

In situ detection of trace aerosol uranium using a handheld photometer and solid reagent kit

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Yaxing Yang,^a Saijin Xiao,^b Ye Zhang,^a Longzhu Huang^b and Qingcheng Liu^{*a}

The public's concern about post-Fukushima radiation in the air and in their food has triggered the development of rapid and simple methods for the detection of trace uranium in air and food. Conventional uranium detection methods including atomic absorption spectrometry, phosphorimetry, and inductively coupled plasma mass spectrometry are highly sensitive. However, the expensive instruments, sophisticated operation procedures and the high skill needed for the interpretation of results obtained by these methods keeps uranium detection mostly in well equipped analytical laboratories. Though *in situ* and real-time detection of uranium is difficult, it is also the most desirable for assessing uranium contamination problems and exploring uranium mines. Driven by these requirements, a new simple *in situ* real-time method for field analysis of trace aerosol uranium in the air was developed in this contribution using a homemade handheld photometer and uranium solid reagent kit. Based on the chromogenic reaction between uranium and arsenazo III, trace aerosol uranium in air samples from above uranium ores could be successfully detected by the method presented herein, and no uranium was detected in air samples from above ores that did not contain uranium, suggesting that the present field method could be utilized for environment control and validation in the case of nuclear accident emergencies. Moreover, the measured uranium concentrations in air samples increased with the uranium content of ores, which suggests that the present field method could be applied for the discrimination of uranium ores and ores without uranium showing great promise for the exploration of uranium mines.

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Introduction

Uranium is an important long-term radioactive element and has several civilian and military applications.^{1–3} In recent years, nuclear power plants have developed rapidly all over the world because of the urgency to solve energy problems, however, the nuclear disaster that happened at Fukushima has triggered governments to make new assessments of the security of nuclear power, and has aroused serious concerns about post-radiation in the air and food. Thus, the detection of radioactive uranium in the air is profoundly important not only for the assessment of the safety of the nuclear industry but also for monitoring biological health and environmental quality. Driven by these requirements, rapid and sensitive methods for the *in situ* detection of uranium in air are urgently needed.

Conventional uranium detection methods including atomic absorption spectrometry,⁴ phosphorimetry,^{5,6} and inductively coupled plasma mass spectrometry⁷ are based on intrinsic

physical properties of the element. Being very sensitive, the expensive instruments, sophisticated operation procedures and the high skill needed for interpretation of results obtained by these methods keeps uranium detection mostly in well equipped analytical laboratories. Though *in situ* and real-time detection of uranium is difficult,⁸ it is also the most desirable for assessing uranium contamination problems and exploring uranium mines. Towards *in situ* real-time uranium analysis, remarkable progress has been achieved in the development of sensors using a wide body of techniques including surface plasmon resonance,⁹ colorimetry,^{10–12} electrochemistry,^{13,14} and fluorescence.^{15–18} In spite of this progress, most of these methods cannot yet fulfill instrument-based detection as a result of sensitivity and selectivity problems. Accordingly, a new simple field method independent of expensive instruments and reagents was developed for the *in situ* detection of trace aerosol uranium in air samples.

Field methods have stricter demands than laboratory methods in terms of equipment and reagents, and are needed for trace aerosol uranium detection in air samples because of the practical need for *in situ* real-time detection. With the purpose of fulfilling the demands of field analysis, a homemade portable photometer possessing the advantages of being compact, lightweight (about 1.5 kg), having a high degree of

^aKey Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense, East China Institute of Technology, Nanchang, Jiangxi Province, 330013, P. R. China. E-mail: qchliu@ecit.cn

^bJiangxi Key Laboratory of Mass Spectrometry and Instrumentation, East China Institute of Technology, Nanchang, Jiangxi Province, 330013, P. R. China

automation, energy-saving (working more than 50 hours with a 9 V battery), and a homemade solid reagent kit avoiding multi-step processing were prepared firstly according to our pioneering work.^{19–21} Then, a new field method was developed based on the chromogenic reaction between uranium and arsenazo III in the solid reagent kit using the homemade handheld photometer as the detector. The results showed that uranium could be successfully detected and there was a good relationship between the enhanced absorbance or the absorbance ratio (A_{650}/A_{535}) and uranium concentrations in the range of 0.141–4.503 $\mu\text{g mL}^{-1}$. It was found that the developed field method could detect trace aerosol uranium in the air samples above uranium ores, and the results were well in accordance with those obtained by ICP-MS showing the high accuracy of the present field method. Moreover, uranium concentrations in air samples increased with the uranium content of ores, which suggests that the present field method could be applied for the discrimination of uranium ores and ores not containing uranium, thus showing great promise for the exploration of uranium mines.

