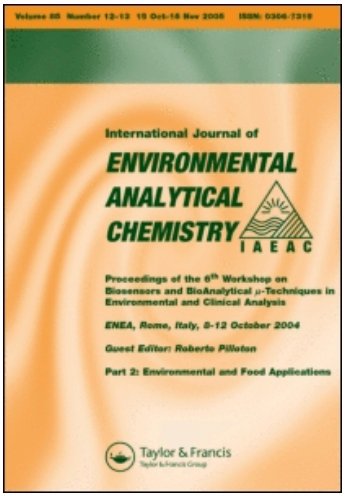

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Challenge to ultra-trace analytical techniques of nuclear materials in environmental samples for safeguards at JAERI: methodologies for physical and chemical form estimation

Shigekazu Usuda[a]; Kenichiro Yasuda[a]; Yoko Saito-Kokubu[a]; Fumitaka Esaka[a]; Chi-Gyu Lee[a]; Masaaki Magara[a]; Satoshi Sakurai[a]; Kazuo Watanabe[a]; Fumio Hirayama[a]; Hiroyasu Fukuyama[a]; Konomi Takai Esaka[a]; Kazunari Iguchi[a]; Yutaka Miyamoto[a]; Jian-Yu Chai[a]
[a] Department of Environmental Sciences, Japan Atomic Energy Research Institute, Naka-gun, Ibaraki-ken, 319-1195, Japan

To cite this Article Usuda, Shigekazu , Yasuda, Kenichiro , Saito-Kokubu, Yoko , Esaka, Fumitaka , Lee, Chi-Gyu , Magara, Masaaki , Sakurai, Satoshi , Watanabe, Kazuo , Hirayama, Fumio , Fukuyama, Hiroyasu , Esaka, Konomi Takai , Iguchi, Kazunari , Miyamoto, Yutaka and Chai, Jian-Yu(2006) 'Challenge to ultra-trace analytical techniques of nuclear materials in environmental samples for safeguards at JAERI: methodologies for physical and chemical form estimation', International Journal of Environmental Analytical Chemistry, 86: 9, 663 — 675
To link to this Article: DOI: 10.1080/03067310600583733
URL: http://dx.doi.org/10.1080/03067310600583733

Intern. J. Environ. Anal. Chem.
Vol. 86, No. 9, 10 August 2006, 663–675

Taylor & Francis
Taylor & Francis Group

Challenge to ultra-trace analytical techniques of nuclear materials in environmental samples for safeguards at JAERI: methodologies for physical and chemical form estimation

SHIGEKAZU USUDA*, KENICHIRO YASUDA, YOKO SAITO-KOKUBU, FUMITAKA ESAKA, CHI-GYU LEE, MASAAKI MAGARA, SATOSHI SAKURAI, KAZUO WATANABE, FUMIO HIRAYAMA, HIROYASU FUKUYAMA, KONOMI TAKAI ESAKA, KAZUNARI IGUCHI, YUTAKA MIYAMOTO and JIAN-YU CHAI

Department of Environmental Sciences, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan

(*Received 7 April 2005; in final form 9 November 2005*)

From a viewpoint of physical and chemical form estimation, ultra-trace analytical techniques of nuclear materials in environmental samples for safeguards have been investigated at Japan Atomic Energy Research Institute. This article deals with (1) an outline of the developed techniques for bulk and particle analyses of uranium and plutonium in the safeguards environmental samples; (2) current R&D on techniques relating to estimation of the physical and chemical form, such as SEM images and EDX spectra for fine particles of nuclear materials and fission track observation applicable to fissile materials; and (3) possible analytical methodologies, as future works, applicable to ultra-trace amounts of nuclear materials in environmental samples.

Keywords: Ultra-trace analysis; Nuclear materials; Environmental samples; Safeguards; Physical and chemical form

1. Introduction

In 1995, the IAEA introduced the environmental sample analysis method, as a powerful tool to detect undeclared nuclear activities, into a strengthened safeguards system based on the Programme 93 + 2 [1]. The method is based on the principle that 'nuclear signatures' can be evidenced if trace amounts of nuclear materials in environmental samples taken from the inside and outside nuclear facilities are accurately analysed.

In such a situation, a cleanroom facility, Clean Laboratory for Environmental Analysis and Research (CLEAR), was constructed at Japan Atomic Energy Research

*Corresponding author. Fax: +81-29-284-3665. Email: usuda.shigekazu@jaea.go.jp

International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310600583733

Institute (JAERI) in 2001, and the development of analytical techniques for ultra-trace amounts of nuclear materials in the environmental samples was started under the auspices of the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) [2]. In the beginning of 2004, JAERI became a member of the IAEA Network of Analytical Laboratories. Since then JAERI has contributed to the international safeguards as well as domestic safeguards, by carrying out environmental sample analyses.

