
UNDERWATER LASER ABLATION AS A METHOD FOR PREPARING SOLUTIONS OF NONSOLUBLE TIN- AND LEAD-BASED COMPOUNDS

S.E. ZELENSKY, A.S. KOLESNIK, A.V. KOPYSHINSKY,
B.A. OKHRIMENKO

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Taras Shevchenko National University of Kyiv, Faculty of Physics
(64, Volodymyrska Str., Kyiv 01601, Ukraine; e-mail: kopyshinsky@univ.kiev.ua)

A method for preparing aqueous electrolyte solutions of nonsoluble tin- and lead-based compounds has been developed. It is based on the underwater laser ablation stimulated by a neodymium Q-switched laser. Absorption and luminescence spectra of the solutions obtained have been studied.

1. Introduction

With the appearance of lasers, researches of interaction processes between powerful laser-emitted radiation and condensed media have been started and intensively carried out till now. The laser-induced ablation, in particular, the ablation of solid targets located under a liquid surface [1–7] is an important aspect of this interaction. Among products of the laser ablation, microparticles composed of a target material, which are thrown out into the liquid at the laser irradiation, are of the largest interest. However, soluble products of the underwater laser ablation have not been studied in full measure.

In this work, the underwater laser ablation is considered as a method for preparation of aqueous solutions. In particular, a possibility to obtain solutions of heavy metals from their compounds that are insoluble in water is analyzed.

In the first report [8] on the underwater laser ablation of thallium compounds, a possibility to obtain an aqueous thallium solution from its insoluble oxide was demonstrated. The spectral characteristics of thallium solutions obtained by the laser ablation method were found to coincide with those of the known solutions of thallium salts in water and aqueous electrolyte solutions with a high content of halogen ions.

As a continuation of researches reported in work [8], we will consider water-soluble products of the laser ablation of lead- and tin-based compounds. Various Hg-like ions (Tl, Pb, Bi, In, Sn, Sb) are known to reveal similar optical characteristics in aqueous electrolyte solutions [9–13], which evidences the common nature of physico-chemical processes that take place in such objects at their interaction with optical radiation. In this connection, it is logical to assume that, under the laser ablation condition, the similarity of properties of Hg-like ions would also take place. This hypothesis is checked in the presented work.

The practical value of the work is predetermined, to a great extent, by a wide application of compounds involving Hg-like elements in technology. It is worth noting a high toxicity of compounds with Hg-like ions. This circumstance makes the researches of the properties of solutions with Hg-like ions and the elaboration of methods—including those, which apply optical spectroscopy—for monitoring the content of Hg-like ions challenging.

2. Experimental Technique

The ablation of tin- and lead-based compounds was carried out in distilled water at room temperature with the help of a Q-switched YAG:Nd³⁺ laser. The radiation wavelength was 1.064 μm , the pulse length was about 15 ns, the power density of laser radiation was approximately 200 MW/cm², and the laser pulse repetition frequency was 12.5 Hz. Specimens were irradiated in a quartz cuvette ($V = 2 \text{ cm}^3$ and $d = 1 \text{ cm}$).

A substance to be irradiated with a laser was located in a quartz cuvette, which was filled with distilled water.

Laser radiation was focused through a lateral wall of the cuvette onto the surface of the substance concerned by means of a lens with a focal length of 5 cm. The power density of a laser radiation was about 200 MW/cm², but the accurate determination of the laser radiation intensity faced difficulties, since the products of the laser ablation attenuated the laser radiation, which could not be taken into account. Substance particles formed a suspension that scattered the laser light considerably.

In the case where the irradiated substance was a powder, its suspension in water was prepared. The cuvette contents were permanently stirred up during the irradiation.

It should be noted that, in this work, when carrying out the laser ablation experiments, we used only water-insoluble compounds of Hg-like elements, such as SnO. In experiments with the laser ablation of lead compounds, a TF-5 x-ray protective glass was used.

In the course of experiments, we checked that the target substance did not form a solution with water at their interface within several minutes without irradiation by a laser beam. As was found out, metallic tin and lead, when contacting with distilled water, form corresponding aqueous solutions within several seconds. The concentration of Hg-like ions in those solutions is sufficient to be detected using the optical absorption technique. This circumstance made it impossible to use metallic lead and tin as objects of concern in the framework of the underwater laser ablation studies.

After the laser irradiation, a suspension of laser ablation products was formed in the cuvette. Afterwards, the suspension was allowed to settle at room temperature. After the suspension particle had settled, the cuvette contents looked like a transparent solution, without visible traces of coloring. We studied the spectral characteristics (luminescence and absorption spectra) of such solutions obtained due to the action of laser radiation on the insoluble compound. The spectral characteristics of such solutions of Hg-like ions remained constant at least within several days.

Absorption and luminescence spectra were measured on automated spectrometers with ordinary monochromators. Luminescence was excited by radiation of a DKSL-1000 xenon lamp passed through a DMP-4 double monochromator. The excitation wavelength was selected to correspond to the maximum in the absorption spectrum of the solution under study. No correction for the non-uniformity of a spectral sensitivity at the luminescence spectrum registration was made.

