

DESTRUCTIVE ASSAY OF URANIUM CONCENTRATION BY RELIABLE LASER INDUCED KINETIC PHOSPHORIMETRY ANALYSIS (KPA)

A.I. Humaid¹, Reem Al-Marboui¹, Sayed A. El-Mongy²

1 Main chemical Lab., Armed forces, United Arab Emirates (UAE)

2 On Leave Atomic Energy Authority, Cairo, Egypt

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In the present work, a destructive assay system based on tunable pulsed laser KPA has been used for determination of uranium concentration. The system has lower detection limit of 0.01 ng/ml. Calibration of the system was carried out before analysis. Precision (reproducibility) of the results was investigated for different uranium concentrations. The bias does not exceed 2.5%. Samples containing uranium concentrations from 0.01 to 200 ng/ml were precisely analyzed. Uranium in ore and reference solid samples were determined after radiochemical separation. The extraction of uranium was carried out with recovery percentage of more than 80%. Linearity of response of the system was studied for uranyl nitrate solutions of different molarities; 10^{-1} - 10^{-5} M. Urine and water samples spiked by uranium were also investigated for quenching testing. Detection limit as low as 0.004 ng/ml was obtained. The observed results were found to be satisfactory and highly accurate. The method can be efficiently applied for quality control and analysis of uranium for nuclear safeguards.

Keywords: *Uranium / Destructive assay/ KPA Laser analysis /nuclear safeguards.*

INTRODUCTION

Using of reliable techniques is very vital for verification and control of uranium in the field of nuclear safeguards and ultra-trace environmental analysis

In the field of nuclear safeguards and environmental signature analysis, accurate destructive and non-destructive techniques must be used to get results of high confidence level. In the framework of the international safeguards, uranium in all stages of the nuclear fuel cycle must be quantitatively and precisely determined. Moreover, increasing field of peaceful and military uses of depleted uranium, its assessment is also required to be carried out by sensitive techniques [1].

In this work, for the first time in the Gulf region, a bench-top instrument that rapidly performs quench-corrected analysis for trace uranium has been used. Study of the sensitivity and reliability of the method for assay of ultra-trace uranium for nuclear safeguard purposes is also targeted.

EXPERIMENTAL WORK

I Aspects of the Laser Kinetic Phosphorimetry Analysis:

The system used is time resolved kinetic phosphorescence analysis (model KPA-11 of Chemchek instruments). The uranium samples and reference are excited by firing the nitrogen laser of 337nm. This excites the dye laser (stilbene-420) to produce an excitation wavelength of 420nm. A 515 –nm band-pass filter is used to filter the emission signal and to pass the 515nm uranium peak. Sensitive photomultiplier tubes and photon counting circuitry count the phosphorescent decay events emitted from the sample and reference. The reference measurement normalizes the sample measurements for interference fluctuations such as laser brightness, temperature drifts and high voltage drifts. Each analysis is a repetition of 50 second cycles. A 3 nsec. laser pulse initiates each cycle [2]. The laser pulse reacts with uranyl ions $[UO_2]^{+2}$ in samples. The pulse energy of nitrogen and dye (stilben-420) are 120 μ J and 20 μ J, respectively. Their peak output powers are 40 and 5 kW, respectively [2]. High precision was achieved using 1000 laser pulses in each measurement. The system has low detection limit of 0.01 ng/ml. The main characteristics of the system are given in the Ttable 1.

Table 1. The main characteristics of the KPA

Parameter	Laser KPA
Selectivity	Tunable for U, Eu, Sm. analysis
Laser source	Nitrogen laser of 337nm
Pulse duration	3 nsec.
Repetition rate	20 pulses/sec
Emission wavelength	515nm for U
Pulse power	120 μ J
Buffer	Uraplex
Sample volume	1 ml
MDL	0.01ng/ml (0.13mBq/l)
Precision (RSD)	1-3% at U> 0.01 ng/ml 7-10% at U< 0.01 ng/ml
Analysis range	0.01 – 500,000 ng/ml
Data processing	Computer software

To achieve high precision, the uranyl ion must be protected from various intermolecular mechanisms (competing interferences) which rapidly quench the uranyl luminescence.

II Calculation of Uranium Concentration:

Following Roiss et al, the intensity (I) of the phosphorescence signal is proportional to the concentration of the emitting species, can be given as [3]:

$$\ln I_t = \ln I_0 - (k_p + k_q) t \quad (1)$$

Where I_t is the number of detected photons at time t and is proportional to the number of excited ions (uranyl ions). k_p and k_q are the rate constants of phosphorescent decay and all other relaxation processes respectively. The luminescence from the analyte is related to its concentration using the intercept (I_0) in the calibration equation obtained with known uranium standards.

