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Light Induce Fluorescence by using L45 System for Uranium determination in Soil

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Abstract:

Light induced fluorescence technique is used for the investigation of selected soil samples from local sites to account for a suspected pollutants that may be included containing uranium amounts. Different excitation sources are used including xenon lamps(**7w,50Hz**) and high repetition xenon lamp(**450w,40kHz**), are used to excite both investigated soil sample uncontaminated and induced contaminated with uranium standard samples and uranium standards with different concentration and the excitation wave length used are (**280,295,337,340,370,450** nm). Fluorescence measurement are carried on for the investigated samples for the steady state. The excitation with the 295 nm wavelength gave best emission results.

Keywords: Soil Sample, xenon lamps, pollution.

استحثاث الضوء باستخدام نظام L45 لتقدير اليورانيوم في التربة

الملخص:

تم استخدام تقنية الفلورسنس المحفزة بواسطة الضوء للتحقيق في عينات التربة المختارة من المواقع المحلية للتحقق من وجود ملوثات مشتبه فيها قد تحتوي على كميات من اليورانيوم. تم استخدام مصادر تحفيز مختلفة ، بما في ذلك مصابيح الزينون (7 وات ، 50 هرتز) ومصابيح الزينون عالية التكرار (450 وات ، 40 كيلوهرتز) لتحفيز كل من العينات الأرضية المستقرة والتي تم تلويثها بشكل مستنتج بعينات قياسية تحتوي على اليورانيوم ومعايير اليورانيوم بتراكيز مختلفة. تم استخدام طول الموجة للتحفيز هو (280، 295، 337، 340، 370، 450 نانومتر). تم إجراء قياسات الفلورسنس للعينات المستقرة باستمرار. أظهر تحفيز بطول موجة 295 نانومتر أفضل نتائج الانبعاث.

Introduction:

Luminescence is the emission of light from any substance, and occurs from electronically excited states. Luminescence is formally divided into two categories—fluorescence and phosphorescence—depending on the nature of the excited state. In excited singlet states, the electron in the excited orbital is paired (by opposite spin) to the second electron in the ground-state orbital. Consequently, return to the ground state is spin allowed and occurs rapidly by emission of a photon. The emission rates of fluorescence are typically 10^9 s^{-1}, so that a typical fluorescence lifetime is near 10 ns. The lifetime of a fluorophore is the average time between its excitation and return to the ground state. Many fluorophores display sub nanosecond lifetimes. Because of the short timescale of fluorescence, measurement of the time-resolved emission requires sophisticated optics and electronics. In spite of the added complexity, time-resolved fluorescence is widely used because of the increased information available from the data, as compared with stationary or steady-state measurements. Additionally, advances in technology have made time-resolved measurements easier, even when using microscopes.[1]

During the past 20 years there has been a remarkable growth in the use of fluorescence in the biological sciences. Fluorescence spectroscopy and time-resolved fluorescence are considered to be primarily research tools in biochemistry and biophysics. This emphasis has changed, and the use of fluorescence has expanded. Fluorescence is now a domiant methodology used extensively in biotechnology, flow cytometry, medical diagnostics, DNA sequencing, forensics, and genetic analysis, to name a few. Fluorescence detection is highly sensitive, and there is no

longer the need for the expense and difficulties of handling radioactive tracers for most biochemical measurements. There has been dramatic growth in the use of fluorescence for cellular and molecular imaging. Fluorescence imaging can reveal the localization and measurements of intracellular molecules, sometimes at the level of single-molecule detection [1].

Lieberman et.al.[2] presented a Fiber optics-based fluorometer system that use a pulsed laser to induce fluorescence and a time-gated linear photodiode array coupled to a spectrograph for rapid measurements of fluorescence emission spectra and fluorescence decay times. James et.al. [3] presented simulation of the laser-induced Raman fluorescence spectra (LIRFS) produced by laser irradiation of the water column. This is a method of extracting the Raman signal from the fluorescence spectra using multiple laser excitation wavelengths. Leung et al [4] studied the fluorescence properties of uranyl nitrates. Their paper reported the fluorescence spectra of uranyl nitrate hexhydrate, trihydrate, and dihydrate at 77K. The fluorescence lifetime of the hexahydrate, trihydrate and dehydrate at 77K were observed to be 699, 838 and 499 second respectively. Boychuk et al [5] is by analsizing seawater fluorescence band directly with sensitive instruments, and with the method of fluorimetry of variable gating (a variant of the kinetic fluorimetry). Jackman et. al. [6] reported in new analytical data for 43 different elements from a regional stream sediment and water geochemistry survey on the charlotte islands. For the determination of uranium using laser induced fluorescence method the detection limit was found about 0.05 ppb while by using the method of instrumental neutron activation analysis the uranium detection limit was 0.5ppm. Zhong et al [7] used a laser fluorescence microprobe for the determination of fluorescence characteristics of various macerals and related to hydrogen content. Elena et al [8] had discussed new possibilities of fluorescence spectroscopy for diagnostics of oil pollutions in natural water.