Currently, isotope ratios of nuclear materials in 'swipe' (surface wipe) samples are mainly measured and collected in operational plant buildings of nuclear facilities by the IAEA inspectors. In future, environmental sample analyses will likely expand to soil, sediment, vegetation, water, and airborne dust taken from outside the nuclear facilities. Generally, for uranium and plutonium, and if possible for other actinides, fission, and activation products in these environmental samples, analytical techniques, such as mass spectrometry and radiometric methods, are effective and may provide information about nuclear activities on present and previous nuclear activities.

In addition, if the physical and chemical form of the nuclear materials in the environmental samples is identified, we will be able to estimate the origin, treatment process and migration behaviour of the nuclear materials. For example, if fluorine is found in uranium particles, the particles contain uranium fluoride compounds and possibly come from an enrichment or conversion process. For the aim of safeguards, such information is also significant. In this article, from the viewpoint of estimating the physical and chemical form, the analytical techniques developed for the safeguards environmental samples and their applications are presented.

2. Developed analytical techniques

The environmental sample analysis for ultra-trace amounts of uranium and plutonium should be carried out at a cleanroom facility in order to avoid cross-contamination from analytical surroundings. The cleanliness of CLEAR is ISO Class 5–7 in every cleanroom and Class 4 in every hood and bench [3].

Figure 1 shows the flow diagram of the safeguards environmental sample analysis developed at JAERI. After receiving the swipe samples from the IAEA or MEXT, they are screened by radiometric methods, and then bulk and/or particle analyses are performed. Samples with less than 1 Bq order of uranium and plutonium are acceptable into CLEAR, while samples that contain much more radioactivity are treated as 'hot-cell samples' and analysed, in principle, at a radiochemical laboratory, NUCEF (Nuclear Fuel Cycle Safety Engineering Research Facility). In addition, γ-ray emitters, such as fission and activation products, are determined by a Ge(Li) detector using the Compton suppression technique [4] and so on.

2.1 *Bulk analysis*

In order to determine the concentrations and mean values of isotope ratios for uranium and plutonium in a swipe sample, the basic bulk analytical technique was successfully established. The technique consists of dry ashing, acidic digestion,

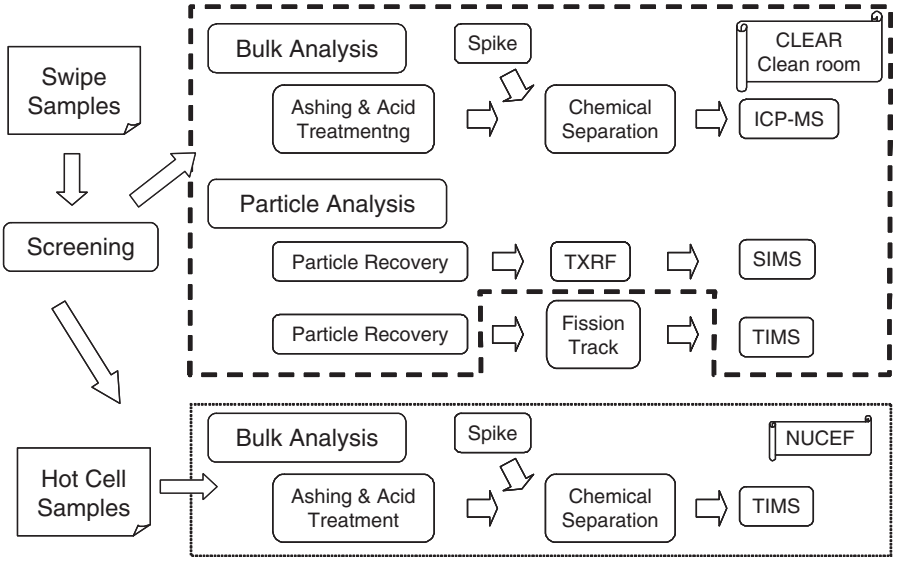

Figure 1. Flow diagram of the safeguards for environmental sample analysis.

and chemical separation. Figure 2 shows a chemical-separation scheme with an anion-exchange column [5].

Uranium and plutonium were successfully determined with a double-focusing high-resolution inductively coupled plasma mass spectrometer (ICP-MS) and thermal ionization mass spectrometer (TIMS) using the isotope dilution method (IDM), while other minor actinides with short half-lives were analysed by α-ray spectrometry. In order to obtain the reliable isotope ratios by the ICP-MS, interference of polyatomic ions with of uranium and plutonium was studied [6, 7].

Consequently, the $^{235}U/^{238}U$ ratio of 0.01 was measured with a relative precision of about 3% when using 5 mL of 3 ppt U solution (10 pg U) and the $^{240}Pu/^{239}Pu$ ratio of 0.07 within 1% when using 5 mL of 0.1 ppt Pu solution (0.5 pg Pu). The uranium blank for whole process was achieved in the range of 5–10 pg during bulk analysis at CLEAR.

