E6-2013-37

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DETECTION OF LANTHANIDES AND ACTINIDES
IN SOLUTIONS BY LASER-INDUCED LUMINESCENCE
AND CHEMILUMINESCENCE

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Детектирование лантанидов и актинидов в растворах
с помощью люминесценции и хемилюминесценции,
индуцированных лазерным излучением

Обсуждается применение лазерной люминесцентной и хемилюминесцентной спектроскопии с временным разрешением для детектирования лантанидов и актинидов в растворах. Проанализированы характеристики хемилюминесценции, инициированной при возбуждении актинидных и лантанидных комплексов в растворах. Также обсуждена возможность использования хемилюминесценции для селективного детектирования ионов актинидов и лантанидов в растворах. Показано, что селективность детектирования может быть повышена с использованием многоступенчатой схемы возбуждения хемилюминесценции. Сделан вывод о том, что лазерная люминесцентная и хемилюминесцентная спектроскопия с временным разрешением может успешно применяться для селективного детектирования лантанидов и актинидов в растворах.

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Detection of Lanthanides and Actinides in Solutions
by Laser-Induced Luminescence and Chemiluminescence

Application of time-resolved laser-induced luminescence spectroscopy and time-resolved laser-induced chemiluminescence spectroscopy to detection of lanthanides and actinides in solutions is discussed. The characteristics of chemiluminescence induced by excited lanthanide and actinide complexes in solutions are considered. A possibility of using chemiluminescence for selective detection of actinide and lanthanide ions having no intrinsic luminescence is discussed. It was shown that high selectivity of detection can be reached with the use of multistep scheme of chemiluminescence excitation. It is concluded that time-resolved luminescence or chemiluminescence laser spectroscopy can be successfully used for selective detection of lanthanides and actinides in solutions.

# 1. INTRODUCTION

Development of laser spectroscopy with tunable lasers gives rise to new procedures for detection of trace amounts of various substances in various media. A possibility to tune a wavelength of laser radiation allows selective action on certain atoms and molecules and, hence, selective detection of these species.

For a practical standpoint, liquids are the most suitable media for analysis since atoms and molecules in liquids are permanently located in the area of interaction with laser radiation. The methods of laser spectroscopy allow determination of valence states and types of molecules. The methods based on luminescence of atoms and molecules are the most sensitive in analysis of solutions. The limit of detection (LOD) determined without preconcentration reaches $10^{-13}$ M and only 1 ml of the solution is required for analysis. Thus, the LOD for a sample can reach $10^{-16}$ moles per 1 ml. To suppress a background, the time-resolved (TR) technique based on a time delay between the beginning of luminescence detection and laser pulse is usually used [1–6].

Unfortunately, Pu, Np, and some U compounds do not give direct luminescence in solutions and commonly adopted TR procedure with registration of luminescence cannot be used for their detection in solutions. At present, the chemiluminescence methods are widely used in biology and medicine for detection of various substances with LOD $10^{-6}$–$10^{-13}$ M and parallel determination of valence states. We, first, demonstrated a possibility of using chemiluminescence method for detection of some actinides and determination of valence states of Pu, Np, and U in solutions [4, 5]. We showed that under irradiation of solutions with laser dissolved Pu, Np, and U species produce chemiluminescence. The most important of all is that we observed a delay of chemiluminescence with respect to laser pulse. This allows us to decrease significantly the background and to use highly sensitive methods of time-resolved laser spectroscopy for chemiluminescence detection.

In this work, the features of luminescence and chemiluminescence in solutions containing lanthanides, actinides and luminol are discussed. A key problem of chemiluminescence application for detection of lanthanides and actinides in solutions is increase in the selectivity of detection. A multistep scheme of chemiluminescence excitation makes this procedure not only highly sensitive but also

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highly selective procedure of detection of various substances. In our experiments, appropriate selectivity was reached when chemiluminescence was initiated by transitions within $4f$- or $5f$-electron shell of lanthanide or actinide ions, which corresponds to visible spectral range. Since the energy of one-quantum excitation in visible range is insufficient for initiation of luminol chemiluminescence, we excited selectively lanthanide or actinide ion by multi-quantum absorption of visible light. Chemiluminescence of luminol was induced by two-quantum excitation of lanthanide or actinide ions in the range of $4f$- or $5f$-electron transitions by the scheme two steps – one color, i.e., in irradiation of actinide-containing solution by one dye laser and by the scheme two steps – two colors, when a solution is irradiated by two dye lasers operating at different wavelengths.