In present work the light induced fluorescence technique is applied through the use different wavelength xenon lamp source (295,337,340,370,450nm) to detect uranium in soil samples. different concentration of standard uranium are prepared including (2,5, 10, 20, 50, 100 ppb) and (1, 2 ,5, 15, 40, 50, 100, 500 ppm). soil samples are also prepared after making the required operation necessary for the measurements.

Experimental Work:

- Preparations of uranium standard.

The preparation of uranium standard samples also in a similar procedure to that mentioned before about 20 standard uranium samples are prepared with dilution concentration $C_1V_1=C_2V_2$ formula in ppm and ppb. Uranium nitrate hexahydrate (UO_2 $(NO_3)_2.6H_2O$) available in the vinca institute.

A 200ml volume of stock standard uranium is prepared (1000 ppm) firstly and kept a glass flask. A next stage of preparation was performed using separate plastic in a container (75ml) to be ready for different concentration which is calculated according to previous formula. The procedure for the Preparation of uranium standards (Preparing a solution of 1000 ppm stock solution) is by dissolving 0.4218 gm of UO_2 $(NO_3)_2.6H_2O$ in 200 ml distilled water. The following standards were prepared utilizing the $C_1V_1=C_2V_2$ formula.

Table (1): the procedure prepared of uranium standard

No.	Standard	Procedure
1.	1 ppm	0.2 ml in 100ml distilled water
2.	2 ppm	0.4 ml in 100 ml d. water
3.	4 ppm	0.4 ml in 100 ml d. water
4.	5 ppm	0.5 ml in 100 ml d. water
5.	10 ppm	1 ml in 100 ml d. water
6.	15 ppm	1.5 ml in 100 ml d. water
7.	20 ppm	2 ml in 100 ml d. water
8.	30 ppm	3 ml in 100 ml d. water
9.	40 ppm	4 ml in 100 ml d. water
10.	50 ppm	5 ml in 100 ml d. water
11.	100 ppm	10 ml in 100 ml d. water
12.	500 ppm	50 ml in 100 ml d. water
13.	2 ppb	0.2 ml in 100 ml d. water
14.	5 ppb	0.5 ml in 100 ml d. water
15.	10 ppb	1 ml in 100 ml d. water
16.	15 ppb	1.5 ml in 100 ml d. water

17.	20 ppb	2 ml in 100 ml d. water
18.	50 ppb	5 ml in 100 ml d. water
19.	100 ppb	10ml in 100 ml d. water

Measurement of absorption spectra.

1 . Absorption spectra of uranium standards.

For the measurements of the absorption spectra of uranium sample we used UV-VIS spectrophotometer (EVOLUTION 6000). The range of this device is (200-850nm).

Initially 15 uranium standard samples were measured, 6 with concentrations (2, 8, 10, 17, 20, 100, 1000) ppb and the other 9 with (10, 15, 40, 100, 1000, 2000, 4000, 10000, 15000) ppm, these spectra are shown in Figures (1). The wavelengths determined from these spectra were in the range (200- 400 nm)

