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NEW SPECTROFLUOROMETER WITH PULSED INTENSIFIED PHOTODIODES ARRAY FOR DIRECT TRACE DETERMINATION OF ACTINIDES AND LANTHANIDES IN SOLUTIONS

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NEW SPECTROFLUOROMETER WITH PULSED INTENSIFIED PHOTODIODES ARRAY FOR DIRECT TRACE DETERMINATION OF ACTINIDES AND LANTHANIDES IN SOLUTIONS

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INTRODUCTION

The determination of actinides and lanthanides in solution at very low level is required in several fields : nuclear, geological, medical, biological. Time-Resolved Laser -Induced Spectrofluorometry (TRLIS) with pulsed intensified photodiodes array detection permits these determinations. Temporal resolution allows discrimination against short lifetime fluorescence and measurement of fluorescence lifetime in various matrices. The use of laser source leads to excitation selectivity and high sensitivity. Multichannel detection allows to cover the entire wavelength range of interest which leads to emission selectivity and rapidity. These different advantages are present in the newly commercialized spectrofluorometer "FLUO 2001"[*] together with specially analytical adapted software. The apparatus and performances obtained for several actinides and lanthanides are presented.

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APPARATUS

In general a Time-Resolved Spectrofluorometer consists of :

- a pulsed excitation source
- a cell for receiving the solution to be analysed
- an optical system which selects the fluorescence emission
- a detector of fluorescence
- a control unit that allows measurements delayed in relation to the excitation.

A diagram of the principle of the spectrofluorometer "FLUO 2001" is given in Figure 1.

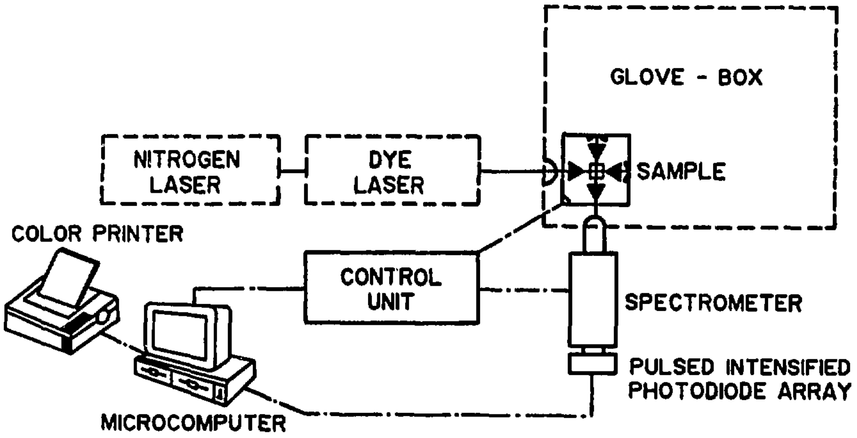


Fig. I

Excitation source **

A nitrogen laser (Model 804 or 2000, 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 the excitation source. For several applications (lanthanides), it could be used to pump a dye laser (Model E1, JOBIN-YVON) delivering about 10 % of the energy of the nitrogen laser. The laser beam is focused into the cell by a quartz lens.

** The laser source is not provided with the FLUO 2001

Measuring Cell

A cell 10 x 10 mm contains the solution to be analysed. In order to increase the sensitivity of the device, two concave mirrors, placed on the cell holder double the distance travelled by the excitation and the fluorescence emission.

Selection system for the emission of fluorescence

The radiation coming from the cell is focused on the entrance slit of the monochromator. This device allows to record fluorescence spectra with a resolution of 2.4 nm. Taking into account the dispersion of the holographic grating (300 l/mm) used in the monochromator, the measurement range extends to approximately 200 nm.

Multichannel detection

This consists of an intensified photodiodes array positioned at the exit of the monochromator. The intensifier plays an essential role in both assuring a high detection sensitivity and performing time-resolved fluorescence measurements. The recording of spectra is performed by the integration on 512 photodiodes (cooled by Peltier effect) of the pulsed light signal given by the intensifier. The integration time is adjustable between 1 s and 99 s. The choice of this time allows for variation in detection sensitivity.

Control unit

This device both assures the pulsed functioning of the intensifier and the photodiodes array. The temporal reference is given by a photodiode located in the vicinity of the cell such that a portion of the excitation laser beam is received. This device gives, with each laser pulse, a reference signal from which command signals for the high voltage supply of the intensifier are elaborated. The logic circuit used to generate the signals allows measurements with a delay which can be set from 0.1 to 9999 µs during an adjustable time of 1 to 99 µs. With this command device, the operation of the intensifier can be assimilated to the one of a fast obturator.