Experimental section

2.1 Apparatus

A homemade handheld photometer was used to measure the absorbance, a KQ-100 ultrasonic processor (Kunshan Ultrasonic Instruments Factory, Jiangsu, China) was employed for the dissociation of solutions.

2.2 Materials

56.29 mg mL^{-1} uranium standard solutions were kindly provided by the Analytical and Testing Center of East China Institute of Technology. Potassium hydrogen sulfate, arsenazo III, disodium ethylene-diamine-tetraacetic acid, potassium hydroxide, nitric acid and sodium silicate were of analytical grade and were purchased from Shantou Xilong Chemical Factory (Shantou, P. R. China). The deionized water (18.1 $\text{M}\Omega\text{ cm}$) was prepared by Thermo Scientific Barnstead Nanopure (Marietta, Ohio, USA).

2.3 Construction of the homemade portable photometer

The homemade handheld photometer was constructed according to our pioneering work with some modifications,^{20,21} Fig. 1 shows a schematic of the homemade photometer. Compared with common photometers, the homemade handheld photometer possesses the following properties. Firstly, the handheld photometer is compact and lightweight, and the size is $20 \times 20 \times 30\text{ cm}^3$ and the weight is 1.5 kg. Secondly, a light-emitting diode (LED) which has a relatively long useful time ($>10^5$ hours) was used as the light source for the homemade handheld photometer. To further reduce the power consumption, the LED light was lit only at the moment of sample determination. Thirdly, a TS-5 sensor that directly converted the optical signals to digitalized frequency signals was used as the detector, thereby omitting the photoelectric conversion process and effectively improving the signal to noise ratio.

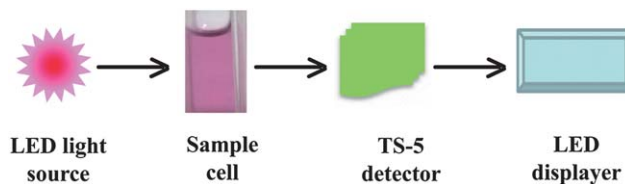


Fig. 1 Schematic of the homemade portable photometer.

2.4 Preparation of the solid reagent kit

The solid reagent kit for uranium detection was made according to our previous work with some modifications.¹⁹ Briefly, the solid reagent kit consists of three compounds, including potassium bisulfate (solid), arsenazo III (solid), and ethylene diamine tetraacetic acid (EDTA, solid). Solid potassium bisulfate is used to control the solution acidity, solid arsenazo III is the chromogenic agent, solid EDTA is the masking agent, masking the interference of other metal ions. To make the solid reagent kit, the three compounds were carefully weighed, ground, and mixed well, then a certain amount of the mixture was placed in plastic bags enclosed with foil paper, to give the finished products, *i.e.*, the solid reagents, and these were kept in a tumbler dryer.

2.5 General procedure for the detection of uranium

A certain amount of uranium standard solution or 2.5 mL of eluted nitrate solution was incubated with a pack of solid reagent kit (1.30 mg) at room temperature for 60 seconds, then distilled water was added to the mixture to give a total volume of 10.0 mL. After mixing completely, the samples were detected by the homemade handheld photometer.

2.6 Collection of air samples above ores

For the collection of trace aerosol uranium in the air samples, a new sample collection device was constructed according to our previous work,²² as seen in Fig. 2. The ore was put into the jar and a rubber stopper was firmly put into the mouth of the jar. 0.12 m^3 air was pumped through a glass tube close to the surface of the ore at a certain lashing velocity which was controlled by an airflow controller, the

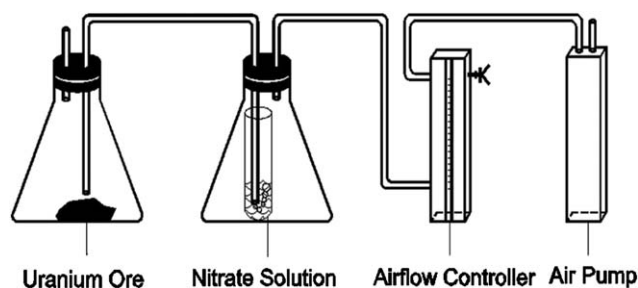


Fig. 2 The collection device for air samples.

trace aerosol uranium in the air was eluted with nitrate solution (2.5 mL), then the pH of the eluted solution was adjusted to 2.0 with potassium hydroxide solution (3.0 mol L⁻¹) and the solution was diluted to 10.0 mL with water acidified with nitric acid (pH 2.0) followed by the addition of a pack of solid reagent kit.