## 2. DETECTION OF LANTHANIDES AND ACTINIDES WITH THE USE OF TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY (TRLIF)

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.

The limit of detection of dissolved substances is governed by the luminescence of impurities and the intensity of scattered light. Efficient optical systems of light collection using to suppress background and luminescence is measured in the wavelength range different from the range of excitation radiation. However, these precautions do not allow suppression of luminescence background from many impurities. Nevertheless, for lanthanides and actinides, the background can be efficiently suppressed using time resolution technique [1–6]. The point is that the characteristic lifetimes of luminescence for impurities are $10^{-8}-10^{-9}$ s, while for lanthanides and actinides, they fall in the range of $10^{-3}-10^{-6}$ s. This difference is due to the fact that for many lanthanide and actinide compounds in liquids, the luminescence is controlled by the electron transitions within the $f$ shell, which are forbidden as dipole $E1$ transitions; this results in the increase of luminescence lifetimes. Thus, the background radiation can be efficiently suppressed by using pulse laser radiation for solution excitation and measurement of the luminescence with a delay ($10^{-3}-10^{-6}$ s) after laser pulse.

The solution to be analyzed is exposed to a pulse ($10^{-8}-10^{-9}$ s) laser beam. The luminescence spectrum is measured with a delay of $10^{-3}-10^{-6}$ s with respect to the laser pulse (Fig. 1). This method has been termed time-resolved laser-induced fluorescence (TRLIF). The TRLIF method allows detection of lanthanides and actinides with concentration less than $10^{-13}$ M [1, 4]. The TRLIF technique features selectivity in four parameters: laser radiation wavelength, mea-
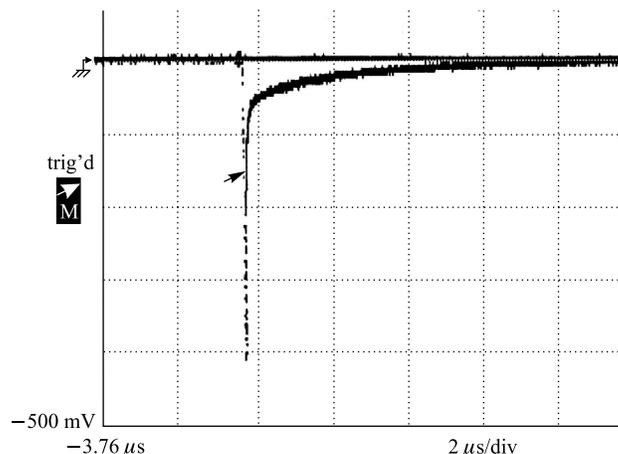
Fig. 1. Intensity of uranyl luminescence in a 4.5 M $H_2SO_4$ solution as a function of time. Start point is a nitrogen laser pulse. The short-lived background luminescence is clearly seen, as well as the relatively long-lived uranyl luminescence. The background luminescence can be significantly suppressed by measuring the luminescence with a delay of several microseconds after laser pulse (TRLIF method)

sured radiation wavelength, measured delay with respect to the pulse laser, and measured time.

The LOD of actinides and lanthanides by TRLIF method reached to the present time is summarized in Table 1 and Table 2.

