N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

1

DETERMINATION OF URANIUM ISOTOPE CONCENTRATIONS IN PRECIPITATION IN THE VICINITY OF LIGNITE-FIRED POWER PLANTS

by

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Coal- and lignite-fired power plants produce significant amounts of fly ash, which in many cases contains high concentrations of naturally occurring radionuclides such as ^{238}U. This is of importance from the radio-environmental point of view since a small portion of the fly ash escapes from the power plant filtering system and disperses in the surrounding atmosphere. In addition, coal- and lignite-fired plants related activities such as fuel mining and ash deposition contribute to the suspended matter in the air with particles containing naturally occurring radionuclides. In this study, rainwater samples were collected in the Megalopolis lignite field basin of the Arcadia prefecture in Greece, where lignite-fired power plants are in operation and related activities are fully developed. The samples were preconcentrated and analyzed with alpha spectrometry and kinetic phosphorescence analysis in order to determine the levels of uranium isotope concentrations in precipitation in the Megalopolis basin. A control rainwater sample was also collected in the Athens area to account for reference purposes. Concentrations determined via the two techniques were found to be in statistical agreement. The concentration of ^{238}U in the samples collected at the Megalopolis basin varies from 2.2 ± 0.6 to 90 ± 14 mBq/L, and is 5-40 times higher than the concentration of ^{238}U in the sample collected in Athens. This could be attributed to the operation of the lignite-fired power plants, the fossil fuel mines, and the ash depositories.

Key words: fly ash, uranium, precipitation, wet deposition, alpha spectrometry, kinetic phosphorimetry, lignite-fired power plants

INTRODUCTION

Fossil fuels such as coal and lignite are used for electric power generation worldwide. These fuels contain traces of incombustible minerals including naturally occurring radionuclides such as ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{40}K. Coal and lignite combustion produces significant amounts of ash. Enrichment of the ash in incombustibles takes place during the combustion process and results in greater concentrations of naturally occurring radionuclides in ash than those in coal [1, 2]. The produced ash is partitioned between bottom ash that falls inside the boiler and fly ash that is suspended in the flue gas. The plant filtering system retains most of the fly ash; however, a small amount of fine-sized fly ash particles escapes from the stack and disperses in the surrounding atmosphere. Possible fossil fuel opencast mining and fuel conveyor belt transportation and/or track transportation activities in the same area may contribute to the number of particles bearing radionuclides that disperse in the atmosphere. In addition, resuspension of fly and/or bottom ash particles from a nearby operation of ash deposition fields further adds to the radioactivity concentration in the air. If the plant area in question is inhabited, then some contribution in this radioactivity is anticipated as a result of traffic and other common anthropogenic activities.

All such main airborne particle sources, namely the stack escaping fly ash, the mined and transported fuel dust and the resuspended ash from the deposits are of concern from the radio-environmental point of view, because they lead to the dispersion of particles in the atmosphere in the power plant area, which are ultimately deposited on the surrounding ground and vegetation. These particles, when in the air, are inhalable

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2

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

and can be deposited in the respiratory system [3], while if deposited on vegetation they can be ingested. Washout is one of the main atmospheric particle deposition processes; therefore, the determination of naturally occurring radionuclides such as the uranium isotopes in rainwater samples is of importance. Several investigations have been made in the past in order to determine the uranium levels in precipitation in several places around the world [4-9].

According to the 2010 data, published monthly by the Public Power Corporation of Greece S. A., about 6 GW or 50% of total available electricity power in Greece is produced by lignite-fired power plants. Two such power plants, with a total capacity of 850 MW_e, are in operation in the Megalopolis lignite field basin in Arcadia prefecture at the Peloponnese peninsula. Therefore, the Megalopolis basin is a typical example of a fossil fuel power producing area, where all mentioned three main airborne particle sources are present and active. Plant A has a rated capacity of 550 MW_e and plant B of 300 MW_e [10]. Public Power Corporation of Greece S. A. runs both plants. Megalopolis lignite is classified as a low-rank coal. It presents high ash content (~30 wt.% dry) and low calorific value (~10 MJ/kg dry). In numbers, at full load the plants consume approximately 22-25 10^6 kg of pulverized dry lignite per day, which is opencast-mined locally. The respective ash production rate varies between 6.6 to 7.5 10^6 kg per day. It can be estimated that about 80% of this is fly ash. The stack electrostatic precipitators nominally collect 99.6% of the fly ash. However, in practice, as mentioned for the Megalopolis plants in [11], the collection efficiency maybe as low as 95-96%. This may happen for reasons well accounted for in the electrostatic precipitator theory of operation, namely years of operation, quality of electric field, particles resistivity and "back-corona" effects, presence of particles of submicron size, non-uniform flows, fly ash sulphur content, *etc*.

The Nuclear Engineering Department of the National Technical University of Athens (NED-NTUA) has been conducting research in the Megalopolis basin since 1983. In the course of this research, it has been well established that the lignite natural radioactivity content is high [12], resulting in high radioactivity content in bottom and fly ash, with ^{226}Ra, and ^{238}U activity concentration in some cases exceeding 1 kBq/kg [2]. According to the findings in [2], at the last stage of the electrostatic filtering system, the collected fly ash particles are of the mean size of 20 μm. Therefore, it can be assumed that the fly ash particles released from the stack of the plants A and B are of a size between sub microns to several microns. To our best knowledge, no data exist on the particle size of resuspended matter originating at the mines and at the ash depositories.

