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## Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water

By

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With 11 Figures

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In the last decade an increasing demand for uranium prospecting has initiated the development of new methods. One of these is hydrochemical prospecting by determination of uranium in water. As such an investigation requires analysis of a large number of samples, it is important to use a fast method for the determination to keep the costs low. Since the average content of uranium in surface water or ground water is below 1 ng/ml (we have found in surface water in a certain region of Germany an average value of 0.57 ng/ml) 0.1 ng/ml or less should be measurable. In Table I a survey is given of methods which have been used up till now. The survey is far from complete, but it shows that most of the methods use a pre-concentration or separation step, which improves the detection limit and eliminates interfering elements.

Recently a new instrument has been developed<sup>1</sup>, which is based on laser-induced fluorescence. Its use is described by Robbins<sup>2</sup>. The aim of our investigation was a critical study of the performance of this instrument. We have looked for possible interferences in surface water or ground water, and even in solid samples which had been fused and dissolved.

The principles of the method have been described in detail by Robbins<sup>2</sup>, so we will give only a very short survey. A nitrogen laser emitting ultraviolet radiation of 337 nm is used as excitation source. As any fluorescence from organic matter in the water is superim-

Table I. Comparison of Methods for the Determination of Uranium in Surface or Ground Water

No.	Method	Enrichment or separation	Volume, ml	Enrichment factor	Detection method	Detection limit	Reference
1	Laser-induced fluorescence	direct	5	—	fluorescence	0.05 ng/ml	2 and this study
2	Xenon arc lamp induced fluorescence	ion-exchange sulphuric acid	200	22	fluorescence	0.3 ng/ml	3
3	Xenon lamp with Fluran	direct	5	—	fluorescence	2 ng/ml	this study
4	Solid fluorescence of NaF beads	extraction	5	—	fluorescence	0.5 ng/ml	4, 5
5	X-ray fluorescence	separation with Hyphan exchange	500	$5 \times 10^4$	X-ray fluorescence	0.3 ng/ml	6
6	Neutron activation	Chelex 100	1000	$5 \times 10^3$	$\gamma$ -spectroscopy	0.3 ng/ml	7
7	Delayed neutron counting	ion-exchange sulphuric acid	1000	1000	neutron counting	1 ng/ml	8
8	Nuclear track method	direct	0.025	—	track counting	0.1 ng/ml	9
9	Spectrophotometric determination (Arsenazo III)	AlPO <sub>4</sub> precipitation	500	100	absorption spectroscopy (665 nm)	2 ng/ml	10
10	AAS flame	ion-exchange	1000	40	detrn. of Cu	25 ng/ml	11
11	AAS non-flame	ion-exchange	1000	40	detrn. of Cu	2 ng/ml	11
12	Flame atomic emission	direct	—	—	atomic absorp.	30 ppm	} 12
	Atomic fluorescence	direct	—	—	atomic emiss.	10 ppm	
	Polarography	direct	—	—	atomic fluores.	3 ppm	
13	Polarography	precipitation with Fe(OH) <sub>3</sub> and extraction	2000	—	polarography	2 ng/ml	13
14	ICP emission spectroscopy	direct	—	—	atomic emiss.	1—10 ng/ml	14
15	ICP emission spectroscopy	direct	—	—	atomic emiss.	1.5 ng/ml	15
16	CMP emission spectroscopy	direct	—	—	atomic emiss.	30 ppm	16
17	AES carbon furnace	direct	—	—	atomic emiss.	2.5 ppm	17

posed on the  $\text{UO}_2^{2+}$  fluorescence, a discrimination by time and wavelength is provided.

For wavelength discrimination a green filter is arranged between the sample and the photomultiplier. Fig. 1 shows the timing for the measurement cycle. The laser is pulsed at a repetition rate of 15 pulses per sec. After a laser pulse, about 1000 nsec are gated off in order to suppress the strong but short-lived organic fluorescence.

