Analysis of Some Synthetic Samples. Table I gives results for some synthetic samples, showing that the method is satisfactory.

TABLE I. Recovery of Cerium Added to Selected Synthetic Samples.

Added (ΣY)	Ce, μg Added	Ce, μg Found	Recovery (%)
2	7	6.9	98.6
5	10	10.3	103.0
5	12	12.2	101.0
7	15	14.6	97.3
10	10	11.0	110.0

Applications. The proposed method has been applied to the determination of cerium sub-group elements in nodular cast iron and low alloy steel (Table II).

TABLE II. Determination of Cerium Sub-group Elements in Iron and Steel.

Sample	Composition %	Found %	
Low alloy steel			
1	0.052	0.0508	0.051
2	0.029	0.0293	0.0297
3	0.031	0.0313	0.031
4	0.0205	0.0203	0.0203
5	0.0354	0.0346	0.0342
6	0.082	0.0814	0.0814
Nodular cast iron			
1	0.022	0.0236	0.0236
2	0.046	0.0468	0.0468
3	0.085	0.082	0.082

Table II gives results for some typical samples showing the method is considered satisfactory.

1 S. B. Savvin, T. V. Petrova and P. N. Romanov, *Talanta*, 1972, *19*, 1437.

2 Chemistry Department of Wuhan University, *Fenxi Huaxue*, 1975, *3*, 109.

3 Hsu Chung-gin, Hu Chao-sheng, Jia Xi-ping and Pan Jiao-mai, *Anal. Chim. Acta*, 1981, *121*, 177.

E14

A New Fluorimetric Technique for Low Levels Uranium Determination using Lifetime Measurements

P. MAUCHIEN

Commissariat à l'Energie Atomique, DCAEA/SEACC, B. P. 6, F92260 Fontenay-aux-Roses, France

A current method used for the determination of trace uranium is the fluorimetric technique. Many scientists studied the emission mechanism and it has been showed that phosphoric complexes give the best fluorescence efficiency.

In 1976 a commercially available laser was introduced by Scintrex Ltd for the direct determination of trace amounts of uranium in water. This new instrument is based on laser induced fluorescence. Its use was described in details by Robbins [1] and a critical study of the performances was made by Campen and Bächmann [2]. The excitation source is a nitrogen laser emitting ultraviolet radiation of 3371 Å. As any fluorescence from organic matter in the water is superimposed on the uranyl phosphate complex fluorescence, a discrimination by time is provided. After each pulse an electronic gating system is employed to separate the very long uranyl fluorescence from the very intense but very short organic matter fluorescence.

This technique is suitable for detection of uranium at very low levels (about 0.05 μg l^{-1}), however the apparatus has some drawbacks:

– Uranium fluorescence spectrum which is characteristic, cannot be obtained.

– Lifetime acquisition allowing to stress the presence of quenching species in solution is not possible. Due to the very long lifetime of uranyl in the excited state (100 to 200 μs in 0.75 *M* phosphoric acid medium), a lot of constituents can participate to quench fluorescence.

As a result this procedure for the determination of trace implies to use the internal standard method, which is time consuming and increases analytical waste. This last point can be a severe drawback to this technique for the determination of trace uranium in radioactive waste [3].

We developped in our laboratory a new technique, by-passing the previous problem of the internal standard method for the determination of trace uranium. The idea is that the laser pulse duration being very short compared to the fluorescent lifetime in the excited state, population of the excited molecules will not reach the steady state before the end of irradiation.

With some assumptions, concentration in excited molecules at the end of irradiation time ($|UO_2{}^{2+}|^*_{t.irr}$) leads to eqn. (1):

$$|UO_2{}^{2+}|^*_{t.irr} = \epsilon I_1 |UO_2{}^{2+}| x t.irr \qquad (1)$$

ϵ = molar absorption coefficient in e-basis. I_1 = intensity of the excitation radiation. $|UO_2{}^{2+}|$ = unknown concentration. t.irr = duration of laser pulse.

Fluorescence being proportional to concentration in excited molecules, it leads to eqn. (2):

$$F_{t.irr} = \frac{1}{\tau_o} k \epsilon I_1 t.irr |UO_2{}^{2+}| \qquad (2)$$

k = apparatus factor. τ_o = natural lifetime of the excited state. $F_{t.irr}$ = fluorescence just after laser pulse.