2.2 *Particle analysis*

In order to measure the isotope ratios of uranium in individual particles, we have established a total reflection X-ray fluorescence spectrometry and secondary ion mass spectrometry (TXRF-SIMS) technique, in which particles are recovered onto a carrier by an impactor-type sampler and screened by TXRF; the isotope ratios are then analysed by SIMS [8–10]. Although the TXRF-SIMS technique is excellent and effective for the particles with a diameter of more than 1 μm (approximately 4 pg), it seemed difficult to analyse the smaller particles owing to limitations in the sensitivity of SIMS.

Therefore, we started to develop a fission track (FT)-TIMS technique [11, 12], which is known to be effective for the analysis of submicron particles. The outline of our technique is as follows. Particles were collected from a swipe sample onto

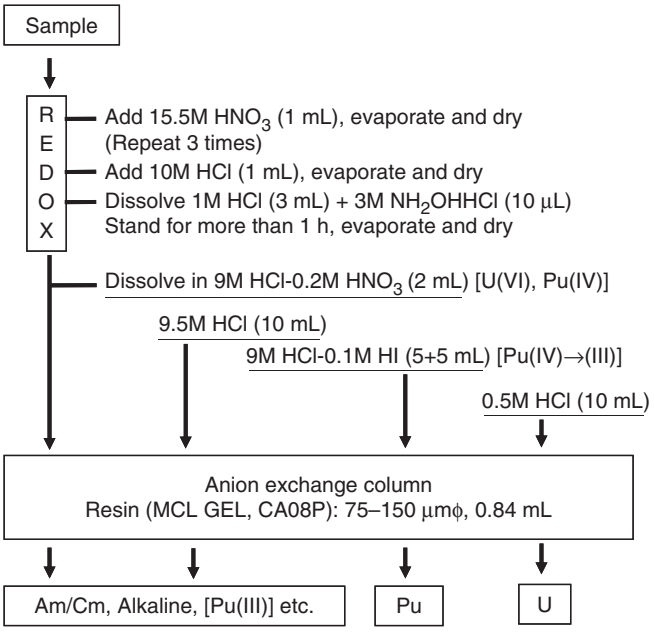

Figure 2. Chemical separation scheme by anion exchange.

a polycarbonate membrane filter (pore size: 0.1 μm) by means of a suction pump. The filter was dissolved in a solvent. The solution was spread on a slide glass and dried up to make a track detector of polycarbonate films (thickness: 5–10 μm) containing the particles, which were irradiated with thermal neutrons. The film detectors were chemically etched, and the fission tracks formed in it were observed with a digital microscope. A small portion of the film containing a fission track was cut off with a laser beam and picked up onto a refined Re filament for isotope ratio measurement by TIMS.

3. Physical and chemical form estimation in practice

In the bulk analysis of the environmental samples, the techniques of estimating physical and chemical form are less significant for the swipe samples, because the analysis provides information on the average composition of particles in each sample.

On the other hand, the particle analysis is more meaningful. The reason is that the particle analysis involves determination of the elemental and isotopic composition of each particle but also its morphology. Four typical examples relating to the estimation of physical and chemical form are introduced.

3.1 *TXRF-SIMS analysis*

Figure 3 shows an example of TXRF spectrum for quantitative analysis to survey elements in whole particles recovered from a swipe sample onto a carrier.

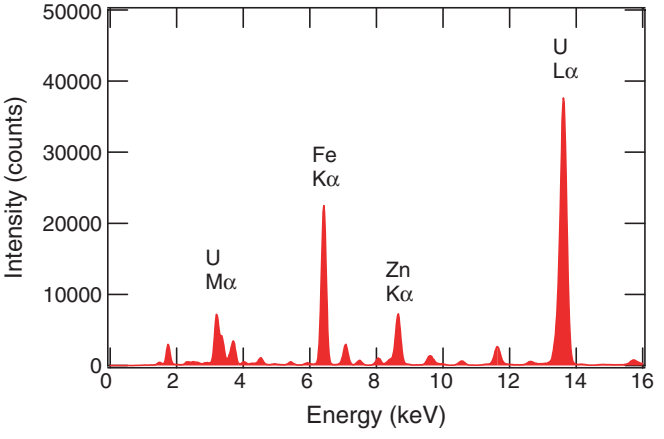

Figure 3. Typical TXRF spectrum of the recovered whole particles.

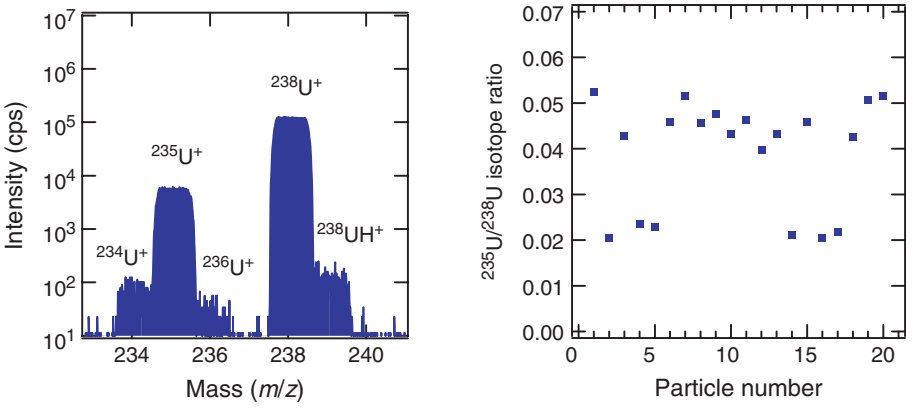

Figure 4. Typical mass spectrum of 3.7% enriched uranium in a single particle (left) and the obtained $^{235}U/^{238}U$ ratios of the particles (right), measured by SIMS.

