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MULTISTEP EXCITATION SCHEMES IN LASER SPECTROSCOPY AND DETECTION OF ACTINIDES AND LANTHANIDES IN SOLUTIONS

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Многоступенчатые схемы возбуждения в лазерной спектроскопии и детектирование актинидов и лантанидов в растворах

Применение лазеров с перестраиваемой длиной волны позволяет селективно возбуждать различные молекулярные и валентные формы актинидов и лантанидов с последующим их детектированием при регистрации люминесценции / хемилюминесценции. Данная работа посвящена применению методов лазерной люминесцентной (TRLIF) / хемилюминесцентной (TRLIC) спектроскопии с временным разрешением для детектирования лантанидов и актинидов в растворах. Показано, что применение многоступенчатых схем возбуждения хемилюминесценции обеспечивает высокую чувствительность и селективность TRLIC метода детектирования лантанидов и актинидов в растворах.

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Multistep Excitation Schemes in Laser Spectroscopy and Detection of Actinides and Lanthanides in Solutions

The use of laser radiation with tunable wavelength allows selective excitation of actinide / lanthanide species with subsequent registration of luminescence / chemiluminescence for their detection. This work is devoted to applications of the time-resolved laser-induced luminescence spectroscopy (TRLIF) and time-resolved laser-induced chemiluminescence spectroscopy (TRLIC) for detection of lanthanides and actinides in solutions. It is shown that a multistep scheme of chemiluminescence excitation provides highly sensitive and highly selective TRLIC procedure of detection of lanthanides and actinides in solutions.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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INTRODUCTION

The use of laser radiation with tunable wavelength allows [1–4] selective excitation of actinide / lanthanide species with subsequent registration of luminescence or chemiluminescence. The practical application of laser spectroscopy to analysis of different samples is confronted with one essential difficulty, namely, the element to be detected must be permanently located in the area of interaction with laser radiation. Therefore, the use of solutions of the substances to be analyzed is the most attractive from the practical standpoint. When the pulse (1 ns) UV radiation produced by nitrogen laser is used for lanthanide and actinide excitation in solutions, the UV radiation is absorbed with different molecules, and as a consequence the background radiation is increased. Using short laser pulses for excitation of molecules and ions in liquids and time resolution (TR) for registration of luminescence (TRLIF) and chemiluminescence (TRLIC) produced by actinide and lanthanide ions, we can efficiently separate target signals from short-lived background luminescence [1–6]. Selective excitation of detectable molecules and multistep excitation schemes of luminescence / chemilumunescence can additionally decrease the intensity of background radiation. The limits of detection (LOD) for spectrometers using the registration of chemiluminescence are in the range from 10^{-6} till 10^{-13} mol/l depending on the type of solutions and type of detected molecule. Chemiluminescence is widely used as a detection method in many fields, such as flow injection analysis, chromatography, biology, medicine, etc. [7]. UV radiation is absorbed with chemiluminogen (luminol in our experiments) molecules, which makes it difficult to interpret the results of chemiluminescence registration. Therefore, a key problem of chemiluminescence application to detection of lanthanides and actinides in solutions is an increase in the selectivity of detection. Appropriate selectivity of lanthanide or actinide molecules excitation can be reached by initiation of transitions within $4f$- or $5f$-electron shell, which correspond to visible spectral range of absorbed laser radiation. Since the energy of one-quantum excitation in visible range may be insufficient for initiation of chemiluminescence, it was proposed [1–4] to excite lanthanide or actinide ion by multiquantum absorption of visible light. The *two step–one color* scheme [1–4], i.e., in irradiation of actinide-containing solution by one laser (two photons absorbed from one laser pulse), and the *two step–two color* scheme, when a solution is irradiated by two lasers operating at different wavelengths (two photons absorbed from two synchronized laser pulses), were used for excitation of actinide ions in the range of $5f$-electron transitions.

The details of multistep excitation of luminescence / chemiluminescence in solutions are considered. It is shown that a multistep scheme of luminescence / chemiluminescence excitation increases both the sensitivity and selectivity of detection of substances.

1. TRLIF, SINGLE-STEP EXCITATION SCHEME

The background radiation can be efficiently suppressed by using pulse laser radiation to excite solutions and measuring the luminescence with a delay (10^{-3}–10^{-6} s) after laser pulse. The solution to be analyzed is exposed to a pulsed (10^{-8}–10^{-9} s) laser beam. The luminescence spectrum is measured with a delay (10^{-3}–10^{-6} s) with respect to the laser pulse (Figs. 1 and 2). This method has been termed "time-resolved laser-induced fluorescence" (TRLIF). The TRLIF method allows detection of lanthanide and actinide concentrations down to 10^{-13} mol/l [5]. The TRLIF technique features selectivity in four parameters: laser radiation wavelength, measured luminescence spectra (Fig. 3), measured delay with respect to the pulse laser, and measured time (Fig. 2). Also, selectivity and sensitivity depend on excitation scheme (single-step or multistep) and excitation wavelength [1–4].

