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Direct Determination of Ultra-trace Plutonium Nanoparticles in Downstream of a Six-Stage HEPA Filter by Inductively-Coupled-Plasma Mass Spectrometry: A Field Application

Zhi-Ming Li, Yong-Yang Su, Xiang-Jun Ren, Jiang Xu, Guo-Qing Zhou, Li-Hua Zhai, Long-Bo Liu, Guan-Yi Wei, and Neng-Bin Huang

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In this work, plutonium aerosol generated from a plutonium reprocessing facility is filtered by a six-stage High Efficiency Particulate Air (HEPA) filter system and analyzed in laboratory within a week. Through on-line monitoring of number concentration of particles above 10 nm by a commercial condensation particle counter and off-line monitoring of ²³⁹Pu activity concentration by ²⁴²Pu isotope dilution Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), it is confirmed that the HEPA filter system works properly during the field operation. Direct determination of plutonium aerosol by two types of ICP-MS, Finnigan ELEMENT ICP-MS and Nu MC-ICP-MS, has been conducted. The results show that the detection limits of ELEMENT and Nu for plutonium concentration are 5.0 \times 10⁻³ Bq/m³ and 5.5 \times 10⁻⁴ Bq/m³, respectively. Plutonium concentrations in the filtered gas samples are on the order of 2.0 \times 10⁻² Bq/m³ while the blank value is 5.7 \times 10⁻³ Bq/m³. It's discovered that some plutonium nanoparticles have penetrated the six-stage HEPA filter system. This phenomenon is also observed in the repeated works of last two years. The size of the penetrated plutonium nanoparticles is investigated by ELEMENT in single particle mode. The preliminary results indicate that the penetrated plutonium nanoparticles are smaller than 10 nm and assume the form of ²³⁹PuO₂.

INTRODUCTION

Nuclear energy is an attractive choice to meet the increasing electrical demands of the society. Many nuclear facilities, such as nuclear fuel fabrication plants, nuclear reactors, and radioactive waste reprocessing plants are under operation while many old ones are planned to be decommissioned. In order to remove the plutonium-containing aerosol generated from these facilities, High Efficiency Particulate Air (HEPA) filtration is widely used, and continuous monitoring methods are utilized.

Owing to high toxicity and inhalation harm for plutonium aerosol, it's vital to evaluate the performance of multiple stages HEPA filter system for removing plutonium aerosol. Ettinger et al (1974) generated ²³⁸PuO₂ particles with Activity Median Aerodynamic Diameter in the range of $0.3 \sim 0.5 \ \mu$ m, and used membrane filter samplers and Anderson impactor to determine the filtration efficiencies of different involved stages. They found that the efficiencies of the first and second stages exceeded 99.98% and that of the third stage was 99.75%. Plutonium particles behave differently from normal aerosol due to a special phenomenon called α recoil. Nanoparticles or atom clusters of several nanometers as daughter products could be ejected into air when plutonium decay takes place (Cheng et al. 2005). At the same time, the residual particle could resuspend and migrate because of the released energy (Icenhour 2005). Early researchers have found that α recoil might be the reason for migration and penetration of plutonium particles captured in the filter (McDowell and Seeley 1976, Yamada et al. 1999). Therefore, special attention must be paid to the filtration efficiency of plutonium particles.

Diffusion capture is the main capture mechanism for nanoparticles in the filter. Cheng and Yeh (1980) developed a classical theory to predict the penetration efficiency of particles after n-layer filter screen. Single fiber efficiency is defined as the product of the collision efficiency (η) and the adhesion efficiency (ε). Assuming that a particle is permanently removed from the aerosol stream if it contacts the fiber, an empirical equation for η from experimental data is derived (Cheng et al. 1990). Taking account of the rebound probability for particles attached to the filter surface, Wang and Kasper (1991) developed a thermal rebound model to predict the penetration efficiency of nanoparticles especially below 10 nm. Mechanical constants

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of particles (K_p), mechanical constants of screen wire (K_s), and specific adhesion energy between particle and screen wire surface ($\sigma_{p,s}$) are introduced to describe the collision and adhesion processes in detail.

