

Determination of trace uranium in environment by laser induced fluorescence method

Wu Jinhai, Yuan Zhengang, Li Jinquan, Zhang Chuanzuo, Ren Lihua

Institute of Radiation Medicine, Shanghai 200032, China

Abstract— The analytical technique of trace uranium has been developed rapidly since Robbins first reported the laser uranium analyzer in 1978. Because of the complicated operation and experimental procedure of the normal spectrophotometer, neutron activation and solid fluorescence, they have been replaced gradually by the laser induced fluorescence method. According to high sensitivity and low detection limit of the fluorescence, it can determine the trace uranium. The uranium content in the lake water, underground water and rain etc. can be measured directly without pretreatment. The range of the method for determining uranium is from 0.05 ppb to 20 ppb, and the detection limit is 0.05 ppb.

Keywords: laser analysis; environmental uranium; fluorescence.

1 Instrument and reagents

Instrument: WGJ-I model Laser Uranium Analyzer made in China

Reagents: Standard solution of uranium; $\mu\text{g/ml}$; Fluorescence enhancing agents; (pyrophosphate and polyphosphate mixed).

2 Experimental methods

2.1 Determination of uranium fluorescence and organic fluorescence

Uranium exists in the form of uranyl ion in liquid. When fluorescence enhancing agents were added, fluorescence effects were raised. It produced 494, 516, 540 nm wavelength fluorescence (Fig. 1). The strength of the fluorescence is directly proportional to uranium content, so that quantitative analysis can be carried out. Other substances contained in the sample may produce the fluorescence. Because there are the different life time of the fluorescence and post filter, uranyl fluorescence is only passed for the instrument. Enhancing agents can quench the fluorescence of Fe^{3+} ,

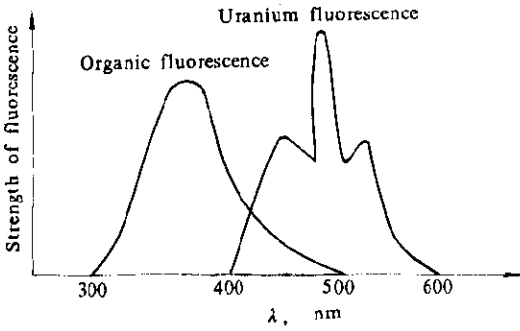


Fig.1 Spectrum figure of uranium and organic fluorescence

Mn²⁺ ion and so on. After the fluorescence that was produced by other matter was quenched, the signal was produced only by the fluorescence of the whole uranyl complex and was accepted by the instrument.

2.2 Effects of acidity

The acidity of the sample exerts prominent influence on the determination, so that suitable acidity for stable determination must be established. So the different sample acidity was made up and every sample was added 5 μl standard solution of 1ppm uranium. The relation between the determination value and acidity is shown in Fig. 2. At same time, effective buffer range of fluorescence enhancing agent is provided. It is pH 4 to 10.

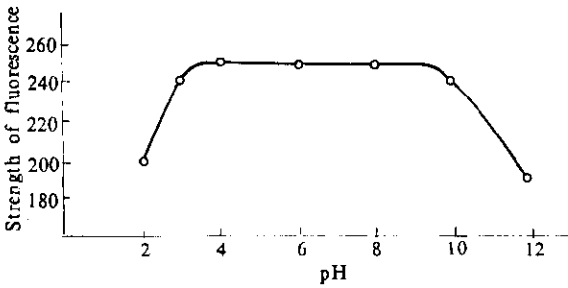


Fig. 2 Effect of acidity for determination

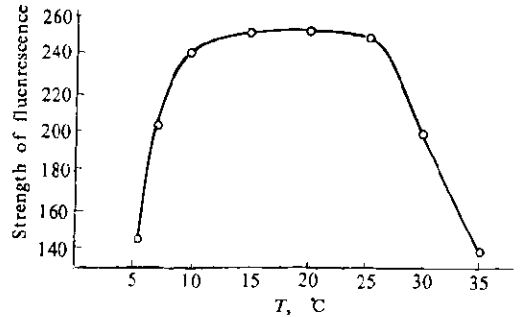


Fig. 3 Effect of temperature for determination

2.3 Effects of temperature

When the temperature was below 6°C, crystal will be arose from solution of fluorescence enhancing agents. Strength of the fluorescence is reduced at high temperature. The relation between the determination value and temperature is shown in Fig. 3.