For Eu, Sm, and U analysis we used luminescence method with pulse (1 ns) nitrogen laser excitation of the solution and time resolution for the signal registration (single-step excitation TRLIF). One of the most convenient ways is the use of sodium polysilicate solution having a low self-background and providing limit of uranyl detection in our experiments up to 0.005 ng/ml. However, this method is suitable only for analysis of inorganic samples. Biological samples containing a large amount of organic substances should be preliminary mineralized. Typical concentration of uranium in blood plasma is about 0.05–0.5 ng/ml, in urine it is about 0.2–5 ng/ml. Solution (2.2 ml) was placed into a quartz cuvette and the background luminescence was measured. Then, an aliquot of the solution to be analyzed (in common case, 0.05–0.2 ml) was added and the total intensity of background and the sample was determined. The decay time of uranium lumi-

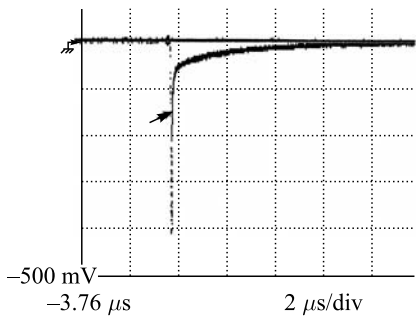

Fig. 1. Time dependence of the uranyl luminescence in a 4.5 M H_2SO_4 solution. Start is a nitrogen laser pulse. The short-lived background luminescence is clearly seen, as well as the relatively long-lived uranyl luminescence. The background luminescence can be significantly suppressed by measuring the luminescence with a delay of several microseconds after laser pulse

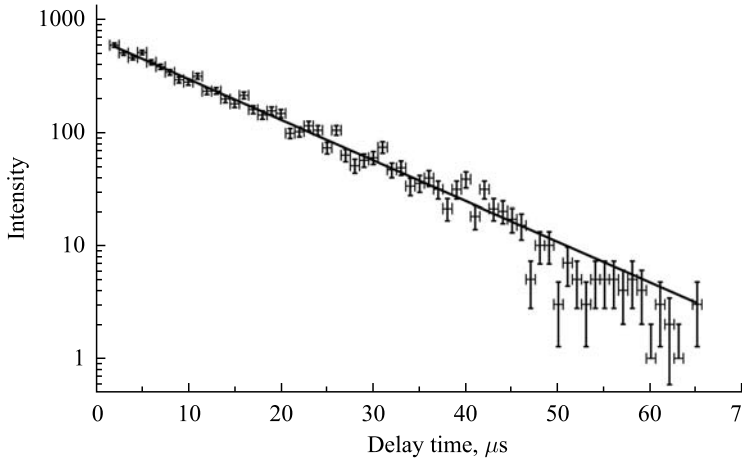

Fig. 2. Photoluminescence of $UO_2F_5^{3-}$ in $H_2O + CsF$ (42%) solution. pH = 9.0. Excitation by nitrogen pulse (10 ns) laser. Registration at $\lambda = 520$ nm, $\delta\lambda = 9$ nm. Gate time 1 μs. 200 laser pulses per channel were made. Laser beam diameter 5 mm, power in laser pulse 15 kW. Luminescence lifetime $\tau = 12.08 \pm 0.25$ μs

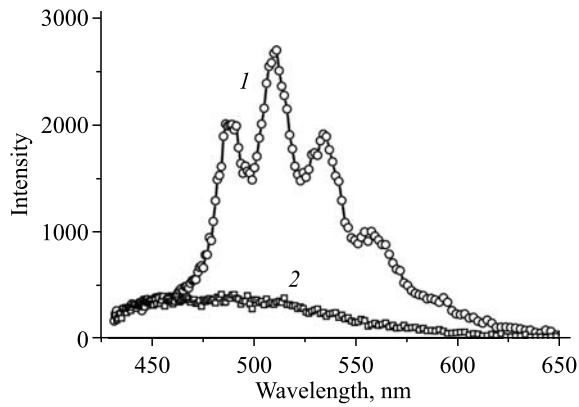

Fig. 3. *1* — photoluminescence of $UO_2F_5^{3-}$ (0.005 M) in $CsF\,(42\%) + H_2O +$ luminol (10^{-4} M); *2* — luminol 10^{-4} M in $CsF\,(42\%) + H_2O$, pH 10.07. Excitation by pulsed (10 ns) nitrogen laser. Delay time 2 μs. Gate time 100 μs

nescence in polysilicate was approximately 500 μs. After mineralization of the sample and preparation of a solution for analysis the decay time of uranium luminescence was about 300 μs. The limit of detection decreases by a factor of 1.5–2 in passing of blood plasma added into solution from 0.05 to 0.15–0.25 ml. Thus,