Figure 4 shows a typical mass spectrum of 3.7% enriched uranium (EU) in a single particle and the obtained $^{235}U/^{238}U$ ratios of the particles measured by SIMS (which means that two kinds of EU existed in the swipe sample).

Scanning electron microscope-energy dispersive X-ray analysis (SEM-EDX) is one of the most effective and sensitive tools to determine the morphology and to estimate the chemical composition for each particle, as shown in figure 5.

3.2 *FT-TIMS analysis*

The FT-TIMS technique was applied to the submicron uranium particles. Figure 6 shows an SEM image of a submicron particle, which passed through a polycarbonate membrane filter with 1 μm pores and was collected on another filter with 0.1 μm pores.

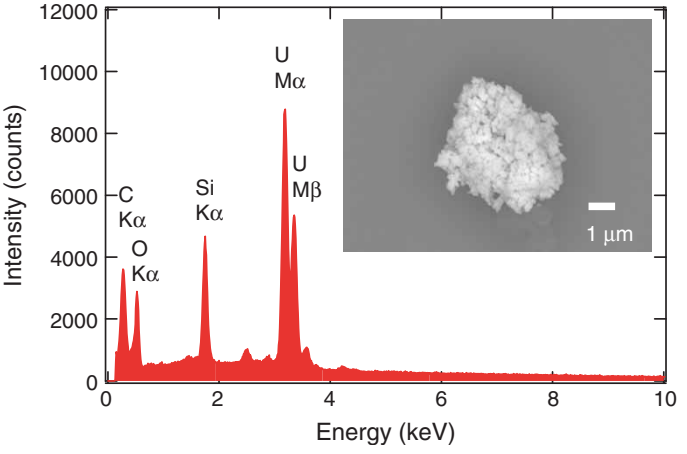

Figure 5. EDX spectrum and SEM image of a single particle.

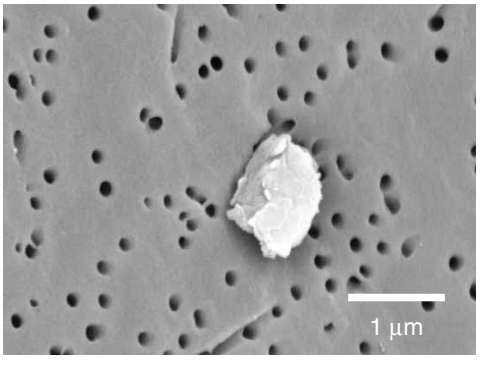

Figure 6. SEM image of a submicron particle.

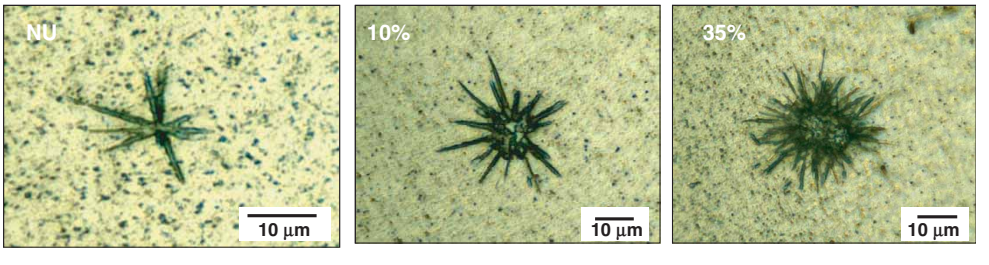

Figure 7. Digital microscope images of fission tracks of the submicron uranium particles, formed on polycarbonate films (left: natural U; middle: 10% EU; right: 35% EU).

Figure 7 shows digital microscope images of fission tracks of the submicron uranium particles with different enrichments observed on polycarbonate films. The fission track method is the most sensitive for distribution detection of fissile materials, such as ^{235}U and ^{239}Pu. Furthermore, the enrichment of each submicron uranium particle might be roughly estimated by observing the images of fission tracks.

