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LASER-INDUCED TIME-RESOLVED SPECTROFLUOROMETRY AND THERMAL LENSING: APPLICATIONS IN THE NUCLEAR INDUSTRY

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LASER-INDUCED TIME-RESOLVED SPECTROFLUOROMETRY AND THERMAL LENSING : APPLICATIONS IN THE NUCLEAR INDUSTRY*

P. DECAMBOX, N. DELORME, P. MAUCHIEN, C. MOULIN**

ABSTRACT

Sensitive spectroscopic methods for the determination of actinides and lanthanides in various media are required in the nuclear industry. Laser-Induced Time-Resolved Spectrofluorometry (LITRS) for several actinides and lanthanides at very low levels and thermal lensing (TL) for oxidation state characterization allow these determinations.

The set-up of LITRS is presented. Spectra, limit of detections and lifetimes obtained for U, Cm, Am, Eu, Gd, Tb, Dy, Ce, Sm, Tm are shown. Detection limit as low as 5.10^{-12} M can be achieved. Examples of matrices encountered for the determination of uranium are given as well as comparison with mass spectrometry /1/ and alpha counting. The set-up of TL and performances obtained on plutonium /2/ as well as future developments are presented.

/1/ Anal. Chem, 60, 1296, 1988.
/2/ Radiochim. Acta 44/45, 103, 1988.

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* Communication présentée à l'occasion de "International Conference on analytical chemistry in nuclear Technology". 5-9 Juin 1989/KARLSRUHE (RFA).

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SECOND KARLSRUHE INTERNATIONAL CONFERENCE
ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