the permissible volume of blood plasma does not exceed 0.15–0.25 ml. Comparing concentrations of uranyl in blood plasma and in urine one can estimate the time when the uranyl was got into organism. Without mineralization the limit of uranyl detection in blood plasma was 0.1 ng/ml and after mineralization it was up to 8–10 pg/ml. The limit of uranyl detection in urine in our TRLIF experiments was up to 5 pg/ml. We applied TRLIF for samarium and europium detection in urine. We found that a high sensitivity of europium and samarium detection in aqueous solutions can be reached in the case of complex formation of these elements with fluorinated β diketones and trioctylphosphine oxide (TOPO) in the presence of nonionic surfactants. In this work, we used pyvaloyltrifluoroacetone (PTFA), TOPO, and Triton X-100. The use of PTFA provides a low limit of detection of europium and samarium. The strongest luminescence radiation in the spectra of europium and samarium was observed at 614 and 643 nm, respectively. The wavelength of radiation maximum for both elements does not vary in passing from neat solution to a solution with addition of urea samples. The lifetimes of europium and samarium luminescence are 800 and 60 μs, respectively, in both neat solution and solutions with addition of urine samples. By this is meant that in this case there is no dynamic quenching of luminescence, and the variation of luminescence intensity is apparently caused by absorption of exciting laser radiation in the solution in addition of urine sample. When 0.2 ml of urine is added into 2.2 ml solution, the intensity of luminescence decreases by a factor of more than 2; hence, the volume of the sample required for analysis should be increased. The limit of detection was estimated from the 3σ background criterion, where σ is the standard deviation of the background measurements. In pure solution the limit of detection of europium was 0.005 ng/ml and samarium, 0.07 ng/ml. After addition of 0.2 ml of urine the limit of detection of europium was 0.015 ng/ml and samarium, 0.2 ng/ml.

Unfortunately, Pu, Np, and also a number of valence forms of uranium give no direct luminescence in solutions. For determination of valence forms of Pu, Np, and a number of valence forms of U not most sensitive methods of laser spectroscopy are used. Among them [1] are laser-induced photoacoustic spectroscopy (LIPAS) with LOD 10^{-7} M, absorption spectroscopy with LOD 10^{-5} M, and laser spectroscopy with the use of effects of thermal lens (TLS) with LOD 10^{-6} M. We proposed to use high-sensitive chemiluminescence method (TRLIC) for detection of such actinides [1, 8].

2. TRLIC, SINGLE-STEP EXCITATION SCHEME

The behavior of the UO_2^{2+} ion excited by radiation of pulse nitrogen laser in aqueous solutions with a high content of CsF and luminol was studied at various pH in [1, 9]. Under the action of radiation of nitrogen laser luminol gives the luminescence in the same spectral range as the luminescence of uranyl ion (Fig. 3).

Naturally (Figs. 3 and 4), there are two complexes ($UO_2F_5^{3-}$ and $UO_2F_4OH^{3-}$) in such a solution [1, 9]. $UO_2F_5^{3-}$ is a luminescent complex (Fig. 3). $UO_2F_4OH^{3-}$ is a nonluminescent complex, but after proper excitation it generates OH radicals, which can be detected from the enhancement of the luminol luminescence (Fig. 4, *c*).

Chemiluminescence of luminol under the action of OH radicals appearing in the solution was considered. In Fig. 4, *a–c*, the kinetic data on luminol luminescence in uranyl-free and uranyl-containing solutions are presented. It is evident that with increasing pH to 11.85 the ratio of the intensity of uranyl luminescence at the maximum of luminol luminescence in the solution containing uranyl increases in comparison with that of the solution containing no uranyl. An increase in pH results in the increase of the concentration of $UO_2F_4OH^{3-}$ complexes in the solution, an increase in the number of quanta absorbed by these complexes, and a decrease in the number of quanta absorbed by luminol molecules [1, 9]. The decrease in the chemiluminescence efficiency with increasing pH of the solution from 8.19 to 9.86 (Fig. 4, *a* and *b*) suggests that the quantum efficiency of chemiluminescence under excitation of $UO_2F_4OH^{3-}$ is lower than that under optical excitation of luminol. The decrease in the luminol chemiluminescence owing to decrease in the light absorption of luminol with increasing pH is not compensated