Safety remarks. Special permission was required for the handling of radioactive substances. The nitrate acid eluted solutions and the wastes were carefully collected for proper handling by another nuclear chemistry lab. The most important thing is to ensure that no radionuclides are emitted into the laboratory atmosphere.

Results and discussion

3.1 Detection of uranium based on the new developed field method

The detection of uranium with the homemade solid reagent kit is based on the interaction between uranium and arsenazo III. Fig. 3 shows the absorption spectra obtained by incubating the homemade solid reagent kit with different concentrations of uranium. A characteristic peak was observed at 535 nm for arsenazo III in the presence of only the homemade solid reagent kit. In the presence of uranium, however, the absorbance of arsenazo III decreased gradually and a new peak was observed at 650 nm which increased as the concentration of uranium increased. This phenomenon is similar to that demonstrated by a previously published report,²³ in which it was reported that 1 : 1 complexes are formed when arsenazo III is incubated with uranium and these complexes have a characteristic absorbance peak at 650 nm. The absorbance changes could also be visualized directly through digital pictures (inset photographs in Fig. 3). The red color shown in photograph 1 is due to the absorption of arsenazo III, and the blue color, which is due to the absorption of the 1 : 1 complexes of uranium and arsenazo III, becomes more and more obvious as the uranium concentrations increase gradually (photographs 2–6). On the basis of the color changes, a semi-quantitative colorimetric method could be developed for field uranium detection based on the present field method using the homemade portable photometer and solid reagent kit.

According to the absorbance changes characterized at 535 nm and 650 nm, a good linear relationship was obtained between the enhanced absorbance and uranium concentrations, which could be expressed as $\Delta A = 0.0025 + 0.098 c_{\text{Uranium}}$ in the range of 0.141–4.503 $\mu\text{g mL}^{-1}$ with a correlation coefficient of $R = 0.996$ ($n = 7$) and a limit of detection of 0.053 $\mu\text{g mL}^{-1}$ (3σ), as seen in Fig. 4. Wavelength-dependent ratiometry is considered to be one of the more effective methods for the detection of intracellular oxygen,²⁴ metal ions,²⁵ aminophenol,²⁶ DNA²⁷ and so on. Therefore, an absorbance ratiometric method was also applied for uranium detection, as seen in Fig. 4, there was also a good linear relationship between the absorbance ratio characterized at 535 nm and 650 nm ($A_{650/535}$) and uranium concentrations, which could be expressed as $A_{650/535} = -0.081 + 0.346 c_{\text{Uranium}}$ in the range of 0.141–4.503 $\mu\text{g mL}^{-1}$ with a correlation coefficient of $R = 0.995$