Since the 1990s, numerous experimental studies on single fiber efficiency of nanoparticles have been conducted to examine the theories mentioned above. Many of these works demonstrate that the Cheng and Yeh theory is valid for particles above several nanometers (Cheng et al. 1990; Alonso et al. 1997; Heim et al. 2005, 2006; Huang et al. 2007; Japuntich et al. 2007; Kim et al. 2007; Shin et al. 2008; Heim et al. 2010). Yet other observations show an enormous increase of penetration efficiency for particles in the same range, which is attributed to thermal rebound (Otani et al. 1995; Ichitsubo et al. 1996; Chen and Pui 2000; Kim et al. 2006; van Gulijk et al. 2009). Further progress is still needed in both theoretical and experimental studies to achieve a clear conclusion. It's necessary to develop highly sensitive detection methods for nanoparticles. Nowadays Faraday Cage Electrometer (FCE) and Condensation Particle Counter (CPC) are two main instruments used for the number concentration measurement of nanoparticles. FCE is able to perform absolute measurement but unable to detect neutral particle. Moreover, the detectable particle is governed by the filter collection efficiency and the minimum detectable concentration ($\sim 1000/\text{cm}^3$) is limited by the electric current background. Commercial CPC instrument is able to detect particles down to about 3 nm no matter whether the particle is charged or not. However, the counting efficiency curves are different from each other and influenced by operation conditions (Heim et al. 2005).

Plutonium aerosol continuous monitor is now widely used for on-line monitoring of plutonium concentration in air. However, its performance is seriously affected by filter collection efficiency, the interference of radon progeny, and the attenuation of α particle energy due to accumulated dust (Baron and Willeke 2001). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is the most popular inorganic mass spectrometry used for multi-element and isotope analysis. It has the advantages of fast analysis, low detection limit (DL), high sensitivity, and wide dynamic range. Off-line analysis of ultra-trace plutonium in atmospheric aerosols has been achieved in our laboratory with a technique using a high-volume filter sampler and isotope dilution ICP-MS (Zhou et al. 2002). The results show that the DL for 239 Pu is on the order of 10^{-8} Bg/m³. On-line analysis of artificially generated heavy metal particles using ICP-MS has been reported by Kaneco et al (1995) and Nomizu et al (2002). Results show that the DL for lead and zinc in aerosols are down to sub-femto-gram (fg) level.

Recently, a series of studies have been carried out in our laboratory to develop a real-time monitoring technique for plutonium aerosol by ICP-MS. When the sample introduction conditions of ICP-MS remain the same, the counting efficiency of the instrument for particle number approaches unity and its sensitivity is independent of particle size within the range of $0.4 \sim 3 \mu m$ (physical diameter) (Su et al. 2009a). However, quantitative

analysis has not been reported before, because matrix effects are serious when real aerosol sample is directly introduced into ICP torch. In order to overcome this problem, nanoparticles nebulized from standard solution are introduced to calibrate the instrument sensitivity in real time (Su et al. 2011). The key point is accurate determination of the introduction rate of atoms in the added nanoparticles aerosol. Monodisperse natural uranium particles have been generated by a commercial Vibrating Orifice Aerosol Generator. Then on-line analysis of ²³⁸U amount in a single particle has been conducted to examine this method (Su et al. 2010a). Agreement between measurement results and theoretical predictions demonstrates that the calibration method is valid for single particle analysis. This technique has been used for fast determination of ²³⁹Pu concentration in environmental aerosols (Su et al. 2010b). Preliminary results show that DL for ²³⁹Pu in the air is of the order of 10^{-3} Bq/m³.

In a plutonium reprocessing facility, the exhaust gases carrying plutonium aerosol were compressed into a sealed container for temporal storage. These gases were then passed through a six-stage HEPA filter system to remove the radioactive and toxic particles. In this work, samples of the filtered gas were collected in cylinder samplers and transported to the laboratory for plutonium analysis. Ultra-trace plutonium concentration in these gas samples was directly determined using two types of ICP-MS. Finally, analytical results were used to estimate the size of the possible penetrated particle.

EXPERIMENT AND METHOD

Instruments and Reagents

Instruments used in this study include a magnetic sector ICP-MS (ELEMENT, Finnigan MAT), Multi-Collector magnetic sector ICP-MS (Nu Plasma, Nu Instrument), Aridus membrane desolvation introduction system (CETAC Inc.), and Model 3010 CPC (TSI Inc.). Analytical standards include a natural uranium standard solution (238 U: 1004 μ g/g, RSD = 0.3%; SPEX Inc.) and a 242 Pu standard solution (Yi et al. 2007). New Al-alloy seamless cylinder gas samplers (Shen Yang ZhongFu KeJin Pressure Vessels Inc.) are vacuumized to be below 0.1 kPa, and used as passive aerosol samplers.