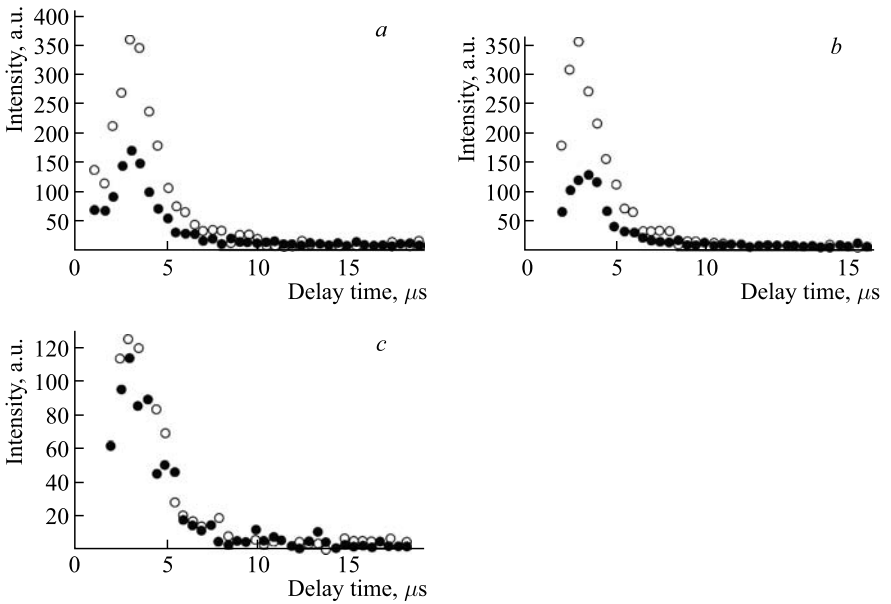

Fig. 4. Kinetics of luminol luminescence at the wavelength 459 nm in 42% solution of CsF in H_2O. pH: 8.19 (*a*), 9.86 (*b*), 11.85 (*c*). Open circles — without uranium, filled circles — 0.009 M of UO_2^{2+}. Luminol concentration 10^{-4}. Gate time 1 μs

at this pH by chemiluminescence generated by excitation of $UO_2F_4OH^{3-}$. Further increase in pH (Fig. 4, *c*) results in increase in the total chemiluminescence efficiency. As a result, we can conclude that the main source of OH radicals is [9] electron transfer in the hydrolyzed uranyl complex from the ligand (OH^-) to uranyl ion $UO_2F_4OH^{3-}$.

Data on luminol chemiluminescence in solutions containing complexes $AnO_2F_4OH^{3-}$ (An = U, Pu, Np) were analyzed in [9–12]. The luminescence was excited by nitrogen laser radiation. In the presence of uranyl, plutonyl, and neptunyl hydroxyfluoride complexes, luminol chemiluminescence sensitized by OH radical was observed. Hydroxy radicals are generated by phototransfer of electrons from hydroxy ligand to the metal. The fact that the intensity of chemiluminescence initiated by photoexcited $AnO_2F_4OH^{3-}$ is comparable with that of chemiluminescence initiated after direct absorption of laser radiation with luminol molecules [9–11] indicates that the luminol chemiluminescence can be used to determine actinide traces in solutions.

The possibility of observation of chemiluminescence caused by the reaction of OH radical with luminol molecule allows detecting the presence of actinyl ions UO_2^{2+}, PuO_2^{2+}, NpO_2^{2+}, and probably AmO_2^{2+} in the solution. The results we obtained [9–11] allowed a conclusion that absorption of UV radiation with UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} ions forming mixed hydroxyfluoride complexes under the experimental conditions leads to generation of OH radicals. Their formation results from an electronic transition with charge transfer from the hydroxide ion coordinated with AnO_2^{2+} to the actinide ion. Actually, this is a photochemical reduction of actinide ion [9–11]. The arising OH radicals initiate chemiluminescence, oxidizing luminol molecules. Thus, absorption of a laser pulse gives rise to relatively long-lived chemiluminescence trace (Figs. 4 and 5) allowing detection

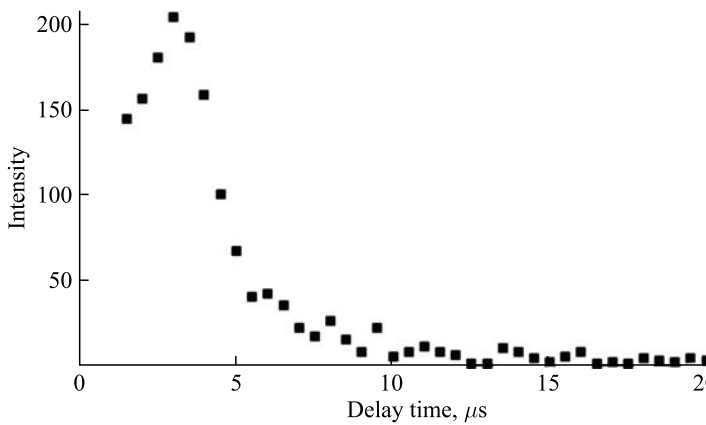

Fig. 5. Kinetic curve of luminol chemiluminescence induced by excitation of plutonyl in solution