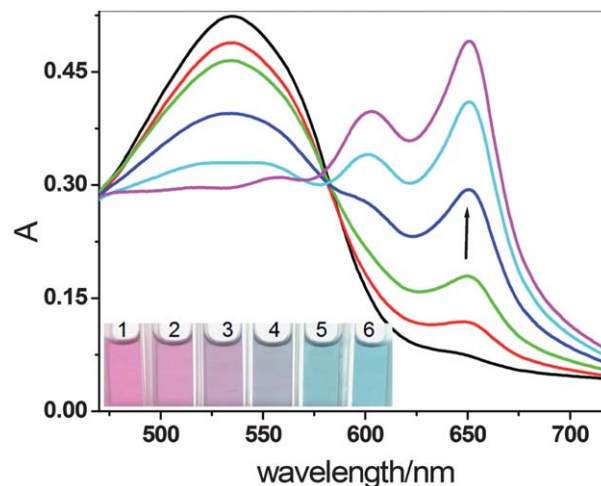


Fig. 3 The absorption spectra obtained by incubating the homemade solid reagent kit with different concentrations of uranium. Homemade solid reagent kit: 1.39 mg (potassium bisulfate: 0.54 mg; arsenazo III: 0.25 mg; EDTA: 0.60 mg); uranium concentrations from bottom to top are 0.00, 0.563, 1.126, 2.251, 3.377, 4.503 $\mu\text{g mL}^{-1}$, respectively. The inset images were photographed using a Fujin digital camera (FinePix Z909EXR), 1.39 mg of the homemade solid reagent kit was used and the uranium concentrations ($\mu\text{g mL}^{-1}$) from left to right were 0, 1.126, 4.503, 9.006, 11.26, 16.89, respectively.

($n = 7$). A comparison of the linear equation based on absorbance ratio with that based on enhanced absorbance, showed that the sensitivity of the absorbance ratiometric method is higher than that of the normal method, but the linear relationship based on the enhanced absorbance will be more suitable in field analysis considering the complexity and speed of the analysis.

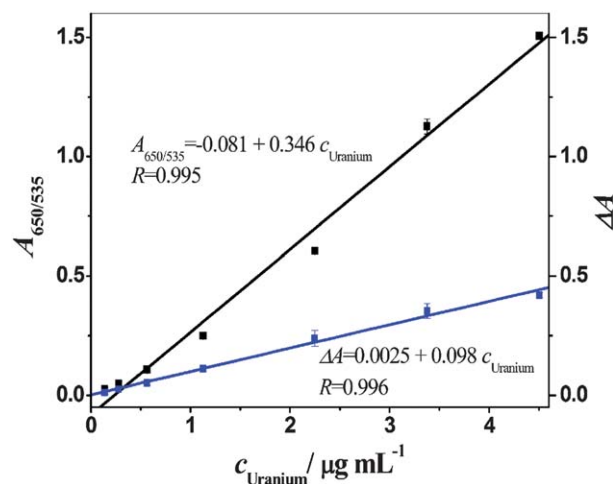


Fig. 4 Plot curve of homemade solid kit incubated with increasing concentrations of uranium. The black line represents the linear relationship between the absorbance ratio characterized at 650 nm and 535 nm ($A_{650/535}$) and uranium concentrations, whereas the red line is the linear relationship between the enhanced absorbance and uranium concentrations. All data were collected from three measurements, and the error bars indicate the standard deviation.

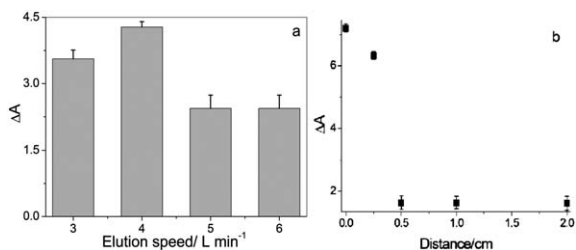


Fig. 5 The influence of elution speed (a) and sampling distance (b) on uranium detection in air samples. The air samples were collected above the uranium ores 10–56. Homemade solid reagent kit: 1.39 mg, the absorbance was measured at 650 nm.

3.2 The influence of elution speed and sampling distance on air sample analysis

It has been reported that radioactive uranium might absorb on dust or become enclosed in aerosols, and then diffuse into the air with the dust or aerosols.^{28,29} The diffused uranium in the air can enter into animals and the human body through skin, the respiratory tract, directly radioactive or other ways.^{30,31} Thus, the detection of radioactive uranium in air is profoundly important for human health and environment control. In order to validate the feasibility of the new developed field method for the detection of trace uranium in air, the air samples above uranium ores and ores without uranium were analyzed.

As the elution speed and the sampling distance might significantly influence the detection results, the two parameters were optimized firstly. Fig. 5a shows the results of the influence of elution speed, it can be seen that the detected uranium concentrations were related to the elution speed, and the highest uranium concentration could be detected when the elution speed was 4.0 L min⁻¹. We suspect that the reason for this is that the interaction between uranium and nitrate acid is inadequate when the elution speed is high, and thus less uranium in air samples could be detected. However, when the elution speed is low, uranium in air samples can interact with nitrate acid adequately and thus more uranium could be measured in air samples. When the elution speed is lower than 4.0 L min⁻¹, the content of eluted uranium is less due to the insufficient velocity of the pump. Then the sampling distance was optimized, as shown in Fig. 5b, the detected uranium concentrations in air samples decreased gradually when the



Fig. 6 The color changes of air samples above uranium ores. The air samples from left to right were control, uranium ore T-3, uranium ore 10–56, uranium ore 5–110, uranium ore H-90, respectively. 1.39 mg homemade solid reagent kit was added into each air sample.

sampling distances were increased, and the highest uranium concentration was obtained when the sampling distance was 0 cm.

