

# On the use of sonoluminescence spectra for determination of the elemental composition of liquid media

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Sonoluminescence (cavitation glow) spectra of argon-saturated aqueous solutions of sodium, magnesium, and calcium at different values of the hydroacoustic pressure have been investigated. The results indicate that the increase in the solution pressure leads to a fast increase in the spectral intensity of the excited metal lines. This effect can be explained by the temperature growth inside cavitation bubbles, and it allows sonoluminescence spectra to be used efficiently for determination of the content of metals in liquid media.

## Introduction

The exposure of a liquid medium to ultrasound gives rise to acoustic cavitation, namely, the formation of nonlinearly pulsating vapor-gas bubbles in the liquid. The impetuous contraction of cavitation bubbles is accompanied by sound-chemical reactions and the emission of light in a wide frequency band – sonoluminescence (SL).<sup>1,2</sup> The sonoluminescence is caused by the efficient concentration of energy of the acoustic field, leading to formation of the excited states of atoms and molecular particles inside a bubble.<sup>3</sup>

The SL spectra are used in studying the mechanism and energy of the processes occurring inside a cavitation bubble.<sup>4</sup> The spectral composition of SL is mostly determined by the nature of the liquid and substances dissolved in it. Upon the exposure of aqueous solutions of metal salts to ultrasound, emission lines due to the excited states of metal atoms are observed in SL spectra.<sup>5</sup> The sonoluminescence can be used as a method for determination of the qualitative and quantitative composition of liquid media and solutions.

Taylor and Jarman<sup>6</sup> have proposed a technique for determination of the concentration of alkaline and alkaline earth metals (sodium, magnesium, calcium) in solutions of sodium chloride and the table salt from the SL spectra. It has been shown that at high concentrations of metals the SL method provides for much better metrological characteristics as compared to the atomic absorption method, because it does not require the multiple dilution of samples. At the low concentrations of metals, the use of the SL method was difficult because of the low intensity of metal emission lines in the spectra.

It is well-known<sup>7</sup> that the intensity of metal lines in the SL spectra depends on the ultrasound frequency and intensity and on the dissolved gas. The effect of the hydrostatic pressure on the intensity of

metal lines in the SL spectra of aqueous solutions of metal salts has not been studied yet.

In this paper, we study the SL spectra of aqueous solutions of sodium, magnesium, and calcium chlorides saturated with argon under variable hydrostatic pressure. The results obtained indicate that the intensity of metal emission lines in the SL spectra of aqueous solutions of salts can be significantly increased due to the increase of the hydrostatic pressure in the solution.

## Experiment

To study the SL spectra, we used a specially designed experimental setup (Fig. 1),<sup>8</sup> whose key part was an original ultrasonic cell, being a cylinder from a stainless steel (inner diameter of 2 cm, volume of 50 ml), equipped with a cooling jacket.



Fig. 1. Experimental setup for recording the sonoluminescence spectra.

A tip of a magnetostrictive emitter connected to an UZDN-2T ultrasonic dispersant was inserted into the cell from one end. This allowed the generation of ultrasonic oscillations with the frequency of 22 kHz and the intensity of 23 W/cm<sup>2</sup> to be performed inside the cell. Another end of the cell was closed by

a quartz window, matched with a monochromator window. The cell was equipped with a thermistor and a manometer for monitoring of the temperature and pressure in the solution. The spectra were obtained from the intense cavitation area near the source of ultrasound (the distance between the emitter tip and the quartz window of the ultrasonic cell was 10 mm).

A weighted sample of a salt (1.5 M) was dissolved in 1 liter of bidistillate. The exact content of a metal was determined by titration of the solution. The solution was saturated with argon for 2 hours before the experiment and during the experiment in a thermostatically controlled glass flask (the solution volume was 0.5 l) and continuously pumped through the ultrasonic cell. The extra pressure in the cell was generated with a peristaltic pump. The solution temperature inside the cell was maintained equal to  $(9 \pm 1)^\circ\text{C}$ .

The SL spectra were analyzed with an MDR-23 monochromator (focal length of 0.6 m, diffraction grating with 1200 grooves/mm, inverse linear dispersion of 1.3 nm/mm). A FEU-100 photomultiplier tube calibrated in a region from 200 to 800 nm served a detector. The spectral scanning and data processing were carried out with a computer. The data were processed with the use of standard software: Microsoft Excel, Microcal Origin, and MathCad.