Naturally occurring isotope deposition studies in the vicinity of lignite-fired power plants are in fact both time-consuming and labor-intensive. A lot of time is needed for attaining deposition samples of activity beyond the lower limit of detection and much highly specialized labor should be devoted for the radiochemical extraction and measurement of the investigated isotopes. The aim of the present study was to time- and labor-effectively investigate the concentration of uranium isotopes in precipitation samples in the Megalopolis basin both in terms of sample collection and also in terms of isotope measurement. For this purpose, a limited number of rainwater samples was collected in two locations in the area. To account for reference purposes a control rainwater sampling took place at the NTUA campus in Athens as well. All samples were radiochemically treated and analyzed by alpha spectrometry and kinetic phosphorescence analysis (KPA) in order to determine uranium isotopes and the total uranium concentration. Alpha spectrometry is a very accurate but rather time-consuming method capable of determining the ^{238}U, and ^{234}U isotopes concentrations. Contrarily, KPA is a very fast method for determining total uranium in water samples but does not provide isotopic information, while it is subject to analytical quality problems when samples are not sufficiently transparent. However, when using KPA, there is practically no need for major radiochemical treatment of samples. To our best knowledge, the measurements presented herein are the first uranium isotopes concentration results reported for wet deposition in the vicinity of a lignite-fired power plant in Greece. In addition, this work communicates a KPA measurement optimization procedure, specific for environmental precipitation samples. This procedure has been verified with the aid of alpha spectrometry. Nevertheless, since it is in essence a convergence method, it can also be safely applied autonomously.

SAMPLING

The rain samplers used are presented in fig. 1, and consist of a HD polyethylene cylindrical container with the diameter of 30 cm, and height of 38 cm, and a

Figure 1. Precipitation sample collectors (power plants flue gas and humidity plumes front ahead)

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

3

plastic funnel with the diameter of 23 cm. The funnel is mounted on the container using a tight gasket. The samplers aim in collecting only wet deposition since the funnel is supposed to hinder the entry of dry deposition matter into the container; however, some dry deposition interference could not be avoided. If temperature within the sampling period is low, evaporation from the HD polyethylene cylindrical container and diffusion of the collected water back to the outer environment is considered negligible given the small diameter of the funnel output, the depth of the funnel insertion in the container, the height and diameter of the container, the almost saturated conditions within the container, and finally, the radiation reflecting color of the sampling assembly.

For the purposes of this work four rain samplings were organized. Control sample #1 was collected, for reference purposes, at the NTUA Campus in Athens, on the roof of the two-storey NED-NTUA building. Sample #2 was collected at the flat roof of a two-storey private residence in the town of Megalopolis. Samples #3 and #4 were collected at the ground level near power plant A. The geographical co-ordinates of the sampling locations and the sampling periods are presented in tab. 1. The map in fig. 2 illustrates the sampling locations of samples #2, #3, and #4 in relation to the position of power plants A and B. The main criterion for the selected locations was to indicatively investigate the outdoors living and working environment of the Megalopolis inhabitants. Location #2 was selected within the 5 km radius from both plants inside the city of Megalopolis in order to provide a measurement of uranium isotopes wet deposition in an inhabited area under the close influence of the plume and quite near to lignite mines and ash depositories operating at a distance less than 5 km southwards. Locations #3 and #4 were selected in the immediate vicinity of plant A works in order to provide worst-case measurements in the working environment.

Each sampling period lasted about 2.5-3.5 months covering late winter and most of spring. The sampling periods were designed this way in order to (a) ensure there was rain, (b) minimize to negligence the evaporation effect, and finally and most importantly, (c) to allow for a close estimation of the yearly