3.3 Field method for the analysis of air samples above uranium ores

Under the optimized conditions, the air samples above uranium ores were analysed by the developed field method, the results are shown in Table 1. The trace aerosol uranium in air samples above uranium ores could be successfully detected by the present method based on the homemade solid reagent kit and homemade portable photometer, and no uranium was detected in air samples taken from above ore which did not contain uranium, suggesting that the present field method could be utilized for environmental control and validation in nuclear accident emergencies. The trace aerosol uranium in air samples could also be observed by the naked eye, see Fig. 6. Little color change could be observed from the air sample above uranium ore T-3 while the colors of air samples above uranium ores 10–56 and 5–110 significantly changed compared with that of the control sample. To demonstrate the accuracy of the present field method, the data were compared with those obtained by ICP-MS, and the results illustrate that the uranium concentrations obtained by the present field method are well in accordance with those obtained by ICP-MS, indicating a high accuracy of the present field method. Moreover, it could also be found that the detected uranium concentrations in air samples were increased with the uranium content of the ores, which suggested that the present field method could be applied for the discrimination of uranium ores and ores without uranium showing a great promise in exploration of uranium mines.

Table 1 Analysis of air samples above uranium ores^a

Samples no.	Field method		ICP-MS	
	Air samples ^b /mg m ⁻³	RSD (%)	Air samples ^b /mg m ⁻³	RSD (%)
Uranium ore T-3	0.093	2.88	0.091	3.12
Uranium ore 10–56	0.200	2.30	0.182	3.11
Uranium ore 5–110	0.166	3.50	0.174	1.30
Uranium ore H-90	0.062	4.13	0.0043	1.30
Ore without uranium	Non-detected		Non-detected	

^a The amount of homemade solid reagent kit used for each air sample was 1.39 mg (potassium bisulfate: 0.54 mg; arsenazo III: 0.25 mg; EDTA: 0.60 mg). ^b The results were obtained from three experiments.

Conclusions

On the basis of the homemade portable photometer and solid reagent kit, a new field method was developed for the *in situ* real-time detection of trace aerosol uranium in air samples. The results showed that uranium could be successfully detected based on the interaction with the homemade solid reagent kit and there was a good relationship between the enhanced absorbance and uranium concentrations. The linear equation was $\Delta A = 0.0025 + 0.098 C_{\text{Uranium}}$ in the range of 0.141–4.503 $\mu\text{g mL}^{-1}$ with a correlation co-efficient of $R = 0.996$. To illustrate the feasibility of the new developed field method for the analysis of real samples, air samples above ores were analysed. It was found that the developed field method could successfully detect the trace uranium from air samples above uranium ores, and the results were well in accordance with those obtained by ICP-MS which suggested that the new field developed method has high accuracy. Moreover, uranium ores could also be discriminated from ores not containing uranium, and higher uranium concentration could be detected from uranium ores with high uranium content, suggesting that air samples above uranium ores might be applied in exploration of uranium mines. Compared with conventional methods, the field method holds at least three advantages. Firstly, the new field method achieves *in situ* field analysis of trace uranium in air samples, which is significantly important for emergencies and uranium mining control. Secondly, the new field method is very simple and does not have to be carried out by a professional analyst. Thirdly, the new developed field method can be used for the detection of trace uranium and can discriminate uranium ores from other ores which do not contain uranium, and shows great promise for uranium control and uranium mining.