Generally, due to the presence of an organic matter fluorescence, $F_{t.irr}$ cannot be directly reached in the experimental part. However using fluorescence lifetime, $F_{t.irr}$ can be calculated. Emission intensity decreases with time according to eqn. (3):

$$F_{(t)} = F_{t.irr} e^{-t/\tau} \qquad (3)$$

By measuring F(t) for different t values and plotting eqn. (4), τ and $F_{t.irr}$ can be obtained:

$$\mathrm{Ln}\, F(t) = \mathrm{Ln}\, F_{t.irr} - t/\tau \qquad (4)$$

$F_{t.irr}$ being independent of τ, the determination of trace is made by comparing results obtained for the unknown concentration with those for a reference concentration.

Eqn. (5) leads to the concentration $|UO_2^{2+}|$:

$$|UO_2^{2+}| = \frac{F_{t.irr}}{F_{t.irr\,(ref)}} |UO_2^{2+}|_{ref} \qquad (5)$$

$F_{t.irr}$ = fluorescence intensity of the unknown solution. $F_{t.irr(ref)}$ = fluorescence intensity of the reference solution.

This technique is of a great interest in laboratories where there is a high rate of determination of trace uranium. Thus, this method provides an important gain of time and decreases waste.

For illustration, Fig. 1, is the plot of eqn. (4), for two solutions of equal uranium concentration (60mg l^{-1}).

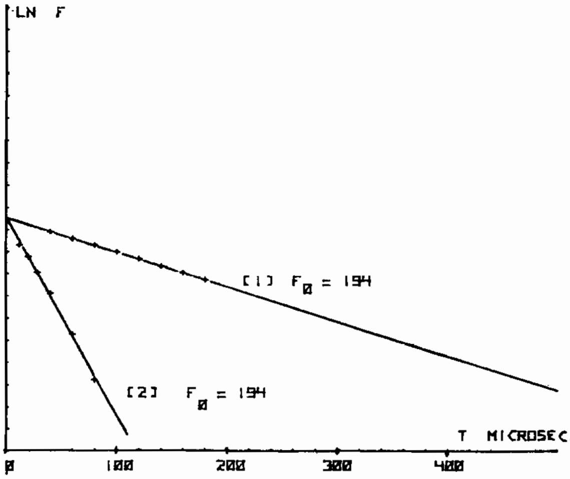

Fig. 1. =1], uranium = 60 mg/l, life = 129 μs; [2], uranium = 60 mg/l, neodyme = 400 mg/l, life = 22 μs.

The first solution is pure and the second one contains 400 mg l^{-1} of Neodyme which is a quenching element. Lifetimes are respectively 129 μs and 22 μs while fluorescence intensities at the beginning are the same. This result is a confirmation to the validity of the procedure.

TABLE I. Results Obtained for Solutions Containing Humic Acids and Quenching Species. The two parts of this table correspond to different adjustments of apparatus.

Solution	Dilution X times	Lifetime μs	$F_{t.irr}$	Calculated concentration (μg l^{-1})
1	50	74	887	80.6
Reference solution (24 μg l^{-1})	–	168	264	–
2	50	84	2416	67.6
3	50	144	291	8.1
4	10	116	820	23
5	10	128	857	24
Reference solution (60 μg l^{-1})	–	164	2143	–

TABLE II. Comparison between the Results Obtained by Two Different Techniques.

Solution	Fluorimetric technique	
	Using an electronic gating system	Using intensity at the beginning
1	3.4 mg l^{-1}	4.03 mg l^{-1}
2	3.6 mg l^{-1}	3.38 mg l^{-1}
3	413 μg l^{-1}	407 μg l^{-1}
4	230 μg l^{-1}	230 μg l^{-1}
5	230 μg l^{-1}	240 μg l^{-1}

Table I is an example of determination of trace in more complex solutions and with lower concentrations. Solution 1 is very strongly contaminated with humic acids and with a quenching species which decreases lifetime by a factor of 2 after 50 times dilution.

By comparison, we used the fluorimetric technique (with a gated pulse integration system) implying the internal standards for the determination of trace in previous samples. Results are shown in Table II and the agreement between the two methods is quite good, differences are lower than 5% except for solution 1 where the result is lower with our new method. However, by looking at results for solution 3 which comes from solution 1 with a 10 times dilution, we may conclude that the second method is closer to reality. Sensitivity of this technique seems to be lower than 1 μg l^{-1}. The two main drawbacks come from absorbents within solutions and species giving complexes with uranium more stable than phosphoric complexes.

When the quenching effect is too important, the reduction of lifetime in the excited state is so strong that differentiation between fluorescence from uranium and organic matter is impossible; thus, the method doesn't work so well for the other methods using fluorescence measurements but it is interesting to point out that, most of the time, solutions for measurement of trace are very dilute, this fact avoiding problems due to quenching and inner filter effect.