**Table 1. Limit of detection (LOD) of lanthanides by TRLIF method**

| Element | $Eu^{3+}$ | $Tb^{3+}$ | $Gd^{3+}$ | $Dy^{3+}$ | $Sm^{3+}$ | $Ce^{3+}$ | $Tm^{3+}$ |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| LOD (M) | $10^{-12}$ | $10^{-9}$ | $10^{-8}$ | $10^{-10}$ | $10^{-10}$ | $10^{-9}$ | $10^{-6}$ |

**Table 2. Limit of detection (LOD) of actinides by TRLIF**

| Element | $UO^{2+}$ | $Cm^{3+}$ | $Am^{3+}$ |
|---------|-----------|-----------|-----------|
| LOD | $10^{-13}$ M (27 pg/l) | $10^{-13}$ M (24 pg/l) | $10^{-9}$ M (240 ng/l) |

At present, the luminescence of only $UO_2^{2+}$ (Fig. 2), $Am^{3+}$, $Cm^{3+}$, $Cf^{3+}$, $Bk^{3+}$ and $Es^{3+}$ is known. The $UO_2^{2+}$ and $Cm^{3+}$ ions have enough large energy gap ($> 10^4$ cm$^{-1}$) for luminescence level [6]. The other actinide ions have lesser energy gap (4500 cm$^{-1}$–5000 cm$^{-1}$) and the quantum yields of luminescence for these ions are very sensitive to the type of solvent and vibration of ligands bonded to actinide ion in the complexes. The $Np^{3+}$ and $Pu^{3+}$ ions have the energy gap less than 3000 cm$^{-1}$, and for $PuO_2^{2+}$, the energy gap is about 1500 cm$^{-1}$. Therefore, an observation of direct luminescence of Np and Pu in solutions

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(vibration energy for O–H band is about 3600 cm$^{-1}$) is practically impossible in most cases because of very strong rate of radiationless deactivation. For this reason, at present, direct application of the TRLIF method to the detection of Pu and Np in solutions seems to be impossible. The other laser spectroscopy methods, which are not so sensitive as TRLIF, are used now to detect Pu and Np in solutions. In addition, the TRLIF method is applicable to the detection of only certain valence of lanthanides and actinides (see Table 1 and Table 2) and limited group of complexes in solutions.

However, many of the characteristics of lanthanides and actinides, including characteristics of migration in the environment, depend on the valence state and type of molecules. Therefore, the problem of development of highly sensitive laser spectroscopy methods for detection of lanthanides and actinides (including Pu and Np) in solutions for various valence states and type of molecules is of great importance for analytical purposes.

## 3. DETECTION OF LANTHANIDES AND ACTINIDES WITH THE USE OF TIME-RESOLVED LASER-INDUCED CHEMILUMINESCENCE SPECTROSCOPY

The luminescence method based on excitation of intrinsic luminescence of actinide and lanthanide ions is one of the most sensitive procedures of detection of actinides and lanthanides in aqueous solutions [1–6]. The distinctive feature of this method is high selectivity caused by the individuality of luminescence spectra of these elements (Fig. 2). However, lanthanides and actinides in various
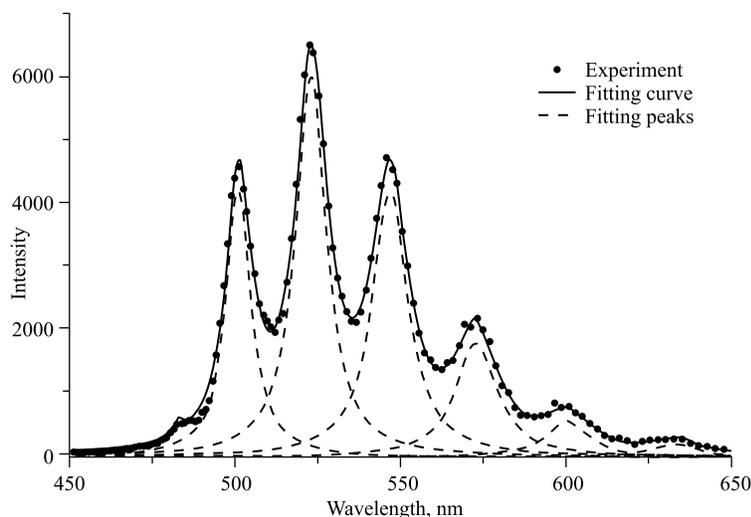