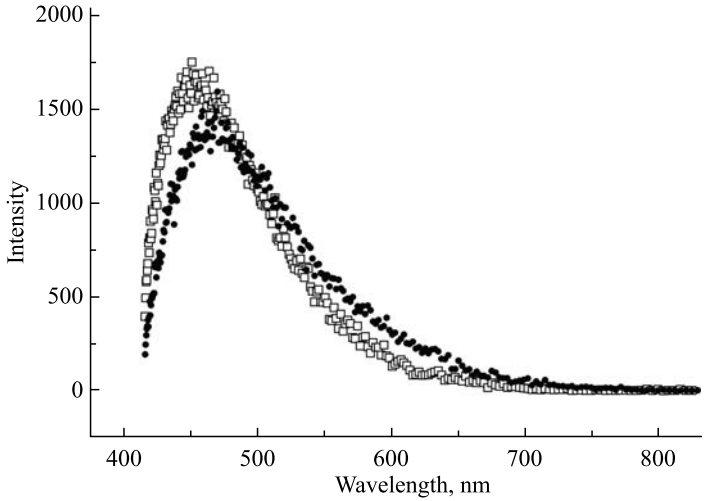

Fig. 6. Photoluminescence of $PuO_2F_5^{3-}$ (0.001 M) + luminol 10^{-4} M in CsF (42%) + H_2O (dots) and luminol 10^{-4} M in CsF (42%) + H_2O (open squares). pH = 8.5. Excitation by pulsed (10 ns) nitrogen laser. 200 laser pulse were made per channel at spectrum measurement, laser beam diameter 5 mm, power in laser pulse 15 kW. Delay time 2 μs. Gate time 50 μs

of actinide ions in solution using Time Resolved (TR) method [1, 8]. This method allows detection both of ions that cannot be detected by intrinsic luminescence.

Chemiluminescence initiation by UV radiation of a nitrogen laser is unselective (Fig. 6), and this does not allow identification of actinides and, the more so, of their valence forms [1, 8]. In addition, UV radiation is absorbed with luminol molecules, which makes it difficult to interpret the results. A key problem of chemiluminescence application to detection of lanthanides and actinides in solutions is an increase in the selectivity of detection.

3. TRLIC, TWO-STEP EXCITATION SCHEMES (TWO STEP–TWO COLOR AND TWO STEP–ONE COLOR)

Chemiluminescence initiation by radiation with $\lambda \leqslant 400$ nm is unselective (Fig. 7). Furthermore, UV radiation is absorbed by luminol molecules, which additionally complicates interpretation of the results obtained. Appropriate selectivity can be reached when chemiluminescence is initiated by transitions within $5f\,/\,4f$ electron shell of actinide / lanthanide ions [1–4, 8, 12], which correspond to visible spectral range (Fig. 7, curve *1*). Since the energy of single-quantum excitation in visible range is insufficient for initiation of luminol chemiluminescence, it was proposed to excite actinide ion by multiquantum absorption of visible light.

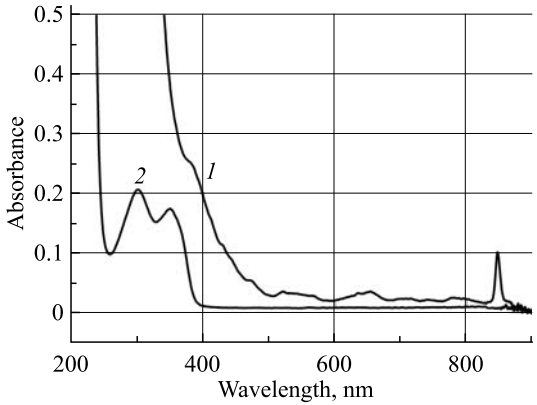

Fig. 7. Absorption spectra: *1* — PuO_2^{2+} (0.003 M) in solution 42% $CsF + H_2O$; *2* — luminol (0.001 M) in solution 42% $CsF + H_2O$; pH = 10.5

It is evident that for realization of this idea one needs to use light sources with sufficiently high power. We used two pulse-tunable dye lasers (Fig. 8) excited with nitrogen laser [1–4]. The *two step–two color* and *two step–one color* [1–4] schemes were used for chemiluminescence excitation. The intensity of chemiluminescence as a function of wavelength generated by the tunable laser (spectrum of chemiluminescence excitation) was measured (Figs. 9–12).

