Pu, Np and U Determination by Chemiluminescence and Time-Resolved Pulse Laser Spectroscopy

Igor Izosimov

Khlopin Radium Institute, 2nd Murinski avn.28, St. Petersburg 19402, Russia

Actinide elements trace amounts detection in the different samples presents today major importance for ecology, radiative waste handling and control, rehabilitation of contaminated areas and risk assessment. The behavior of actinides in environment is determined by actinides valence states and type of molecules. Information about actinide valence states in trace analysis is essential to fix the actinides emission source and the propagation history. The most sensitive (for example – TRLIF) laser spectroscopy methods (with time resolution (TR) use photoluminescence for detection) do not provide information about valence states; and for some actinides and lanthanides detection in solutions [1,2] have limit of detection (LOD) up to 10^{-13} mol/l(M) (Table 1).

Table 1. LOD by Time Resolved Laser Induced Fluorescence (TRLIF) method.

Element	UO^{2+}	Cm^{3+}	Am^{3+}	Eu^{3+}	Tb^{3+}	Gd^{3+}	Dy^{3+}	Sm^{3+}	Ce^{3+}
LOD(M)	10^{-13}	10^{-13}	10^{-9}	10^{-13}	10^{-9}	10^{-8}	10^{-10}	10^{-10}	10^{-9}

Pu, Np and some valence form of U does not give the photoluminescence in solutions and for it's detection not most sensitive (LOD – 10^{-5}-10^{-7}M) laser spectroscopy methods are used.

Today the chemiluminescence effects are used in biology and medicine [3] for trace amount detection of different substances with LOD up to 10^{-9} – 10^{-13} M and it is possible to determine the elements valence states and type of molecules. In our experiments [4,5] we observed the chemiluminescence of solutions induced by Pu, Np and U after excitation by pulse laser radiation. High sensitive TR methods may be used for this chemiluminescence detection (Fig. 1).

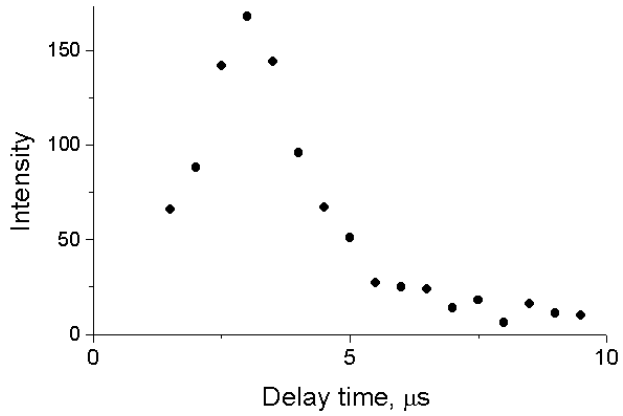

Fig. 1: Kinetic curve of luminol chemiluminescence induced by excited plutonyl complexes.

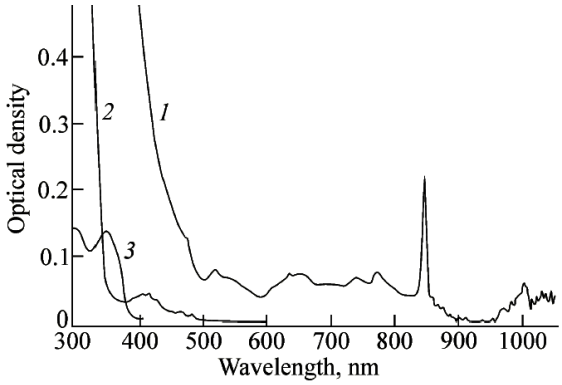

Fig. 2: Absorption spectra of (1) – PuO_2^{2+}, (2) – UO_2^{2+}, (3) – luminol.

By proper selection of lasers radiation wavelengths (Fig. 2 and 3), one or multi-step actinides complexes excitation scheme and chemiluminogenic label, it is possible to induce chemiluminescence by selective excitation of detectable actinide complexes only.

There is possibility open for chemiluminescence application in *Nuclear Chemistry.*

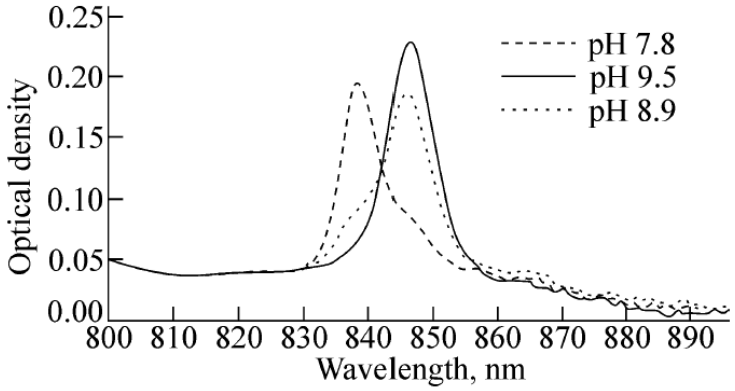

Fig. 3: Absorption spectra of plutonyl complexes in 42 % CsF + H_2O solutions at different *p*H values. Two complexes are in solution: $PuO_2F_5^{3-}$ (band 839 nm) and $PuO_2F_4OH^{3-}$ (band 846.5 nm).

The chemiluminescence effects using allows to essentially spread scope for trace amount detection of actinide in solutions, determination of the actinide valence states in solutions and determination of the molecule type containing actinide. Especially perspective is to use the chemiluminescence effects for detection of actinides and complexes containing actinides in solution in the cases when in such systems actinide does not give direct luminescence but can induce chemiluminescence. Multi step chemiluminescence excitation scheme may be efficiently used for detection selectivity increasing [5].

The sensitivity of the chemiluminescence methods is higher than sensitivity of other methods (LIPAS for example) which are used for non-luminescent actinides and molecules detection now. The combinations of the chemiluminescence effects with high sensitivity and high selectivity laser spectroscopy methods make it possible to carry out an effective detection both of luminescent and *non-luminescent* actinides and molecules containing actinides (especially U, Pu and Np) in different solutions.

In this report a different multi-step schemes of chemiluminescence excitation and it's applications for selectivity increasing are discussed. It is shown that the two-step chemiluminescence excitation schemes in combination with TR laser spectroscopy method may be efficient for actinides detection in solution.

This work was supported by International Science and Technology Centre (ISTC), project ISTC 3694.

References

[1] C.Moulin, P.Decambox, and P.Mauchien, Anal.Chem. **68** (1996) 3204.
[2] I.N.Izosimov, *Proc. 4th International Workshop "Laser spectroscopy on beams of radioactive nuclei",* May 24–27, 1999, Poznan, Poland. Ed.JINR, Dubna, E15-2000-75, p.169.
[3] C.Dodeigne, L.Thunus and R.Lejeune, Talanta **51** (2000) 415.
[4] I.N.Izosimov et al., *Proc. Intern. Conf. "Actinides 2005"*, Manchester, UK, 2005, p.779.
[5] I.N.Izosimov, Phys. Part. Nucl. **38 (**2007) 177.