Hardware - Software

The signal acquisition is performed via DMA. All the functions of the apparatus (temporel delay, gate width, integration time, reading of spectra) are programable by the use of an IEEE 488 interface. The whole system is piloted by an IBM AT (EGA, 20 Mo) supplied with a color printer for hardcopy. The analytical software automatically performs lifetime measurements and calculates concentrations, whether by the standard addition or the initial fluorescence methods /1/.

APPLICATIONS

The FLUO 2001 spectrofluorometer is particularly designed for the determination of fluorescent elements with long lifetime. For the moment, the most interesting results have been obtained for elements in the series of actinides and lanthanides /2/ but could be extended to other fluorescent elements.

ACTINIDES

At present, the actinides known for their natural properties of fluorescence are : **uranium, curium, americium, bekerlium, einsteinium** /3,4,5/. Among these elements, only uranium and curium present long lifetime in aqueous solution and are extensively studied by TRLIS.

Uranium

Determination of uranium takes place in phosphoric or sulphuric medium. The most quenching elements are the ions Cl^-, Ag^+, I^-, Br^-, Pb^{2+}, Fe^{2+} but their influence can be drastically reduced by dilution of the solution to be analysed. Due to the high sensitivity and selectivity of the apparatus, uranium is analysed in the whole nuclear fuel cycle. Just some of the examples that could be given are : underground water prospection, medical control, environment control, process control solutions, purity qualification (PuO_2 for example) /6/. The limit of detection for uranium in solution of 1 ppt (1 ng/l) is the lowest reported for this element. Figure 2 and 3 respectively show spectrum and lifetime of uranium (10 µg/l) in phosphoric medium obtained with the FLUO 2001.

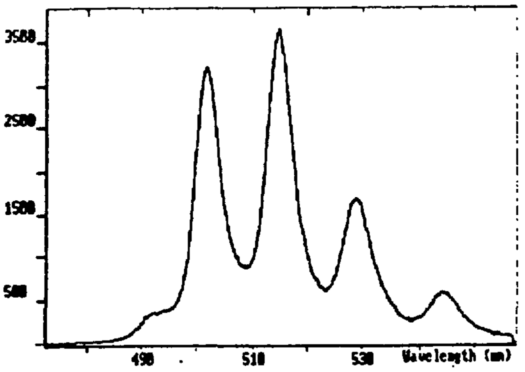
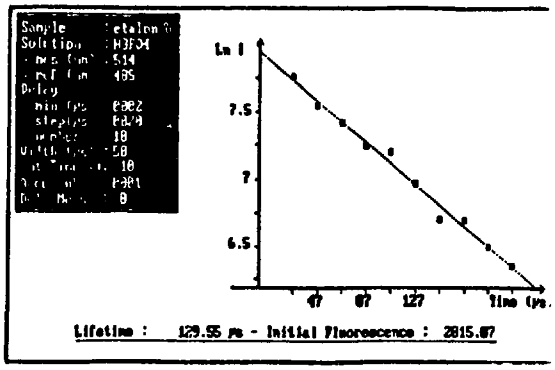


Figure 2



Lifetime : 129.55 µs - Initial Fluorescence : 2815.87

Figure 3

Curium

The analyse of curium can take place in various media (HNO_3, HCl, H_2SO_4..) but the most favourable medium is carbonate. The detection limit in this medium is 10 pg/ml (5.10^{-11}M). Very few elements have influence on the fluorescence of curium /7/. Curium causes many of the long term radiological and thermal problems associated with nuclear plant waste disposal. Hence, TRLIS is an appropriate technique for curium monitoring.

LANTHANIDES

Of the 14 elements from this series, 7 have natural properties of fluorescence /8,9/. The seven are : **cerium, samarium, europium, gadolinium, terbium, dysprosium and thulium.** Various media can be used, but the most favourable is the carbonate medium. The fluorescence of these elements is hardly affected by the composition of the solution and due to the selectivity of the apparatus, each of them can be determined in the presence of other elements of the series. Several lanthanides are used for their fluorometric properties in numerous immunoassay and biological determinations /10/ as well as geological traceurs.

Table 1 shows lifetimes, detection limits obtained with the FLUO 2001 and a classical fluorometer (continuous excitation with no temporal resolution). It should be pointed out that TRLIS lowers the detection limit by two to four orders of magnitude (except for cerium due to its very short lifetime).