Table 1. Rainwater sampling details

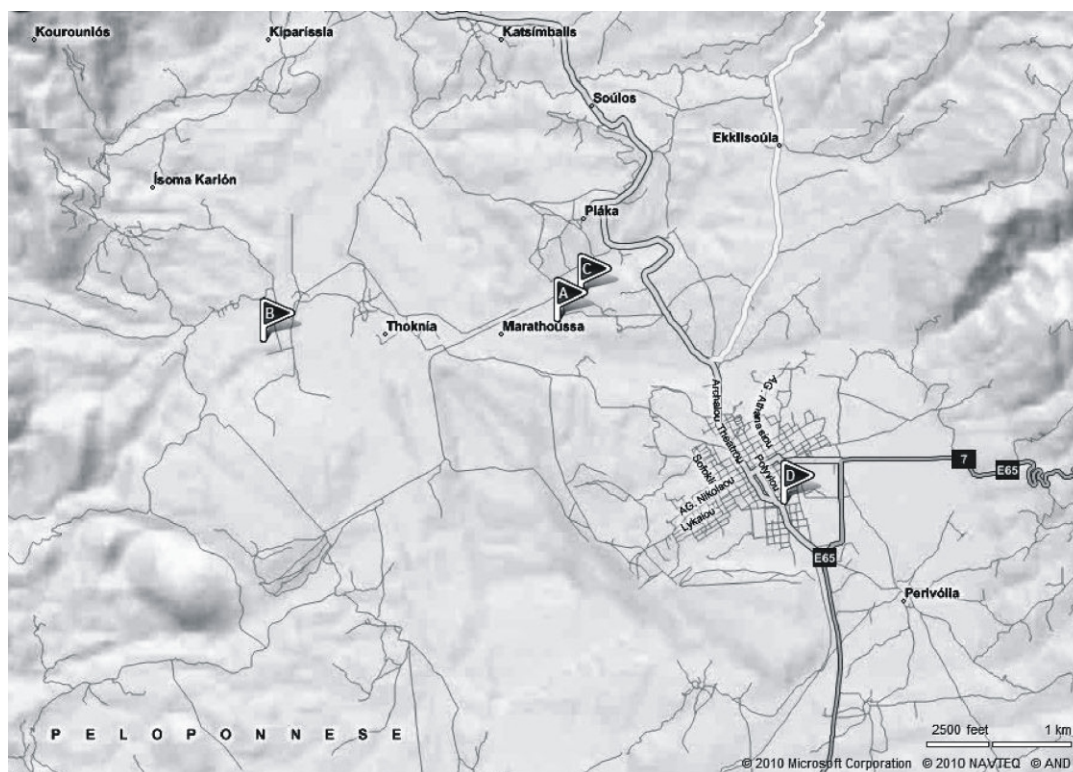| Sample	Sample period	Sample location	Longitude [°]	Latitude [°]	Volume [L]
1	February 14-April 20, 2007	NTUA Campus	37.9782	23.7849	4.63
2	February 14-April 20, 2007	Megalopolis (City)	37.3970	22.1403	6.11
3	January 26-May 11, 2008	Megapolis (Plant A)	37.4205	22.1113	6.29
4	January 26-May 11, 2008	Megapolis (Plant A)	37.4205	22.1113	7.72

Figure 2. Rainwater sampling locations map; A – plant A, B – plant B, C – locations #3 and #4, D – location #2 (map courtesy of Microsoft Corporation Bing Aplication)

4

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

average in terms of the ^{238}U wet deposition. In terms of seasonal characteristics and according to the climatological data available for Arcadia and the greater Peloponnese peninsula by the Hellenic National Meteorological Service (http://www.hnms.gr/) the applied sampling period is quite representative of the whole year as far as monthly precipitation height and number of rainy days per month are concerned. Data published for the nearby city of Tripolis give an average monthly precipitation height of 65 mm both for the year duration and for the time frame of February to May. For the same city the yearly average number of rainy days per month is 10, and the February to May average is 12. In addition, the average temperature in the area for the time frame in question is estimated to 10.6 °C, which does not give significant rise to evaporation interference questions. It is worthwhile to add that the sampling locations were close to some of the locations chosen in the previous work [11], which, among other things, investigated bulk (*i. e.* total = wet plus dry) ^{238}U deposition in the same area, so that to facilitate comparisons and support the experimental verification of a fly ash dispersion model investigated in [13]. The data for the ^{238}U bulk deposition collected on a monthly basis for 12 months in [11] average between late winter and most of spring at the values quite close (within error) to the yearly average and support our sampling period choice.

At the end of each sampling period the funnel was removed and the container was transported to the Radiochemistry Laboratory of NED-NTUA. Each sample was weighted, and the rainwater volume collected was found to range from 4.63 to 7.72 L. As expected, samples #3 and #4, having been collected on the ground and very close to plant A, were found to be somewhat contaminated by organic and other matter.

SAMPLE PRECONCENTRATION AND SCREENING

Before the radiochemical processing of the samples mainly for the purposes of alpha spectrometry measurements, an initial screening was performed by gamma spectrometry. To this end, immediately after the arrival at the Laboratory, any foreign matter such as insects and tree leaves were removed from the samples, especially samples #3 and #4, using a coarse sieve (approx. 2 mm). Subsequently, all the samples went through a preconcentration treatment using gentle evaporation to a low volume. For this purpose, the content of each sampling container was gradually transferred to a 3 L beaker, and placed in a water bath at 80 °C. When the container was totally empty, the sides and the bottom were scrubbed with a rubber spatula. The container was successively washed with two 500 mL portions of distilled water and 500 mL of 5% HNO_3, and the washings were transferred to the 3 L

beaker. The contents of the 3 L beaker were gradually transferred to a smaller, 800 mL beaker and evaporation continued at 80 °C in a fume hood due to the presence of HNO_3. The empty 3 L beaker was washed with 5% HNO_3 and the sides and the bottom were again scrubbed with a rubber spatula. The slurry was transferred gradually to the 800 mL beaker. The evaporation continued until the volume of each sample was below 150 mL. To facilitate the analysis of the entire sample in a standardized geometry the slurry was then transferred to our plastic cylindrical containers of 282 mL calibrated for gamma-spectroscopy analysis and the 800 mL beaker was washed with 5% HNO_3 and scrubbed with the rubber spatula. Finally, the remaining contents of the beaker were also transferred to the plastic container. The remaining empty volume of the container was filled with distilled water and the container was sealed with a silicone adhesive.

