.08	3.70	1.06
$\text{CaCl}_2$	0.10	–	0.03	0.10	0.19	0.05
	0.20	–	0.05	0.21	0.37	0.11
	0.40	–	0.10	0.40	0.72	0.21
	1.00	0.14	1.03	1.03	1.84	0.51
	2.00	0.26	2.04	2.02	3.61	1.05
$\text{MgCl}_2$	0.10	–	–	0.07	0.17	–
	0.20	–	0.04	0.15	0.32	0.06
	0.40	–	0.07	0.57	0.56	0.11
	1.00	0.10	0.17	0.76	1.45	0.51
	2.00	0.18	0.36	1.51	2.90	1.06

Note: \* – Frequency of LF ultrasound is 22 kHz. The intensity of LF ultrasound is  $1.5 \text{ W}/\text{cm}^2$ . The intensity of UHF ultrasound is  $20 \text{ W}/\text{cm}^2$ .

The presence of NaCl results in the increase of the intensity of sonoluminescence of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> under simultaneous exposure to UHF and LF ultrasound (Table 5).

Moreover, as in the case of using LF ultrasound to initiate sonoluminescence, the increase of the sonoluminescence intensity for KCl-containing solutions starts at concentration of NaCl of 20 g/dm<sup>3</sup>, and it reaches the maximum at NaCl concentration of 30 g/dm<sup>3</sup> and at higher NaCl concentrations it remains unchanged. For LiCl, the rise of the sonoluminescence intensity starts from NaCl concentration 20 g/dm<sup>3</sup> and reaches the maximum at NaCl concentration of 50 g/dm<sup>3</sup>. For CaCl<sub>2</sub> the corresponding concentrations are 15 g/dm<sup>3</sup> and 50 g/dm<sup>3</sup> and for MgCl<sub>2</sub>, they are 10 g/dm<sup>3</sup> and 100 g/dm<sup>3</sup>, respectively. This could be caused by different boiling temperatures of the corresponding metals and ionization energies [5,14].

The results show that the maximum intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> sonoluminescence is achieved at a LF ultrasound frequency of 19–22 kHz. It is probable that in a given frequency range of LF ultrasound frequency the maximum possible number

of cavitation bubbles for a given system is formed (Table 6).

At a LF ultrasound intensity of less than 1.3 W/cm<sup>2</sup>, the cavitation activity of the system is negligible (Table 7). This shows the significant increase in the intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> sonoluminescence with the increase of LF ultrasound intensity from 1.2 to 1.3 W/cm<sup>2</sup>. Thus, the intensity of sonoluminescence increased from 0.19 to 0.80 for KCl, while it increased from 0.18 to 0.81 for LiCl, from 0.14 to 0.73 for CaCl<sub>2</sub>, and from 0.12 to 0.56 for MgCl<sub>2</sub> (Table 7).

The influence of UHF ultrasound intensity on the sonoluminescence intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> is less than the effect of LF ultrasound (Table 8). Thus, in the studied range of UHF ultrasound intensities of 16–20 W/cm<sup>2</sup>, it can be seen that the intensity of sonoluminescence of KCl varied from 0.24 to 0.82, LiCl – from 0.22 to 0.80, CaCl<sub>2</sub> – from 0.21 to 0.72, MgCl<sub>2</sub> – from 0.19 to 0.56 (Table 8). This shows the effect of UHF ultrasound intensity on the synergy of the simultaneous action of ultrahigh and low frequency ultrasound [5,7,8].

Table 5

**Effect of NaCl concentration on sonoluminescence intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> admixtures at different concentrations\***