## Results and discussion

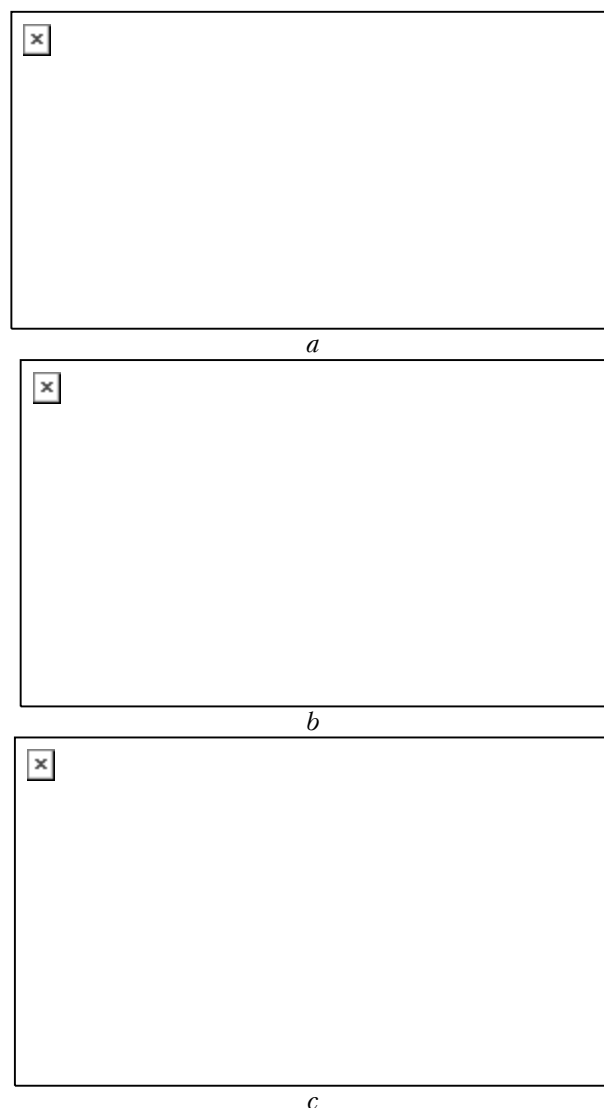
The experimental results are shown in Figs. 2–4. The SL spectra of aqueous solutions of salts of alkaline and alkaline earth metals, saturated with an inert gas, include a wide continuum formed by several overlapping emission bands,<sup>3</sup> the emission lines of the excited hydroxyl radical at 280, 310, and 340 nm, and the atomic emission bands of metals, observed against the background of the continuum (Fig. 2).

The increase of the hydrostatic pressure ( $P_h$ ) in the solutions led to changes in the SL spectra.

As  $P_h$  increased from 1 to 1.8 atm, the intensities of the emission lines of  $\text{Na}^*$  at a wavelength of 590 nm (see Fig. 2*a*) and  $\text{Mg}^*$  at 285 nm (see Fig. 2*b*) increased by 9 and 6 times, respectively (the concentration of sodium in the solution was 34 g/liter, and that of magnesium of 32.4 g/liter). In the SL spectra of the solution of calcium chloride (see Fig. 2*c*) (the metal content of 54 g/liter), as  $P_h$  increased from 1 to 2.6 atm, the intensity of the  $\text{Ca}^*$  line at 423 nm increased 13 times. Figure 3 clearly demonstrates these changes in the intensities of the metal emission lines in the SL spectra.

The further increase of  $P_h$  led to a decrease of the total SL intensity (as a result of the decrease in the number of cavitation bubbles, emitting the radiation<sup>9</sup>), and the intensity of metal lines in the spectra decreased as well (see Fig. 3). Nevertheless,

the relative intensity of the  $\text{Na}^*$ ,  $\text{Mg}^*$ , and  $\text{Ca}^*$  lines (relative to the integral intensity of the continuum  $I_c$ , see Fig. 4) in the SL spectra remained rather high.



**Fig. 2.** SL spectra of argon-saturated aqueous solutions of NaCl (*a*),  $\text{MgCl}_2$  (*b*), and  $\text{CaCl}_2$  (*c*).



**Fig. 3.** Intensity of the emission lines of metal atoms in SL spectra of aqueous solutions of NaCl,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$  as a function of pressure. The values are normalized to the intensity at the normal pressure.



Fig. 4. Ratio of the intensity of emission lines of metal atoms to the integral intensity of continuum ( $I_V/I_C$ ) in SL spectra for different values of the hydrostatic pressure.

This effect (the faster growth of the metal emission intensity in comparison with the SL continuum with the increase of the hydrostatic pressure in the solution) was observed for the first time.

The mechanism of the appearance of the metal emission lines in the SL spectra is still unclear. The extreme conditions inside the cavitation bubble (up to 3000–5000 K and 500 atm by the time of emission) are sufficient for the excitation of atoms to higher energy levels. It is unclear in what way neutral atoms are formed from ions. It is possible to suppose that the impetuous collapse of the bubble, accompanied by the fast increase of the temperature inside the bubble, leads to a sharp evaporation of the solution from the bubble/solution interface. Under the effect of high temperature, the salt inside the bubble loses its water, and the salt molecules dissociate with formation of the excited metal atoms. The elementary processes of dissociation and excitation of halides MeHal are described by the equation



The observed increase of the intensity of metal emission in the SL spectra means that the number of salt molecules, falling within cavitation bubbles, increase with pressure. The increase of the hydrostatic pressure in the solution leads to a more intense collapse of cavitation bubbles and, as a consequence, to the increase in the temperature attained inside the cavitation bubble during its impetuous contraction. It should be noted that the increase of the ultimate temperature significantly affects the SL spectral distribution.<sup>10,11</sup> At a higher temperature inside a cavitation bubble, the processes of evaporation and dissociation of halides occur more intensely. Thus, the cause for the increase in the

intensity of emission lines of metal atoms in the SL spectra of aqueous solutions of salts is the increase of the ultimate temperature inside the cavitation bubbles due to the increase of the pressure in the solution.

## Conclusions

The effect discovered in this work, namely, the fast increase in the metal emission with the increasing hydrostatic pressure in the solution, is interesting not only for the further investigation into the mechanism of appearance of emission lines corresponding to the excited states of metal atoms in the SL spectra, but also for the more efficient use of the spectra in determination of the metal content in liquid media. The use of SL spectra as an analytical tool is possible for a wide range of problems connected, for example, with monitoring of pollution of aqueous media, analysis of the elemental composition of biological objects, such as plant cells and zooblasts, in particular, phytoplankton cells.

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