Measurements were performed using the extended range germanium (XtRa) detector of NED-NTUA, with a FWHM of 1003 eV at 122 keV and a relative efficiency of 107% [14]. It was shown that the radioactivity of ^{238}U in all the samples was at the same magnitude as the detection limits of the gamma spectroscopy method, *i. e.*, 0.58 Bq/L. It was therefore concluded that gamma spectrometry results could not be considered reliable for determining the uranium isotopes in the samples and further analysis employing radiochemical techniques was undertaken. Details about the gamma spectroscopy techniques may be found in [2, 12, 14].

ALPHA SPECTROMETRY

Radiochemical separation of uranium isotopes followed by alpha spectroscopic determination was performed on all samples. The method as applied in NED-NTUA has been verified during the latest ALMERA Network Laboratories Intercomparison Exercise [15]; NED-NTUA is an ALMERA Network member. A weighed 50 mL portion of each preconcentrated sample was pipetted to a small beaker. In order to evaluate recovery efficiency, 0.75 mL of calibrated ^{232}U solution, traceable to UK's National Physical Laboratory, was added to each sample. The activity concentration of ^{232}U in the tracer solution was calculated to 0.103 ± 0.004 Bq/g, while the exact amount added to each sample was determined by weight.

After the tracer addition, 25 mL of HNO_3 (65%) were added to each beaker and the sample was evaporated to near dryness. This procedure was repeated twice. The residue was evaporated twice with 25 mL of HCl and finally diluted in 30 mL of 7N HCL. The separation of uranium isotopes was performed by ion exchange, using Biorad AG1-X4 resin. Ion exchange columns were prepared with AG1-X4 resin, conditioned in 7N HCl. Each sample solution was passed

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

5

through the corresponding column, which was subsequently washed with 400 mL 7N HCl. Uranium was eluted with 1N HCl and the eluate was collected in a small beaker. Then 25 mL of HNO_3 (65%) was added to the eluate and it was evaporated until dryness. This procedure was repeated twice and subsequently the sample was diluted in 40 mL of 8M HNO_3. The second ion exchange column with AG1-X4 resin conditioned with 8M HNO_3 was prepared and the sample solution was passed through the column. Uranium was eluted with 50 mL of 8M HNO_3. The eluate was electrodeposited on a stainless steel plate following [16].

Spectra from each source were collected with a solid state CANBERRA PIPS 450 mm^2 detector for 72000 seconds. The source was placed at a distance of 9 mm, achieving a geometric efficiency of 18.72%. As an example, the spectrum of sample #3 is presented in fig. 3. The spectra were analyzed by the in-house developed XAlpha software [17], applying Levenber-Marquardt fitting algorithm. All four samples were analyzed by these techniques. The concentration of ^{238}U and ^{234}U in the samples is presented in tab. 2, referring to the initial sample volume before preconcentration. The total recovery of this method for each sample was also calculated and is presented in tab. 2. Although the recovery values were not as high as anticipated, determination of uranium isotopes concentration was possible in all cases. In the calculations of the concentrations of uranium isotopes in th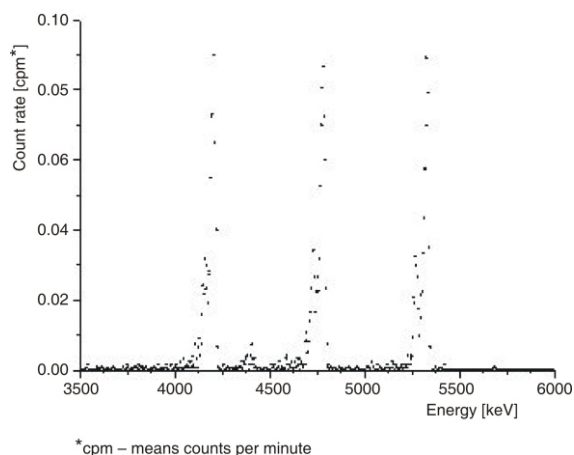e rain samples the following uncertainty components were included: (a) the uncertainty of the radioactivity of the ^{232}U tracer, (b) the uncertainty of the area of each peak in the collected spectrum, and (c) the uncertainty of the sample mass measurement.

In order to compare the concentration of ^{238}U and ^{234}U, u-tests, as described in [18], were conducted at a confidence level of 95%. The results of the tests show that the concentrations of the two isotopes do not differ significantly at this confidence level. It is therefore concluded that ^{238}U and ^{234}U are in radioactive equilibrium in the rainwater samples both in Megalopolis and in the NTUA Campus in Athens. Samples #3 and #4 that were collected at the same place and the same time have been found to have statistically equal concentrations of ^{238}U according to a u-test at a 95% confidence level. The same conclusion is valid for the concentrations of ^{234}U in these samples. This shows that the radiochemical separation was preformed successfully and in the same manner for both samples.