Admixture	c, g/dm <sup>3</sup>	Sonoluminescence intensity of NaCl at different concentrations									
		5 g/dm <sup>3</sup>	10 g/dm <sup>3</sup>	15 g/dm <sup>3</sup>	20 g/dm <sup>3</sup>	30 g/dm <sup>3</sup>	50 g/dm <sup>3</sup>	100 g/dm <sup>3</sup>	200 g/dm <sup>3</sup>	300 g/dm <sup>3</sup>	400 g/dm <sup>3</sup>
KCl	0.20	0.18	0.25	0.29	0.33	0.38	0.37	0.39	0.37	0.39	0.39
	1.00	0.92	1.23	1.44	1.55	1.90	1.88	1.92	1.90	1.92	2.01
LiCl	0.20	0.12	0.13	0.16	0.32	0.33	0.36	0.36	0.37	0.37	0.37
	1.00	0.58	0.62	0.80	1.60	1.63	1.80	1.78	1.84	1.83	1.85
CaCl <sub>2</sub>	1.00	0.53	0.50	1.30	1.45	1.50	1.80	1.82	1.81	1.80	1.84
	2.00	1.03	1.03	2.60	2.89	3.03	3.59	3.56	3.60	3.60	3.61
MgCl <sub>2</sub>	1.00	0.50	0.61	0.89	1.10	1.23	1.34	1.44	1.43	1.45	1.45
	2.00	1.07	1.19	1.77	2.16	2.42	2.65	2.85	2.87	2.90	2.90

Note: \* – The frequency of UHF ultrasound is 22 MHz. The frequency of LF ultrasound is 22 kHz. The intensity of LF ultrasound is 1.5 W/cm<sup>2</sup>. The intensity of UHF ultrasound is 20 W/cm<sup>2</sup>.

Table 6

**Dependence of sonoluminescence intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> on the frequency of LF ultrasound \***

Admixture	Sonoluminescence intensity at ultrasound frequency, kHz				
	18	19	20	22	23
KCl	0.43	0.82	0.81	0.82	0.19
LiCl	0.29	0.80	0.79	0.80	0.15
CaCl <sub>2</sub>	0.37	0.72	0.71	0.72	0.25
MgCl <sub>2</sub>	0.32	0.57	0.57	0.56	0.21

Note: \* – Frequency of UHF ultrasound is 20 MHz. The intensity of LF ultrasound is 1.5 W/cm<sup>2</sup>. The intensity of UHF ultrasound is 20 W/cm<sup>2</sup>.

From the results given in Tables 4–8, it can be seen that at the use of the simultaneous ultrasonic exposure of UHF and LF the lower limit of detection of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> in brines decreased by 10–12 times as compared with the use of HF and LF ultrasound and it is 0.10 g/dm<sup>3</sup> comparing with atomic absorption method, AAM (Table 9) [3]. The best results were obtained with simultaneous exposure to UHF ultrasound with a frequency of 20–22 MHz, an intensity of 20 W/cm<sup>2</sup> and LF ultrasound with a frequency of 19–22 kHz, an intensity of 1.3–1.5 W/cm<sup>2</sup> (Table 4–8).

Thus, a new method to determine KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> in natural and synthetic brines was developed. The correctness of the technique was checked by «added-found» method, as well as by the analysis of the same samples by alternative methods: sonoluminescence spectroscopy using LF ultrasound to initiate sonoluminescence, sonoluminescence spectroscopy using simultaneous exposure of HF and LF (Table 9).

It can be seen from Table 9 that the method of atomic absorption spectrometry has better metrological characteristics in the determination of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> in brines than the proposed method of sonoluminescence spectroscopy. However, the use of two methods of analysis makes it practically impossible for the simultaneous determination of the main salt component directly in the well before placing the brine into the vacuum evaporator.

### Conclusions

The use of UHF ultrasound to initiate sonoluminescence in the sonoluminescence spectroscopy for the analysis of salt solutions and natural brines was studied. UHF ultrasound (10–25 MHz) was used to initiate sonoluminescence in determining the content of the main substance in natural brines and highly concentrated solutions – salt coolants based on CsCl (400 and 600 g/dm<sup>3</sup>) and LiCl (400 g/dm<sup>3</sup>).

The relative standard deviations of cesium, lithium and sodium determination in highly mineralized solutions of their salts decrease with an increase in the frequency of ultrasound, which initiates sonoluminescence and reach minimum at the ultrasound frequency of 20–22 MHz and intensity of 20 W/cm<sup>2</sup>.

A method to determine the content of the main substance in solutions of salt coolants of nuclear power plants and brines was developed. The correctness of the methodic was checked by the «added-found» method, as well as by the analysis of the same samples by alternative methods: gravimetry and atomic absorption spectrometry.

