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CHEMILUMINESCENCE INITIATED
BY LASER-INDUCED EXCITATION OF LANTHANIDE
AND ACTINIDE IONS IN AQUEOUS SOLUTIONS

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Хемилюминесценция, инициированная при лазерном возбуждении ионов
лантанидов и актинидов в водных растворах

Представлены данные по инициированию хемилюминесценции люминола в растворах, содержащих Sm(III), U(IV) и Pu(IV). Хемилюминесценция инициировалась путем многоквантового возбуждения ионов лантанидов и актинидов в области 4f- и 5f-переходов по схемам: две ступени — один цвет и две ступени — два цвета с использованием лазеров на красителях. Мы наблюдали хемилюминесценцию хемилюминогена (люминола), инициированную многоквантовым лазерным возбуждением лантанидов и актинидов в водных растворах. Применение многоквантовой схемы возбуждения хемилюминесценции делает эту методику не только высокочувствительной, но и высокоселективной при детектировании различных веществ.

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Chemiluminescence Initiated by Laser-Induced Excitation of Lanthanide
and Actinide Ions in Aqueous Solutions

Data on luminol chemiluminescence in solutions containing Sm(III), U(IV), and Pu(IV) are presented. Chemiluminescence was induced by multiquantum excitation of lanthanide and actinide ions in the range of 4f- and 5f-electron transitions by the schemes: two steps — one color and two steps — two colors with the use of dye lasers. We observed chemiluminescence of chemiluminogen (luminol) caused by multiquantum excitation of lanthanides and actinides in aqueous solutions by laser radiation. A multistep scheme of chemiluminescence excitation makes this procedure not only highly sensitive but also highly selective procedure of detection of substances.

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

INTRODUCTION

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 [1–6]. The LOD in solutions depends on the impurity luminescence and scattered-light intensity. Efficient optical systems of light collection are used to suppress background, and luminescence is measured in the wavelength range different from the excitation radiation wavelength. However, these precautions do not allow suppression of luminescence background from many impurities. Nevertheless, the background can be efficiently suppressed for lanthanides and actinides using time resolution [1–6]. The point is that the characteristic luminescence lifetime for impurities is $10^{-8}-10^{-9}$ s, while it is $10^{-3}-10^{-6}$ s for lanthanides and actinides. This difference is due to the fact that the luminescence in liquids for many lanthanides and actinides and their compounds is controlled by electron transitions inside the f shell, which are forbidden as dipole $E1$ transitions, therefore, the luminescence lifetime increases. Thus, 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. If the delay time is about a few nanoseconds [3] then the sensitivity of detection will be not so high as for microsecond delay time.

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 are [7–9] 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.

Direct luminescence of Pu, Np, and some U compounds in liquids was not observed due to strong nonradiative deactivation. However, using chemiluminescence of solutions, it is possible to develop detection technique for Pu, Np, and U in liquids with high sensitivity, exciting actinides using various pulsed laser [4, 5]. The Limits of Detection (LOD) for spectrometers using the registration of chemiluminescence [10–12] are in the range from 10^{-6} mol/l to 10^{-13} mol/l depending on the type of solutions and type of detectable molecule. Chemiluminescence is widely used as a detection methods in many fields, such as flow injection analysis, chromatography, biology, medicine, etc.

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A key problem of chemiluminescence application for lanthanides and actinides detection in solutions is the increase of the selectivity of detection. Appropriate selectivity can be reached when chemiluminescence is initiated by transitions within 4f- or 5f-electron shell of lanthanide and actinide ions, which correspond to visible spectral range. Since the energy of one-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 [4, 5].

