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ON THE USE OF TIME-RESOLVED LASER-INDUCED SPECTROFLUOROMETRY IN THE NUCLEAR FUEL CYCLE

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Abstract

Time Resolved Laser-Induced Spectrofluorometry (TRLIS) has been used for actinides trace analysis and complexation analysis in the nuclear fuel cycle. Results obtained in the different fields such as in geology, in the Purex process, in the environment, in the medical and in waste storage assessment are presented.

Introduction

Fast and sensitive methods are more and more required in the nuclear fuel cycle for ultratrace determinations of actinides and lanthanides. Time-Resolved Laser-Induced Spectrofluorometry (TRLIS) is a method of choice for such determinations and has been used for now more than 10 years. The principle of this technique consists in pulsed laser excitation followed by temporal resolution of the fluorescence signal which leads to the elimination of short lifetime fluorescence. The main advantage of TRLIS aside rapidity and sensitivity is its triple selectivity. Excitation selectivity by the proper choice of the laser excitation wavelength, emission selectivity since each fluorescent element gives a characteristic fluorescence spectrum and finally time resolution selectivity which characterizes the fluorescent element environment. Among the actinides and lanthanides, the ones that are fluorescent in solution are uranium, curium, americium and europium, terbium, dysprosium, samarium, gadolinium, cerium, thulium. These elements have been studied in different complexing media (nitric, phosphoric, sulphuric, carbonate, micellar) and can be analysed from ppt and sub ppt level for uranium and curium to ppb level for lanthanides and americium /1-3/.

The different fields of interest in the nuclear fuel cycle where TRLIS has been used are in :

- Geology, for ultratrace determination of uranium (ng/l level) in waters from different localities in order to obtain a better understanding of uranium mobilization under natural reducing conditions and so to validate thermodynamic data /4/;
- All the different steps of the Purex process, in plutonium matrices for quality control, in organic matrices (TBP, TPH) where uranium used as tracer allows to calculate decontamination factors of new installations and hence to ameliorate performances of the process ;
- Medical surveillance for direct and fast determination of uranium in human urines. Hence, based on the uranium concentration in urine, metabolic models are established to estimate the body burden of uranium from persons exposed to uranium ambience /5/ ;
- Environment control for uranium determination in water and soil samples in order to have a "cartography" of specific areas ;
- Waste storage assessment, for the determination of complexing constants at very low level between actinides and organic matters. TRLIS allows to work directly at trace level and has been applied to curium /6/.

Moreover, in Purex process control, remote measurements are performed in hot cell with the adaptation of fibre-optics and optode and would be used for in-line control in the nuclear fuel process. This feature allows real time analysis.

Material and Methods

Apparatus

The experimental set-up is schematically shown in Fig. 1.

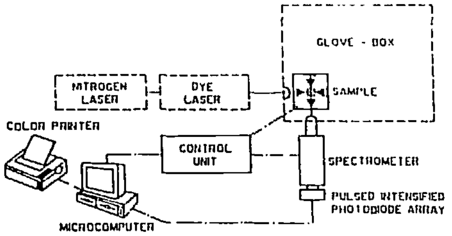

Figure 1 : TRLIS experimental set-up.

A nitrogen laser (Model 804, SOPRA) operating at 337 nm and delivering about 1.5 mJ of energy in a 5 ns pulse with a repetition rate of 25 Hz is used as excitation source. The laser beam is focused into the cell of the spectrofluorometer "FLUO 2001" (DILOR, Lille, France) by a quartz lens. In order to increase the sensitivity, two concave mirrors placed in the cell holder double the distance travelled by excitation and fluorescence emission. The radiation coming from the cell is focused on the entrance slit of the monochromator. Taking into account dispersion of the holographic grating used in the monochromator, measurement range extends to approximately 200 nm into the visible spectrum. The detection is performed by an intensified photodiodes (512) array cooled by Peltier effect and positioned at the monochromator exit. Recording of spectra is performed by integration of the pulsed light signal given by the intensifier. The integration time adjustable from 0.1 to 30 s allows for variation in detection sensitivity. Time-resolution is obtained by the control unit that assures pulsed running of the intensifier and the photodiodes array. A photodiode located in the vicinity of the cell produces with each laser pulse, a reference signal from which command signals for the high voltage are obtained. The logic circuit used to generate the signals allows measurements with a delay adjustable from 1 to 999 µs during a time of 1 to 99 µs. The signal acquisition is performed via DMA (direct memory access). All functions of the apparatus (temporal delay, gate width, integration time, reading of spectra, ...) are programmable by the use of an IEEE 488 interface. The whole system is controlled by a PC-AT microcomputer. Analytical software automatically calculates concentrations by the standard addition or the initial fluorescence methods.