2.4 Effects of interfering ions

Natural water contains some cation and anion, it has different content. There

are no effects of fluorescence strength from a 100000-time amount of K^+ , Na^+ , Ca^{2+} and Mg^{2+} , and a 1000-time amount of Mn^{2+} and Fe^{3+} on the experimental results. In normal condition, foreign ions are not over it, therefore there no interference for trace uranium determination (Table 1).

Table 1 Effects of interfering ion

Ion in samples	Added ion, ppm	Uranium content, ppb	Relative fluorescence strength
K^+	1000	3	100
Na^+	10000	3	100
Ca^{2+}	100	3	100
	300	3	81
Mg^{2+}	100	3	100
	300	3	88
Fe^{3+}	10	3	90
	30	3	84
Mn^{2+}	1	3	100
	3	3	91

3 Operative methods

There are two kinds of determination method for the instrument, the method of standard addition and of standard curve. Uranium solutions of different concentration were prepared, a curve that can check directly the content of the uranium in a sample was then constructed. It is the method of standard curve, but this method requires more for temperature control. Now, many laboratories use the method of standard addition, which is addition of quantity of standard uranium solution compared with that of no standard uranium solution. In present study the method of standard addition was used. Determination step is as follows: (1) Removed 5 ml sample's water in a beaker and placed it in the samples' room, closed the small door of the samples' room, turned on high voltage, a count F_0 was recorded; (2) Turned off high voltage, opened the small door of the samples' room, 0.5 ml fluorescence enhancing agents was added to the sample, a count F_1 was recorded; (3) Opened the sample door, 10 μ l uranium of 1 ppm was added, and a count F_2 was recorded.

4 Calculative methods

Formula:
$$C_x = \frac{F_2 - F_0}{F_2 - F_1} \cdot \frac{V_s}{V_x} \cdot C_s \quad (1)$$

V_x is volume of sample solution (ml); C_x is uranium concentration in sample ($\mu\text{g/L}$); F_0 is strength of fluorescence uranium before addition enhancing agents; F_1 is strength of fluorescence uranium after addition fluorescence enhancing agents; F_2 is strength of fluorescence uranium after addition solution of standard uranium; V_s is volume of addition standard solution (ml); C_s is concentration of standard uranium solution ($\mu\text{g/L}$).

Two kinds of laser uranium analyzers were used in China now, they are Canada VA-3 and China WGJ-1, and VA-3 has a switch of balance change. Because the structure is different, the calculative methods are also different. VA-3 is used $F_0=0$. The calculative formula is the following:

$$C_x = \frac{F_1}{F_2 - F_1} \cdot \frac{V_s}{V_x} \cdot C_s \quad (2)$$

It notes instrument model and function at application, both formula (1) and (2) are prerequisite, it is $\frac{V_s}{V_x} \leq 1/100$, $\frac{C_s}{C_x} \geq 100$. If formula is $\frac{V_s}{V_x} > 1/100$, $\frac{C_s}{C_x} < 100$, it must be considered dilute function of the standard uranium solution of addition. The calculative formula of the uranium concentration is the following.

$$C_x = \frac{(F_1 - F_0) \cdot (V_x + V_f)}{F_2 (V_x + V_f + V_s) - F_1 \cdot (V_x + V_f)} \cdot \frac{V_s}{V_x} \cdot C_s \quad (3)$$

V_f is volume of addition enhancing agents (ml).

5 Results and discussion

In the article, the method of standard addition was used for determining uranium in samples of Huangpu River, Yangtze River, tap water, rain and snow in Shanghai (Table 2 to 5). Rate of recovery of samples' determination see Table 6, contrast of two kinds of analytical methods see Table 7.

Now trace uranium is determined conveniently with high sensitivity by laser induced fluorescence method which has the advantages of simple operation, rapid determination, high sensitivity, and so on. The acidity of samples must be controlled between pH 4 to 10. Temperature must be controlled between 10 to 25 °C. Solid samples, ore and soil and plants and so on were determined after pretreatment.