Fig. 2. Luminescence spectrum of uranyl ion

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valence states do not all exhibit luminescence properties. For selective detection of valence forms of actinides having no intrinsic luminescence in solutions, laser spectroscopy methods are commonly used [7–9] but these methods have lower sensitivity than those based on detection of luminescence. Of some interest was to use advantages of luminescence procedure for selective detection of actinides and lanthanides having no intrinsic luminescence by initiation of luminescence of some agents as an example luminol (5-amino-1,2,3,4-tetrahydro-1,4-phthalazindione) via excitation of the element to be detected, the so-called chemiluminescence. The use of chemiluminescence methods for detection of actinides in solutions allows the sensitivity to reach the limit of detection from $10^{-6}$ to $10^{-13}$ M depending on chemical form of actinide in a solution [10–12]. It is because of its high sensitivity that chemiluminescence is widely used in many fields such as flow injection analysis, chromatography, biology, medicine, etc. [11].

Initially, studies of this kind were performed for $AnO_2^{2+}$ ions (An = U, Np, Pu) [4, 5, 13, 14] at different pH and excitation of $AnO_2^{2+}$ ion with UV radiation produced by nitrogen laser. We have concluded that in moderately acid and alkaline solutions the OH radical is formed as a result of excitation of $AnO_2^{2+}$ ion and in turn the OH radical reacts with luminol molecule to initiate chemiluminescence. We observed experimentally the presence of a time delay between the pulse of laser radiation and the chemiluminescence response for solutions containing luminol and actinide complexes (An = U, Np, Pu) (Fig. 3). This fact is of great importance since it allows using time resolution (TR) procedure for detection of chemiluminescence. The TR procedure is based on registration of chemiluminescence in a 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. The sensitivity of detection can be additionally increased with the use of wavelength range corresponded to the maximum of chemiluminescence spectrum (Fig. 4) for chemiluminescence registration.
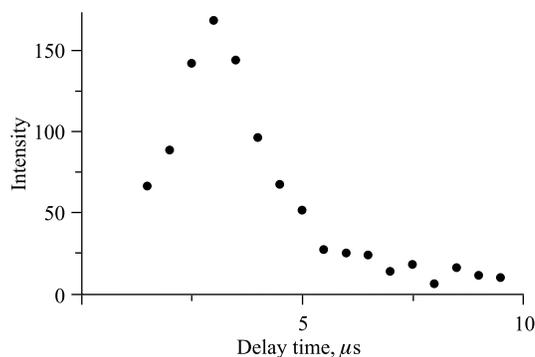


Fig. 3. Kinetic curve of luminol chemiluminescence induced by excitation of plutonyl ion in aqueous solution

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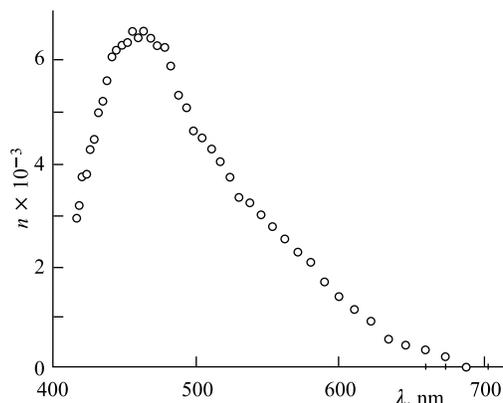
Fig. 4. Typical spectrum of luminol chemiluminescence

