

UV Radiation Influence of Uranine Fluorescence in Water Samples

LILJANA R. KOLA*, ELIDA B. BYLYKU and PRANVERA LAZO

Department of Chemistry, Faculty of Natural Sciences, CANP, University of Tirana, Tirana, Albania

*Corresponding author: E-mail: kolaliljana@yahoo.it

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Fluorescence ability of uranine (fluorescence) enables its using as artificial tracer in the water system. Problem has to do with injection of uranine to trace and determine water movements within the karstic system and underground waters. Uranine has been used as an artificial tracer for the first times in Albania on 'Mali me Gropa' system study in year 2002. Fluorescence intensity (I_F) of tracers in water samples depends on their physical and chemical properties, such as pH, temperature, presence of oxidants, *etc.* Besides that, UV radiation may induce photochemical decomposition of the dyes which can cause large measurement errors. This paper presents the influence of UV radiation on uranine fluorescence intensity in water samples in different conditions so-called: 'in light', 'in shadow', 'in colourless and brown glass bottle'. Concentration and synchronous scan methods were used for the measurement of uranine fluorescence by the means of a Perkin Elmer LS 55 luminescence spectrometer. Photodecomposition results help us to determine if the dye can be used or not in a water system study with tracing experiment. According to these results we can decide the conditions of the transport and storing of the water samples, too.

Key Words: Spectral determination, Uranine, Fluorescence intensity, Synchronous scan, Artificial tracer.

INTRODUCTION

Modern techniques of tracers in hydrology are elaborated to know aquatic systems and study them in order to assess their water usability as well as to find optimum and sustainable ways of water management. The introduction of fluorescent tracers has led to enormous methodological and instrumental developments^{1,2}. The problems deal with various water systems might be grouped into different groups, according to where is flowing groundwater to, from where it comes, whether exist underground hydraulic connections between different points of the system or not, how is flowing the groundwater in (to) and/or through the system under the study, *etc.*³.

System's water is labeled through fluorescent dyes as artificial tracers and then their presence is monitored from time to time in various parts of the system under the study. When measured in water samples uranine fluorescence intensity depends on different physical and chemical properties of the sample matrix-pH, temperature, oxidants' presence, *etc.*, as shown by Käss³, Benischke⁴ and Kola⁵. Besides that, UV radiation may induce photochemical decomposition of the dyes. That's why we decided to monitor during four months the influence of UV radiation on uranine fluorescence intensity in water samples, in different conditions.

EXPERIMENTAL

"Blank" solutions sampled from the different points of the water system were analyzed in order to assess the natural presence of uranine-fluorescence in environment and to determine the so called "background".

A special software package (FL WinLab) manages different application programs the instrument LS 55 offers. We have detected and measured tracer contents in water samples and standard solutions by using the Synchronous Scan and Concentration Applications. First, the instrument validation should be realized through Raman spectra (Raman Peak Wavelength, Raman Peak Intensity and Raman S/N ratio) from a sealed water cell and a reference material, anthracene. Instrument stability is checked with regard to fluorescence intensity by the means of a reference material (anthracene). The instrument's parameters are organized so as through synchronous and concentration applications. The method elaborated to measure uranine content in water samples is made up of the following parameters: excitation wavelength-491 nm; emission wavelength-512 nm; excitation slit-10.0 nm; emission slit-10.0 nm; $\Delta\lambda$ -21 nm; auto background subtract, *etc.* The characteristic peak wavelength was verified before hand by some preliminary synchronous scans. Instrument was previously calibrated with six uranine standard solutions by the means of the calibration application (Lazo⁶) for uranine determinations.

RESULTS AND DISCUSSION

Influence of the UV radiation on uranine fluorescence intensity:

UV radiation may induce photochemical decomposition of uranine which can cause large measurement errors⁷. To investigate this phenomenon it was prepared uranine standard solution with the concentration $C_0 = 1$ ppb (solvent: distilled water). Two colourless glass bottles and two brown coloured bottles were filled with this prepared uranine standard solution. We placed one colourless glass bottle and one brown colourless glass bottle in the first situation 'in light' and one other uncoloured bottle and one brown coloured flask (pyrex) in the second situation 'in shadow'. Uranine fluorescence intensities of these four flasks were measured at the same time and day according to one preliminary schedule. At the beginning, the measurements were frequently and after some times were more rarely than before.

The supervision of this process continued four months (March-July 2007). The obtained results of uranine photodecomposition in different conditions are shown in Table and Fig. 1. The results of the Table-1 show the decay of the fluorescence of uranine standard solution in the colourless glass bottles exposed to daylight in the so called condition 'in light' and 'in shadow'.

It is obvious from the results above that UV radiation decay sensibly uranine fluorescence. Daylight destroys 33.46 % of the total fluorescence intensity after one day in the colourless bottle 'in light' and 78.05 % of its fluorescence after two days exposure. After 14 days exposure on daylight uranine fluorescence has been destroyed 100 %. The obtained results present clearly that uranine is too sensible *versus* to daylight.

UV radiation decay totally uranine fluorescence after 16 days in the colourless bottle 'in shadow', so 3 days later than 'in light' condition.

Fig. 1 shows the results of uranine fluorescence intensity (I_F) decay after the exposure to daylight in brown glass bottle, 'in light' condition.