The selective excitation of actinide gives rise 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 detected. 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. The optimum choice of laser radiation wavelength on the basis of absorption spectra, scheme of luminescence excitation, 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 about a few microseconds between the pulse of laser radiation and the chemiluminescence pulse is extremely significant feature [4, 5, 13, 14]. This fact allows using time resolution (TR) procedure for detection of chemiluminescence. The TR procedure is based on registration of chemiluminescence in some time window with a delay relative to the pulse of laser radiation, which allows significant suppression of the background and increasing sensitivity of this method. In this work an effort was made to realize this approach by initiation of chemiluminescence of luminol through excitation of Sm(III), U(IV) and Pu(IV) ions with laser radiation. Data on luminol chemiluminescence in solutions containing Sm(III), U(IV), and Pu(IV) are presented. Chemiluminescence was induced by two-quanta excitation of lanthanide or actinide ions in the range of 4f- or 5f-electron transitions by the schemes [5]: two steps — one color and two steps two — colors with the use of dye lasers. A multistep scheme of chemiluminescence excitation makes this procedure not only highly sensitive but also highly selective procedure of detection of substances.

1. EXPERIMENTAL

In our experiments for lanthanide and actinide ions excitation following by chemiluminescence initiation we used dye lasers (models OBB-1011 and OBB-1012) pumping by nitrogen laser (model OBB-1010).

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The OBB-1010 Nitrogen Laser delivers a crisp pulse at 337 nm with a hefty 2.4 MWt of peak power. With a pulse width of 1 ns, that results in a pulse energy of 1.45 MWt. We got the specified power with the specified pulse characteristics every time.

The OBB-1011 Dye Laser is built around a single stage Littrow configuration cavity, providing continuously tunable output from 360 to 900 nm. The pulse energy at 500 nm is 250 μJ. With a pulse width of 1 ns and a bandwidth of 1 to 3 nm, the OBB-1011 model is perfect for general spectroscopy.

The OBB-1012 Dye Laser 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.

The radiation generated by nitrogen laser was simultaneously derived to both dye lasers through a beam splitter (Fig. 1). This scheme allows synchronization
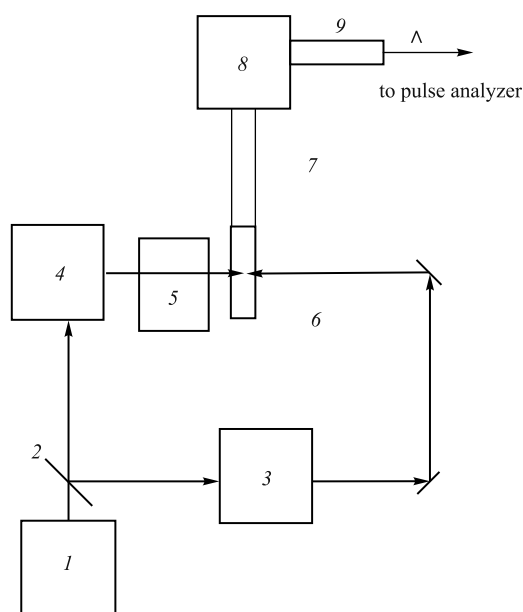

Fig. 1. Block-scheme of the experimental set up. *1* — nitrogen laser (model OBB-1010); *2* — beam splitter; *3* — dye laser (model OBB-1011); *4* — dye laser (model OBB-1012); *5* — optical delay line OPD-1; *6* — cuvette with analyzing solution; *7* — optical fiber; *8* — monochromator DMR-4; *9* — photomultiplier

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. Optical delay line OPD-1 was used for synchronization. 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 of 1 cm in thickness. 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 detected by photomultiplier working in the photon counting mode with the use of gating technique at a wavelength of 460 nm corresponding to the maximum of luminol chemiluminescence. The length [5] of gating impulse (strobe) was 10 μs, delay time, 2 μs.

A radiation wavelength of laser OBB-1011 was fixed. A radiation wavelength of laser OBB-1012 was tuned in the limits of absorption band of detectable actinide valence or molecular form (two colors — two steps chemiluminescence excitation scheme). 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 second 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 only during the strobe pulse duration with the proper delay time after laser pulse (Time-Resolved or TR method). Thus, background radiation can be efficiently suppressed [5] and chemiluminescence signal will be more clear.