The experiments were performed on an installation (Fig. 8) consisting of pulse nitrogen laser OBB-1010 with a pulse length of 1 ns and generation power of approximately 1.4 MW and two dye lasers — OBB-1012 and OBB-1011. When using two dye lasers, the radiation generated by nitrogen laser was simultaneously

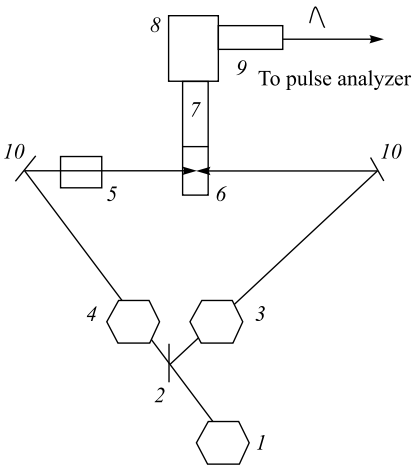

Fig. 8. Scheme of the experimental setup: *1* — nitrogen laser OBB-1010; *2* — beam splitter; *3* — dye laser OBB-1011; *4* — dye laser OBB-1012; *5* — optical delay line OPD-1; *6* — cuvette with solution; *7* — optical fiber; *8* — monochromator DMR-4; *9* — photomultiplier; *10* — mirror

derived to both dye lasers through a beam splitter. This scheme allows synchronization of laser pulses in a cuvette within an accuracy of 10 ps at generation pulse length of 800 ps for laser OBB-1012 and 1 ns for laser OBB-1011. A laser beam splitter was oriented at an angle of 45° to the direction of laser beam generated by nitrogen laser and divided this beam to two beams with equal intensities. Laser beams generated by two dye lasers were aligned in the opposite directions and directed to a cuvette 1 cm thick. Dye laser of OBB-1012 incorporates a grazing incident design laser cavity for high resolution followed by a secondary amplifier cell to boost the power. The result is a narrow 0.04 nm output from 360 to 900 nm, a pulse width of 1 ns, and an energy of 220 μJ per pulse at 500 nm. With the addition of OBB's OL-403 Frequency Doubler, tunable wavelengths from 235 to 345 nm can be attained.

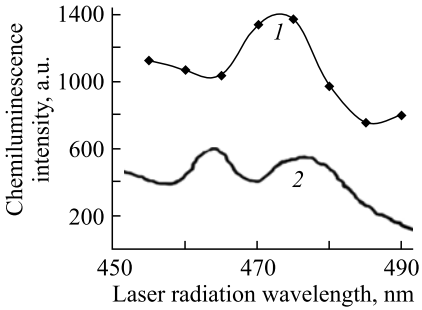

Fig. 9. *1* — spectrum of chemiluminescence excitation by the *two step–one color* scheme in luminol + Sm(III) solution; *2* — absorption spectrum of Sm^{3+}

Chemiluminescence of luminol was collected with a lense whose optical axis was oriented at an angle of 39° to the direction of laser beams and was transferred to the entrance slit of double prismatic monochromator DMR-4 with flexible optical fiber. Chemiluminescence was recorded in the quantum counting mode with the use of gating technique at a wavelength of 460 nm corresponding to the maximum of luminol chemiluminescence. The length of gating impulse (strobe) was 10 μs, delay time, 2 μs.

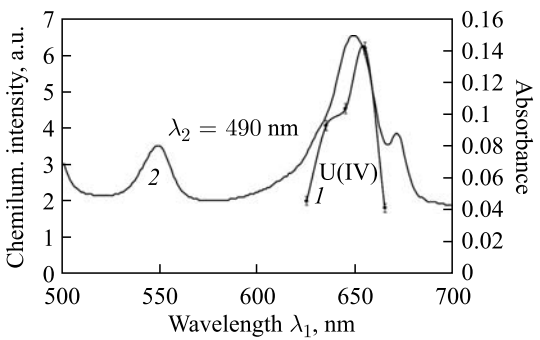

Fig. 10. *1* — spectrum of chemiluminescence excitation by the *two step–two color* scheme in luminol + U(IV) solution; *2* — absorption spectrum of U(IV) in aqueous HCl solution

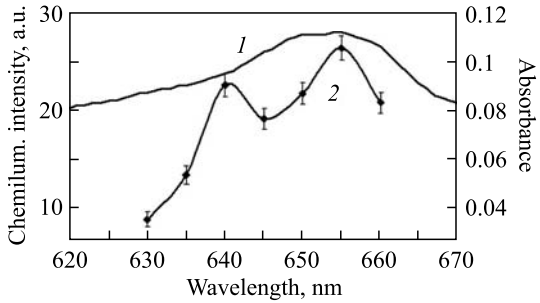

Fig. 11. *1* — the absorption spectrum of Pu(IV) in solution. *2* — chemiluminescence excitation spectrum for the luminol + Pu(IV) + CsF solution using the *two step–one color scheme*

