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Application of multi-step excitation schemes for detection of actinides and lanthanides in solutions by luminescence/chemiluminescence laser spectroscopy

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Abstract

The use of laser radiation with tunable wavelength allows the 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 and time-resolved laser-induced chemiluminescence spectroscopy for the detection of lanthanides and actinides. Results of the experiments on U, Eu, and Sm detection by TRLIF method in blood plasma and urine are presented. Data on luminol chemiluminescence in solutions containing Sm(III), U(IV), and Pu(IV) are analyzed. It is shown that appropriate selectivity of lanthanide/actinide detection can be reached when chemiluminescence is initiated by transitions within *4f*- or *5f*-electron shell of lanthanide/actinide ions corresponding to the visible spectral range. In this case chemiluminescence of chemiluminogen (luminol) arises when the ion of *f* element is excited by multi-quantum absorption of visible light. The multi-photon scheme of chemiluminescence excitation makes chemiluminescence not only a highly sensitive but also a highly selective tool for the detection of lanthanide/actinide species in solutions.

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1. Introduction

The use of luminescence methods for detection of lanthanides/actinides in solutions allows the sensitivity to reach the limit of detection (*LOD*) up to 10^{-13} mol/l (M). The background can be efficiently suppressed for lanthanides and actinides by using time resolution¹⁻³. Results of the experiments on U, Eu, and Sm detection by Time Resolved Laser Induced Fluorescence (TRLIF) method in blood plasma and urine are presented. Pu, Np, and some U compounds do not produce direct luminescence in solutions, but when excited by laser radiation, they can induce chemiluminescence of some chemiluminogen (luminol in our experiments)¹⁻³. It is because of its high sensitivity (*LOD* from 10^{-6} M to 10^{-13} M) that chemiluminescence is widely used in many fields^{4,5}. Of some interest was to use advantages of luminescence procedure for selective detection of actinides and lanthanides having no intrinsic luminescence by initiation of chemiluminescence of some agents as an example luminol via excitation of the element to be detected. The selective excitation of actinide leads to a chemical reaction between molecule or complex containing excited actinide and chemiluminescence agent added into solution. As a result of the reaction, light is emitted (chemiluminescence) and registered by a photomultiplier. Using laser radiation with tunable wavelength, we can selectively excite various valence forms and molecules of actinides with subsequent registration of chemiluminescence. When knowing the wavelength at which chemiluminescence appears and the intensity of this chemiluminescence, we can determine the concentration of a certain valence form of a given actinide and the structure of the complex containing this actinide. The optimum choice of the laser radiation wavelength on the basis of absorption spectra, scheme of luminescence excitation (one-step or multi-step), and chemiluminescence agent is extremely significant for selective and efficient luminescence/chemiluminescence induction. It should be noted that the presence of a time delay between the pulse of the laser radiation and the chemiluminescence pulse is an extremely significant feature¹⁻³. This fact 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 the laser radiation. This allows a significant suppression of the background and an increased sensitivity of TR chemiluminescence method.

A key problem of chemiluminescence application to the 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 a visible spectral range. Since the energy of one quantum excitation in the visible range is insufficient for initiating luminol chemiluminescence, it was proposed¹⁻³ to excite lanthanide and actinide ions by multi-quantum absorption of visible light. Data on luminol chemiluminescence in solutions containing Sm(III), U(IV), and Pu(IV) are presented. Chemiluminescence was initiated by two-quantum excitation of lanthanide/actinide ions in the range of $4f/5f$ electron transitions by the following schemes: two steps—one colour (two photons are absorbed during one laser pulse) and two steps—two colours (two photons are absorbed from two synchronized laser pulses)¹⁻³.

The experiments on chemiluminescence were carried out at f element concentrations in the range of 10^{-3} M. Because the *LOD* for the chemiluminescence method of detection^{4,5} may reach 10^{-13} M, 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. It is shown that a multi-photon scheme of chemiluminescence excitation makes chemiluminescence not only a highly sensitive but also a highly selective tool for the detection of lanthanide/actinide species in solutions.

2. Time-resolved laser spectroscopy in solutions

The practical use of the laser spectroscopy methods in the analysis of different samples encounters one essential difficulty, namely it is necessary to get the investigated element from the sample to a zone of interaction with laser radiation. That is why the most attractive approach from a practical point of view is to use the solutions of investigated samples. But in this case, as a rule, one cannot determine the isotopic composition of a sample.

The detection limit in solutions depends on the luminescence of impurities and the scattered-light intensity. Efficient optical systems of light collection are used to suppress the background, and the luminescence is measured in a wavelength range different from the excitation radiation wavelength. However, these precautions do not allow the suppression of the luminescence background from many impurities. Nevertheless, the background can be efficiently suppressed for lanthanides and actinides using time resolution^{6,7}. The point is that the characteristic luminescence lifetime for impurities is 10^{-8} s – 10^{-9} s, while it is 10^{-3} s – 10^{-6} s for lanthanides and actinides. This

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