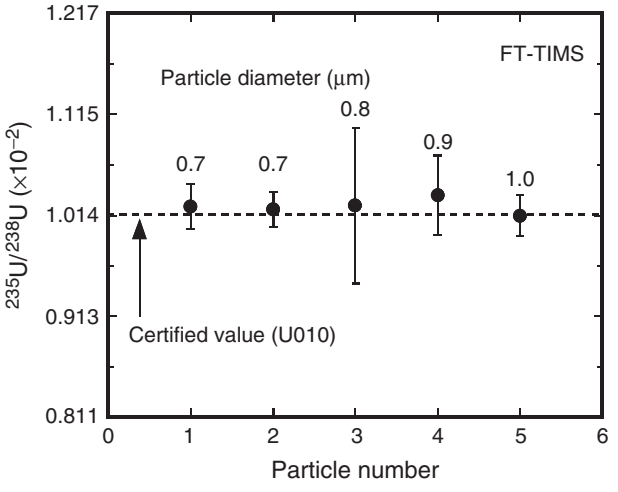

Figure 8. TIMS analytical result on submicron particles of the EU working standard (NBS U010, $^{235}U/^{238}U$: 0.01014).

At present, the applicability of TIMS to the measurement of isotope ratios of the submicron uranium particles is being investigated. Figure 8 shows analytical results on submicron particles for a working standard of EU (NBS U010, $^{235}U/^{238}U$: 0.01014).

3.3 *Hot-particle detection*

Hot particles were surveyed efficiently with IP (imaging plate: BAS-TR2040 for tritium detection), thus enabling us to detect particles with ultra-low level radioactivity in a large aria ($200 \times 400\,mm^2$), simply by exposing the IP over samples [13].

Figure 9 shows the distribution of hot particles in the Chernobyl soil sample obtained with the IP, which was exposed for about 1 h in a shield Pb box. The hot particles could be easily found in the positions where the IP was exposed strongly to turn black (dark portions in the image).

Figure 10 shows an EDX spectrum and SEM image of a single hot particle in the soil sample, which revealed that the hot particle was composed of uranium (the Au peaks observed are from a gold coating ($0.06\,mg\,cm^{-2}$) over the sample, used to avoid the electrostatic effect). On the other hand, α emitters, such as $^{239+240}Pu$ and ^{238}Pu ($+^{241}Am$), were detected by α-ray spectrometry on the particle, as shown in figure 11. That is, the hot particle also contained plutonium, which played a major part in radioactivity but a minor part in the elemental component.

3.4 *Search for traces of the Nagasaki atomic bomb*

Traces of the Nagasaki atomic bomb recorded in sediments at Nishiyama reservoir have been investigated as one of the applications of ultra-trace analysis. The reservoir is located about 3 km east of the hypocentre and experienced the 'black rain' just after the bombardment. Bulk analysis of the sediments revealed that the $^{240}Pu/^{239}Pu$ ratios

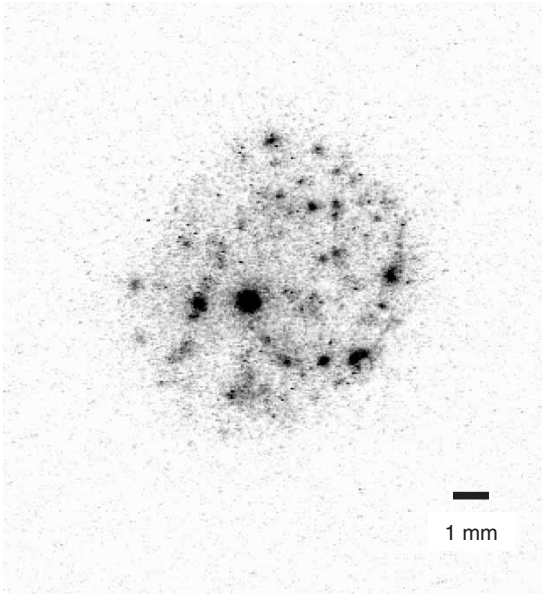

Figure 9. Radioactivity distribution in the Chernobyl soil, observed by IP.

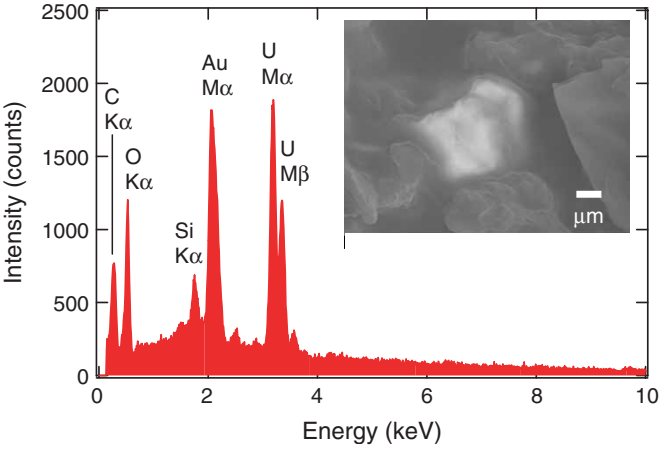

Figure 10. EDX spectrum and SEM image of a single hot particle in the Chernobyl soil.

were approximately 0.03, which is quite different from the global fallout value of 0.18, and it was concluded that these originated from the atomic bomb [14].