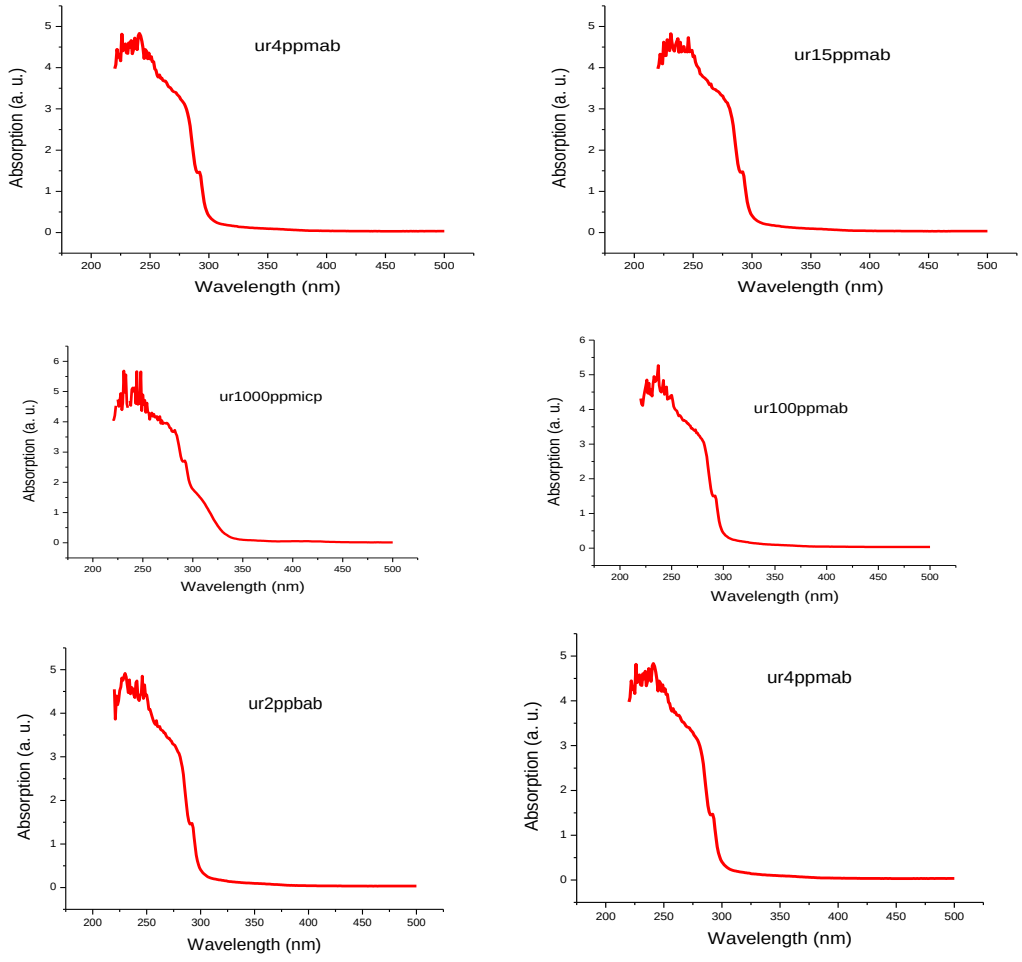


Fig (1) absorption spectra of uranium standard (evolution 6000)