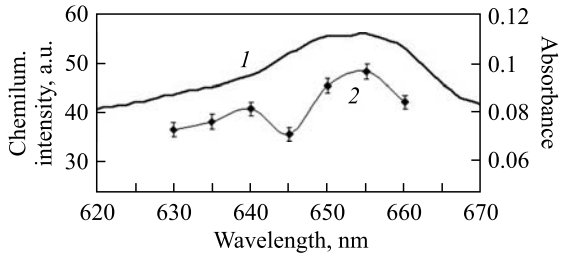

Fig. 12. Comparison of (*1*) the absorption spectrum of Pu(IV) and (*2*) the intensity of chemiluminescence at various wavelengths of radiation generated by the OBB-1012 dye laser (*two step–two color scheme*)

A radiation wavelength (λ_1) of laser OBB-1012 was tuned in the limits of absorption band of detectable actinide valence or molecular form. A radiation wavelength of laser OBB-1011 was fixed in the region $\lambda_2 = 490{-}500$ nm (*two color–two step* chemiluminescence excitation scheme). In *one step–one color* (two laser photons absorbed from one laser pulse) only tunable OBB-1012 (λ_1) laser was used. The intensity of chemiluminescence as a function of wavelength generated by the tunable laser (spectrum of chemiluminescence excitation) was measured. The presence of absorption band of detectable actinide in the range of tuning of the first (λ_1) laser wavelength results in appearance of a peak of luminol chemiluminescence. Peaks in the spectrum of chemiluminescence excitation are connected with the definite valence or molecular forms of detectable actinides. The intensity of chemiluminescence was measured [2–4] only during the strobe pulse duration with the proper delay time after laser pulse (TRLIC). Thus, background radiation can be efficiently suppressed and the chemiluminescence signal will be more clear.

The experiments were carried out at concentrations of f element of the order of 10^{-3} M. It is shown that a multistep scheme of chemiluminescence excitation increases the selectivity of the f element detection. Because the LOD for the chemiluminescence method of detection may reach 10^{-13} M [7], the multistep excitation scheme for the chemiluminescence initiation is promising for further development of a method that may become competitive in sensitivity and selectivity with ICP-MS and other trace detection methods [1].

We recorded the spectra of chemiluminescence excitation as a result of excitation of Sm^{3+} ions with dye laser by using *two step–one color* scheme [2–4].

There is no complete similarity of the spectrum of chemiluminescence excitation to absorption spectrum (Fig. 9). This experimental fact is connected with the difference in the selection rule for single-quantum and multiquantum absorption [2–4].

Figure 10 shows a portion of the U(IV) absorption spectrum and the chemiluminescence intensity varying with variation of the generation wavelength of the OBB-1012 tunable laser. As can be seen, the chemiluminescence excitation spectrum on varying the generation wavelength of the first laser is similar to the uranium absorption spectrum in the tuning range. The presence of the U(IV) absorption band in the region of tuning of the emission wavelength of the first laser gives rise to a peak of the luminol chemiluminescence intensity. This fact undoubtedly reflects the selective mechanism of the chemiluminescence excitation [2–4].

Initiation of chemiluminescence as a result of excitation of Pu(IV) with one (Fig. 11) and two (Fig. 12) dye lasers was demonstrated for a solution containing CsF, luminol, and Pu(IV). A solution composition was chosen [2–4] in such a way as to provide favorable conditions for observation of luminol chemiluminescence and to avoid formation of colloidal species of hydrolyzed Pu(IV). As is seen, the spectrum of chemiluminescence excitation is in close agreement with absorption spectrum of Pu(IV) which indicates high selectivity of chemiluminescence excitation.

A comparison of run of the curves presented in Figs. 11 and 12 shows that in the *two step–one color* mechanism (Fig. 11) the slop of the spectral curves is sharper than that in the *two step–two color* mechanism (Fig. 12). The spectrum of chemiluminescence excitation correlated with the absorption spectrum of Pu(IV). In both schemes we realized selective excitation of chemiluminescence, and this selectivity is caused by the features of absorption spectra of Pu(IV) solutions.

Measurement of the spectrum of chemiluminescence excitation requires correct consideration of contribution of the following processes:

(1) Initiation of luminol chemiluminescence as a result of two-quantum excitation of An(IV) by the *two step–one color* scheme, i.e., as a result of absorption by An(IV) of two quanta radiated by one laser.

(2) Initiation of luminol chemiluminescence as a result of two-quantum excitation of An(IV) by the *two step–two color* scheme, i.e., as a result of absorption by An(IV) of two quanta radiated by two lasers.

(3) Initiation of luminol chemiluminescence as a result of two-quantum excitation of luminol molecules.

Of course, the process (3) is a background process and its spectrum of chemiluminescence initiation does not correlate with the absorption spectrum of An(IV).

For detection of small amounts of actinides with the use of chemiluminescence recording, it is necessary to exclude a possibility of registration of luminol luminescence having nature different from chemiluminescence. In this connection, we studied the kinetics of this luminescence in alcoholic solutions with various water content.