While we could not find any hot particles using the radiometric method mentioned above, several particles of metallic copper and its alloy were observed with SEM-EDX in sediments at a certain depth, which had a high plutonium content. Figure 12 shows an EDX spectrum and SEM image of an example of the metallic copper particles. Since the chemical form of copper in nature is $CuFeS_2$, Cu_2S, $Cu_2CO_3(OH)_2$, and so on, these metallic particles are artificial and might be supporting evidence for traces of the atomic bomb.

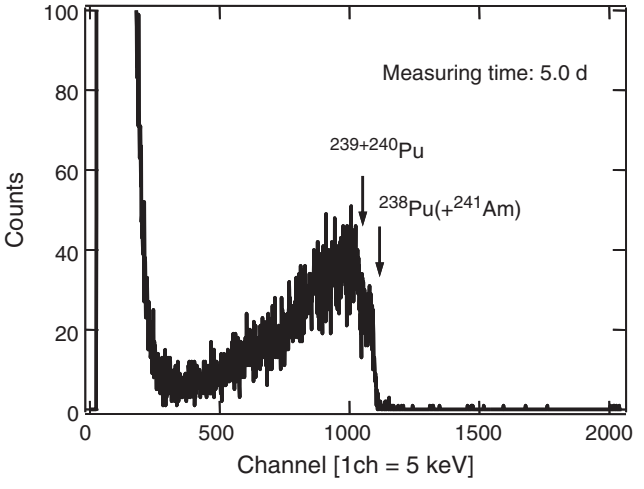

Figure 11. α-ray spectrum of the single hot particle in the Chernobyl soil.

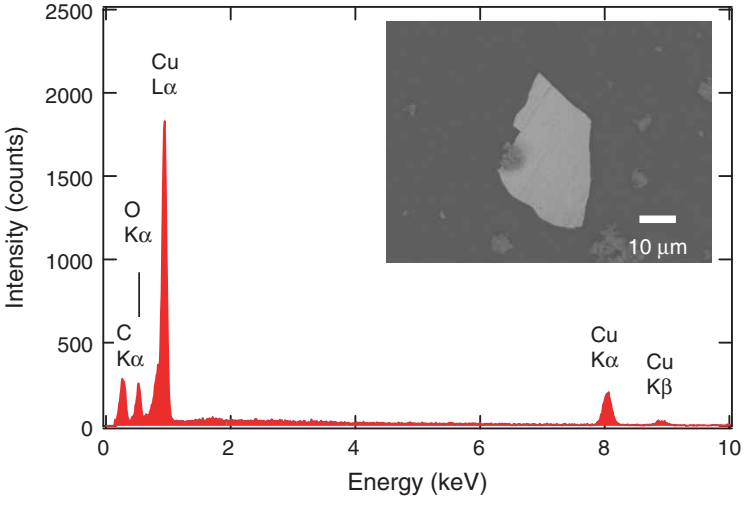

Figure 12. EDX spectrum and SEM image of a metallic copper particle in Nishiyama sediment at a depth of 227 cm.

4. Possible analytical methodologies

4.1 *Chemical analysis*

In an ultra-trace bulk analysis of environmental samples, differences in chemical behaviour during the separation process, such as ion exchange and extraction chromatography, will provide significant information on the speciation in the same way as 'single atom chemistry' details the chemical properties of super-heavy elements [15].

In the case of the anion-exchange separation shown in figure 2, for example, Pu(III) is eluted into the Am/Cm fraction, and then Pu(IV) is reduced to Pu(III) with HI to be eluted into the Pu fractions, unless the reduction–oxidation (REDOX) process is applied. If we use 4 M HCl solution instead of 9 M HCl–0.1 M HI eluent for Pu(IV), Pu(VI) may be recovered in the U(VI) fraction with 0.1 M HCl eluent.

4.2 *Instrumental analysis*

Instrumental methods, such as the electro-probe micro analysis (EPMA), photothermal spectroscopy, X-ray fluorescence, X-ray microscopy, nuclear magnetic resonance (NMR), and spectrophotometry, will help to directly estimate the physical and chemical form. Especially, techniques developed and/or under development in the field of high-energy photon and synchrotron radiation science will be utilized as promising tools for environmental nanotechnology [16–18].

For the purpose of determining chemical composition of nuclear materials, analysis of light elements as well as heavy elements is meaningful. As an example, the existence of fluorine in a nuclear particle provides important information from the viewpoint of safeguards, as described in section 1. However, it is difficult to analyse fluoride complex in practical fine particles. Besides SEM-EDX, analysis of trace fluorine is possibly performed by instrumental neutron-activation analysis (INAA) using the reaction of $^{19}F(n,\gamma)^{20}F$ ($T_{1/2}$: 11 s, sensitivity: $10^{-2}-10^{0}$ μg) [19], by detection of $^{19}F(\gamma,n)^{18}F$ ($T_{1/2}$: 110 min, sensitivity: $10^{-3}-10^{-1}$ μg), and also by atomic absorption spectrophotometry (sensitivity: subnanogram) [20].