The use simultaneous of ultrahigh (10–25 MHz) and low (18–23 kHz) ultrasound in the sonoluminescence spectroscopy was studied to determine the content of macroimpurities in NaCl brines: KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>.

At the simultaneous exposure to ultrahigh and

Table 7

**Dependence of sonoluminescence intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> on the intensity of low frequency ultrasound\***

Admixture	Sonoluminescence intensity of low frequency ultrasound				
	1.2 W/cm <sup>2</sup>	1.3 W/cm <sup>2</sup>	1.4 W/cm <sup>2</sup>	1.5 W/cm <sup>2</sup>	1.6 W/cm <sup>2</sup>
KCl	0.19	0.80	0.83	0.82	0.24
LiCl	0.18	0.81	0.80	0.80	0.22
CaCl <sub>2</sub>	0.14	0.73	0.73	0.72	0.20
MgCl <sub>2</sub>	0.12	0.56	0.56	0.56	0.17

Note: \* – The frequency of LF ultrasound is 22 kHz. The intensity of LF ultrasound is 1.5 W/cm<sup>2</sup>. The intensity of UHF ultrasound is 20 W/cm<sup>2</sup>.

Table 8

**Dependence of sonoluminescence intensity of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> on the intensity of UHF ultrasound\***

Admixture	Sonoluminescence intensity of UHF ultrasound				
	16 W/cm <sup>2</sup>	17 W/cm <sup>2</sup>	18 W/cm <sup>2</sup>	19 W/cm <sup>2</sup>	20 W/cm <sup>2</sup>
KCl	0.24	0.36	0.39	0.81	0.82
LiCl	0.22	0.30	0.36	0.79	0.80
CaCl <sub>2</sub>	0.21	0.36	0.39	0.67	0.72
MgCl <sub>2</sub>	0.19	0.32	0.34	0.52	0.56

Note: \* – Frequency of UHF ultrasound is 20 MHz. The frequency of LF ultrasound is 22 kHz. The intensity of UHF ultrasound is 20 W/cm<sup>2</sup>.

low frequency ultrasound, the lower limit for determining the content of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> in the brines decreased by 10 times compared to the use of HF and LF ultrasound and it is 0.10 g/dm<sup>3</sup>.

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Table 9

### The results of the determination of KCl, LiCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> in different brines

Admixtu re	Added main component, g/dm <sup>3</sup>	Found, g/dm <sup>3</sup>							
		Sonoluminescence method at different ultrasound frequency						AAM [10]	
		22.0 kHz		22.0 kHz+4 MHz		22.0 kHz+22 MHz		$\bar{C}$	S <sub>r</sub>
		$\bar{C}$	S <sub>r</sub>	$\bar{C}$	S <sub>r</sub>	$\bar{C}$	S <sub>r</sub>		
Synthetic NaCl brine: 400 g/dm <sup>3</sup> of NaCl and KCl, LiCl CaCl <sub>2</sub> , and MgCl <sub>2</sub> (all 40 g/dm <sup>3</sup> )									
KCl	–	–	–	–	–	0.38	0.021	0.40	0.015
	0.20	–	–	0.53	0.051	0.57	0.023	0.59	0.014
LiCl	–	–	–	–	–	0.37	0.021	0.39	0.015
	0.20	–	–	0.52	0.052	0.54	0.023	0.58	0.014
CaCl <sub>2</sub>	–	–	–	–	–	0.36	0.024	0.40	0.019
	1.00	–	–	1.25	0.055	1.35	0.023	1.39	0.017
MgCl <sub>2</sub>	–	–	–	–	–	0.38	0.022	0.38	0.017
	1.00	–	–	1.28	0.053	1.34	0.021	1.37	0.018
The brine of Slavyansk deposit									
KCl	–	–	–	0.07	0.060	0.08	0.022	0.09	0.015
	0.20	–	–	0.25	0.061	0.25	0.020	0.28	0.014
LiCl	–	–	–	0.14	0.061	0.14	0.023	0.14	0.014
	0.20	–	–	0.31	0.062	0.32	0.023	0.33	0.015
CaCl <sub>2</sub>	–	–	–	0.53	0.065	0.58	0.027	0.54	0.017
	5.00	3.90	0.094	5.09	0.067	5.43	0.025	5.47	0.018
MgCl <sub>2</sub>	–	–	–	0.95	0.067	0.99	0.026	1.02	0.017
	5.00	4.24	0.097	5.53	0.068	5.85	0.028	5.97	0.019
The brine of Drogobych deposit									
KCl	–	–	–	2.14	0.064	2.34	0.021	2.23	0.016
	1.00	2.69	0.096	3.02	0.061	3.25	0.022	3.20	0.015
LiCl	–	–	–	1.56	0.064	1.80	0.023	1.86	0.015
	1.00	2.43	0.097	2.43	0.065	2.65	0.020	2.79	0.018
CaCl <sub>2</sub>	–	–	–	–	–	0.12	0.037	0.21	0.020
	5.00	3.94	0.092	4.78	0.084	5.08	0.023	5.14	0.019
MgCl <sub>2</sub>	–	–	–	–	–	0.32	0.024	0.34	0.018
	5.00	4.20	0.097	4.89	0.080	5.24	0.023	5.32	0.019