However, initiation of chemiluminescence via excitation of $AnO_2^{2+}$ ion with UV radiation is not selective. In addition, UV radiation is absorbed with luminol molecules, which makes difficult interpretation of the results. 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 can be reached when chemiluminescence is 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, it was proposed to excite lanthanide and actinide ions by multi-quantum absorption of visible light [4–5]. The selective excitation of $f$ element gives rise to light-induced reduction of the element with formation of OH radical. As a result of the reaction between OH radical and chemiluminescence agent, the light is emitted. In the case of luminol, the key intermediate of this process is an $\alpha$-hydroxyperoxyde formed in oxidation of heterocyclic ring [11]. This intermediate decomposes to form 3-aminophthalate ion in the excited state. When the ion relaxes to the ground state, the light is emitted. The use of laser radiation with tunable wavelength allows selective excitation of actinide or lanthanide species with subsequent registration of chemiluminescence. In so doing, it is of value to have a time delay between the laser pulse and beginning of chemiluminescence registration, which is reached by using time resolution procedure for chemiluminescence detection. We have made an effort to realize this approach by initiation of luminol chemiluminescence via excitation of Sm(III), U(IV) and Pu(IV) ions with laser radiation. Here, data on luminol chemiluminescence in solutions containing Sm(III), U(IV), and Pu(IV) are presented.

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Chemiluminescence was initiated by two-quantum excitation of lanthanide or actinide ions in the range of $4f$- or $5f$-electron transitions by the schemes: two steps – one color and two steps two – colors. Experiments were performed on an installation [15–17] comprising an OBB 1010 pulse nitrogen laser with a generation pulse length of 1 ns and a power of approximately 1.4 MW and two dye lasers, OBB 1012 and OBB 1011 (Fig. 5). The radiation generated by nitrogen laser passed through a beam splitter to both dye lasers. This scheme allowed synchronization of laser pulses in the cell with an accuracy of 10 ps at the generation pulse lengths of 800 ps for OBB 1012 laser and 1 ns for OBB 1011 laser. The beam splitter was oriented at an angle of $45°$ to the direction of the nitrogen laser radiation and split the beam into two beams of equal intensity. The laser beams from two dye lasers were directed to a cell of 1 cm in thickness toward each other. The chemiluminescence radiation of luminol was collected by a lens with the optical axis oriented at an angle of $39°$ to the di-
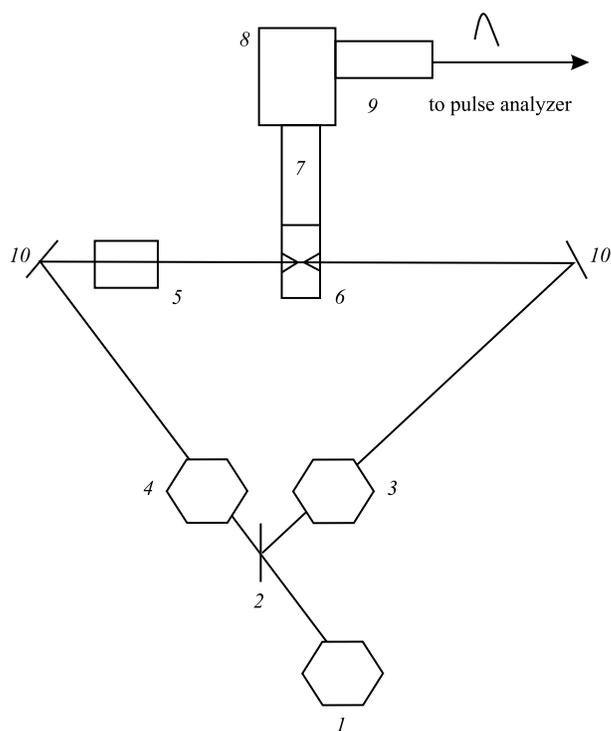


Fig. 5. Scheme of the experimental installation: nitrogen laser OBB-1010 (*1*); beam splitter (*2*); dye laser OBB-1011 (*3*); dye laser OBB-1012 (*4*); optical delay line OPD-1 (*5*); cuvette with solution (*6*); optical fiber (*7*); monochromator DMR-4 (*8*); photomultiplier (*9*); mirror (*10*)

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rection of the laser beams and was transmitted using a flexible light guide to the inlet slit of a DMR-4 double prism monochromator. Data were recorded at a wavelength of 460 nm corresponding to the maximum of the luminol chemiluminescence. The gate length was 10 $\mu$s, and the delay time was 2 $\mu$s. The pulse repetition frequency of the nitrogen laser was 6 Hz. In spectra presented in Figs. 6–9, the chemiluminescence intensity was normalized to the power generated by dye laser.