KARLSRUHE JUNE 5-9,1989

LASER-INDUCED TIME-RESOLVED SPECTROFLUOROMETRY AND THERMAL LENSING:APPLICATIONS IN THE NUCLEAR INDUSTRY

C.MOULIN

LASER SPECTROSCOPY GROUP

IRDI/DERDCA/DCAEA/SEA

CEA FONTENAY AUX ROSES

FRANCE

TRLIS AND TL IN THE NUCLEAR FUEL CYCLE

GEOLOGICAL SURVEY

TRLIS

U at the ppt level in groundwaters

TRLIS

U,Cm,Am at the ppb level in complex matrices

NUCLEAR PROCESS

MEDICAL AND ENVIRONMENT CONTROL

TRLIS

U at the ppt level in soils and urines

TRLIS and TL

complexation phenomena for lanthanides and actinides

WASTE DISPOSAL

TIME-RESOLVED LASER INDUCED SPECTROFLUOROMETRY

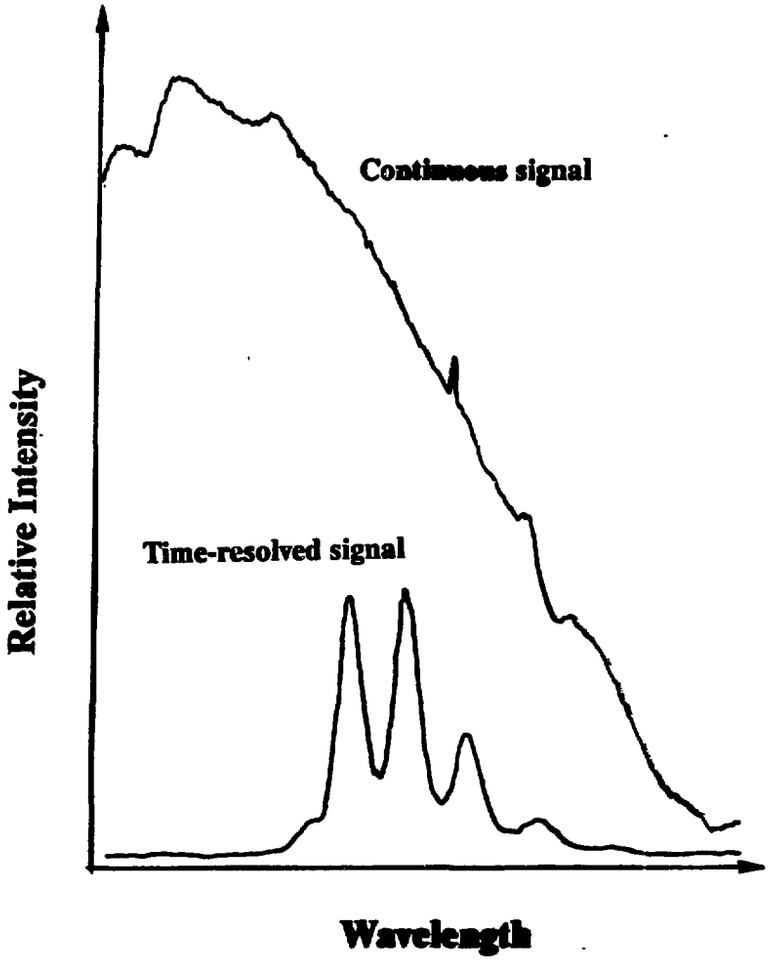