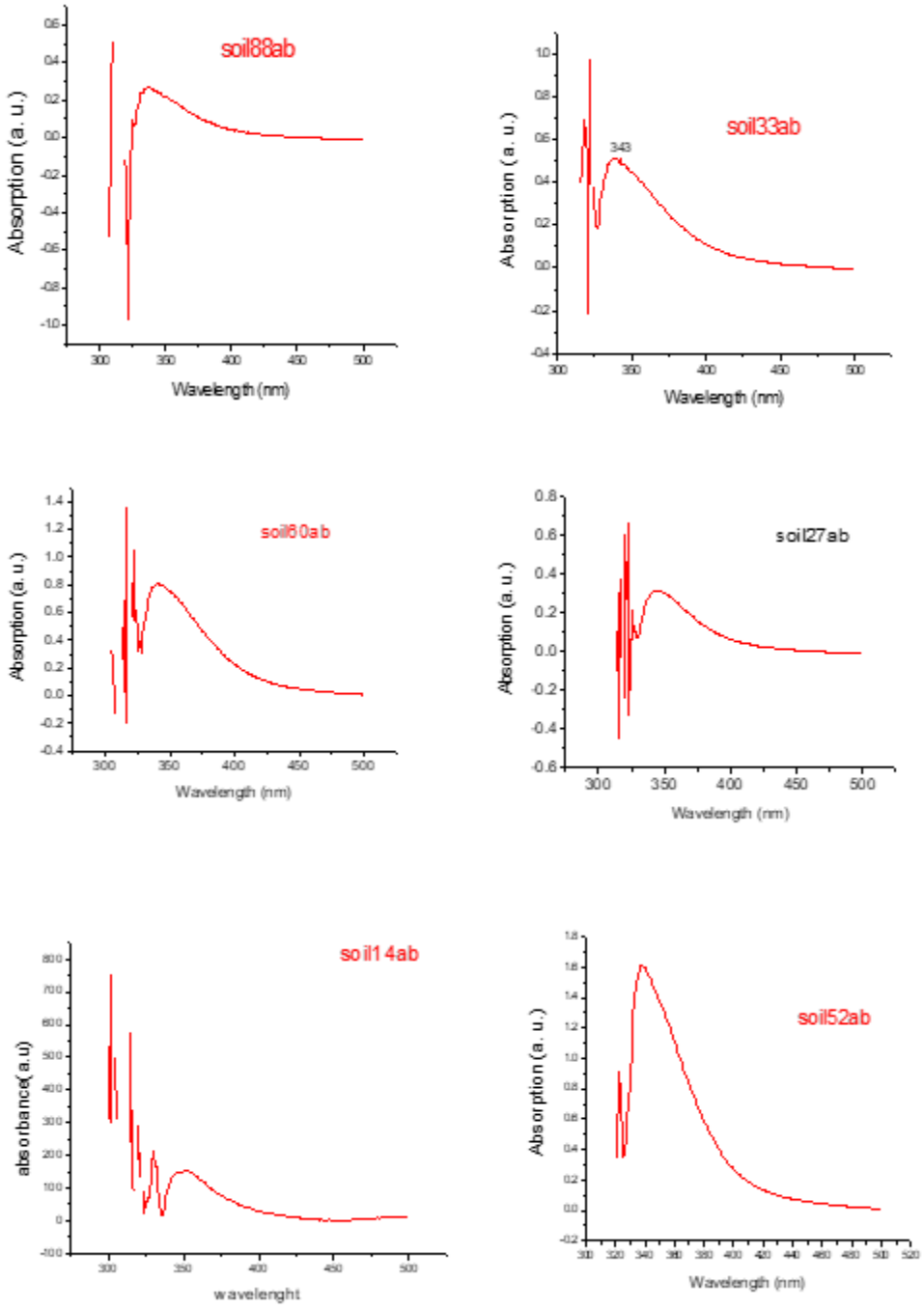


Fig (2) absorption spectra of soil sample (evaluation 6000)

1-Fluorescence spectra measurements by using luminescence L45 (Perkin Elmer).

The system used in obtaining the fluorescence spectra in this technician is(Perkins Elmer).the system consists of a Xe lamp, sample holders and PMT detector coupled to PC. The light source is a Xe lamp(7.3 W average power,50 Hz) with quartz envelope and very little ozone and the wavelength range operation is (200-800 nm). The detector used is photomultiplier tube (PMT)type R928(range 200-650 nm, high voltage 650V). The sample is positioned using a sample holder of rectangular configuration to contain the solution cuvette. The sample holder is at right angle with the light source to in sure best emission and to avoid the scattering the light source, the coveter is transpire in the surrounding directions.

A monochromater is used before the sample to choose the specified wavelength used (200- 1100nm). The slits are localized in different Positions and are used to obtain better resolution and accuracy. The first slit is before the sample while the second is after the sample. The width of each slit is variable, but we have fixed the width of both the slits at 10 nm for the measurements. The system is programmed using a built-in program. The scan rate (emission) is 100nm/min.

The operation of the luminescence L45 (Perkin Elmer) requires providing the device with certain information. This includes excitation wavelength value, emission wavelength range and slits value and scan rate value. To estimate range of emission spectrum for a certain excitation wavelength. initially we have prepared a volume of 100ml with a concentration of 1000ppm as a stock solution. from this stock solution the concentration (13) are prepared for each one every time by using one flask (100ml) and according $C_1V_1=C_2V_2$ formula (3 ml) of last prepared concentration is taken direct for the measurement using the coveter (3ml) this process is repeated using the same flask for all the (13) uranium standard concentration we standard the perpetration in an increasing miner for low to higher concentration. we used this procedure becomes of the an variability of separate plastic container of with the same number of concentration., however, and due to the problems in continuing in such procedure including the slow rate of operation, possibility of an accuracy in the values in concentration due a mixture between previous and succeeding concentration (contamination of one concentration by

another) that may affect the results, we used another method of preparing concentration in separated container each with 75 ml plastic container. A sample of standard uranium of this stock solution concentration (1000ppm, 100ml) is measured by the system. A fairly broad emission spectrum is obtained by these measurements using (420-540 nm) this range is fixed for later measurements this technique.

Using a similar procedure is also used for the determination of the input parameters required by the measurement of soil samples (380-540nm), the range of emission spectra detection for this case is (380-540) emission. The selection of the range of emission spectra for both uranium standards and soil samples is made according to the region of interest of studying emission spectra besides avoiding saturation effect in the spectra. The emission spectra of uranyl ion as determined in literature [9], has three distinct peaks at 499,517,530nm and for reasonable measurements these peaks should be well distinguished in the emission spectra of UO_2^{+2}.using the system (luminescence L45(Perkin Elmer)) we made the measurement for both uranium standard and soil samples with changing excitation source wavelength value (280, 295, 337, 340, 370, 450nm).

Results and discussion:

Twenty uranium standard samples obtained for the stock solution of 3ml size were measured using this system for short period necessary to obtain the emission spectrum. Three different excitation wavelengths are used in the measurements at (280,295 and 337 nm) for the twenty different uranium standard concentrations which are (2, 8, 10, 100, 1000) ppb, and (1, 4, 10, 15, 40, 100, 1000, 2000, 4000, 10000, 15000) pm. The emission spectra obtained for these measurements are shown in Figure (3).