First, we performed experiments on initiation of luminol chemiluminescence as a result of excitation of Sm(III) hydroxo complexes with laser radiation. The wavelength of dye laser radiation for the first step of excitation was chosen based on absorption spectra of solutions containing Sm(III) and luminol. Since the end of luminol absorption is close to the strongest line in the spectrum of samarium at 401 nm, the experiments on samarium reduction with laser radiation were performed at the wavelength of 477.5 nm. This facilitates excitation of $Sm(OH)_3$ complex to the energy allowing electron transfer from ligand $OH^-$ to the central ion and abstraction of OH radical under two-quantum absorption of radiation of 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 molecules with laser radiation is the lowest. The chemiluminescence arises as a result of oxidation of luminol molecule with OH radical induced by Sm(III) under light radiation. We recorded the spectra of chemiluminescence excitation as a result of excitation of $Sm^{3+}$ ions with dye laser by the scheme two steps – one color [5, 15, 16] (Fig. 6) (two photons are absorbed during one laser pulse).
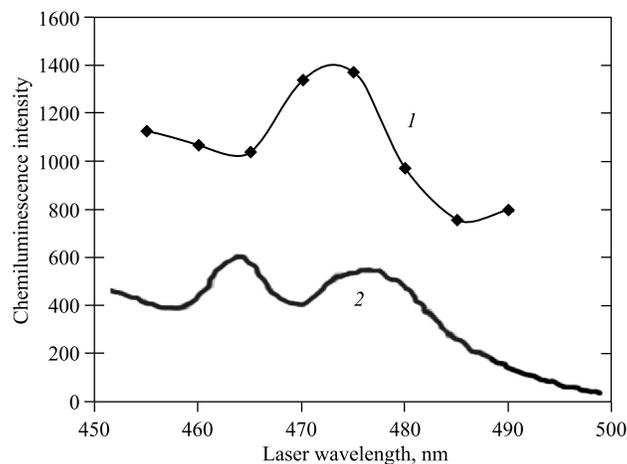


Fig. 6. Spectrum of chemiluminescence excitation by the scheme two steps – one color in luminol + Sm(III) solution (*1*); absorption spectrum of $Sm^{3+}$(*2*)

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At a power of laser radiation not exceeding $10^8$ W·cm$^{-2}$ per a pulse (the length of laser pulse is in the order of 800 ps, spectral width $\delta\lambda = 0.04$ nm) chemiluminescence arises only after addition of samarium to the solution. 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 to initiate luminol chemiluminescence. However, with further increase in the power of laser radiation above $10^8$ W·cm$^{-2}$ per a pulse the chemiluminescence arises even the wavelength of laser radiation is outside the range of Sm$^{3+}$ absorption. This fact suggests two-quantum mechanism of chemiluminescence excitation via virtual intermediate level of Sm$^{3+}$ ion. It should be noted that there is no complete similarity between the spectrum of chemiluminescence excitation and absorption spectrum. This experimental fact can be explained by the difference in the selection rules for single-quantum and multi-quantum absorption.

In the experiments on initiation of luminol chemiluminescence, as a result of U(IV) excitation, we used a $2 \cdot 10^{-3}$ M solution of U(IV) in 0.3 M HCl, containing $5 \cdot 10^{-5}$ M luminol. In such a solution, U(IV) does not undergo hydrolysis and luminol is still capable of chemiluminescence. For the excitation, we used the two steps – two colors scheme. The OBB 1011 laser emitted light with a fixed wavelength of 490 nm. The emission wavelength of the OBB 1012 laser was tuned within the limits of the U(IV) analytical absorption band with a maximum at 650 nm (PLD 644 dye was used). We measured the intensity of the chemiluminescence arising upon solution irradiation and the generation energy of the tunable laser. 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. Figure 7 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 (data for five wavelengths). As can be seen, the chemiluminescence excitation spectrum on varying the generation wavelength of the second laser is similar to the uranium absorption spectrum in the tuning range. The presence of the U(IV) absorption band in the tuning range of the second laser gives rise to a peak of the luminol chemiluminescence. This fact undoubtedly confirms the selective mechanism of chemiluminescence excitation.