KINETIC PHOSPHORESCENCE ANALYSIS

Kinetic phosphorescence analysis, or KPA, is a sensitive, selective, and fast method for total uranium concentration determination in aqueous samples, which requires a minimum of radiochemical treatment. KPA measures total uranium irrespective of isotopic composition. For natural uranium, ^{238}U accounts for 99.3% of the total uranium mass [19] and the activity of ^{238}U using KPA can be derived simply by using ^{238}U specific activity equal to 12395.33 mBq/kg [20].

The method is based on a pulsed laser excitation of the sample, and temporal detection and analysis of uranyl ion phosphorescence [21]; its capabilities have been investigated in NED-NTUA during the course of the research in [22], and it has also been verified during the latest ALMERA Network Laboratories Intercomparison Exercise [15]. In the present work, the method was applied using a KPA-11 Unit, provided by ChemChek™ Instruments Ltd. Aqueous samples are pipetted into special quartz vials (cuvettes) with the addition of a proprietary complexing reagent (Uraplex®), which protects phosphorescence from quenching [23]. The total solution volume is 2.5 mL, at a sample-to-complexant volume ratio of 1:1.5.

The unit is calibrated using a set of 9 standards ranging from 50 ppt to 1 ppm total uranium, prepared at the Laboratory by gravimetric dilution from a uranium standard solution calibrated by alpha spectrometry. Provided that samples are in aqueous form and sufficiently transparent, measurements with the KPA-11 unit can be performed without any sample chemical treatment. In the present work, despite the evident coloration and visible suspended impurities, it was attempted to analyze the collected samples di-

*cpm – means counts per minute

Figure 3. The alpha spectrum of sample #3

Table 2. ^{238}U and ^{324}U activity concentrations in rainwater samples according to alpha spectrometry

Sample	^{238}U [mBqL^{-1}]		^{238}U [mBqL^{-1}]		Chemical recovery [%]
1	2.2	0.6	2.0		45
2	10	2	10		57
3	88		88	9	56
4	90	14	91		45

6

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

rectly after preconcentration. For this purpose, the preconcentrated samples were thoroughly mixed and a 1 mL aliquot was withdrawn from each one using an Eppendorf pipette. The samples aliquot was transferred to the KPA cuvette and mixed with 1.5 mL of complexing reagent. The mean lifetime of the resulting phosphorescence in all measurements exceeded the suggested upper limit of 350 µs of the optimum mean lifetime range of 150 to 350 µs, implying that there was plenty of interference luminescence most probably from organic matter present in the samples, which did not allow for a safe derivation of uranium concentration, especially in the case of the contaminated samples #3 and #4 collected in the close vicinity of plant A. An attempt was made to clarify the samples by simple filtration. Small sample aliquots were filtered by gravity through Whatman No. 42 filter paper, and analyzed in the KPA-11. However, measurement quality characteristics did not improve.

Following these unsatisfactory initial investigations, it was decided to apply chemical pretreatment according to [24]: 5 mL of each sample were pipetted to a small beaker, 1 mL of concentrated HNO_3, and a few drops of 30% H_2O_2 were added and the solution was brought to dryness. This step was repeated four to five times, or in the case of the contaminated #3 and #4 samples up to 15 times, before dissolving the residue of the last iteration in 1 mL of 4N HNO_3, and 4 mL of deionized water. From this freshly prepared 5 mL sample, 1 mL was pipetted in a cuvette with the added complexing reagent to be measured by the KPA-11 unit. By treating all samples according to this method, the measurement quality characteristics of all the samples were improved, since most of the heavy impurities and pollutants were evidently dissolved. However, the problem of reduced sample transparency was not sufficiently addressed. Persisting slight opaqueness was attributed to non-fully dissolved micro-particles and air bubbles present in the sample that gave the treated liquid samples a characteristic grayish hue, a remnant of the polluted matrix of the original liquid samples. Micro-particles and air bubbles can act as potent luminescence quenchers that reduce phosphorescence mean lifetime. For this reason, despite the measurement quality characteristics improvement, the resulting phosphorescence mean lifetimes were this time found to be below 150 s, a value which is not considered adequate for evaluating total uranium concentration in the samples.

To overcome this problem, the method of standard addition was applied to obtain a recovery factor for the KPA method. Five mL of sample #4 were treated once according to [24], and were then measured. Then 5 mL of sample #4 were spiked with a uranium calibration solution, and an aliquot was formed and named #4s. Aliquot #4s was treated once according to [24] as well and was measured. The recovery factor ε of the method can be calculated by:

$$\varepsilon \quad \frac{M_s \quad M}{C_s} \frac{m}{m_s} \qquad (1)$$

where M (in ppt*) is the measurement result as quoted by the KPA unit for the unspiked sample, M_s (in ppt) – the result for the spiked sample, m_s (in g) – the mass of the spike solution added, C_s (in ppt) its uranium concentration, and m – the sample mass before the addition of the spike. Applying this efficiency correction to the results obtained by analyzing #4 did not give satisfactory results. Uranium concentration was found much less than the values obtained by alpha spectrometry, since the recovery of the added standard did not compensate for the severe quenching caused by the polluted matrix.