For the uranium standard concentration in the ppb range the conc. Standard are(2, 8, 10, 17, 20) generally most of the spectrum at different ppb concentrations did not reveal significant peaking for the spectra range but for the case of 10 ppb concentration the appearance of the 515 nm peak is clearly observed for the three excitation wavelengths (280, 295, 337 nm).We tried next to study the response of this method at higher concentrations, namely at (1, 4, 10, 15, 40, 100, 1000, 2000 ppm).the spectra measurement at these concentrations at different excitation wavelengths (280, 295, 337nm)are shown in

Figure(3).in this spectra the emission wavelength of peak at 517nm of UO_2^{+2} is clearly observed and isolated. The intensity of this peaked as we have excited for the three different concentrations, is in general usually proportional with excitation wavelength. The spectra in general have a valles at about 460nm.the region down these values in general is a continuum with out distinct peaks with a intensity that different with standard concentrations.

For the concentrations above 3ppm the emission line at 499 nm begins to appear. The peak of this line becomes clearer and more isolated with increasing the concentration. It should be noted here that the increase in the intensity of this peak is same that corresponding to a decrease in the intensity of the region below the valley at 460nm. Fluorescence measurements are also carried on three additional excitation wavelengths (342, 373 and 458nm). Using the previous procedure we made measurement for (13) uranium standards at (2, 8, 10, 17, 20, 100) ppb and (1, 4, 10, 15, 40, 100, 1000) ppm in addition to higher concentration at (7500, 10000, 15000) ppm. With six soil samples numbered (1, 10, 14, 21, 27, 60) were also studied both in contaminated and uncontaminated cases. The contaminated soil samples included contaminating them with (100ppb, 100ppm) uranium concentrations.

The emission spectra of soil sample were measured by making several tests of spectra at for wavelengths in the range (200-700nm). As mentioned previously in subsection to determine the range of emission wavelengths used in studying the standard uranium samples. And in a similar way the range of emission spectra to be studies is determined for soil sample to be 380-540nm.here we excluded the other wavelengths that belong to excitation wavelengths that may arise as a result of the geometrical arrangement of the experimental.

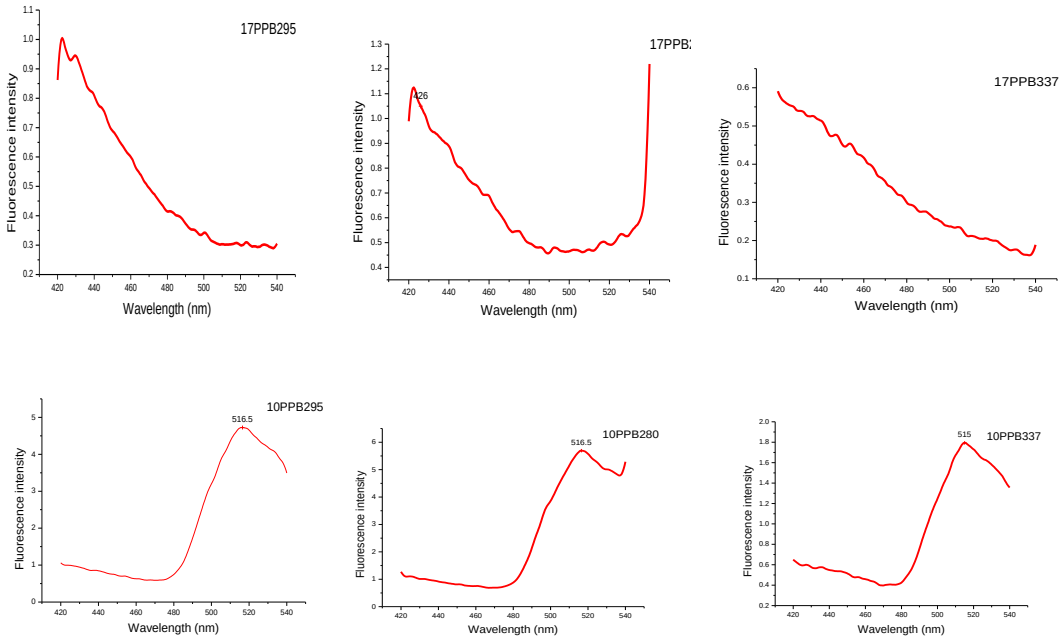
Using one soil sample with excitation using different excitation wavelengths at (280, 295, 337 nm) and under the same operation condition of the system, to select the typical and homogeneous wavelength, this revealed the typical and homogenous excitation wavelength which is 337nm.The decision here is based on the homogeneity of the emission spectra. The other wavelengths at (280nm, 295nm) are excluded due to their in homogeneity and the existence of the fluctuation in the emission spectra. Thus, the excitation wavelength at 337nm is fixed here

for the measurements of the other soil samples which are about 50 samples.