The absorption and luminescence spectra of the solutions prepared by the laser ablation technique were

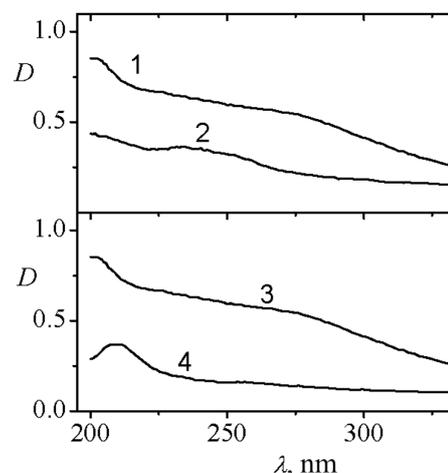


Fig. 1. Absorption spectra of tin (curves 1 and 3) and lead (curves 2 and 4) aqueous solutions. Spectra 1 and 2 were obtained by the method of laser ablation of SnO powder suspension (1) and TF-5 lead glass (2) in water. Curves 3 and 4 are the spectra of water-soluble salts SnCl₂ and PbCl₂, respectively

compared with the corresponding spectra of solutions prepared from soluble salts of the same elements, for example, PbCl₂ and SnCl₂. The spectral characteristics of water-soluble salts of Hg-like ions were studied in detail in work [9].

3. Results and Their Discussion

The absorption spectra of aqueous solutions obtained from the insoluble compounds of Hg-like elements using the laser ablation technique are depicted in Fig. 1 (curves 1 and 2). The tin solution (curve 1) was obtained by irradiating the aqueous suspensions of SnO powder with a neodymium laser. The lead solution (curve 2) was obtained by irradiating a piece of optical glass TF-5 in the cuvette filled with water by a neodymium laser as well. For the sake of comparison, the same figure exhibits the absorption spectra of water-soluble salts SnCl₂ (curve 3) and PbCl₂ (curve 4) [9].

The absorption spectra of tin and lead ions in water are wide bands with a weakly expressed structure. A satisfactory coincidence of ultraviolet absorption band positions observed in Fig. 1 for irradiated water-insoluble and water-soluble tin- and lead-based compounds can be regarded as an evidence for the formation of aqueous solutions of tin and lead Hg-like ions after the insoluble compounds of indicated Hg-like ions having been irradiated with powerful pulse radiation. As is demonstrated below, the difference between spectra 2 and 4 can be explained by the fact that the PbCl₂ solution (curve 4)

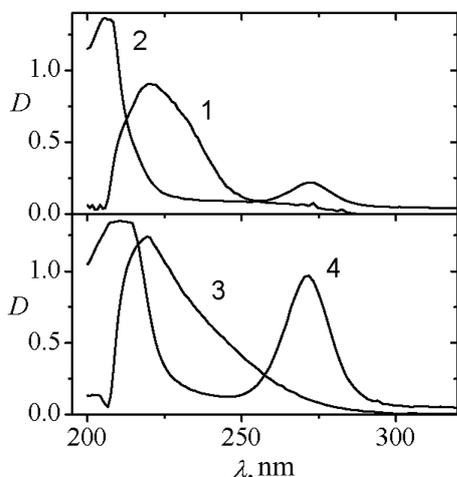


Fig. 2. Absorption spectra of tin (curves 1 and 3) and lead (curves 2 and 4) solutions in the aqueous electrolyte $\text{H}_2\text{O} + \text{LiCl}$ with the concentration $C_{\text{LiCl}} = 7 \text{ mol/l}$. Spectra 1 and 2 were obtained by the method of laser ablation of SnO powder (1) and TF-5 lead glass (2) suspensions in water followed by the addition of LiCl. Curves 3 and 4 were obtained making use of water-soluble salts $\text{H}_2\text{O} + \text{LiCl} + \text{SnCl}_2$ and $\text{H}_2\text{O} + \text{LiCl} + \text{PbCl}_2$, respectively

contains an admixture (10^{-3} mol/l) of hydrochloric acid [9].

In aqueous electrolyte solutions with an excess of halogen ions, Hg-like ions are known to form stable complexes with the latter [10, 13]. For instance, in aqueous solutions of thallium with an excess of chlorine, limiting complexes TlCl_6 are formed. As a rule, the optical absorption spectra of halogen complexes of Hg-like ions are shifted towards the long-wave range in comparison with those of hydrated Hg-like ions [10]. This circumstance allows one to make an additional composition analysis of the solutions obtained by the method of laser ablation of insoluble compounds of Hg-like ions.