2. INITIATION OF LUMINOL CHEMILUMINESCENCE AS A RESULT OF Sm EXCITATION BY LASER RADIATION

The experiments were performed with hydroxo complexes of Sm(III). The wavelength of dye generation for the first step of excitation was chosen based on absorption spectra of solutions containing Sm(III) and luminol. Absorption spectra of samarium chloride and luminol aqueous solutions are presented in Fig. 2. Since the absorption end of luminol (sodium form) is close to the strongest line of samarium spectrum at 401 nm, the experiments on reduction of samarium with laser radiation were performed at the line of 477.5 nm (Fig. 3). This makes easy excitation of $Sm(OH)_3$ complex in a solution to the energy allowing electron transfer from ligand OH^- to the central ion and splitting off of $OH^\bullet$ radical with the tunable laser operated in visible spectral range, i.e., under conditions of the best selectivity of excitation. In this case, the probability of excitation of luminol
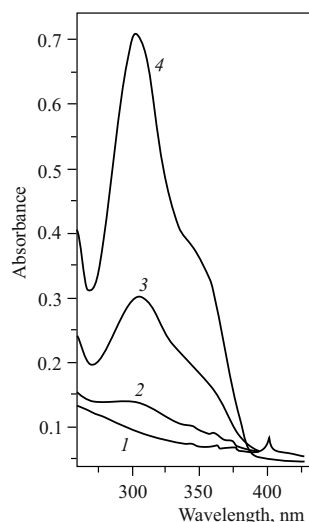
Fig. 2. Absorption spectra of aqueous solutions: *1*) $7.3 \cdot 10^{-3}$ M SmCl$_3$, pH 5.6; *2*) $6.8 \cdot 10^{-3}$ M SmCl$_3$ $+2.9 \cdot 10^{-5}$ M luminol, pH 5.6; *3*) $6.8 \cdot 10^{-3}$ M SmCl$_3$ $+8.79 \cdot 10^{-5}$ M luminol, pH 5.6; *4*) 10^{-4} M luminol, pH 5.6
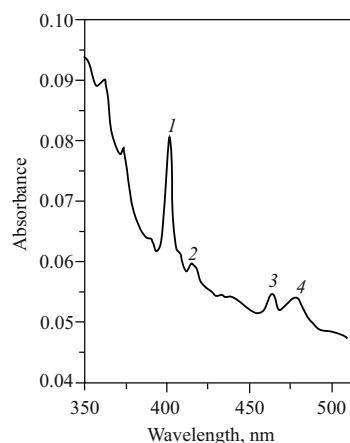
Fig. 3. Absorption spectrum of aqueous solution 10^{-3} M SmCl$_3$ $+2 \cdot 10^{-5}$ M luminol: *1*) 401.0; *2*) 415.0; *3*) 464.0; *4*) 477.5 nm

molecules with laser radiation is minimum. The chemiluminescence arises as a result of oxidation of luminol molecule with OH$^\bullet$ radical induced by light excitation of the ion of the element to be detected (Sm(III)). We successfully recorded the spectra of chemiluminescence excitation (Fig. 4) as a result of excitation of Sm^{3+} ions with dye laser by using two steps — one color scheme [5, 15] (two photons absorbed during one laser pulse).