The uranium concentration in the sample (U_c) is calculated using the following equation [4];

$$U_c = U_t / (W_a + F_b) \quad (2)$$

Where U_t is the total uranium, W_a is the aliquant weight in grams, and F_b is the dilution factor in (gram sample/ gram solution).

The KPA-11 is controlled by KPAWin software operating under Windows for automatic calculation of uranium concentration. The percent relative difference (%RD) is calculated by;

$$\%RD = ((\text{Measured value} - \text{reference value}) / \text{reference value}) \times 100 \quad (3)$$

III) Sample preparation and analysis:

Liquid samples do not need for pretreatment. However, turbidity and suspended matter must be avoided and eliminated. In the presence of quenchers such as Cl^- , dilution is required.

In this work, uranium standards (CLARITAS PPT) of 1, 10, 100, 250 ng/ml were used to calibrate the system for low and high range analysis. Samples of different concentrations; 0.01 – 250 ng/ml were analyzed. One ml of the sample was taken in quartz cuvette with adding 1.5 ml of complexant agent (Uraplex). Uraplex with its stronger complexing power reduces interference problems [2].

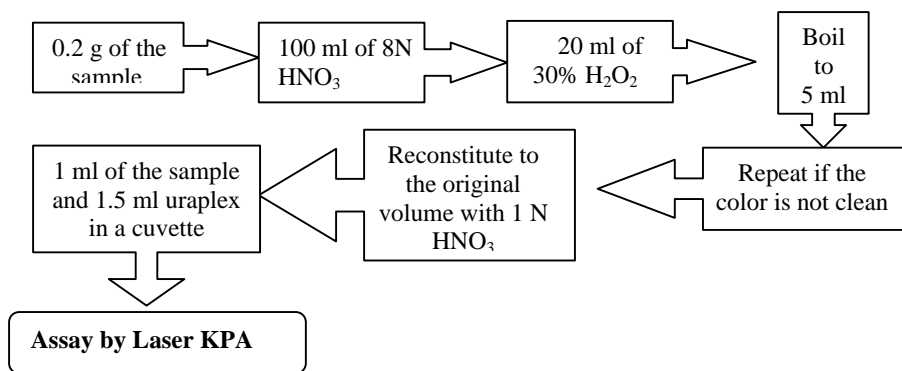


Figure 1. Chart of radiochemical extraction of uranium

Uranyl nitrate solutions of different molarities, spiked urine and reference water samples were also analyzed in this work.

Uranium in ore and reference (IAEA) solid samples was chemically separated according to the following chart given in the Figure 1. The extracted uranium was then analyzed by the KPA [2].

The wet-ash with a nitric acid and hydrogen peroxide mixture is used to eliminate quenchers and fluorescers [2].

RESULTS AND DISCUSSION

The KPA has been used for assay of uranium in biological, environmental and geological samples [1,3,5,6]. In previous works, uranium was analyzed by the KPA with detection limit as low as 0.001 and 0.007 ng/ml respectively [7,8].

In this work, with preparing very low uranium concentrations; less than 0.01ng/ml, in deionized water, a detection limit was found to be 0.004 ng/ml.

The system was calibrated for low and high (1, 10,100 and 250 ng/ml) ranges before measurements using quality control standards. The calibration curve is displayed in the Figure 2.

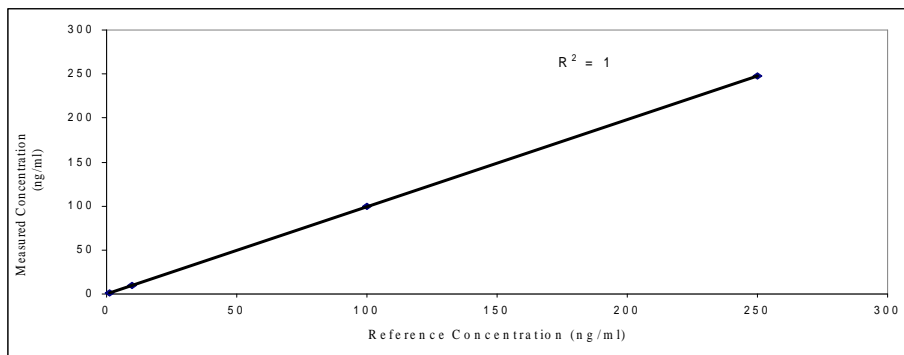


Figure 2. Calibration curve of the pulsed Laser KPA

As shown from the Figure, a precise straight-line with powerful correlation coefficient ($R^2=1$) was obtained.