4.3 *Preparation of reference particles*

The authors would like to emphasize the necessity for reference particles of submicron sizes for reliable estimation of the physical and chemical forms, such as the morphology, and isotopic and elemental composition, for ultra-trace nuclear materials. Therefore, we have applied a technique using a vibrating-orifice aerosol generator to prepare uranium reference particles of a definite size with a fixed isotopic and elemental composition [21].

Preliminary tests with a solution of lead-isotopic reference materials successfully produced mono-disperse lead particles. Figure 13 shows an SEM image of the particles obtained. An EDX spectrum was measured for one of the particles (figure 14); from this, its chemical composition was found to be PbO_2. Such a technique will be applicable to the uranium and plutonium reference particles, which are of great value for accurate calibration in isotope ratio measurements and quantitative analysis for individual particles in practice.

5. Conclusions and future perspectives

Ultra-trace analytical techniques for both bulk and particle analysis of uranium and plutonium in environmental samples have been investigated at JAERI to help strengthen safeguards. In the bulk analysis, chemical purification and ICP-MS

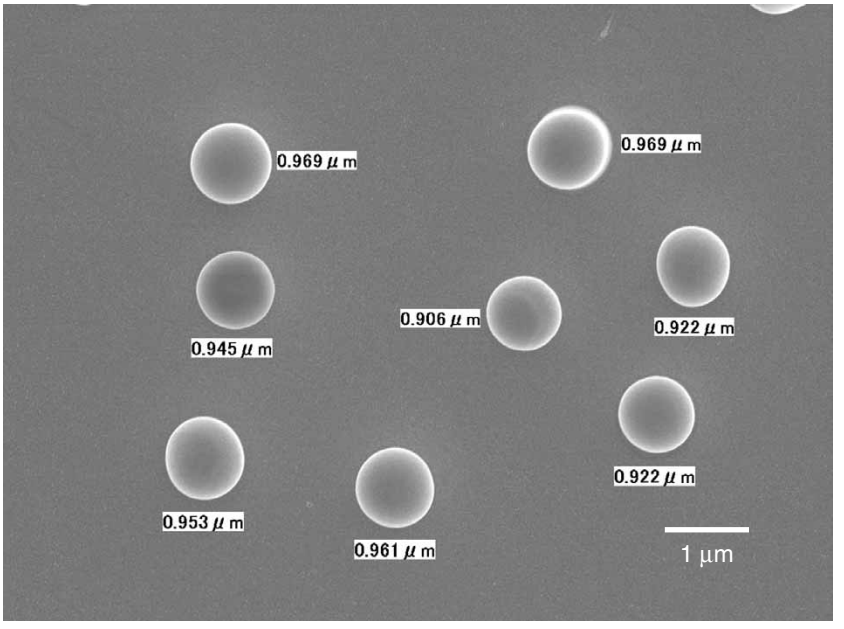

Figure 13. SEM image of lead oxide particles.

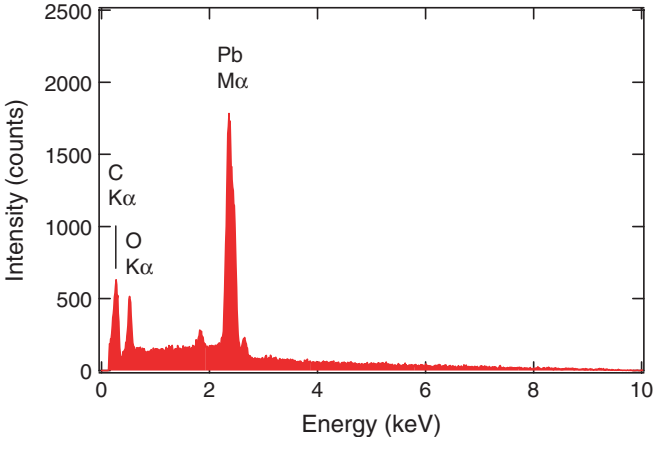

Figure 14. EDX spectrum of a lead oxide particle.

produced satisfactory results for determining the concentrations and isotope ratios. In particle analysis, the TXRF-SIMS technique was excellent for uranium particles with diameters of more than 1 μm, whereas the FT-TIMS technique has been developed for submicron particles.

As a means to estimate the physical and chemical form of the nuclear materials, mass spectrometry, such as ICP-MS, TIMS, and SIMS, was efficient by combining techniques and providing information on chemical behaviour. Radiometric methods,

such as IP and α-ray spectrometry, were sensitive for determining short-lived nuclides. SEM images and EDX spectra were powerful measures for estimating the morphology and elemental composition of fine particles. The FT method was also a sensitive technique for detecting fissile materials.

Such methodologies are useful for detecting current and past nuclear activities and will help to determine the origin and migration behaviour of the ultra-trace nuclear materials in the environment. As a future work, we will attempt to establish more sensitive and reliable methodologies, such as X-ray fluorescence using a synchrotron radiation source. In addition, for quantitative estimation, it will be indispensable to prepare nuclear reference materials of submicron particles.