In a successive attempt to obtain a uranium concentration value close to that given by alpha spectrometry, the process of standard addition was repeated in a different manner. Five mL of sample #4 was again treated once according to [24], but this time the 1 mL aliquot of the treatment product was diluted 10-fold to obtain a clearer matrix (a technique suggested also in [21]). An aliquot like #4s spiked with a uranium calibration solution was also treated once according to [24] as well, but this time the 1 mL aliquot of the treatment product was also diluted 10-fold to obtain a clearer matrix. The mass of the #4s aliquot before standard addition was equal to $m =$ = 6.2401 g. The mass of the added standard in aliquot #4s was equal to $m_s =$ 0.5053 g. The sample #4 uranium concentration measurement result was $M =$ = 13600 ppt 3%, while the uranium concentration of aliquot #4s was found equal to $M_s =$ 23810 ppt 3%. The concentration of the added standard solution was equal to $C_s =$ 1894210 ppt 7.5%. Substituting all the above to eq. (1), the overall recovery factor ε was found equal to 6.6 7%, corresponding to the treatment recovery of 66 7%, when the 10-fold dilution is taken into account. Applying this recovery factor, taking the preconcentration ratio into account, and finally the fact that rainwater contained natural uranium, the initial ^{238}U concentration of sample #4 was calculated to be 100 16 mBq/kg. This value incorporates the uncertainty of the calibration source and also the uncertainty of the calibration curve along with the uncertainty of the KPA measurement.

The same treatment procedure was followed for samples #1 and #3, for which the ^{238}U concentrations calculated using KPA were clearly divergent from the alpha spectrometry values; sample #2 was successfully measured without any standard addition. The procedure yielded recovery factors of 57.6 6%, and 89.3 7%, respectively. KPA ^{238}U concentration measurement results for all the samples referring to the initial collected samples are presented in tab. 3. Uranium-238 activity concentrations as determined by KPA have been compared to those determined by alpha spectrometry by calculat-

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*ppt – means parts per trillion, or parts per 10^{12}

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

7

Table 3. ^{238}U activity concentrations according to kinetic phosphorescence analysis and u-values for comparison with alpha spectrometry results

Sample	^{238}U [mBqL^{-1}]	*u*-value
1	1.8 0.2	0.67
2	8.0 0.9	1.22
3	103 15	1.00
4	100 16	0.51

ing u-values. At a 95% confidence level, where the results are considered significantly different when $u > 1.96$, as it can be seen from tab. 5, KPA and alpha spectrometry measurements do not differ significantly in all cases.

DISCUSSION

Uranium-238 concentrations measured in rainwater samples collected in Alsace and Luxemburg have been found to be in the range of 0.006-0.062 mBq/L [9]. Uranium-238 concentrations measured in rainwater samples collected in Arkansas have been measured in the range of 0.26-2.96 mBq/L [4]. The ^{238}U concentration measurement reported for a rainwater sample [5] was 1.38 mBq/L. Rainwater samples in Seville, South Spain, were also measured and the concentration of ^{238}U was found to be in the range of 1.1-22.5 mBq/L [6]. It is noted that all these measurements were made in places where no sources of uranium isotopes such as coal-fired power plants or uranium mills existed. The ^{238}U concentration of 2.2   0.6 mBq/L in sample #1 collected at the NTUA campus in Athens, where ^{238}U in rainfall is due to natural sources only, agrees well with the above reported values.

On the other hand, a research near a uranium mill in Canada reported ^{238}U concentration values in rainwater in the range of 3.1-7.44 mBq/L [7]. Other measurements in rainwater samples in northern Australia near a uranium mine determined concentration values in the range of 0.5-1270 mBq/L [8]. It is evident that the rainwater uranium isotopes concentration values measured in the present work in the vicinity of the lignite-fired power plants A and B at the Megalopolis lignite field basin are in all cases (samples #2, #3, #4; tab. 2) in the same order of magnitude (*i. e.*, 10-90 mBq/L) providing strong indications that the plants, mines, and depositories operation contribute to the technological enhancement of uranium concentration in local precipitation in close resemblance to what is being observed in other parts of the planet due to similar activities. However, these ^{238}U concentrations are close to those measured elsewhere in river, ground, and bottled waters: values for ^{238}U in river waters in the range of 0.18-49 mBq/L are reported in [25]; the concentration of ^{238}U in bottled mineral waters in Hungary was found to be up to 98 mBq/L in [26]; concentration measurements in ground waters collected from wells in Mexico are reported in the range of

190-840 mBq/L by [27]; a similar study in waters from boreholes in Greece showed a value range from 0.4 to 600 mBq/L [28].

The reference concentration of ^{238}U in control sample #1 collected in the NTUA campus in Athens is about 4.5 times lower than the concentration of sample #2, which was collected inside the town of Megalopolis; both samplings took place during the same period. The concentration of ^{238}U in samples #3 and #4, which were collected near Megalopolis power plant A, are 40 and 40.9 times higher, respectively, than the concentration in sample #1.