PRINCIPLE

* PULSED LASER EXCITATION

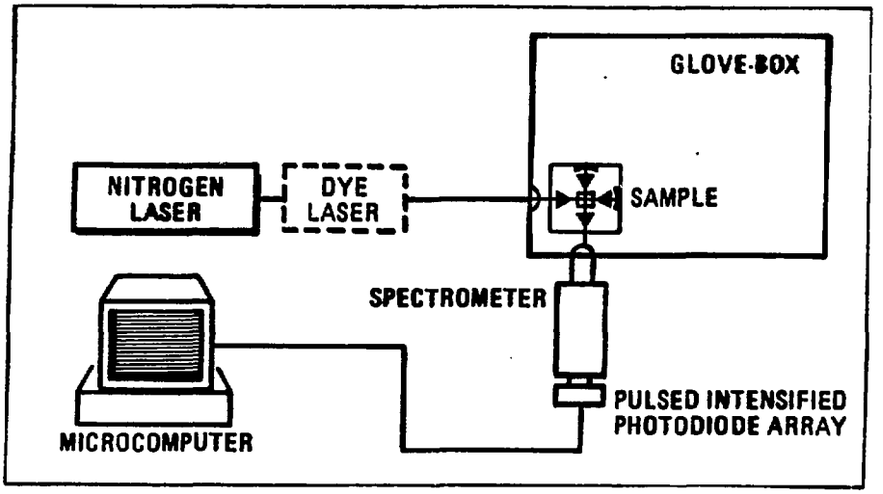
* TEMPORAL RESOLUTION OF THE FLUORESCENCE SIGNAL

* ELIMINATION OF UNWANTED FLUORESCENCE

Fluorescence of a Uranium Solution Containing Humic Acids



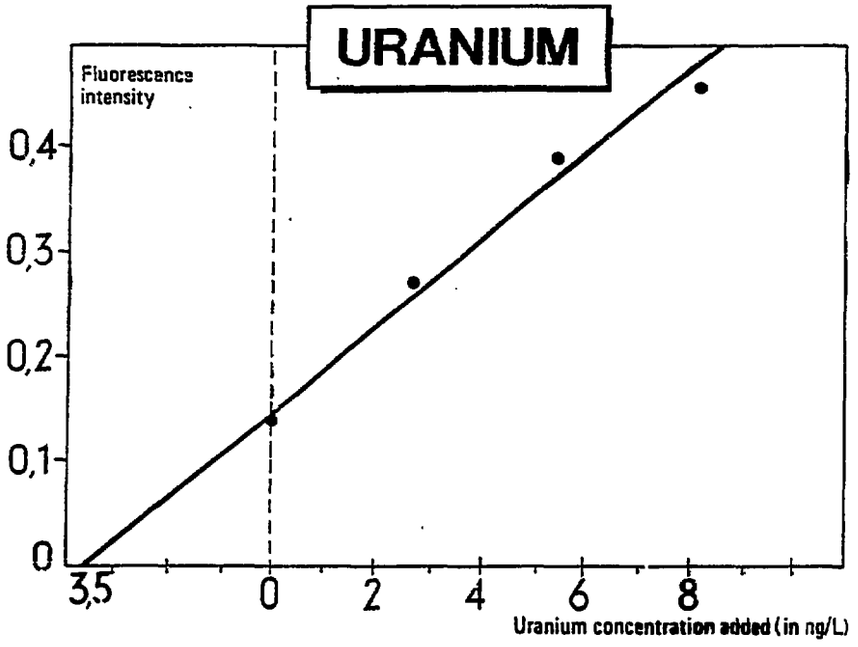
TIME-RESOLVED LASER INDUCED FLUORESCENCE



PERFORMANCES

ELEMENT	LoD (LITRS) (ug/l)	LoD (CF) (ug/l)
URANIUM	0.001	1
CURIUM	0.01	10
AMERICIUM	1	800
CERIUM *	1.5	8
SAMARIUM	1.5	15000
EUROPIUM	0.1	150
TERBIUM	1.0	150
DYSPROSIUM	0.5	16000
GADOLINIUM *	50	15000
THULIUM	850	150000

* frequency doubler



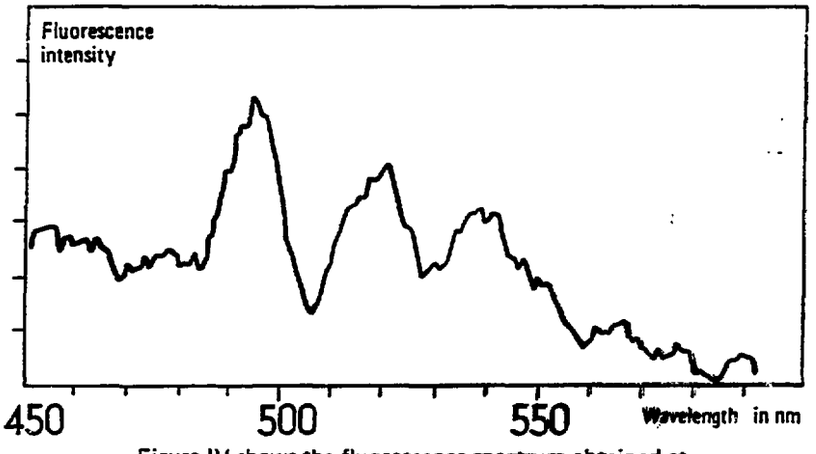
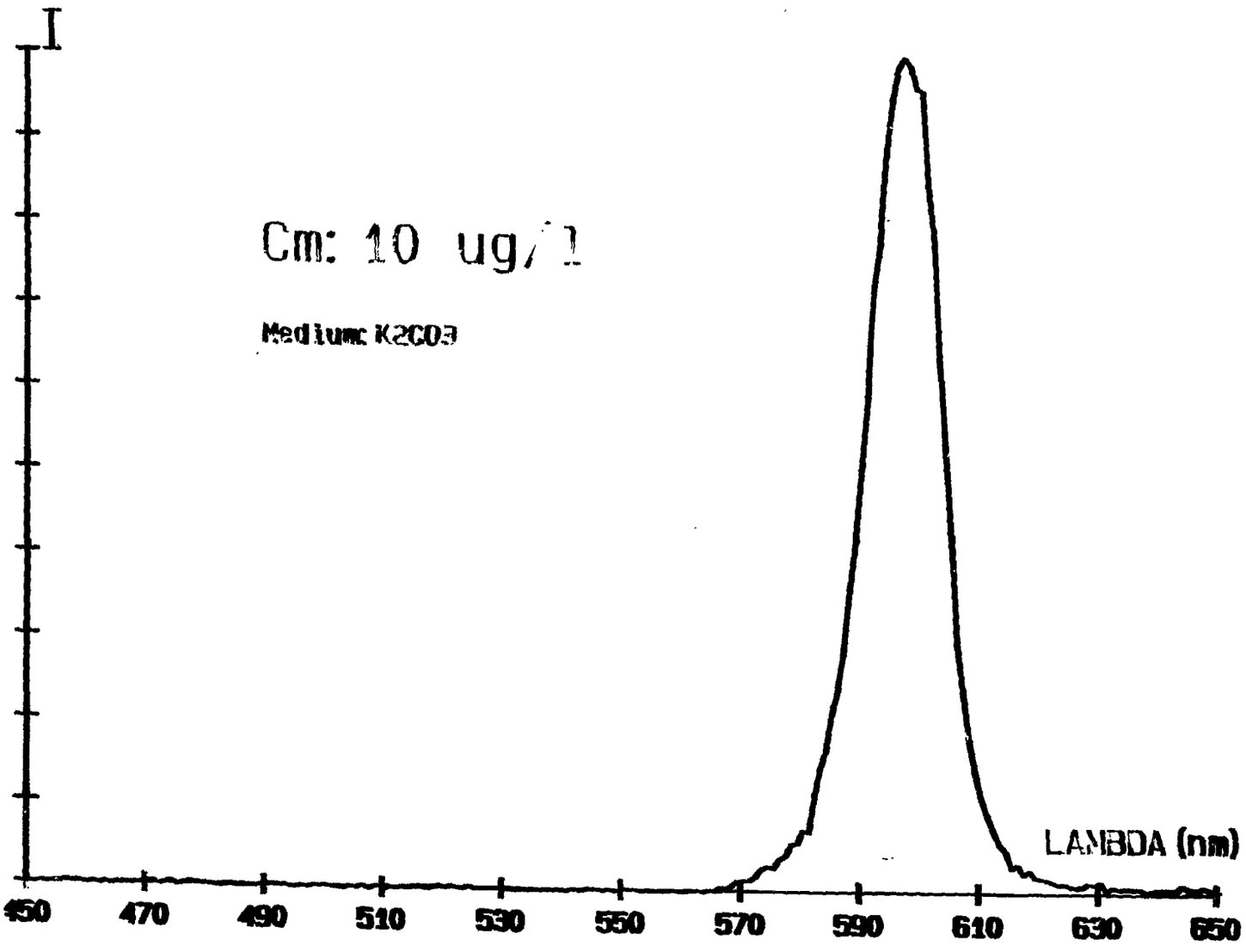