Reproducibility (precision) of the results was determined by analyzing different samples of different uranium concentrations. The results are given in Table 2.

It can be observed from the table that the bias in the results is in the range from 0.12% to 2.5% maximum. Moreover, the results of the measured samples are close to each other.

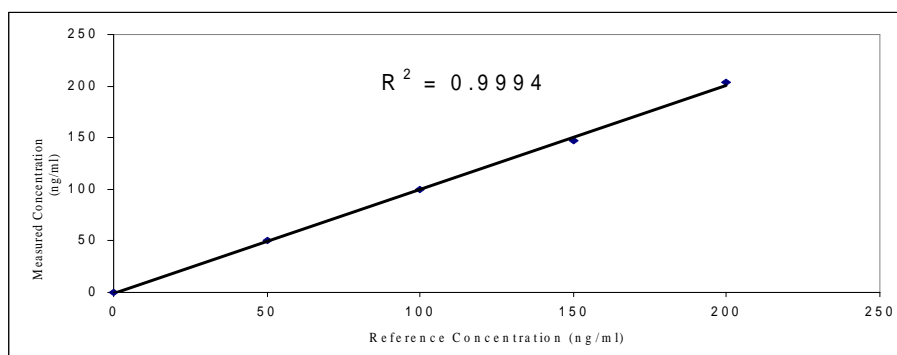
Reference samples of low concentrations were also analyzed. The measured concentrations are also very close to the declared values. The results are listed in the Table 3.

Table 2. Reproducibility (precision) of the results

Reference Value (ng/ml)	Measured Value (ng/ml)	%RD
5	4.98 ± 0.06	-0.40%
	4.89 ± 0.11	-2.20%
	5.04 ± 0.06	0.80%
	5.04 ± 0.06	0.80%
100	98.5 ± 3.0	-1.50%
	97.5 ± 3.1	-2.50%
	99.3 ± 3.1	-0.70%
	98.6 ± 3.1	-1.40%
250	249.7 ± 7.6	- 0.12%
	250.7 ± 7.6	0.28%
	249.5 ± 7.5	- 0.20%
	249.6 ± 7.6	- 0.16%

Table 3. Results of assay of different concentrations of uranium

Reference Concentration (ng/ml)	Measured Concentration (ng/ml)	%RD
0.01	0.009 ± 0.004	-10%
0.05	0.049 ± 0.002	-2%
0.1	0.097 ± 0.003	-3%
0.5	0.49 ± 0.011	- 2%
1.0	0.99 ± 0.011	-1%
20	19.93 ± 0.27	-0.4%

**Figure 3.** Results of high concentrations analysis of reference uranium solutions

The highest difference (10%) was found at the low concentration near the system detection, i.e. at 0.01ng/ml.

Reference samples of high uranium concentrations (50 – 200 ng/ml) were also analyzed. The results are displayed in the Figure 3.

The correlation between the target and measured values is very sharp ($R^2 = 0.999$). This result reflects the accuracy of the measurements.

Linearity of the response to various uranium concentrations was investigated by analysis of uranyl nitrate solutions of molarities from 0.1 to 10^{-5} M. The results are presented in the Figure 4.

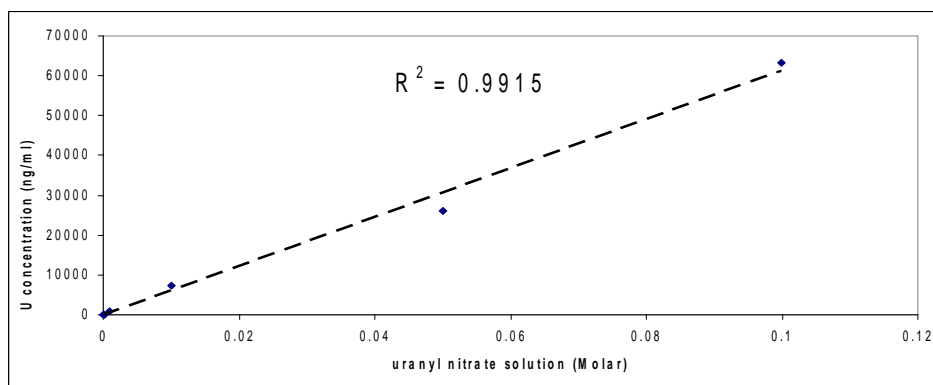


Figure 4. Linearity of response to uranium analysis

A direct relationship between the increase of solution molarities and the measured uranium concentration was found. The correlation coefficient (R^2) is 0.992.