Table 4 presents the average monthly ^{238}U wet deposition rates and the average monthly precipitation at all sampling locations calculated according to the dimensions of the rainwater sampler, as presented in the sampling paragraph. For comparison purposes, tab. 5 summarizes the average monthly ^{238}U bulk (*i. e.* wet plus dry) deposition rates and the average monthly precipitation at similar close sampling locations, compiled herein following the monthly data collected between February 1997 and January 1998 provided in [11]. It has to be explained that (a) sampling location Patras refers to a city of 200 000 inhabitants with urban characteristics quite close to those of Athens of 3 700 000 inhabitants, (b) sampling locations M3 and M4 are in fact really close (within 200 m) to sampling location #2 of this work, and finally, (c) sampling location M5 is in fact really close (within 100 m) to sampling locations #3 and #4 of this work. According to the commentary in [11], the three sampling sites in Patras present no spatial differentiation and can be considered collectively as one sampling location. In addition, there also seems to exist no spatial variation between sampling locations M3 and M4, therefore they could be considered one sampling location as well. Further-

Table 4. Average monthly wet deposition rate of ^{238}U and precipitation (this work)

Sampling location	Average ^{238}U wet deposition rate measurement error [mBqm^{-2} month]	Average precipitation [mm]
1	113	50
2	679 135	67
3	4335 443	43
4	4764 741	43

Table 5. Average monthly bulk deposition rate of ^{238}U and precipitation in Patras and megalopolis [11]

Sampling location	Average ^{238}U bulk deposition rate [mBqm^{-2} month^{-1}]	Bulk deposition range [%]	Average precipitation [mm]	Precipitation range [%]
Patras (3 sampling sites)	<130	ND-161	45	2.2-255
M3	3230	31-254	70	10-353
M4	3705	49-391	70	10-353
M5	9522	58-270	70	10-353

8

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

more, data ranges in tab. 5 indicate significant seasonal influence with no clear origin. An attempt was made to reduce the original respective data of [11] to the monthly precipitation height. This reprocessing actually increased the variation range of the reduced ^{238}U bulk deposition rate, showing that the influence of precipitation variation was not evident or that the variations of airborne concentrations of particulate matter dominated the phenomena.

Having in mind that to our best knowledge, the plants A and B, lignite mines and fly ash depositories performances in 1997-98 were similar to those in 2007-08, and that all recorded average monthly precipitation heights are typically close to those expected from the climatological data of Athens, Patras, and Megalopolis, one could draw some qualitative rather than quantitative conclusions by considering the results of the present work in tab. 4 and those of tab. 5:

(1) The ^{238}U wet deposition results of this work further support the suggestion presented in [11] that there exists a local source of natural radioactivity in the area of the city of Megalopolis. This suggestion is quite consistent to similar observations for the ^{238}U wet deposition in other parts of the planet, where uranium containing ores are being processed as per the literature references already provided.

(2) The results in this work have been compared for reference purposes to the ^{238}U wet deposition in Athens metropolitan area, while the ^{238}U bulk deposition results of [11] have been compared to the data collected in Patras metropolitan area. In both cases reference data are significantly lower than the data collected at the Megalopolis lignite field basin.

(3) All ^{238}U wet deposition results in this work are of the same order of magnitude with the similar bulk deposition results presented in [11]. However, it seems worthy to argue that, as theoretically anticipated: (a) ^{238}U wet deposition seems lower than ^{238}U bulk deposition in respective sampling locations, and (b) ^{238}U wet deposition seems to be a substantial part of the bulk deposition. These conclusions cannot be clearly statistically supported due to the few rainwater samples collected and also due to possible and difficult to estimate dry deposition interference. Nevertheless, it can be mentioned that roughly ^{238}U wet deposition in Megalopolis area might be within 20% to 50%. This percentage range was estimated by calculating the wet to bulk deposition rates at sampling locations #2 and M3 and M4, and at sampling locations #3, #4, and M5. The percentage range as estimated is in agreement with the ~30% percentage of rainy days during the sampling period.

(4) The maximum ^{238}U wet deposition values of this work were recorded at locations #3 and #4. This seems to be well consistent with the fact that the maximum ^{238}U bulk deposition values in [11] were registered at the nearby location M5. Data collected at sampling locations in the close vicinity of these power plants such as #3, #4, and M5 indicate that both ^{238}U fallout and washout close to the plume emission point is quite enhanced due to the appreciably higher concentration of radionuclides in the respective air column.

Regarding the applied measurement techniques, it should be noted that the measurements with alpha spectrometry gave concentrations of ^{238}U in rainwater that did not differ statistically from the measurements with kinetic phosphorescence analysis at the 95% confidence level. However, the latter method provides somewhat better uncertainties and it is notably not as time and labor consuming, since it does not need extended radiochemical sample treatment. Furthermore, when applying this method, measurements are not influenced due to the possible existence of silicate in the matrix. Unless HF is used, silicate may not decompose in the case of sample radiochemical treatment for alpha spectrometry resulting to an incomplete uranium dissolution. In the investigated case, impurities contained in samples #2, #3, and #4 hindered KPA measurements by decreasing reliability. This matrix-related problem was solved by simple treatment following [24] combined with uranium addition of known concentration and sample dilution to improve the measurement sample transparency. The satisfactory application of the treatment, standard addition and dilution technique was verified using the results of alpha spectrometry. In case that no second method is available for the kinetic phosphorescence analysis results verification, it might be suggested that the number of dilutions and standard addition is increased in steps until the resulting phosphorescence measurement quality characteristics get within the optimal range. Attention should be paid so that the uranium addition is as close as possible to the anticipated uranium concentration in the sample. Further dilutions may be necessary until the uranium concentrations measured converge to a steady value, which may be accepted as the final result. Such a trial and error procedure with a kinetic phosphorescence analyzer is far less time consuming than alpha spectrometry.