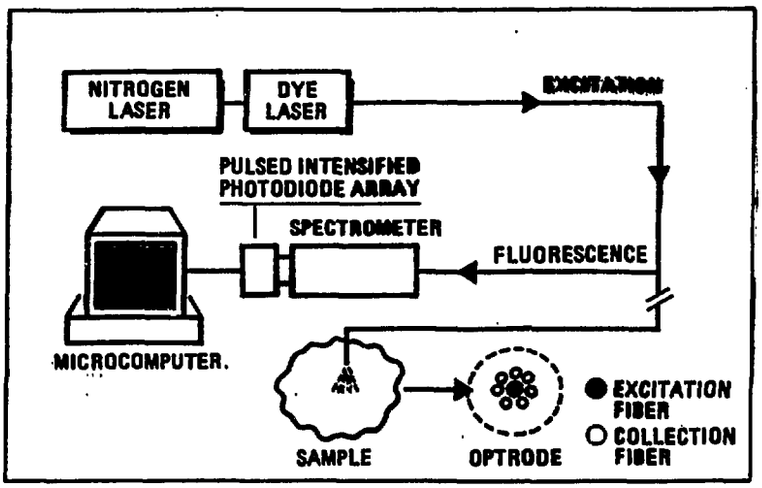
Figure IV shows the fluorescence spectrum obtained at the blank level (3,5 ng/L)


I
Cm: 10 ug/l
Medium: K2CO3
LAMBDA (nm)
450
470
490
510
530
550
570
590
610
630
650

APPLICATIONS

FIELDS	Elt	MATRICES	RANGE	LoD (ug/l)
medical	U	urines	0.1–5	0.05
nuclear	U	sodium	–	0.5
		organic TBP	0.05–500	0.01
		Ac and FP	–	0.02
	Cm	Ac and FP	2–500	0.02
geology	U La	groundwater	LoD–1	0.001
environ-ment	U	soils,grass,..	LoD–10	0.005
comple-xation	U,Cm Am,La	organic matters,..		0.001–10

Time-Resolved Laser-Induced Spectrofluorometry with Fiber Optics for Remote Sensing



Results:

- Patent submitted.
- Optimzation of "optode" geometry.
- No significant loss (in visible) of sensitivity for the lanthanides as compared to conventional method with cuvette.
- Comparable results for uranium excited at 337 nm.
- Installation of Dilor Fluo 2001 with fiber optics in hot lab (Marcoule reprocessing - analysis of solutions originating from the first cycle of the Purex process.