The methodologies introduced in this article are meaningful and attractive technologies for a quantitative discussion of trace-element characterization. The techniques developed are expected to be applied not only to the environmental sample analysis for safeguards but also to basic research on environmental, cosmo- and geo-sciences.

Acknowledgements

The authors thank Messrs. H. Gunji, S. Kurosawa, J. Inagawa, D. Suzuki S. Ichimura, and T. Onodera, for their help in the experimental work. A portion of this work is being performed under the auspices of MEXT of the Japanese government.

References

[1] D.L. Donohue. *J. Alloy. Compd.*, **11**, 271 (1998).
[2] S. Usuda, K. Watanabe, S. Sakurai, M. Magara, F. Esaka, N. Kohno, M. Takahashi, K. Yasuda, C.G. Lee, H. Gunji, S. Kurosawa, J. Inagawa, K. Esaka, Y. Saito, Y. Miyamoto, D. Suzuki, S. Ichimura, H. Fukuyama, K. Iguchi, T. Onodera, J. Chai. In *Proceedings of 44th INMM Annual Meeting*, Phoenix, AZ, 13–17 July (2003) (CD-ROM).
[3] Y. Hanzawa, M. Magara, K. Watanabe, F. Esaka, Y. Miyamoto, K. Yasuda, K. Gunji, S. Sakurai, S. Takano, S. Usuda, T. Adachi. *J. Nucl. Sci. Technol.*, **40**, 49 (2003).
[4] K. Yasuda, M. Mori, Y. Miyamoto, M. Magara, S. Sakurai, S. Usuda. *J. Nucl. Sci. Technol.*, **3**(Suppl), 576 (2002).
[5] M. Takahashi, M. Magara, T. Sakakibara, S. Kurosawa, S. Sakurai, Y. Hanzawa, F. Esaka, K. Watanabe, S. Usuda, T. Adachi. *J. Nucl. Sci. Technol.*, **3**(Suppl), 568 (2002).
[6] M. Magara, T. Sakakibara, S. Kurosawa, M. Takahashi, S. Sakurai, Y. Hanzawa, F. Esaka, K. Watanabe, S. Usuda. *J. Nucl. Sci. Tech.*, **39**, 308 (2002).
[7] M. Magara, T. Sakakibara, S. Kurosawa, M. Takahashi, S. Sakurai, Y. Hanzawa, F. Esaka, K. Watanabe, S. Usuda. *J. Anal. Atomic Spectrometry*, **17**, 1157 (2002).
[8] F. Esaka, K. Watanabe, T. Onodera, T. Taguchi, M. Magara, S. Usuda. *Spectrochim. Acta Part B*, **58**, 2145 (2003).
[9] F. Esaka, K. Watanabe, H. Fukuyama, T. Onodera, K.T. Esaka, M. Magara, S. Sakurai, S. Usuda. *J. Nucl. Sci. Technol.*, **41**, 1027 (2004).
[10] F. Esaka, K. Watanabe, M. Magara, S. Usuda. *Instrum. Sci. Technol.*, **32**, 103 (2004).
[11] K.T. Esaka, F. Esaka, J. Inagawa, K. Iguchi, C.G. Lee, S. Sakurai, K. Watanabe, S. Usuda. *Jpn. J. Appl. Phys.*, **43**, L915 (2004).
[12] K. Iguchi, K.T. Esaka, C.G. Lee, J. Inagawa, F. Esaka, T. Onodera, H. Fukuyama, D. Suzuki, S. Sakurai, K. Watanabe, S. Usuda. *Radiat. Measure.*, **40**, 363 (2005).
[13] K. Yasuda, S. Sakurai, H. Gunji, S. Usuda. *J. Nucl. Sci. Technol.*, **3**(Suppl), 552 (2002).

[14] Y. Saito, F. Esaka, K. Yasuda, M. Magara, Y. Miyamoto, S. Sakurai, S. Usuda, H. Yamazaki, S. Yoshikawa, S. Nagaoka. In *Book of Abstracts of 4th European Meeting on Environmental Chemistry*, Plymouth, UK, 10–13 December (2003).
[15] M. Schädel. *The Chemistry of Superheavy Elements*, Kluwer Academic, Dordrecht (2003).
[16] H. Saisho. *Trends Anal. Chem*., **8**, 209 (1989).
[17] S. Török, J. Osán, L. Vincze, S. Kurunczi, G. Tamborini, M. Betti. *Spectrochim. Acta B*, **59**, 689 (2004).
[18] Research Activities in the Japan Atomic Energy Research Institute Home Page. Available online at: http://www.jaeri.go.jp/english/research.html (accessed 30 March 2005).
[19] C. Yonezawa, S. Ichimura, T, Kurosawa, H. Hatsue. *JAERI-Tech 98-046* (1998) (in Japanese).
[20] U. Kurfürst (Ed.). *Solid Sample Analysis*, Springer, Berlin (1998).
[21] N. Erdmann, M. Betti, O. Stetzer, G. Tamborini, J.V. Kratz, N. Trautmenn, J. van Geel. *Spectrochim. Acta B*, **55**, 1565 (2000).