Procedure

Samples are directly diluted in phosphoric acid (0.75 M), sulphuric acid (4.5 M) or Fluran (10 %) depending on the matrix composition. Then one millilitre of this solution is introduced into the quartz cell. The standard addition method is used for uranium concentration determination. Small quantities of a known uranium solution are successively added in the cell, fluorescence intensity is measured at 494 . nm (phosphoric and sulphuric acid) or 499 nm (Fluran) and then background (450 nm) subtracted. For each solution, uranium concentration in the sample is obtained by plotting fluorescence intensity versus concentration and extrapolating back to the origin.

Results

In this paper, only three examples of the previously quoted fields of application of TRLIS will be given. *In geology*, the acquisition of thermodynamic data for uranium in alkaline solution is hampered by problems such as the ionic strength of the experimental solution, the stability of U (IV) complexes and uraninite and the very low level uranium concentrations. As a result, published data are often conflicting. A set of waters from French Pyrennes at temperature ranging from 60 to 70°C were chosen to check on the accuracy of solubility data. The two possible equilibria between U(VI) and uraninite are considered.

$$U(OH)_4^0 \rightleftharpoons UO_2 + 2\,H_2O \quad (1)$$
$$\text{Log } K = 9.47 \pm 0.3 \quad (100\text{-}300°C)$$

$$U(OH)_5^- + H^+ = UO_2 + 3\,H_2O \quad (2)$$
$$\text{Log } K = -19.86 \pm 0.3 \quad (25°C)$$

From the concentrations determinations of these different sample, figure 2, where the activity of uranium in solution is plotted versus pH was obtained.

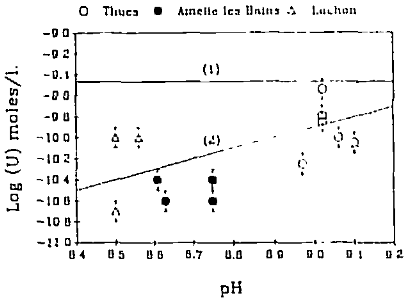

Figure 2 : Activity of uranium versus pH of groundwter samples. Solid lines represent the relation given by Eqns. 1 and 2, respectively; dotted lines give the possible limits with respect to the data accuracy.

From this figure, it seems that with equation 2, the uranium-pH correlation agrees better with the observed trends. This trend seems to confirm that uranium is controlled in solution by a mineral phase.

In the Purex process and recently in the TEO (Organic Waste Treatment) project where the main goal was to determine the decontamination factor (DF) of an installation by using uranium as tracer in the organic phase (TBP, TPH) to simulate radioactive elements behaviour. This installation is briefly shown on figure 3.

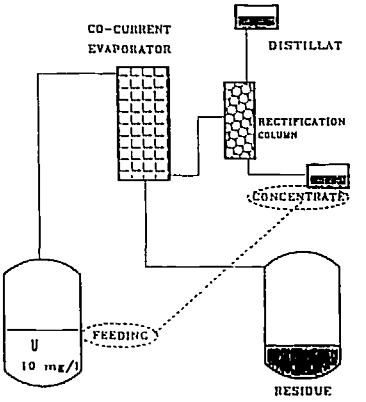

Figure 3 : Oversimplified scheme of the TEO project.

The DF factor simulated by calculation was expected to be in the 10^3 to 10^4 range. The uranium initial concentration in the feeding was set to 10 mg/l and practical measurements by TRLIS in the μg/l to sub μg/l have confirmed previously quoted figures. These numerous data (more than 1000 determinations) have allowed to visualize effects of eventual modifications of the installation on the decontamination factor.

In waste storage assessment, the knowledge of radioelement behaviour is of great importance. In particular, complexation reactions of radioelements with natural organic ligands such as humic substances (humic/fulvic acids) present in aquifer systems are important, because of the strength of complexes that humic substances form with cations, in particular trivalent elements like americium and curium. TRLIS is the only technique that allow to work *directly* at trace levels.

Typical titration curve (fluorescence signal versus humic substance concentration) of curium (III) by humic acids is presented on Figure 4 at fixed pH and ionic strength.

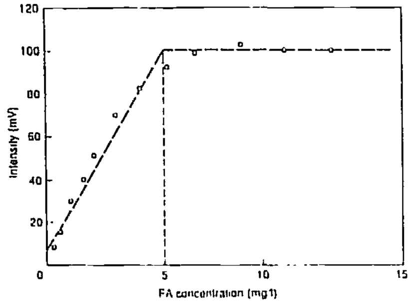

Figure 4 : Curium fluorescence intensity as a function of fulvic acids concentration. [Cm] 2.10^{-7} M,pH 5, I=0.1

The complexation of curium by humic substances leads to an increase of the curium fluorescence signal until saturation of the complexing sites occurs. From similar titration curve, different binding parameters are obtained such as the complexing capacity W (expressed in mmoles/g) and the conditional stability constant β. Several factors such as the concentration, pH and ionic strength have been investigated.

Conclusion

Time-Resolved Laser- Induced Spectrofluorometry is a fast, sensitive and selective technique for uranium determinations in the nuclear fuel cycle Other elements such as curium, americium and several lanthanides can also be analysed. One great advantage of this technique is the possibility to perform in-line measurements by the use of fibber optics and optodes for real time analysis.

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