CONCLUSIONS AND OUTLOOK

The concentrations of ^{238}U in precipitation samples in the Megalopolis lignite field basin were found to be 4.5-40.9 times higher than the concentrations of ^{238}U in a control precipitation sample in NTUA campus in Athens. The concentrations of ^{238}U in precipitation samples in the Megalopolis basin are also higher in comparison with other measurements of ^{238}U in rainwater in the literature, in cases where no known anthropogenic activities entailing uranium redistribution in the environment are in progress. Nevertheless,

N. K. Papadopoulos, *et al.*: Determination of Uranium Isotope Concentrations ...
Nuclear Technology & Radiation Protection: Year 2011, Vol. 26, No. 1, pp. 1-10

9

if such processes, for example uranium mining and milling are considered, the concentrations of ^{238}U in precipitation presented in this work are in the same order of magnitude. As anticipated, the values of ^{238}U wet deposition of this work are lower as compared to the values of ^{238}U bulk deposition presented in another investigation that took place in the same area. It seems, however, that wet deposition is a significant component of bulk deposition, which suggests that, in the absence of rain, bulk deposition from fossil fuel power plants could be far less than bulk deposition in rainy and humid environments.

Both alpha spectrometry and kinetic phosphorescence analysis methods applied for the determination of uranium content in the samples performed accurately. However, time- and labor-wise KPA seems to have a better cost to benefit ratio, even when a sample has to be chemically treated and diluted. The standard addition technique is preferred for the calculation of treated samples recovery factors, when no other trace isotope could be employed for this purpose. Evidently, the standard uranium addition in the case of KPA met this purpose as well.

Focusing on the Megalopolis lignite-fired power plants situation, it should be noted that according to Public Power Corporation of Greece S. A. the works layout is to be changed within the next five years. Power plant A (about 550 MW_e) and its related activities of lignite mines and ash depositories are to be closed down. In its place a natural gas plant is to be deployed, thus completely altering the environmental situation in the vicinity of the city of Megalopolis. It seems therefore necessary to record the uranium wet deposition situation in the area before this happens both in the time and in the space domain. A ten sampling point grid and a monthly long sampling repeated for the months of November to May, when there exists rain seems adequate. Such information could help so that at a later stage and after the decommissioning of power plant A and the commissioning of the natural gas plant, the wet deposition component due to power plant A could be discriminated from that of power plant B. Having obtained, through this work, satisfactory experience regarding the determination of uranium isotope concentrations in precipitation samples in all aspects of the task, that is sampling, preconcentration, chemical treatment, and measurement, the quick reporting of the results of such a study, seems quite feasible especially if kinetic phosphorescence analysis is applied.

ACKNOWLEDGEMENTS

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10

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Ник К. ПАПАДОПУЛОС, Ангелос В. ЕФСТАТОПУЛОС, Димитриос J. КАРАНГЕЛОС, Ник П. ПЕТРОПУЛОС

ОДРЕЂИВАЊЕ ИЗОТОПСКЕ КОНЦЕНТРАЦИЈЕ УРАНИЈУМА У ПАДАВИНАМА У ОКОЛИНИ ТЕРМОЕЛЕКТРАНА НА ЛИГНИТ

Термоелектране на мрки угаљ и лигнит производе значајне количине летећег пепела који често садржи високе концентрације природних радионуклида, као што је ^{238}U. Са становишта радијационог загађења животне средине ово је од значаја, јер мале количине летећег пепела излазе из система за филтрирање нуклеарне електране и расипају се у околну атмосферу. Поред тога, код термоелектрана на мрки угаљ и лигнит, угљенокопи и пепелишта такође доприносе да се у ваздуху налазе повећане количине суспендованих честица које садрже природне радионуклиде. У овом раду, анализирани су сакупљени узорци кишнице са лигнитног копа Мегалополис у области Аркадија у Грчкој – у којој раде термоелектране на лигнит са угљенокопима и пепелиштима. Узорци су осушени и подвргнути алфа-спектрометријској и кинетичко-фосфориметријској анализи са намером да се одреде нивои изотопске концентрације уранијума у падавинама басена Мегалополис. Контролни узорак кишнице сакупљен у подручју Атине, узет је за референтни. Показало се да су концентрације одређене овим двема техникама у статистичкој сагласности. Концентрација ^{238}U у узорцима сакупљеним у басену Мегалополис варира од 2.2   0.6 до 90   14 mBq/kg и виша је од 5 до 40 пута од концентрације ^{238}U у узорцима сакупљеним у Атини. Ово се може приписати раду термоелектрана на лигнит, угљенокопима и пепелиштима.

Кључне речи: летећи пепео, уранијум, падавине, мокро одлагалиште пепела, алфа-спектрометрија, кинетичка фосфориметрија, термоелектрана на лигнит