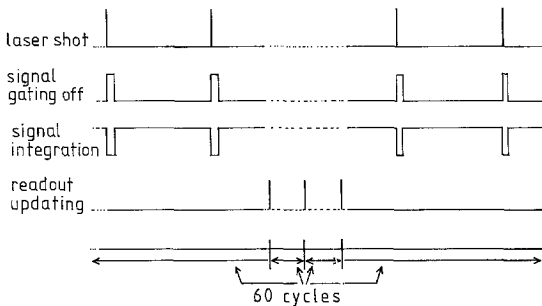


Fig. 1. Timing diagram for the pulsed measurement cycle

Then the signal is integrated until the next laser pulse. To improve stability, the outputs from about 60 cycles are accumulated, which results in an update-cycle of 4 sec for the analogue read-out device. In order to increase the  $\text{UO}_2^{2+}$  fluorescence, "Fluran"\* is added to the sample. Fluran is a compound of a chelating agent and a fluorescence agent<sup>18</sup> which, because of the high stability constant of the  $\text{UO}_2^{2+}$  complex, guarantees that the fluorescence measured always comes from the same species. As the stability of the complex is pH-dependent, Fluran also contains sufficient amount of buffer.

## Experimental

### *Investigation of Interference and Performance*

*Detection limit and calibration curve.* For all measurements 5-ml samples were used. After the zero had been set on the instrument 0.75 ml of Fluran was added. Fig. 2 shows the dependence of the signal on the amount of Fluran added, at a uranium level of 5 ng/ml. For smaller or higher levels the curve does not change, as the fluorescent agent is always present in excess, but a sufficient amount of buffer solution must be added. Since the fluorescence radiation depends on temperature, we have measured the signals

\* Fluran is available from the instrument manufacturer: Scintres Limited, 222 Suidercroft Road, Concord (Toronto), Ontario, Canada.

as a function of temperature and found a strong decrease with increasing temperature (Fig. 3). This means that care must be taken about the temperature of the sample and that errors might be caused by the laser radiation heating up the sample. The reason for the scatter of the measured points

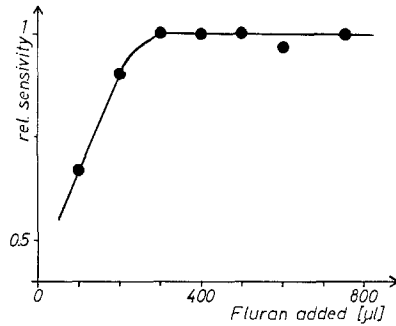


Fig. 2. Dependence of the signal intensity on amount of Fluran added

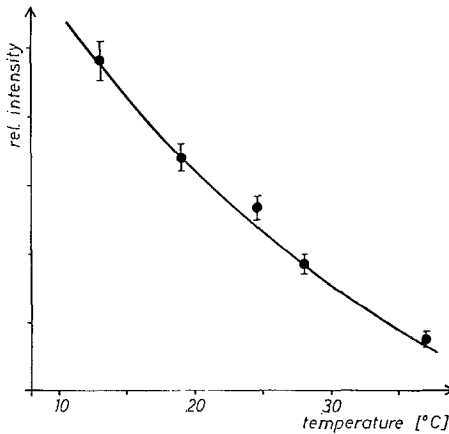


Fig. 3. Dependence of the signal intensity on temperature

in the curves shown is probably the inevitable temperature fluctuation and a certain laser instability.

Fig. 4 shows the calibration curve, obtained with a standard solution of uranyl nitrate. The lower curve is the measured curve and the upper curve is the curve corrected for volume changes caused by adding the Fluran and diluting the samples. The regression coefficient is 0.995. The lower detection limit, taken as three times the standard deviation of the background signal, is 0.05 ng/ml. For the calibration of the instrument, solutions containing 200 ng of uranyl nitrate per ml were used and diluted

at the time of calibration. A second calibration was carried out with solid standards, which were fused, dissolved and diluted; the curve is shown in