It was found that in single-quantum excitation with decreasing water content the intensity of chemiluminescence decreases and luminescence having no burning-up stage typical for chemiluminescence becomes more pronounced. It should be noted that this luminescence (Fig. 13) different from chemiluminescence arises (Fig. 5) in single-quantum UV excitation of luminol molecule and can be significantly depressed in two-quantum excitation induced by radiation with longer wavelength, since in visible region a scheme of two-quantum excitation involving no absorption band of luminol can be chosen (Fig. 7). We showed that this background luminescence of luminol can be significantly depressed in two-quantum excitation of solutions by laser radiation with wavelength longer than 450 nm. This fact is very important in choice of background conditions for recording of trace amounts of actinides in solutions with the use of chemiluminescence.

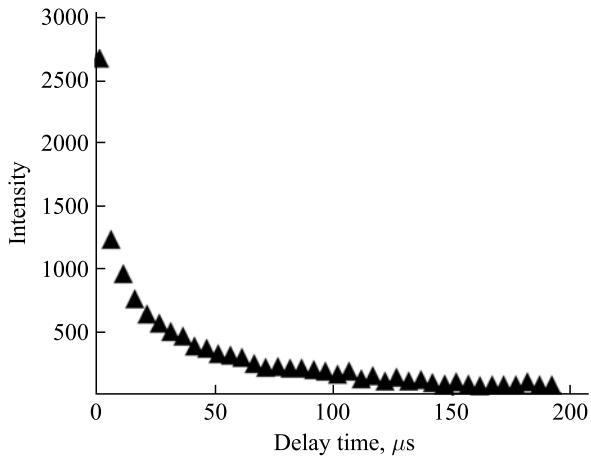

Fig. 13. Kinetics of luminol luminescence in dry methanol

The results we obtained in [13] show that in designing photochemical experiments with powerful light sources (e.g., pulse lasers) it is necessary to take into account the hydrolysis of the excited ions and the concomitant chemical reactions even in strongly acidic solutions. Because of the second-order effects the laser radiation should not be too powerful (usually less than 10^8 W cm^{-2} per a pulse) [2–4]. Thus, when using multistep scheme of chemiluminescence excitation there is a need to choose the power of laser radiation to provide required sensitivity and selectivity.

4. DISCUSSION AND CONCLUSIONS

At present, the most efficient methods of detection of actinides and lanthanides in solutions are methods based on registration of actinides with time resolution, time-resolved laser-induced fluorescence (TRLIF) spectroscopy, having limit of detection (LOD) up to 10^{-13} M [1, 5]. TRLIF may be applied for biological samples analysis. Samples containing a large amount of organic substances should be preliminary mineralized.

Pu, Np, and some U compounds do not produce direct luminescence in solutions, but when excited by laser radiation, they can induce chemiluminescence of chemiluminogen (luminol in our experiments) [1–4]. It is because of its high sensitivity (LOD from 10^{-6} to 10^{-13} M) that chemiluminescence is widely used in many fields [7]. A key problem of chemiluminescence application to detection of lanthanides and actinides in solutions is an increase in the selectivity of detection. Appropriate selectivity can be reached when chemiluminescence is initiated by transitions within $4f\,/\,5f$ electron shell of lanthanide / actinide ions, which correspond to visible spectral range. In some cases chemiluminescence can be simpler to detect than intrinsic luminescence. For example [14], in U(IV) solutions it is possible to excite luminescent transitions, but their lifetimes are shorter than 1 ns, and recording of such transitions is difficult. Since the energy of one-quantum excitation in visible range is insufficient for initiation of luminol chemiluminescence it was proposed [1–4, 8] to excite lanthanide / actinide ion by multiquantum absorption of visible light.

The selective excitation of actinide gives rise to a chemical reaction between molecule or complex containing excited actinide and chemiluminescence agent added into solution. As a result of the reaction, the light is emitted (chemiluminescence) and registered. Using laser radiation with tunable wavelength we can selectively excite various valence forms and molecules of actinides with subsequent registration of chemiluminescence. With knowledge of wavelength at which chemiluminescence appears and the intensity of chemiluminescence, we can determine the concentration of a certain valence form of given actinide and the structure of complex containing this actinide [1–4, 8]. The optimum choice

of laser radiation wavelength on the basis of absorption spectra, scheme of luminescence excitation (single-step or multistep), and chemiluminescence agent is extremely significant for selective and efficient luminescence induction in excitation of actinides. It should be noted that the presence of a time delay between the pulse of laser radiation and the chemiluminescence pulse is an extremely significant feature [1, 8]. This fact allows using time resolution (TR) procedure for detection of chemiluminescence (TRLIC).

Using chemiluminescence of solutions, we found an approach [2–4] to registration of plutonium, uranium, and other elements in solutions with a high sensitivity in excitation of plutonium and uranium with a pulse laser with tunable wavelength. A multistep scheme of chemiluminescence excitation makes this procedure not only highly sensitive but also highly selective method of detection of substances.

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