Reference uranium ($10\mu\text{g/g}$) was accurately investigated with 2% relative difference. The IAEA-381 reference sample was chemically treated and then analyzed. The difference (20%) obtained for QAP003 sample is mainly due to the fact that the certified value given in Table 4, is for ^{238}U only.

Uranium concentrations in ore and reference solid materials; IAEA RGU-1, IAEA375 and QAP003, were also assayed after radiochemical leaching. The dilution factor was corrected. The results are listed in the Table 4.

Table 4. Results of the analyzed reference samples

Analyzed sample	Certified value	Measured	%RD
Ref. uranium solution	10 $\mu\text{g/g}$	9.8	-2%
IAEA-381	3.25 ng/ml (3.01 - 3.8)	3.9	+20%
RGU-1 (ore)	400 $\mu\text{g/g}$ (398 – 402)	415.6	+3.9%
RGU-1 (ore)	400 $\mu\text{g/g}$ (398 – 402)	324.8	-18.8%
IAEA 375	1.86 $\mu\text{g/g}$ (1.66 – 2.05)	1.56	-16%
QAP003	10.3 $\mu\text{g/g}$	8.3	-19.4%

The values given between brackets represents the lower and higher certified levels. The extraction recovery percentages of uranium from the ore and reference samples were found to range from 80 to 104%. The %RD between the measured and certified values are mainly due to the difference in the recovery percentage of uranium.

Uranium concentration in water samples was found to be less than the system detection limit. The sample was then spiked by different concentrations (1,10,100 and 250 ng/ml) of uranium standard. The results are displayed in the Figure 5.

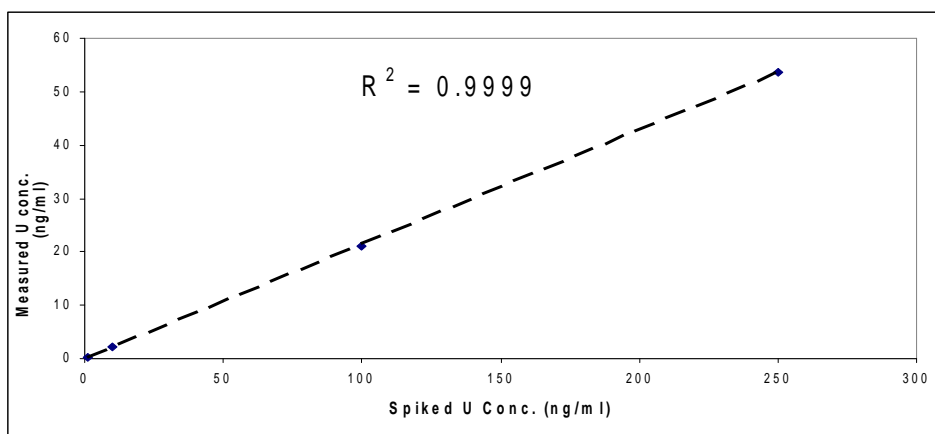


Figure 5. Results of the spiked samples analysis

An excellent correlation coefficient of 0.999 was found. This means that the uranium added to the samples neither quenched nor interfered.

As a matter of fact, urine analysis is used as an indicator of uranium internal contamination (e.g. fuel fabrication workers) [9].

In this work, analysis of urine samples was carried out without pretreatment. **Values lower than the system detection limit were observed.** The samples were then spiked by different uranium concentrations for determining of quenching effect. The results are presented in the Figure 6.

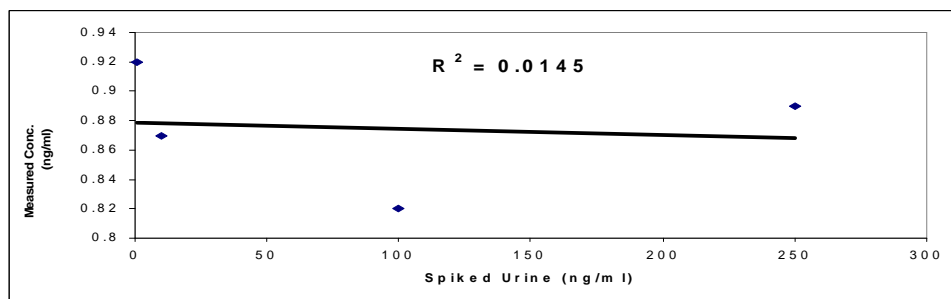


Figure 6. Results of the spiked urine analysis

It was observed that the added uranium was almost totally quenched. Scattered values with very weak correlation factor ($R^2 = 0.0145$) were obtained. This is because of quenchers shorten the excited state lifetime and reduces the luminescence intensity from the uranyl ions (2). Although, the KPA automatically corrects for quenching, an analysis with greater than 80 – 90% quenching cannot be accomplished [2].