The measurements were carried on for fifty samples for two cases. The first case in which the samples were measured with out making any change in their composition, while in the second case the samples were exposed to contamination with uranium standard from the prepared stock solution with two concentrations at 100ppm and 100ppb. The volume prepared for each of these two concentrations is 0.5ml. This volume is completed for the full volume of the cuvette which is 3ml by adding 2ml of the soil sample and 0.5ml of distilled water.

The uncontaminated soil sample measurements were made by fixing the wavelength at 337nm for a certain time of radiation (10 min) the emission of fluorescence spectra are obtained for the required range (380-540nm) and this are shown in Figure (5).

For standard uranium sample it is found that the highest fluorescence intensity obtained is at 280nm. While the fluorescence intensity at the other excitation wavelength (295- 337nm) is relatively lower at the emission peak of 516nm as can be seen in this Figure, general indication is clear for a uranium content in the sample that is characteristic by the wavelengths at (499- 516nm) with in the detection capability of this technique. But we can see as indication for the a presence of peak in the range (440-460nm) with different fluorescence intensity.



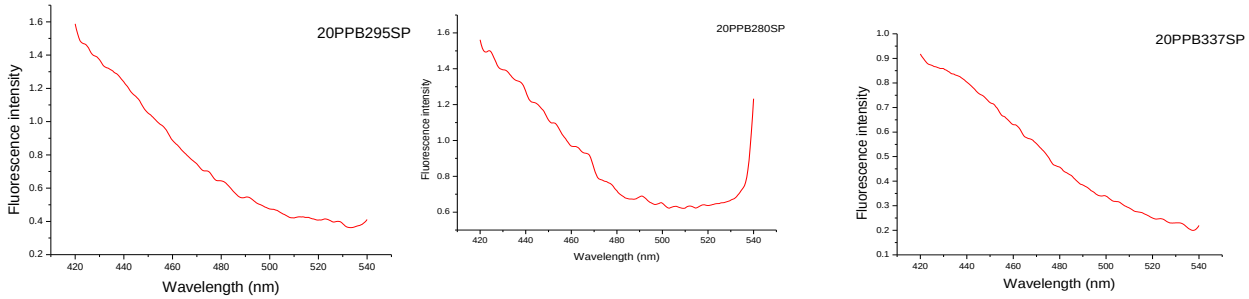


Fig (3) fluorescence spectra uranium standard concentration ppb with 295, 280,337nm (P.K)