ELEMENT	Time Resolved Laser Induced Spectrofluorometry		Classical Spectrofluorometry
	lifetime(µs)°	LOD(µg/l)$^+$	LOD(µg/l)
URANIUM	180	0.001	1
CURIUM	250	0.01	10
SAMARIUM	7	1.5	15000
EUROPIUM	455	0.1	150
GADOLINIUM	290	50	15000
TERBIUM	1000	1.0	150
DYSPROSIUM	9	0.5	16000
CERIUM*	0.07	1.4	8
THULIUM	5	850	150000

*with frequency doubler °in K_2CO_3 except U (H_3PO_4) and Ce (H_2SO_4) $^+$ laser energy normalized to 1 mJ

Table 1

EXAMPLES

To illustrate the performances of the "FLUO 2001", two examples were chosen which show the need to test both the temporal resolution parameters and the fluorescence emission spectra. Figure 4 shows the fluorescence emission spectra of a treating solution of uranium ore. This solution has a high proportion of humic acids which emit a far more intense fluorescence than does uranium. The spectrum recorded without temporal resolution ($\Delta t = 0\ \mu s$) does not allow the distinction of uranium fluorescence. However, with a temporal delay of 20 µs, the short fluorescence of humic acids (< 1 µs) is eliminated and a spectrum characteristic of uranium is recorded, which means that measurements can be performed under proper conditions. Figure 5 presents results obtained on a europium ($\tau = 455\ \mu s$)-samarium ($\tau = 7\ \mu s$) mixture in carbonate medium with excitation at 405 nm. With a temporal delay of 3 µs, a spectrum characteristic of samarium with slight europium overlapping is obtained and samarium determination can be performed at 565 nm. By increasing the temporal delay, samarium fluorescence disappears and a spectrum characteristic of europium is obtained. Europium determination can be performed at 620 nm.

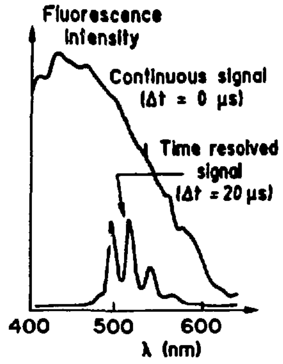


Fig. 4 - Fluorescence of a uranium solution containing humic acids

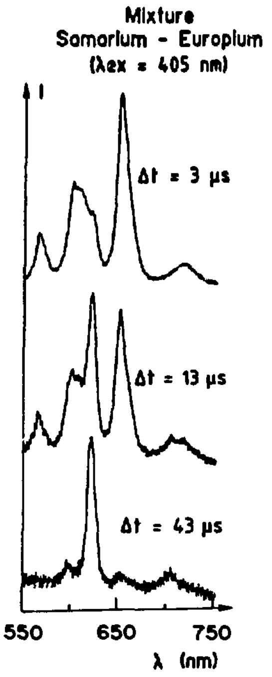


Fig. 5

Moreover, remote measurements with the FLUO 2001 are performed with the adaptation of fiber optics and optrode*. This set-up is presented in Figure 6 and has the advantage of allowing measurements in hostile or difficult to access environments at several tens of meters at several locations with only one central monitor.

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* Optrode and fiber optics adaptation performed by the GIA group (CEN Fontenay-aux-Roses)

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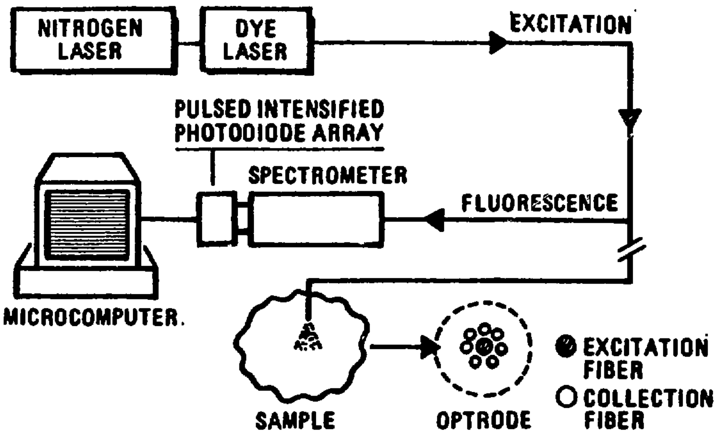
FIGURE 6



CONCLUSION

Time-resolved Laser-Induced Spectrofluorometry is a very sensitive technique for actinides and lanthanides determination in solution. Due to its triple selectivity, determinations in complex matrices can be achieved without chemical pretreatments or separations. Remote sensing with fiber optics are already performed in the nuclear industry. Further developments on faster detection are in progress for short lifetime fluorescence studies. The use of the new FLUO 2001 together with analytical software allows rapid and accurate determinations for routine or control analysis as well as chemical phenomena (complexations, kinetics) studies.

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