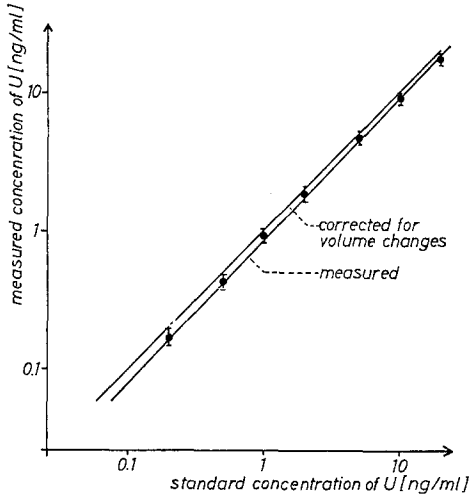


Fig. 4. Calibration curve for liquid samples

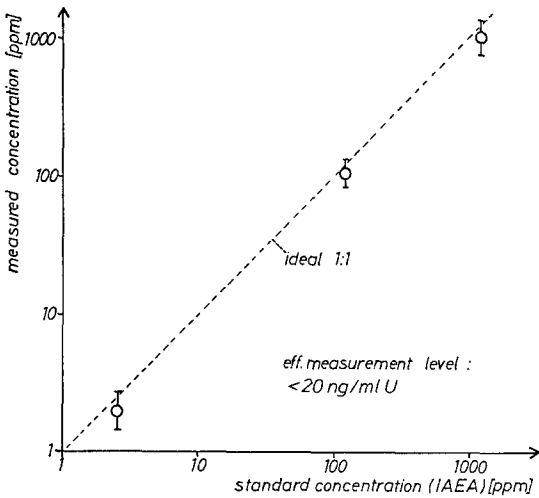


Fig. 5. Calibration curve for solid samples

Fig. 5. For the solid samples the values obtained by laser-induced fluorescence are always about 15% lower than the expected values. The error bars indicate the standard deviation (5 measurements).

Table II. Element Concentrations in Sea-Water and River or Ground Water

Element	Sea-water* µg/ml	Element	Sea-water* µg/ml	Element	Surface or ground water** µg/ml
Chlorine	18 980	Iron	0.002—0.02	Cl <sup>-</sup>	7.8
Sodium	10 561	Manganese	0.001—0.01	Na <sup>+</sup>	6.3
Magnesium	1 272	Copper	0.001—0.01	Mg <sup>2+</sup>	4.1
Sulphur	884	Zinc	0.005	SO <sub>4</sub> <sup>2-</sup>	11.2
Calcium	400	Lead	0.004	K <sup>+</sup>	2.3
Potassium	380	Selenium	0.004	Ca <sup>2+</sup>	15
Bromine	65	Caesium	0.002	HCO <sub>3</sub> <sup>-</sup>	58.4
Carbon	28	Uranium	0.0015	SiO <sub>2</sub>	13.1
Strontium	13	Molybdenum	0.0005	NO <sub>3</sub> <sup>-</sup>	1
Boron	4.6	Thorium	0.0005	Fe	0.67
Silicon	0.02—4.0	Cerium	0.0004		
Fluorine	1.4	Silver	0.0003		
Nitrogen	0.01—0.7	Vanadium	0.0003		
Aluminium	0.5	Lanthanum	0.0003		
Rubidium	0.2	Yttrium	0.0003		
Lithium	0.1	Nickel	0.0001		
Phosphorus	0.001—0.10	Scandium	0.00004		
Barium	0.05	Mercury	0.00003		
Iodine	0.05	Gold	0.000006		
Arsenic	0.01—0.02	Radium	0.2—3 × 10 <sup>-10</sup>		

\* Sverdrup *et al.*, The Oceans, 1942.

\*\* Livingstone, 1963.

*Interference by anions.* Figure 6 shows a curve for the dependence of the signal on the concentration of sodium carbonate. The decrease at about 1000 ppm is due to the carbonate, since it can be shown

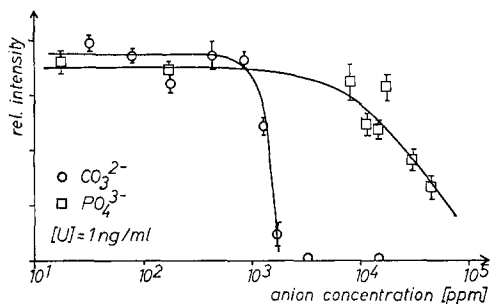


Fig. 6. Dependence of the fluorescence intensity on  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  concentrations

that sodium below 4000 ppm does not influence the uranium fluorescence (Fig. 8). In Figs. 6 and 7 the signal is plotted as a function of the concentration of sodium chloride, sulphate and dihydrogen phosphate monohydrate. Chloride and sulphate show no influence