Future:

- Characterize long distance performances.
- On-line control of uranium in the Purex process.

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THERMAL LENSING SPECTROSCOPY

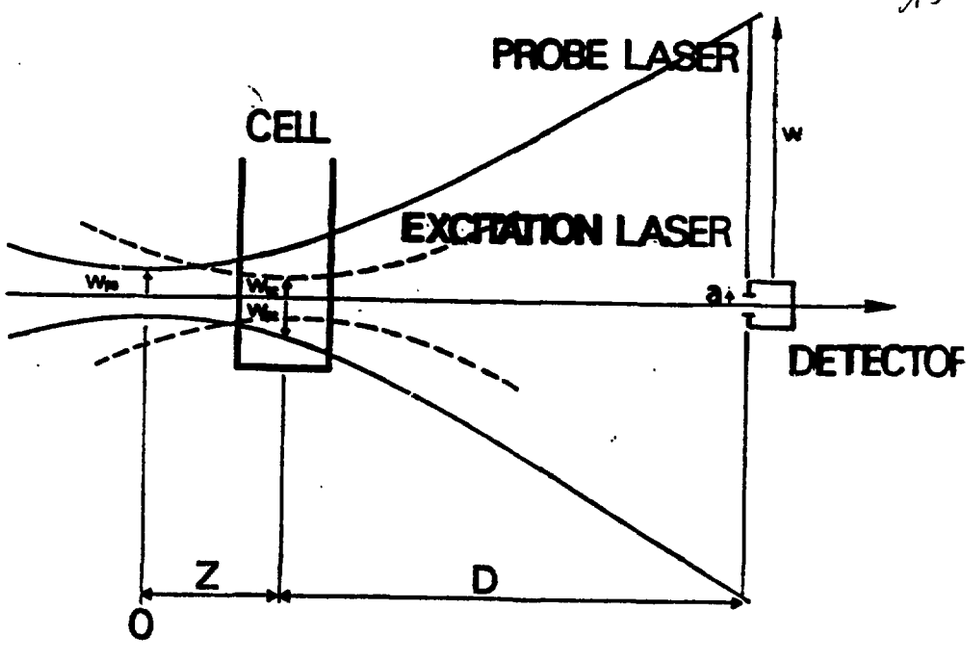
PRINCIPLE

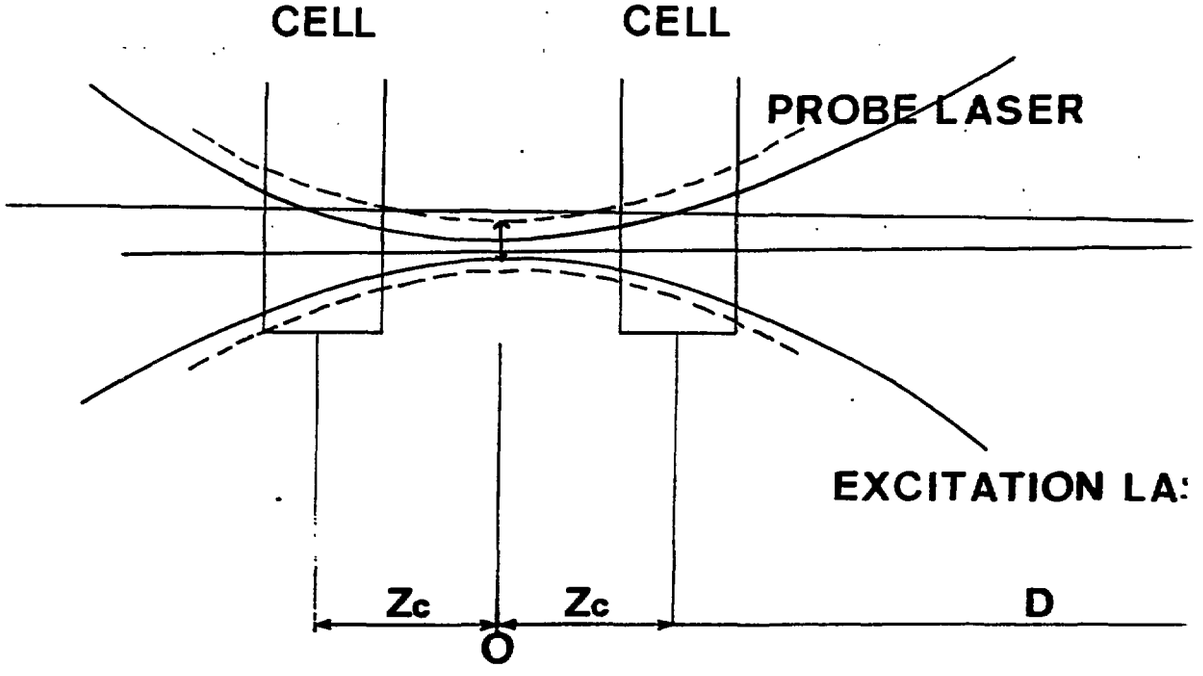
* CW LASER WITH CHOPPED EXCITATION

* ABSORPTION ⟹ INCREASE OF TEMPERATURE

* REFRACTIVE INDEX VARIATION