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## УЛЬТРАВИСОКОЧАСТОТНИЙ УЛЬТРАЗВУК ТА ОДНОЧАСНИЙ ВПЛИВ УЛЬТРАЗВУКУ НАДВИСОКОЇ ТА НИЗЬКОЇ ЧАСТОТИ В СОНОЛЮМІНЕСЦЕНТНИЙ СПЕКТРОСКОПІЇ

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Досліджено використання ініціалізації ультразвуку надвисокої частоти (НВЧ) (10–25 МГц) у сонолюмінесцентному спектроскопічному аналізі. Розроблено і використано методи визначення домішок у висококонцентрованих розчинах та методи визначення вмісту основної речовини в природних розсолах та розчинах CsCl (400 та 600 г/дм<sup>3</sup>) та LiCl (400 г/дм<sup>3</sup>). Досліджено одночасне використання ультразвуку НВЧ та низької (18–23 кГц) частоти (НЧ) для сонолюмінесцентного визначення калію, літію, кальцію та магнію в розсолах NaCl. При одночасному використанні ультразвуку НВЧ та НЧ нижня межа визначення KCl, LiCl, CaCl<sub>2</sub> та MgCl<sub>2</sub> у розсолах зменшується у 5 разів (0,10 г/дм<sup>3</sup>) порівняно з роздільним використанням ультразвуку НВЧ або НЧ. Оптимальними параметрами є: НВЧ – частота 20–22 МГц та інтенсивність 20 Вт/см<sup>2</sup>; НЧ – частота 19–22 кГц і інтенсивність 1,3–1,5 Вт/см<sup>2</sup>.

**Ключові слова:** хлориди, висококонцентровані розчини, сонолюмінесцентна спектроскопія, відносне стандартне відхилення, калій, літій, кальцій, магній.

## ULTRA-HIGH FREQUENCY ULTRASOUND AND SIMULTANEOUS INFLUENCE OF ULTRA-HIGH AND LOW FREQUENCY ULTRASOUND IN SONOLUMINESCENT SPECTROSCOPY

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The use of ultra-high frequency (UHF) ultrasound (10–25 MHz) in sonoluminescence spectroscopy was studied. Methods for determining impurities in highly concentrated solutions were developed and used to determine the main substance content in natural brines and solutions of CsCl (400 and 600 g/dm<sup>3</sup>) and LiCl (400 g/dm<sup>3</sup>). The simultaneous use of UHF and low-frequency (LF) ultrasound (18–23 kHz) for the sonoluminescence determination of potassium, lithium, calcium, and magnesium in NaCl brines was studied. When using the simultaneous action of UHF and LF ultrasound, the lower limit of determination of KCl, LiCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> in brines decreases fivefold (0.10 g/dm<sup>3</sup>) compared with the separate use of UHF or LF ultrasound. The optimal parameters are as follows: UHF: frequency of 20–22 MHz and intensity of 20 W/cm<sup>2</sup>; LF: frequency of 19–22 kHz and intensity of 1.3–1.5 W/cm<sup>2</sup>.

**Keywords:** chlorides; highly concentrated solutions; sonoluminescence spectroscopy; relative standard deviation; potassium; lithium; calcium; magnesium.

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