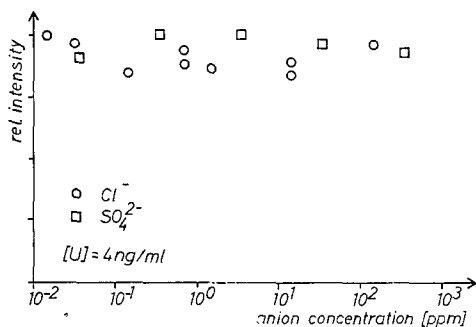


Fig. 7. Dependence of the fluorescence intensity on  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations

on the signal, nor does phosphate in the range expected for natural waters. For solid samples which have a higher phosphate content, a determination by this method is not suitable.

Table II summarizes the normal concentrations of cations and anions in surface water, ground water and ocean water and it can be seen that the concentrations of most of anions are lower than the limit of interference. In ocean water only the high concentration of chloride interferes.

*Interference by cations.* Figs. 8 and 9 show plots of the relative signals as a function of the concentration of the main cations expected in surface or ground water and which might interfere. As

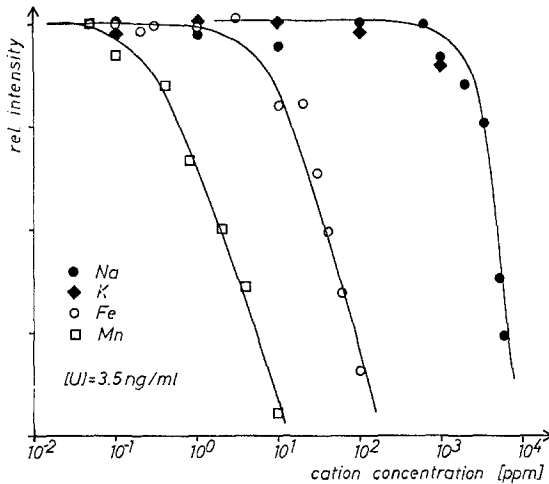
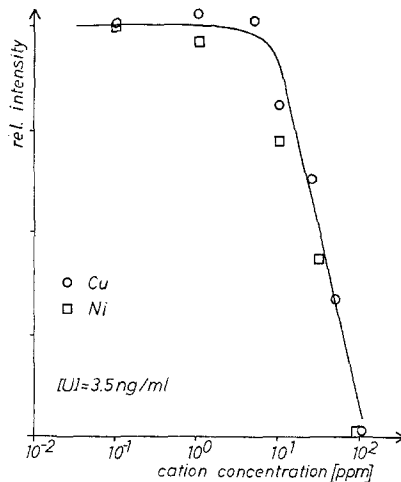


Fig. 8

Dependence of the fluorescence intensity on  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  concentrations

Fig. 9. Dependence of the fluorescence intensity on  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  concentrations

can be seen by comparing with the concentrations in Table II, the most critical elements are Mn and Fe. The curves for these two elements have already been measured by Robbins<sup>2</sup> and are in rather



good agreement with ours. In the case of solid samples severe interference might occur, depending on the composition of the matrix and on the uranium concentration. High uranium concentrations, for example 50 ppm, allow a dilution to 1 ng/ml, which means a dilution factor of  $10^4$  related to the volume of 5 ml. Thus for a solid containing 50 ppm of uranium and 10% iron dissolution and dilution to the 1 ng/ml level for uranium would give an iron concentration of 10 ppm, which is tolerable. Because of variation in the sodium concentration in sea-water, the measurement of uranium should be preceded by a rough sodium determination to decide the dilution necessary to exclude interference by sodium.