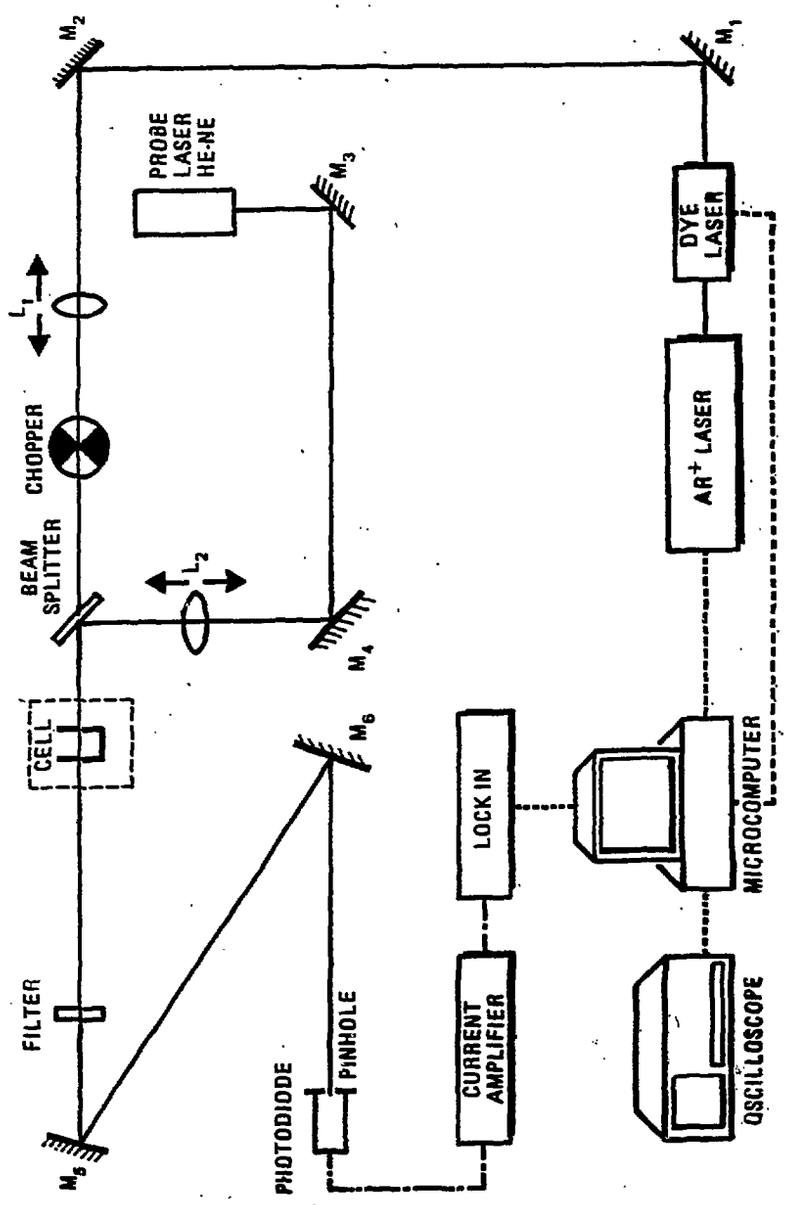
* MEASUREMENT OF THE DIVERGENCE OF THE PROBE BEAM


PROBE LASER
CELL
w
EXCITATION LASER
a
DETECTOR
Z
D
O


CELL
CELL
PROBE LASER
EXCITATION LA
Zc
Zc
D
O

13

14


M2
M1
PROBE LASER HE-NE
M3
DYE LASER
L1
CHOPPER
AR+ LASER
BEAM SPLITTER
L2
M4
CELL
M6
LOCK IN
MICROCOMPUTER
FILTER
CURRENT AMPLIFIER
OSCILLOSCOPE
PINHOLE
PHOTODIODE
M5