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 solution composition was chosen 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 in the previous experiment, the OBB 1011 laser emitted light with a fixed wavelength of 490 nm. The emission wavelength of the OBB 1012 laser was tuned from 630 to 660 nm (PLD-640 dye was used). This range was chosen based on the fact that Pu(IV) has absorption band

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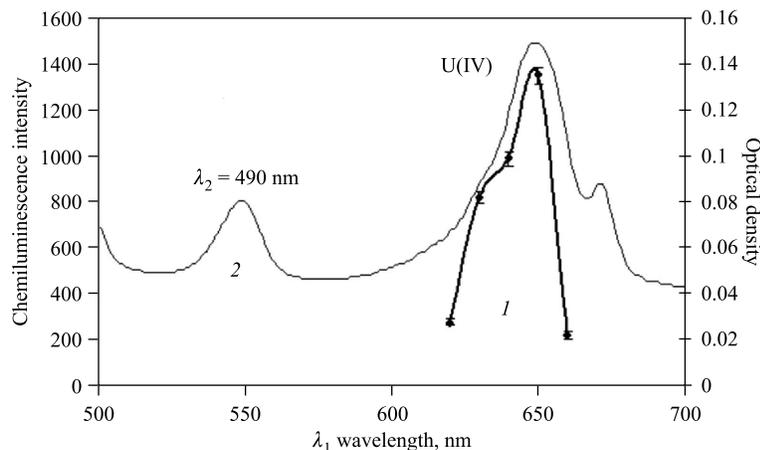
Fig. 7. Spectrum of chemiluminescence excitation by the scheme two steps – two colors in luminol + U(IV) solution (*1*); absorption spectrum of U(IV) in aqueous HCl solution (*2*)

in this range. Figure 8 shows variation of chemiluminescence intensity with variation of the wavelength generated by the OBB 1012 laser. As is seen, the spectrum of chemiluminescence excitation is in close agreement with absorption spectrum of Pu(IV).

In a similar manner, we performed excitation of Pu(IV) chemiluminescence (Fig. 9) by the scheme two steps – one color. For chemiluminescence excitation, only OBB 1012 tunable dye laser was used. The intensity of chemiluminescence at various wavelengths of radiation generated by the OBB 1012 dye laser was measured. As in the previous case, the spectrum of chemiluminescence excitation is in close agreement with the absorption spectrum which indicates high selectivity of chemiluminescence excitation.

A measurement of the spectrum of chemiluminescence excitation requires correct consideration of the following processes contributing to the total process.

1. Luminol chemiluminescence due to two-quantum excitation of An(IV) by the scheme two steps – one color, i.e., An(IV) absorbs two quanta during one laser pulse emitted by one laser.

2. Luminol chemiluminescence due to two-quantum excitation of An(IV) by the scheme two steps – two colors, i.e., An(IV) absorbs two quanta from two laser pulses emitted by two lasers.