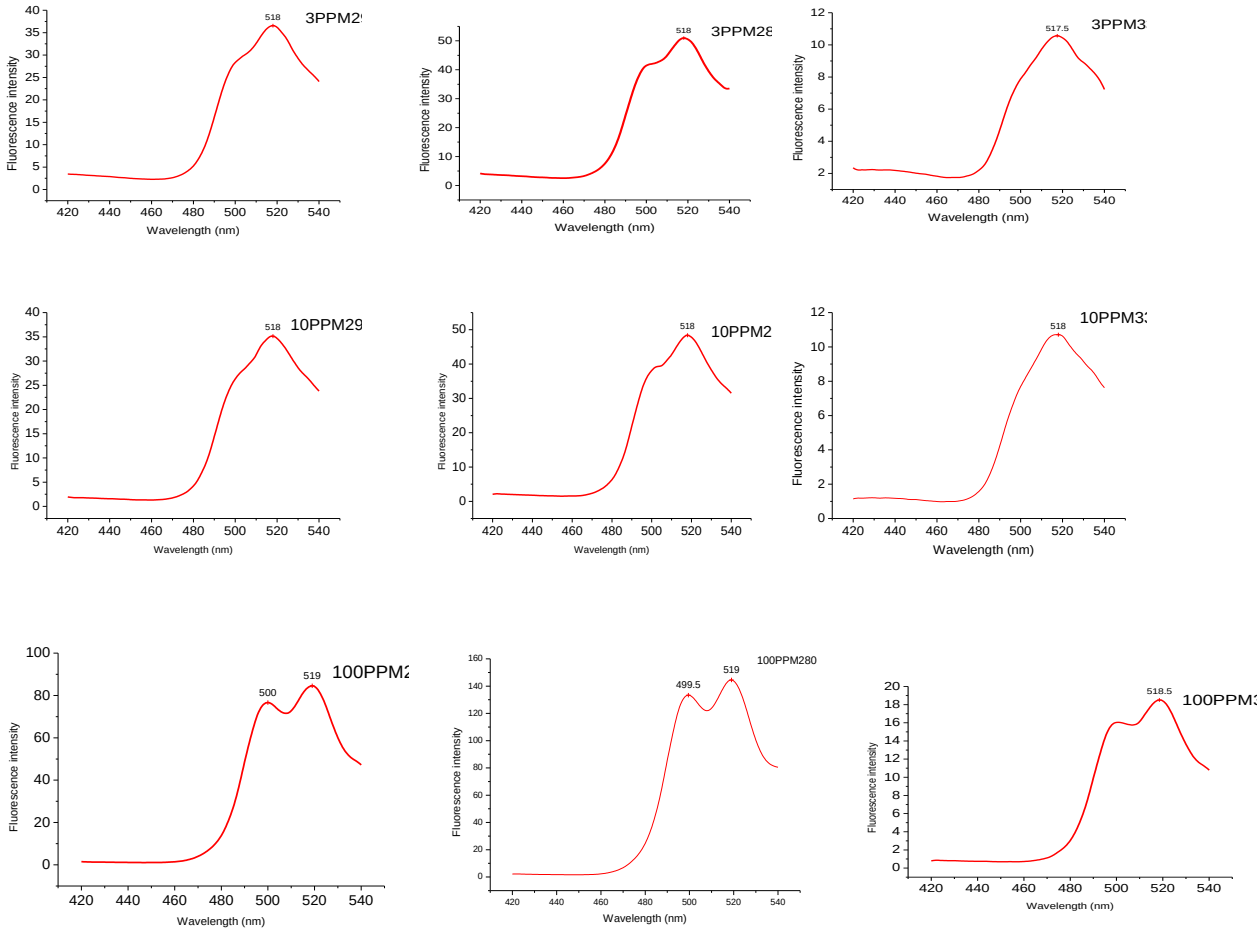


Fig (4) fluorescence spectra uranium standard concentration ppm –xenon lamp at 295, 280,337nm (P.K)

soil content such as silicates and iron in addition to the difference in sampling location, their concentration, soil pH etc..

However, a precise inspection for a number of the soil samples namely (50, 57, 68, 72, 80, 95, and 99) show in Figure (5.11) shows increments even very little. The intensity of the spectrum curve at emission lines of uranium like (499,516,530nm). but a decision on these lines is far from what is available of condition concerning the present technique, and this may be confirmed by a further future research. Next, we made the measurements using the same apparatus but with concentration prepared sup portly using 75ml container for each of the (13) concentration. The measurement is generally similar to that discuss previously for the 100 volume stock used.

We started the measurements using 337nm excitation wavelength to excite the uranium standard sample for the 13 concentration mentioned earlier. A volume of 3ml is taken from the 75ml container for each support concentration and is measured in suitable time. The fluorescence emission intensity value obtained are show in table (1- 2).

As can be observed from these spectra is that until the concentration of 1000ppb. on distinct emission lines can be seen, the peak at 422 nm may belonging to other compound materials rather than uranium as the concentration studied get higher the uranium emission lines are gradually appear. These are clearly observed for the concentration 4ppm. At 517nm with intensity 2.50. for the concentration at (10, 15, 40, 100, 1000) ppm. the two emission lines at (499,517nm) are clearly isolated but increasing intensity. As a primary notes that may be extracted from the emission spectra for the measurement of using both 100ml stock and 75ml is that the later has general low intensities for the emission lines measured at same concentration.