LA:

Conference on analytical chemistry in nuclear Technology".
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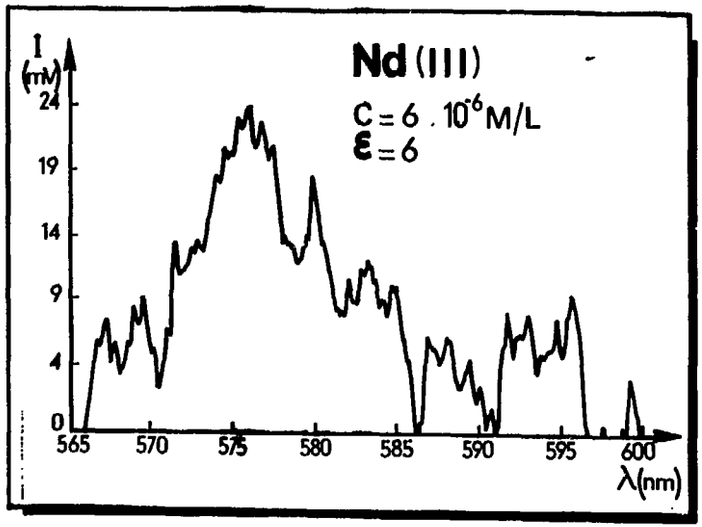
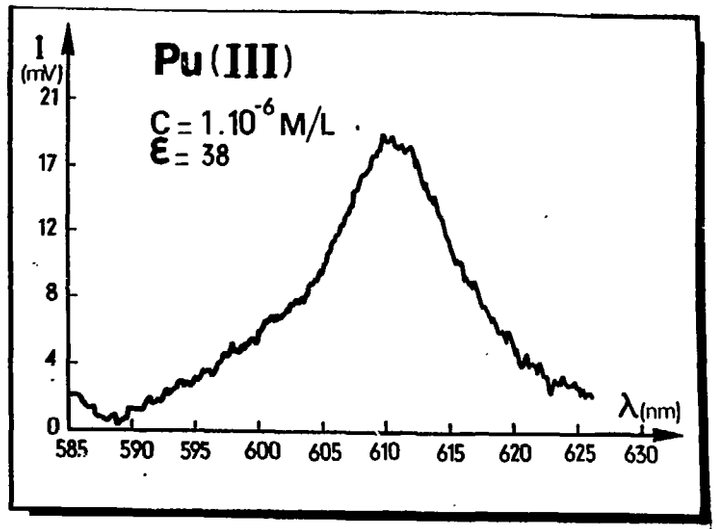
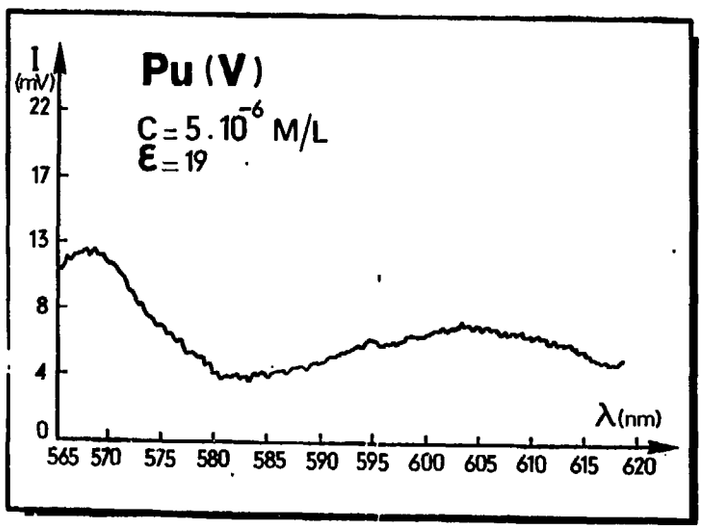
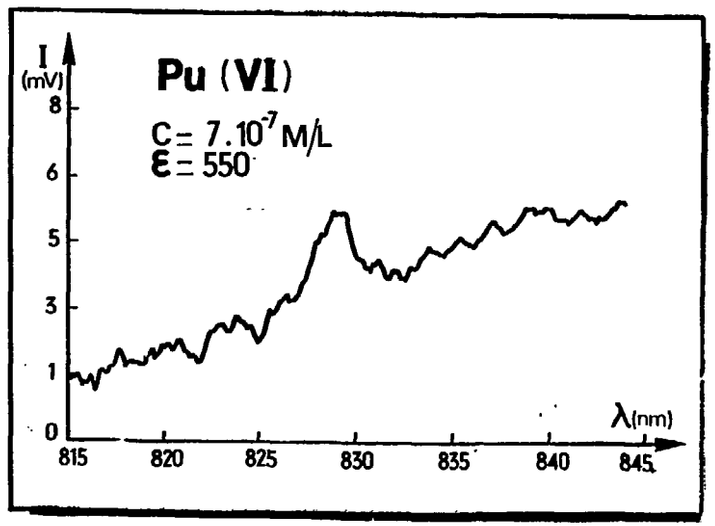
COMPARISON OF THE LOD FOR THE VARIOUS OXYDATION STATES OF PLUTONIUM BY TL AND SPECTROPHOTOMETRY