In other work, uranium in urine samples of Hanford UO_3 plant workers was extracted and found by KPA analysis to be in the range from 0.015 to 0.03ng/ml [6]

The KPA method can be easily converted for work in the field and it was used for on-line determination of uranium in media such as stack gases, uranium in zirconium metal and waste streams.

CONCLUSION

Using the pulsed laser induced kinetic phosphorimetry technique, uranium in different matrices has been accurately and precisely assayed. Uranium was analyzed in uranyl nitrate samples with accuracy between 0.4% and 10% at low concentration. The precision in the results was found to be 2.5 maximum. Detection limit as low as 0.004 ng/ml was achieved. Uranium was amounted in leached samples with recovery percentages from 80 to 104%. The method can provide rapid, sensitive, selective and convenient analytical measurements, without the need for internal standard, for uranium in simple as well as complex matrices for verification of safeguarded nuclear materials.

REFERENCE

- [1] Patricia Horan, Leonard Dietz and Col Asaf Durakovic " The Quantitative Analysis of DU isotopes in British , Canada and U.S Gulf War Veterans " , Military Medicine , Vol.167 , (2002)
- [2] Chemchek instruments, The KPA catalogue and Documents (2006).
- [3] Rossella Brina and Alla G. Miller. "Direct detection of trace levels of uranium by laser-induced kinetic phosphorimetry", Analytical chemistry 67 (1995).
- [4] Paul V. Croatto , Iris W. Frank , Kimberly D. Johnson , Peter B. Mason , and Marianne M. Smith , " Evaluation of Kinetic Phosphorescence Analysis for the Determination of Uranium " Research and Development Report , New Brunswick Laboratory – Illinois ,USA , Dec. (1997)
- [5] Elliston J.T, Glover S.E., and Filby R.H." The Determination of natural Uranium in Human Tissues by recovery corrected KPA " , United State Trasuranium and Uranium Registries (USTUR) -0168 (2000)
- [6] Rossella Brina and Alla G. Miller "Determination of uranium and Lanthanides in real-world samples by kinetic phosphorescence analysis", Spectroscopy, Vol.8 , no.3, (1993).

- [7] Rossella Brina, "Uranium removal from contaminated water by enzymatic reduction with kinetic phosphorimetry detection", American laboratory, USA, May (1995).
- [8] Duane W. Medley, Ronald L. Kathren and Alvin G. Miller, "Diurnal urinary volume and uranium output in uranium workers and unexposed controls", Journal of health physics, Vol. 67,no.2, (1994).
- [9] Van Weers A.W., Voors P.I., de Groot T.J.H, van Maurik C.J.H., Draaisma F.S." Prospects For assessing internal exposure examples from the nuclear and non-nuclear sector ", 3rd European ALARA network workshop, Managing internal exposures (2000)

تحليل اليورانيوم بطريقة الليزر فوسفورمترى المستحث في عينات متعددة التراكيب

حميد اليماحي , ريم المربوعي , سيد علي المنجي

المختبر الكيميائي الرئيسي القوات المسلحة دولة الإمارات العربية المتحدة

في هذا العمل تم تحليل اليورانيوم في عينات مختلفة مثل محاليل نترات اليورانيوم خام يورانيوم بول , بواسطة محلل الليزر فوسفورمترى المستحث الذي يعتمد على إثارة اليورانيوم بنبضات من الليزر قدرها ٢٠ نبضة في الثانية. كما تم قياس الوميض الفوسفوري المنبعث و المعبر عن تركيز اليورانيوم في العينات. تمت معايرة الجهاز قبل إجراء عمليات التحليل ووجد أن معامل الارتباط R^2 هو الواحد الصحيح، كما تم اختبار دقة Precision الجهاز بالقياس المتكرر للعينات حيث وجد أن الفارق في النتائج لم يزيد عن ٢,٥ بالمائة. درست أيضا خطية استجابة الجهاز مع تغير تركيز اليورانيوم في العينات وتبين الحصول على معامل ارتباط خطي واضح. علما بأنه تم قياس اليورانيوم في بعض العينات بتركيزات منخفضة جدا وصلت إلى 0.01 جزء في البليون . كما تم فصل اليورانيوم من عينات الخام وقياسه بدقة بمحلل الليزر. و تشير نتائج التحليل إلى توافق قوي بين تركيزات اليورانيوم المقاسة و القيم العيارية المرجعية مما يعكس الدقة Accuracy في النتائج والتحليل التي أجريت وكذلك الحساسية والثوق في الجهاز المستخدم في التحليل الإشعاعي لليورانيوم.