At a power of laser radiation not exceeding 10^8 W/cm^2 per pulse (the length of laser pulse is in the order of 800 ps, spectral width $\delta\lambda = 0.04$ nm) chemiluminescence arises only under addition of samarium to the solution and when the wavelength of laser generation does not fall into the range of Sm^{3+} absorption chemiluminescence disappears. This means that absorption of two quanta with wavelength of 477.5 nm is sufficient for initiation of luminol chemiluminescence. However, with further increase of the power of laser radiation above 10^8 W/cm^2 per pulse the chemiluminescence begins to burn even the wavelength of laser radiation is outside the range of Sm^{3+} absorption. This means that two-quantum mechanism of excitation via virtual intermediate level of Sm^{+3} ion begins to operate.
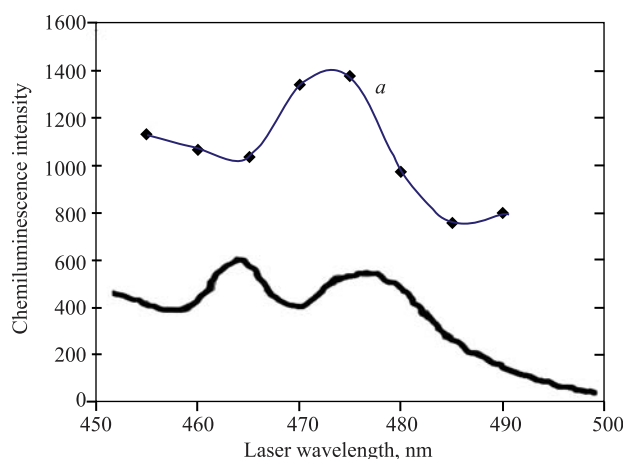
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Fig. 4. Spectrum of excitation of luminol chemiluminescence (*a*) with dye laser in the range of absorption bands of Sm^{3+}. Chemiluminescence is detected at the wavelength of 460 nm. Absorption spectrum of Sm^{3+} is shown below

Thus, when using multistep scheme of chemiluminescence excitation there is a need to choice the power of laser radiation to provide required sensitivity and selectivity.

There is no complete similarity between the spectrum of chemiluminescence excitation and absorption spectrum. This experimental fact connected with the difference in the selection rule for single-quantum and multiquantum absorption.

3. INITIATION OF LUMINOL CHEMILUMINESCENCE AS A RESULT OF U EXCITATION BY LASER RADIATION

We performed experiments on multiquantum excitation of luminol chemiluminescence in solution containing U(IV) with the use of two dye lasers. Luminol was added into the prepared solutions up to concentration of $5 \cdot 10^{-5}$ M. The solution for experiments on multiquantum excitation of chemiluminescence was finely chosen based on the ability of luminol to produce chemiluminescence after excitation of U(IV) and also on the presence of absorption bands in the range of 650 nm typical for U(IV). A characteristic absorption band at approximately 650 nm (PLD 644 dye) was chosen for the first step of two-quantum excitation of U(IV).

In the experiments the OBB-1011 laser was operated at a fixed wavelength of 500 nm. The wavelength of radiation of the OBB-1012 laser was tuned in the limits of the analytical absorption band of U(IV) at 650 nm. We performed

several cycles of chemiluminescence excitation varying wavelength of generation of the OBB-1012 laser. In all cases we recorded variation of chemiluminescence intensity with variation of wavelength. These variations are connected with chemiluminescence of luminol induced by U(IV) excited by laser radiation via two steps — two colors excitation scheme.

The intensity of chemiluminescence of U(IV) solution under irradiation with two lasers varies cymbately with variation of optical density when wavelength of generation of one laser is varied in the limits of absorption band of U(IV) (Fig. 5). This allows conclusion on excitation of chemiluminescence using two steps — two colors excitation scheme under irradiation of a solution with two pulse lasers one of which has wavelength of generation in the limits of absorption band of U(IV). Thus the selectivity of chemiluminescence method of U(IV) detection was provided.

The spectrum of chemiluminescence excitation obtained in retuning of generation wavelength of the second laser is similar to the absorption spectrum of uranium (Fig. 5). The presence of absorption band of U(IV) in the range of retuning of the second laser results in appearance of a peak of luminol chemiluminescence. This fact undeniably confirms the selective mechanism of chemiluminescence excitation.
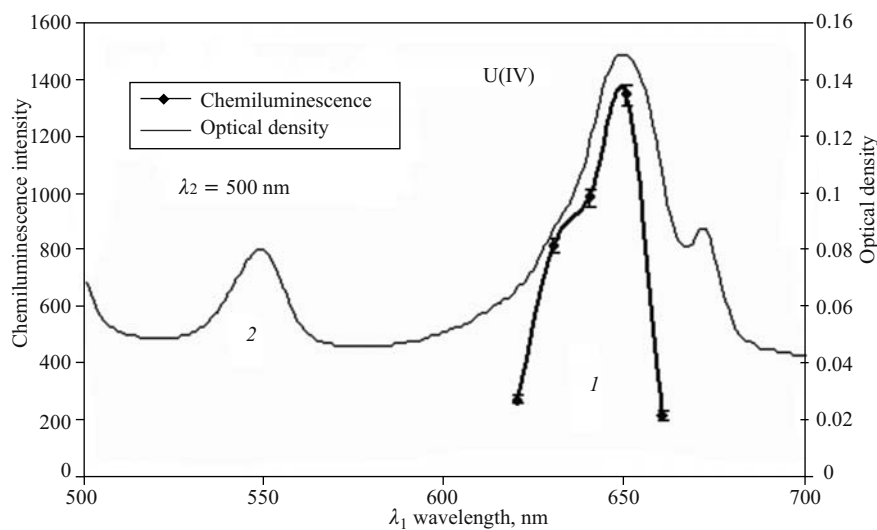