			LoD(10^{-8}M)	
STATE	λ	ε	TL	S
Pu(III)	610	33	1	2500
Pu(IV)	651	36	1	2500
Pu(V)	569	10	3	3000
Pu(VI)	830	550	3	200


Nd (III)
C = 6 . 10⁻⁶ M/L
ε = 6
I (mV)
24
19
14
9
4
0
565 570 575 580 585 590 595 600
λ(nm)


Pu (III)
C = 1.10⁻⁶ M/L
ε = 38
I (mV)
21
17
12
8
4
0
585 590 595 600 605 610 615 620 625 630
λ(nm)


Pu (V)
C = 5.10⁻⁶ M/L
ε = 19
I (mV)
22
17
13
8
4
0
565 570 575 580 585 590 595 600 605 610 615 620
λ(nm)


Pu (VI)
C = 7.10⁻⁷ M/L
ε = 550
I (mV)
8
6
5
3
1
0
815 820 825 830 835 840 845
λ(nm)

CONCLUSION

LASER SPECTROSCOPIC TECHNIQUES (TRLIS,TL,RIMS,ICP-LASER) ALLOW A GAIN IN SENSITIVITY OF A FACTOR 100 TO 1000 RELATIVE TO CONVENTIONAL SPECTROSCOPY

CONSIDERING THE FIGURES OF MERIT FOR THESE TECHNIQUES,THEY WILL WITHOUT DOUBT BE INCREASINGLY USED IN THE FUTURE IN THE FUEL CYCLE WHERE THERE ARE NEEDS FOR HIGH SENSITIVITY AND ON-LINE CONTROL