One can see from the graph that the fluorescence intensity of uranine has been destroyed 100 % after 60 days exposure to daylight, in brown glass flask, 'in light' condition, so 47 days later than in the case of colourless bottle in the same conditions. Uranine fluorescence in colourless bottle 'in light' has been totally destroyed after 14 days exposure to daylight

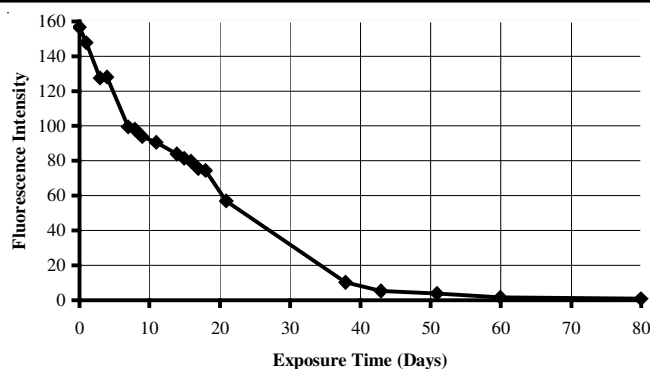


Fig. 1. Photodecomposition of uranine in brown glass bottle, 'in light' ($C_0 = 1$ ppb)

(Table-1), whereas in brown bottle 'in light', in the same date, fluorescence was 53.5 % of its initial value. This proves clearly that brown bottle delay the decomposition of uranine.

The obtained results after exposure to daylight of uranine standard solution in a brown flask in condition 'in shadow' are presented in the Fig. 2.

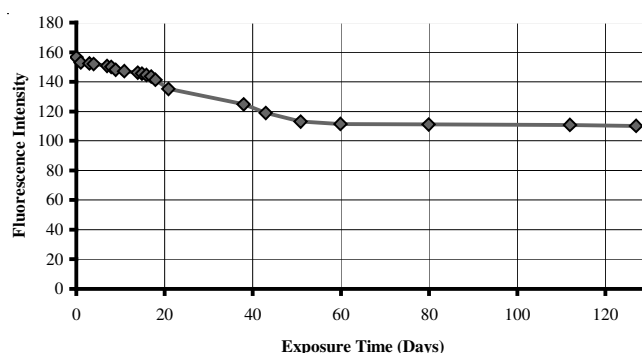


Fig. 2. Photodecomposition of uranine in brown glass flask, 'in shadow' ($C_0 = 1$ ppb)

Results of Fig. 2 show clearly that the decay of uranine fluorescence intensity in brown glass flask, 'in shadow', is more gradual than its decay in the other conditions. In this case, daylight destroys only 29.46 % of uranine total fluorescence intensity at the end of the monitoring (after 127 days).

Comparing the results of the different conditions, it is observed that UV radiation decay 70 % of the initial fluorescence (156,636) in less than one day exposure to daylight in

TABLE-1
PHOTODECOMPOSITION OF URANINE IN COLOURLESS GLASS BOTTLE, 'IN LIGHT' AND 'IN SHADOW'

Uranine standard sol. ($C_0 = 1$ ppb)	I_F of uranine 'in light' condition	Uranine conc. (ppb)	I_F of uranine 'in shadow' condition	Uranine conc. (ppb)	Exposition to daylight (days)
Colourless bottle	156.636	0.987	156.636	0.987	0
Colourless bottle	104.224	0.650	125.047	0.725	1
Colourless bottle	34.393	0.202	80.989	0.503	3
Colourless bottle	28.631	0.165	69.985	0.430	4
Colourless bottle	6.666	0.023	37.768	0.273	7
Colourless bottle	5.529	0.016	19.768	0.107	8
Colourless bottle	5.028	0.013	16.250	0.085	9
Colourless bottle	4.265	0.008	10.707	0.049	11
Colourless bottle	2.104	0.000	6.492	0.022	14
Colourless bottle	1.963	0.000	5.151	0.013	15
Colourless bottle	1.360	0.000	1.177	0.000	16
Colourless bottle	-	-	0.380	0.000	17

colourless 'in light' condition; about two days in colourless bottle 'in shadow'; after about 6 days in brown glass bottle, 'in light' and more than 127 days in brown glass flask, 'in shadow'. These results prove that brown flask delay too much the photo-decomposition of uranine. Fig. 3 shows the dynamics of uranine decomposition after exposure to daylight in four different conditions mentioned above.

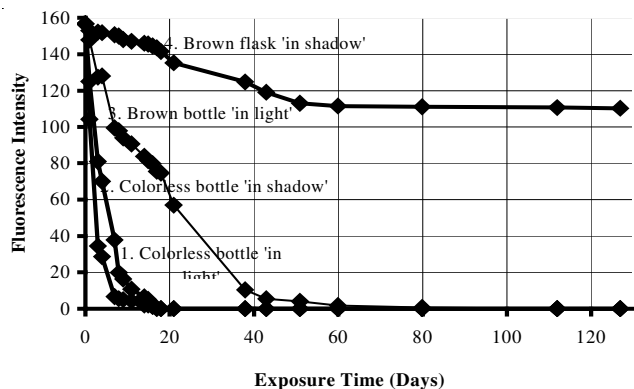


Fig. 3. Decay of the fluorescence of uranine in aqueous solutions exposed to different conditions of daylight

The results show clearly the influence of the UV radiation on uranine fluorescence. It is obvious from the graphs that brown glass bottle (3) and especially brown flask (4) delay the decomposition of uranine fluorescence. We must have these influences in consideration when choose uranine as an artificial tracer for water system studies. We should have in view the influences of UV radiation during the samples transport and standard solutions saving, too.

Conclusion

UV radiation induces the destruction of the uranine fluorescence in the aqueous solution, which can lead to analytical errors, therefore it is indispensable to transport and store the uranine water samples protecting them from day light. UV radiation decay more slowly uranine fluorescence in brown flask in 'shadow' condition than in the other conditions. That's why one should store uranine standard solutions in brown flasks and in the dark. Uranine is affected sensibly by UV radiation; therefore it is better to use uranine in underground water tracing experiments than in surface water studies.

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