Fig. 5. Two steps — two colors excitation of chemiluminescence in solution luminol+U(IV)+HCl. *1* — chemiluminescence intensity dependence on the wavelength of laser radiation at the first excitation step. When the wavelength of laser radiation corresponds to the wavelength of U(IV) absorption band then the intensity of luminol chemiluminescence is increased. The wavelength of laser radiation at the second step was fixed at 500 nm. *2* — absorption spectrum of U(IV) + HCl solution

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4. INITIATION OF LUMINOL CHEMILUMINESCENCE
AS A RESULT OF Pu EXCITATION BY LASER RADIATION

Initiation of chemiluminescence as a result of excitation of Pu(IV) with two dye lasers was demonstrated for a solution containing CsF, luminol, and Pu(IV). A choice of solution composition was made based on an attempt to provide favorable conditions for observation of luminal chemiluminescence and to avoid formation of colloidal species of hydrolyzed Pu(IV).

Settings of the first dye laser OBB-1011 were unchanged. The laser generated light with a wavelength of 490 nm. The wavelength of radiation of the second dye laser was varied in the range from 630 to 660 nm (PLD-640 dye). The wavelength of radiation of the second dye laser was chosen based on the fact that Pu(IV) has absorption band in this range. As is seen from Fig. 6 variation of the wavelength gives rise to variation of chemiluminescence intensity. The spectrum of chemiluminescence excitation reproduces a part of absorption spectrum of Pu(IV). A measurement of the spectrum of chemiluminescence excitation requires correct consideration of contribution of the following processes.
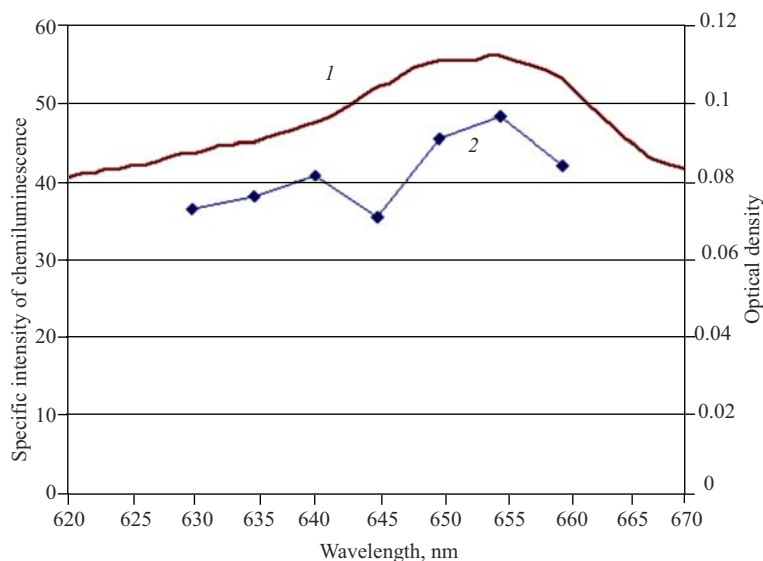

Fig. 6. A comparison of absorption spectrum of Pu(IV) and specific intensity of chemiluminescence at various wavelengthes of radiation generated by the second laser. *1*) Absorption spectrum of the solution to be irradiated. *2*) Specific activity of chemiluminescence of Pu(IV) solution as a function of wavelength of radiation generated by the second laser, wavelength of radiation generated by the first laser — 490 nm. Solution composition: CsF 3.6 M, luminol 10^{-5} M, Pu(IV), solution pH was adjusted by addition of CsOH

1) Initiation of luminol chemiluminescence as a result of two-quantum excitation of An(IV) by the scheme two steps — one color, 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 scheme two steps — two colors, 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.