3. Luminol chemiluminescence as a result of two-quantum excitation of luminol molecules.

The latter process requires additional comments. In the field of laser radiation luminol molecule can pass into excited state after absorption of two light quanta.
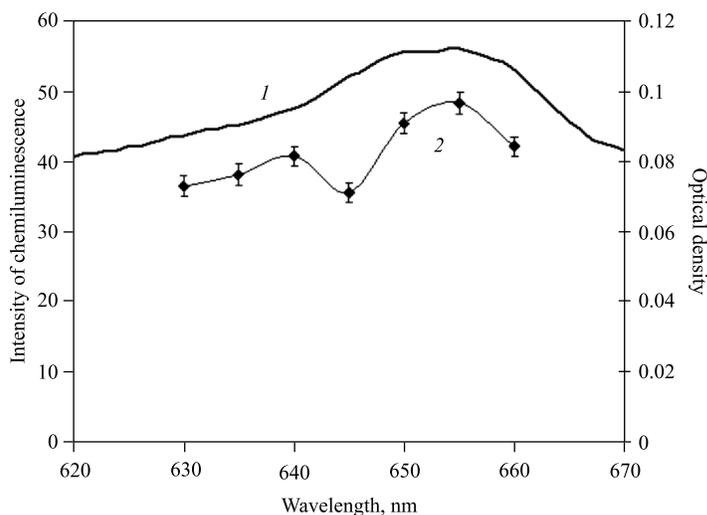
Fig. 8. A comparison of absorption spectrum of Pu(IV) (*1*) and intensity of chemilumines-
cence (*2*) at various wavelengths of radiation generated by the OBB 1012 dye laser (two
steps – two colors scheme)
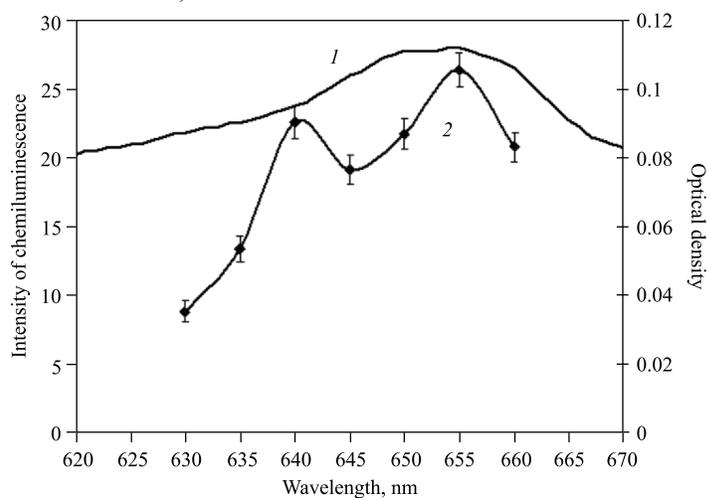


Fig. 9. Absorption spectrum of Pu(IV) in solution (*1*). Spectrum of chemiluminescence
excitation (*2*) by the scheme two steps – one color (two photons are absorbed during one
laser pulse) in luminol + Pu(IV) solution

Chemiluminescence having characteristic spectrum appears as a result of exci-
tation transfer from luminol molecule to molecule of dissolved oxygen. In this
case, oxygen molecule passes into the singlet state becoming capable to oxidize

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luminol molecule. This excitation transfer from molecules of organic compounds to oxygen molecules is well known in biochemistry [18]. A contribution of this process can be evaluated from the luminescence of actinide-free luminol solutions. Process (3) is a background process and its spectrum of chemiluminescence initiation does not correlate with the absorption spectrum of An(IV).

Thus, appropriate selectivity can be reached when chemiluminescence is initiated by transitions within $4f$- or $5f$-electron shell of lanthanide or actinide ions corresponding to visible spectral range. In this case, chemiluminescence of chemiluminogen arises when the ion of $f$ element is excited by multi-quantum absorption of visible light. This multistep scheme of chemiluminescence excitation having high sensitivity and selectivity allows application of chemiluminescence as an essential tool for selective detection of lanthanide and actinide species in solutions.

## CONCLUSION

Using short laser pulses for excitation of molecules and ions in liquids and time resolution for registration of luminescence and chemiluminescence produced by actinide and lanthanide ions, we can efficiently separate target signals from short-lived background luminescence. Additional potential for increase in the sensitivity of laser spectroscopy is in the use of energy transfer within inner electron shell of molecule or ion and also in the use of chemiluminescence effects especially in combination with high-selective laser spectroscopy and time-resolution technique.

A multistep scheme of chemiluminescence excitation makes chemiluminescence procedure not only highly sensitive but also highly selective procedure of detection of various substances. This scheme significantly enlarges the field of application of chemiluminescence for analytical purpose. In particular, we can detect various valence and molecular species of lanthanides and actinides in solutions with significantly higher sensitivity as compared to traditional methods.

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