We studied the solutions of Hg-like ions with an excess of chlorine ones. The latter were introduced into the solution by dissolving the LiCl salt. In this case, Hg-like ions formed complexes with chlorine ions, whereas lithium ions practically did not affect the optical characteristics of the solutions obtained. The experiment showed that the addition of chlorine ions to aqueous solutions of Hg-like ions, which were obtained by laser ablation of their insoluble compounds, gives rise to an appreciable long-wave shift of the admixture-related absorption bands.

For instance, the absorption spectra of aqueous solutions of Hg-like ions with addition of chlorine ones are depicted in Fig. 2. The concentration of chlorine ions was selected to provide the formation of Hg-like ion-

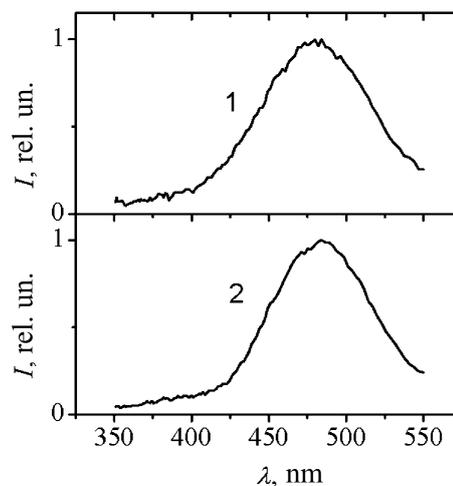


Fig. 3. Luminescence spectra of $\text{H}_2\text{O} + \text{LiCl} + \text{SnCl}_2$ solutions produced by laser ablation (1) and by dissolving SnCl_2 salt in the $\text{H}_2\text{O} + \text{LiCl}$ solution (2)

haloid complexes with the limiting content. As is seen from this figure, the maxima of absorption spectra obtained for halogen solutions of Hg-like ions produced by laser ablation of insoluble compounds and for solutions produced by dissolving soluble salts practically coincide. A good coincidence between the absorption spectra of solutions produced using different techniques testifies in favor of their interpretation given above.

It should also be noted that, in the literature, there are reports on the luminescence of some Hg-like ions in aqueous solutions of electrolytes at the ultra-violet excitation [14]. For instance, the luminescence spectra of aqueous thallium and lead solutions are wide ultra-violet bands without any visible structure, which can be observed, when the excitation is carried out by irradiating the solutions at the wavelength that falls within the corresponding absorption bands of hydrated thallium and lead ions. The luminescence of lead solutions is observed only at low temperatures (in the frozen solutions).

In this work, we detected the luminescence of aqueous tin solutions obtained by the laser ablation technique. We studied the luminescence of solutions at room temperature, when chlorine ions were added. The luminescence spectra of tin complexes in aqueous solutions of electrolytes ($\text{H}_2\text{O} + \text{LiCl}$) are shown in Fig. 3. The excitation wavelength was 230 nm. As is seen from the figure, the shape of luminescence spectra of the solutions produced by the laser ablation technique satisfactorily coincides with that of luminescence spectra of water-soluble salt SnCl_2 , which is an additional confirmation of the fact that the underwater laser ablation of Hg-like ion

compounds results in the formation of aqueous solutions of corresponding Hg-like ions.

It is known that, in the course of ablation, a torch is formed, the composition of which depends on irradiation conditions. Neutral and ionized atoms of target elements, atomic clusters, droplets, and solid particles of various sizes—all in various ratios [15]—can constitute the products of ablation. Large solid particles settle onto the cuvette bottom in approximately 24 h after irradiation; this results in a reduction of light scattering. Ablation products that remained in the solution affect the optical characteristics of the suspension. Some differences in the absorption (Figs. 1 and 2) and luminescence (Fig. 3) spectra of suspensions and reference solutions of Hg-like ions can be explained by the presence of those ablation products (clusters and nanoparticles) that remained in the solution. It is impossible to determine the composition and optical characteristics of those ablation products at this stage.

4. Conclusions

In this work, we have studied the interaction between the powerful pulse laser radiation and compounds of Hg-like ions (lead and tin) under the water surface. The ablation of a substance under the laser irradiation was found to result not only in the formation of aqueous suspensions including insoluble compounds of Hg-like ions, but also in the formation of aqueous solutions of those ions. The spectral characteristics (absorption and luminescence spectra) of water-soluble products of the laser ablation of insoluble lead- and tin-based compounds have been studied.

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ЛАЗЕРНА АБЛЯЦІЯ У ВОДНОМУ СЕРЕДОВИЩІ ЯК МЕТОД ПРИГОТУВАННЯ РОЗЧИНІВ ІЗ НЕРОЗЧИННИХ СПОЛУК ОЛОВА ТА СВИНЦЮ

*С.Є. Зеленський, О.С. Колесник, О.В. Копишинський,
Б.А. Охріменко*

Резюме

Розроблено метод отримання водних розчинів електролітів із нерозчинних сполук олова та свинцю, а також при додаванні LiCl. Основою методу є підводна лазерна абляція із використанням неодимового лазера з модуляцією добротності. Досліджено спектри поглинання і люмінесценції отриманих розчинів.