The latter process (3) requires additional comments. In the field of laser radiation luminol molecule has a possibility to pass into excited state after absorption of two light quanta. Chemiluminescence having characteristic spectrum appears only as a result of excitation transfer to molecule of dissolved oxygen to pass that into active singlet state being efficient oxidant for luminol molecules. This excitation transfer from molecules of organic compounds to oxygen molecules is well known in biochemistry [16]. A contribution of this process can be evaluated from the luminescence of actinide-free luminol solutions. Of course, the process (3) is a background process and its spectrum of chemiluminescence initiation does not correlated with the absorption spectrum of An(IV). Excitation of Pu(IV) chemiluminescence by the mechanism two steps — one color, i.e., without irradiation by the first laser, is demonstrated in Fig. 7.
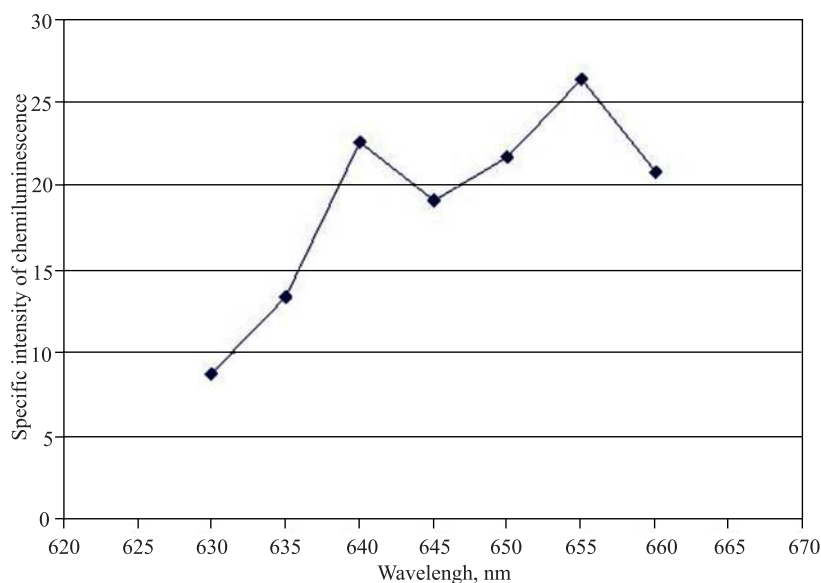

Fig. 7. Specific intensity of chemiluminescence excited by the mechanism two steps — one color in irradiation of Pu(IV) solution by laser OBB-1012 in the range of 630–660 nm

A comparison of run of the curves presented in Figs. 6 and 7 shows that in the mechanism two steps — one color (Fig. 7) the slop of the spectral curves is sharper than that in the mechanism two steps — two colors (Fig. 6). The spectrum of chemiluminescence excitation correlated with 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. The selectivity of chemiluminescence excitation allows us to apply chemiluminescence procedure as a method for selective detection of actinides in various valent states in solutions with the using individual features of valent states absorption spectra.

CONCLUSION

Appropriate selectivity was reached in our experiments when chemiluminescence was initiated by transitions within 4f- or 5f-electron shell of lanthanide or actinide ions, which correspond to visible spectral range. Since the energy of one-quantum excitation in visible range is insufficient for initiation of luminol chemiluminescence, we selectively excited actinide ion by multiquantum absorption of visible light. This fact allows using highly sensitive chemiluminescence procedure for selective detection of various valence lanthanide or actinide species in solutions based on individual features of their absorption spectra.

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