1 J. Robbins, *C.I.M. Bulletin*, May 1978, p. 61.
2 W. Campen and K. Bächmann, *Mikrochim. Acta*, 1979 (2), 159.
3 P. Mauchien, Ph. Cauchetier and J. Grison, 'Nuclear Safeguards Technology 1982'. IAEA-SM-260/25.

E15

Neutron Activation Analysis: a Powerful Tool for Rare-earth Elements Assay in Terrestrial Materials

M. ODDONE, S. MELONI*

Dipartimento di Chimica Generale, University of Pavia, Pavia, Italy

and N. GENOVA

Centro CNR per la Radiochimica e l'Analisi per Attivazione, Dipartimento di Chimica Generale, University of Pavia, Pavia, Italy

The ability of rare-earth elements to act as indicators of physico-chemical processes in the environment has drawn a great interest on the knowledge of their abundance and distribution. This interest is growing with the availability of reliable data on rare-earth element concentrations.

Neutron activation analysis [1–4] is the most used analytical technique for the determination of the rare-earth elements in environmental matrices on account of its high sensitivity, of the possibility of determining all the elements and of the undisputed accuracy and reliability of its results. Both instrumental and destructive techniques may be applied but when the content of all the rare-earth elements is required, the use of destructive methods is compulsory.

Neutron activation analysis methods for rare-earth elements determination in different matrices have been developed at the University of Pavia using the 250 Kw TRIGA Mark II reactor [5]. In the present paper a critical review of both instrumental and destructive methods is presented as well as the indication of the best working conditions for irradiation, counting and radiochemical separations.

The 'optimized' procedures were then utilized in the determination of rare-earth element in standard reference materials of both mineral and biological origin to emphasize a widespread application of the method. The chosen materials were: SRM-278 'Obsidian rock', SRM-1632 'Coal', SRM-1633 'Fly Ash', SRM-1571 'Orchard Leaves' from U.S. National Bureau of Standard and Standard rock NIM-G (South Africa).

All these matrices were submitted to instrumental and radiochemical activation analysis for rare-earth elements determination.

The choice of the nuclear reaction, irradiation and decay times, and of the proper gamma radiation in counting are presented and discussed. The adopted radiochemical procedure is based on the separation of the rare-earth element group by fluoride precipitation, which allows the removal of ^{46}Sc and alkaline, alkaline-earth radionuclides interfering in the high resolution gamma-ray spectrometry.

Results, given as the average of four or more independent determination and relative standard deviation, are reported and discussed. Precision of the methods can be deduced from the reproducibility of data, whereas accuracy is evaluated by comparison with certified information and literature values. Sensitivity limits under the described operational conditions are also reported. In some cases it is the first time that a rare-earth element content is reported, as for instance Pr, Dy, Ho and Er content in NBS-SRM 278 'Obsidian rock', Pr, Nd, Gd, Er and Tm content in NBS-SRM 1633 'Fly Ash' and Er content in NBS-SRM 1571 'Orchard Leaves'.

Trends and correlations among data are discussed as well.

1 A. Benedetti, R. Frache, H. Jaffrezic, J. L. Joron, A. Mazzucotelli, S. Meloni and M. Oddone, *Ofioliti 2* (1977) 29.
2 A. Chattopadhyay and S. A. Katz, *J. Radioanal. Chem.*, *46* (1978) 321.
3 J. E. Whitley, A. B. Moves and P. Bowden, *J. Radioanal. Chem.*, *48* (1979) 147.
4 H. Jaffrezic, J. L. Joron, M. Treuil and D. A. Wood, *J. Radioanal. Chem.*, *55* (1980) 417.
5 S. Meloni, M. Oddone, A. Cecchi and G. Poli, *J. Radioanal. Chem.*, *71* (1982) 429.

E16

Effect of Lanthanium(III) on Noninvasive Tumour Imaging with Gallium-67

S. K. SHUKLA*

Istituto di Cromatografia, C.N.R., Casella Postale 10, I-00016 Monterotondo Stazione (Rome), Italy

C. CIPRIANI, G. B. MANNI

Servizio di Medicina Nucleare, Ospedale S. Eugenio, P.le Umanesimo, I-00144 Rome, Italy

I. BLOTTA and R. MASELLA

Istituto Regina Elena per lo Studio e la Cura dei Tumori, V.le Regina Elena 291, I-00161 Rome, Italy

Gallium-67 citrate is the most widely used noninvasive, positive tumour imaging radiopharmaceutical [1]. Healthy organ uptake of the radionuclide in