Table 2 Uranium content of Huangpu River, $\mu\text{g/L}$

Years	N*	Rainy season	N*	Dry season	Range
1986	18	0.49 ± 0.05	21	0.48 ± 0.05	0.41 - 0.52
1987	18	0.47 ± 0.06	21	0.49 ± 0.06	0.40 - 0.53
1988	18	0.50 ± 0.05	21	0.52 ± 0.06	0.42 - 0.59
1989	18	0.51 ± 0.07	21	0.56 ± 0.07	0.42 - 0.63
1990	18	0.49 ± 0.07	21	0.54 ± 0.09	0.39 - 0.60

*: Numbers

Table 3 Uranium content of Dingshan Lake water, $\mu\text{g/L}$

Years	N	Rainy season	N*	Dry season	Range
1986	20	0.31 ± 0.07	20	0.32 ± 0.09	0.29 - 0.39
1987	20	0.37 ± 0.05	20	0.36 ± 0.07	0.30 - 0.38
1988	20	0.35 ± 0.08	20	0.35 ± 0.08	0.31 - 0.41
1989	20	0.34 ± 0.04	20	0.35 ± 0.07	0.30 - 0.42
1990	20	0.34 ± 0.07	20	0.38 ± 0.05	0.29 - 0.40

Table 4 Uranium content of Yangtze River in Shanghai, $\mu\text{g/L}$

Years	N	Rainy season	N*	Dry season	Range
1986	21	0.52 ± 0.07	20	0.59 ± 0.09	0.47 - 0.65
1987	20	0.58 ± 0.08	18	0.58 ± 0.04	0.46 - 0.68
1988	16	0.55 ± 0.06	16	0.57 ± 0.07	0.42 - 0.69
1989	14	0.54 ± 0.06	14	0.57 ± 0.06	0.46 - 0.70
1990	12	0.51 ± 0.05	12	0.56 ± 0.07	0.44 - 0.67

Table 5 Uranium content of natural water in Shanghai, $\mu\text{g/L}$

Years	N	Tap water	N	Rain water	N	Well water	N	Snow water
1986	24	0.14 ± 0.01	10	0.10 ± 0.07	12	0.47 ± 0.07	5	0.09 ± 0.02
1987	24	0.15 ± 0.02	19	0.12 ± 0.04	12	0.40 ± 0.14	4	0.07 ± 0.03
1988	24	0.16 ± 0.02	16	0.12 ± 0.03	12	0.43 ± 0.12	4	0.08 ± 0.03
1989	24	0.18 ± 0.03	16	0.12 ± 0.03	12	0.44 ± 0.07	2	0.08 ± 0.00
1990	24	0.18 ± 0.05	12	0.11 ± 0.02	12	0.44 ± 0.07	2	0.08 ± 0.00

Table 6 Rate of recovery of samples determination

Uranium content, ppb	Determination value, ppb	Rate of recovery, %
1	1.01 ± 0.12	101.0
3	3.00 ± 0.22	100.0
5	4.90 ± 0.18	98.0
7	6.91 ± 0.42	98.7
9	8.90 ± 0.22	98.8
11	10.61 ± 0.25	96.5
13	12.57 ± 0.39	96.7
15	14.80 ± 0.22	98.7

Table 7 Contrast of two kinds of analysis method, µg/L

Samples	Laser method	P350 extraction method
Yangtze River	0.57	0.55
Huangpu River	0.49	0.48
Dingshan water	0.35	0.32
Well water	0.44	0.42

References

- Chen Weiguo. Radiation Protection, 1981; 6:30
 Cheng Zhiyue, Zheng Zhanghua, Lu Jing, Shu Liyan. Radiation Protection, 1986; 4:309
 Robbins JC CIM (Can Min Metall). BULL, 1978, 71:793
 Wu Jinhai, Li Jinquan, Zhang Chuanzuo. Shanghai Medicine, 1989; 12:713
 Wu Jinhai, Li Jinquan, Yuan Zhengang. Nuclear Electronics and Detection Technology, 1991; 2:127
 Zheng Chike, Wang Ziling, Tan Fuxing, Ye Kaiming. Nuclear Chemistry and Radiation Chemistry, 1981; 1:27
 Zi Bengren, Xue Huizhen. Nuclear Techniques, 1986; 6:48

(Received January 15, 1992)