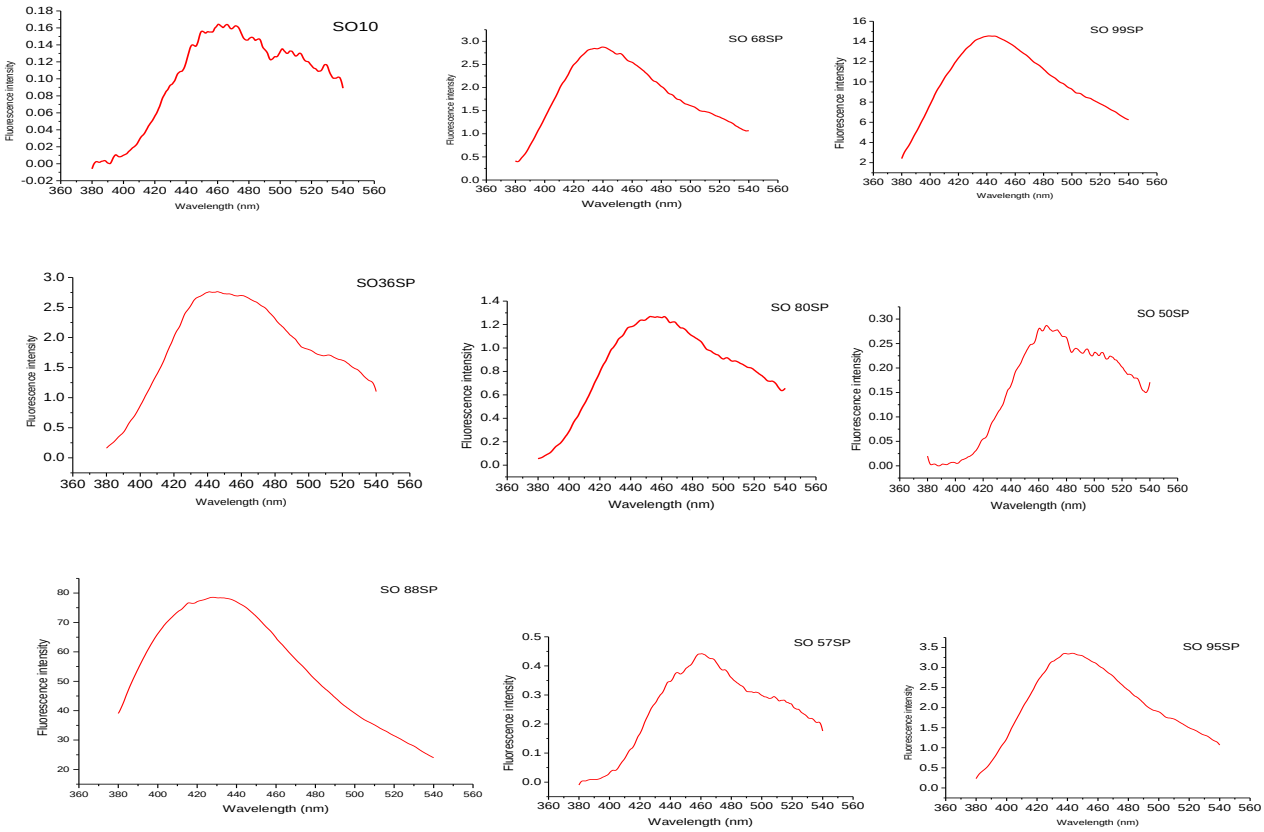


Fig (5) fluorescence spectra of different soil samples _ xenon lamp at 337nm (P.E.)

Table (2) Uranium standard concentration (ppb) with (280,295,337 nm) 0.2 mg of $(UO_2(NO_3)_2.6H_2O)$ in 100 ml . H_2O

No.	S.con.	λ 280nm		λ 295nm		λ 337nm (100ml)		λ 337nm(75ml)	
		λ	Int	λ	Int	λ	Int	λ	
1	8ppb	420	1.27	421.72	1.20	421.89	0.72	422.4	0.89

		540	1.26	x	x	455.91	0.56		
2	10ppb	497.35	3.58	504.43	3.77	515.13	1.74	422.4	0.86
		516.86	5.69	516.17	4.72	x	x		
3	17ppb	422.24	1.12	422.24	1.00	420	0.59	422.2	0.88
		540	1.22	430.35	0.44	x	x		
4	20ppb	420.34	1.54	421.15	1.50	420.17	0.91	421	0.78
		540	1.23	539.65	0.4	539.48	0.21		
5	100ppb	420.17	1.17	422.07	1.11	422.24	0.59	422	1.03
		540.00	1.27	540	0.39	x	x		

Table (3) Uranium standard concentration (ppm) with (280,295,337 nm)

No.	S.con..	λ 280nm		λ 295nm		λ 337nm 100ml		λ337nm 75 ml	
1	1 ppm	516.51	13.01	515.65	10.80	515.48	4.32	422	2.49
2	4 ppm	518.07	50.91	517	36.53	515.65	10.50	516.17	2.26
		517.72						539	1.64
3	15 ppm	500.63	44.16	502.01	30.63	499.59	8.34	499.2	3.41
		518.41	54.78	517.38	38.83	516.86	11.57	517.38	4.00
4	10 ppm	502.01	39.14	504.08	28.27	517.72	10.71	497.6	3.84
		517.55	48.35	517.72	35.14	x	x	517.2	4.2
5	40 ppm	499.07	76.23	500.63	46.00	499.59	10.65	500.2	7.82
		518.76	86.79	518.58	54.00	518.41	13.39	517.89	8.98
6	100 ppm	499.42	133.38	499.25	76.52	499.76	16.02	499.4	12.81
		519.10	144.44	519.10	84.53	518.76	18.50	518.5	13.69
7	1000ppm	498.38	265.07	498.38	195.32	499.25	65.84	498.7	67.48
		518	280.23	518.58	206.78	518.24	69.82	518	70.16

Conclusions:

The main conclusions obtained from this study may be summarized as laser induced

fluorescence technique is used to determine the type of pollutants in certain radiative environmental samples and gave significant results indicating the possibility of applying the method to different environmental studies of close nature.

Acknowledgment

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