### Discussion and Comparison With Other Methods

Most of the methods for determination of uranium in solution need a preconcentration step or even complete separation. The separation lowers the detection limit because of the enrichment factor, and eliminates interfering elements. However, any separation step is time-consuming and expensive. We have not tried to compare the different methods in terms of cost or time, but we feel that any method which includes a separation step is not very suitable for dealing with the several thousands of samples needed in prospecting work. Furthermore we did not try to compare the detection limits in terms of accuracy, reproducibility and possible interferences. Most of the direct methods in Table I have too high a detection limit for use in hydrogeochemical investigation. As for the fluorimetric method (using solid pellets), the great number of interferences leads to large errors. In the nuclear track method the small volume of water used might result in observation of small fluctuations in concentrations, caused by temperature differences or chemical gradients, so the result is not representative of the average value in surface water or ground water. In addition the use of a reactor and the counting of the tracks seems to be more complicated than the laser-induced fluorescence. However, of the direct methods the nuclear track method seems to be the nearest competitor. To decide whether a xenon arc lamp could induce sufficient fluorescence to make a direct measurement possible we have made some measurements, shown in Figs. 10 and 11. Classical fluorescence might be optimized to give a detection limit of perhaps about 0.5 ng/ml, but a value of 0.05 ng/ml seems impossible.

Summarizing, laser-induced fluorescence can be recommended for the measurement of low uranium concentrations when the number of samples is very large. We would suggest as improvements of

the instrumentation, the use of a thermostatic housing for the cuvette, and instead of a simple filter instrument an instrument

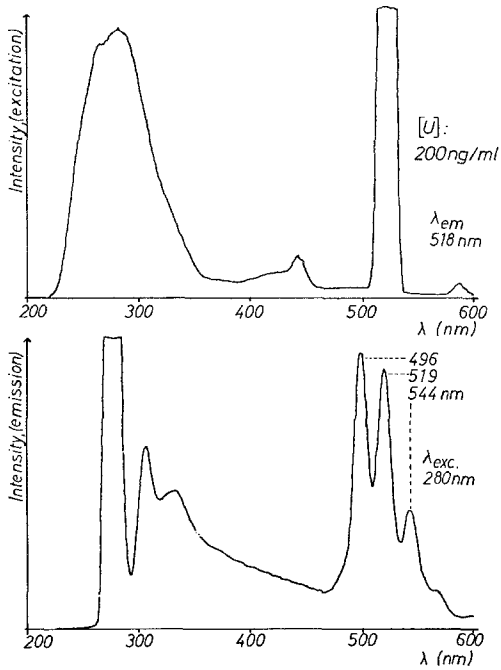


Fig. 10. Excitation spectrum and emission spectrum of an aqueous solution containing 200 ng of uranium per ml

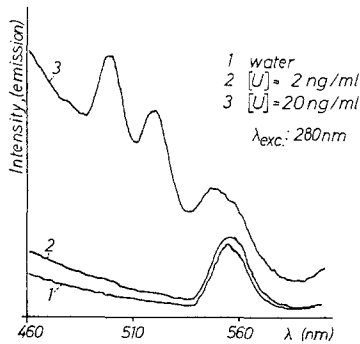


Fig. 11. Emission spectra for 20-ng/ml and 2-ng/ml uranium samples

which measures the whole spectrum either by scanning or with an optical multichannel analyser.

### Acknowledgements

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### Summary

#### *Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water*

The performance of a new analytical device (UA-3-fluorimeter) for the direct measurement of uranium in water has been critically evaluated. The method is based on laser-induced fluorescence. Possible interferences by anions and cations present in natural water have been studied and a critical comparison with other methods has been made.

### Zusammenfassung

#### *Laser-induzierte Fluoreszenz als Grundlage für die direkte Bestimmung kleiner Urankonzentrationen in Wasser*

Eine kritische Beurteilung der Leistungsfähigkeit eines neuen Gerätes (UA-3-Fluorimeter) für die direkte Bestimmung von Uran in Wasser wurde durchgeführt, das sich der Methode der Laser-induzierten Fluoreszenz bedient. Mögliche Störungen durch Kationen und Anionen, die in natürlichen Wässern vorkommen, wurden untersucht. Die Methode wird mit der Leistungsfähigkeit anderer bekannter Methoden verglichen.

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