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Notes and references

- J. K. Gibson and J. Marcalo, *Coord. Chem. Rev.*, 2006, **250**, 776.
- G. S. Groenewold, A. K. Gianotto, K. C. Cossel, M. J. Van Stipdonk, D. T. Moore, N. Polfer, J. Oomens, W. A. de Jong and L. Visscher, *J. Am. Chem. Soc.*, 2006, **128**, 4802.
- S. Handley-Sidhu, M. J. Keith-Roach, J. R. Lloyd and D. J. Vaughan, *Sci. Total Environ.*, 2010, **408**, 5690.
- S. A. Abbasi, *Int. J. Environ. Anal. Chem.*, 1989, **36**, 163.
- R. Brina and A. G. Miller, *Anal. Chem.*, 1992, **64**, 1413.
- R. Kaminski, F. J. Purcell and E. Russavage, *Anal. Chem.*, 1981, **53**, 1093.
- D. W. Boomer and M. J. Powell, *Anal. Chem.*, 1987, **59**, 2810.
- T. P. Rao, P. Metilda and J. M. Gladis, *Talanta*, 2006, **68**, 1047.
- J. Homola and M. Piliarik, *Springer Ser. Chem. Sens. Biosens.*, **4**, 45.
- P. Hazarika, B. Ceyhan and C. M. Niemeyer, *Angew. Chem., Int. Ed.*, 2004, **43**, 6469.
- J. Liu and Y. Lu, *Angew. Chem., Int. Ed.*, 2006, **45**, 90.
- J. H. Lee, Z. D. Wang, J. W. Liu and Y. Lu, *J. Am. Chem. Soc.*, 2008, **130**, 14217.
- D. Li, Y. Yan, A. Wieckowska and I. Willner, *Chem. Commun.*, 2007, 3544.
- I. Willner and M. Zayats, *Angew. Chem., Int. Ed.*, 2007, **46**, 6408.
- E. M. Nolan and S. J. Lippard, *J. Am. Chem. Soc.*, 2007, **129**, 5910.
- S. V. Wegner, A. Okesli, P. Chen and C. He, *J. Am. Chem. Soc.*, 2007, **129**, 3474.
- Y. Xiang, Z. D. Wang, H. Xing, N. Y. Wong and Y. Lu, *Anal. Chem.*, 2010, **82**, 4122.
- J. W. Liu, A. K. Brown, X. L. Meng, D. M. Cropek, J. D. Istok, D. B. Watson and Y. Lu, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 2056.
- L. Z. Huang, S. P. Yang, X. L. Zhang, H. W. Chen and S. J. Xiao, *Uranium Geology*, 2012, **28**, 311.
- R. Hua, X. L. Zhang, Y. M. Zhou, Y. Hu, X. Zhang and H. W. Chen, *Rock Miner. Anal.*, 2008, **27**, 169.
- X. L. Zhang, R. Hua, Y. F. Huan, M. B. Luo, X. Zhang and H. W. Chen, *Uranium Geology*, 2009, **25**, 312.
- Y. X. Yang, S. J. Xiao, Q. C. Liu, L. Z. Huang, D. F. Peng and M. Y. Zheng, *Spectrosc. Spectral Anal.*, 2011, **32**, 1939.
- J. Avivar, L. Ferrer, M. Casas and V. Cerdà, *Anal. Bioanal. Chem.*, 2010, **397**, 871.
- F. R. Kersey, G. Q. Zhang, G. M. Palmer, M. W. Dewhirst and C. L. Fraser, *ACS Nano*, 2010, **4**, 4989.
- Z. X. Han, X. B. Zhang, Z. Li, Y. J. Gong, X. Y. Wu, Z. Jin, C. M. He, L. X. Jian, J. Zhang, G. L. Shen and R. Q. Yu, *Anal. Chem.*, 2010, **82**, 3108.
- X. D. Ge, L. Tolosa and G. Rao, *Anal. Chem.*, 2004, **76**, 1403.
- X. X. Dai, Y. F. Li, W. He, Y. F. Long and C. Z. Huang, *Talanta*, 2006, **70**, 578.
- Z. Karpas, A. Lorber, E. Elish, R. Kol, Y. Roiz, R. Marko, E. Katorza, L. Halicz, J. Riondato, F. Vanhaecke and L. Moens, *Health Phys.*, 1998, **74**, 337.
- X. H. Liu and X. H. Tong, *Geophys. Geochem. Explor.*, 2009, **33**(2), 128.
- M. Kulich, V. Rericha, R. Rericha, D. L. Shore and D. P. Sandler, *Environ. Res.*, 2011, **111**, 400.
- L. Walsh, F. Dufey, M. Mohner, M. Schnelzer, A. Tschense and M. Kreuzer, *Radiat. Environ. Biophys.*, 2010, **50**, 57.