A HEPA filter unit (NIOSH 7580P100) was installed in a steel holder as a single stage and the contract surface was tightly sealed by glue. Nanoparticles were generated by combustion of mosquito coil incenses for filter test. Particle size distribution monitored by Scanning Mobility Particle Sizer (Model 3936L, TSI Inc.) shows that the median diameter is 110 nm with geometric standard deviation of 1.4. The penetration efficiency of each stage filter was determined by dividing the downstream number concentration by the upstream number concentration. The downstream number concentration was maintained to be above 10/ml so that the results had enough statistical precision. Results demonstrate that the filtration efficiency of a single stage HEPA is better than 99.9%, which is consistent with the



FIG. 1. Schematic of plutonium aerosol filtration, monitoring, and sampling system.

nominal value. Then the six-stage HEPA filter system was fabricated using the tested single stage with flange connections. Leak detection of the system through helium leak detector reveals that the leak rate is less than 10^{-8} Pa m³/s. Before field operation, the system is carefully installed to again pass the leak detection test.

Plutonium Aerosol Filtration, Monitoring, and Sampling

As shown in Figure 1, plutonium aerosol is driven by gas pressure through a six-stage HEPA filter when the ball valve is opened. Once the flow drops significantly because of the decreasing upstream pressure, a pump is powered to maintain a nearly constant flow. During the whole filtration process, the volume flow rate is below 50 L/min for normal operation of a HEPA filter.

Three cylinder samplers (numbered S1 to S3) are connected to the main tube in parallel and used to sample the filtered gas at different times. When the ball valve at the inlet of the sampler is opened, the gas injects from the main tube into the sampler because of the pressure difference. Nanoparticles below 100 nm can flow quite well with the carrier gas because of its small inertia. Hence, the ball valves are opened slowly to collect representative samples. After achieving pressure equilibrium, the ball valves are closed and the samplers are disconnected from the tube. The fourth sampler (numbered S0) is used to sample environmental aerosol as a blank sample. Argon is pressured into samplers to achieve the pressure about 200-kPa. These four samplers are sent to laboratory for direct determination of plutonium concentration.

As safety operation is the primary requirement for the filtration and monitoring system, the total leakage rate of the system is required to be less than 10^{-8} Pa m³/s. It is desirable to inject ²⁴²Pu aerosol as internal standard into the tube to correct the efficiencies and losses of the whole process. However, normal nebulizer could not fulfill the leakage requirement under high pressure. So the ²⁴²Pu aerosol of internal standard has not been added in the sampling stage but during measurement.

Another two techniques are used to monitor plutonium particles in the filtered gas for comparison purposes. The particle number concentration is monitored on-line by CPC while the plutonium concentration in the filter sample is determined by a traditional off-line technique (Zhou et al. 2002). A filter sampler installed in the main tube is used to sample the filtered gas during the whole filtration process. Then the filter sampler is sent to laboratory for determination of plutonium concentration using ²⁴²Pu isotope dilution ICP-MS method. The average concentration of plutonium in the gas is determined by dividing the plutonium amount by the recorded air volume through the filter.

Direct Determination of Plutonium Concentration by ICP-MS

A ²⁴²Pu working solution of 2.67 \times 10⁻¹² g/g was prepared. As shown in Figure 2, the gas sample with flow rate controlled



FIG. 2. Schematic of direct introduction and rapid determination of plutonium aerosol with ²⁴²Pu aerosol addition calibration method by ICP-MS.

by MFC1 is directly introduced into ICP torch. Continuous ²⁴²Pu aerosol, nebulized and desolvated by Aridus, is introduced simultaneously to calibrate the instrument sensitivity for ²³⁹Pu. Another argon flow is introduced to help carry the gas sample during the sample introduction period. The tubes are carefully washed by variable argon flow during the washout period.

The ²³⁹Pu activity concentration in the gas sample is determined by

$$C_{\rm s} = \frac{239AC_2 Q_{\rm up} \eta_{\rm a}}{242Q_{\rm s}} \left(\frac{\sum^{239} {\rm Pu}}{\sum^{242} {\rm Pu}} \middle/ k - \frac{R_{9/2,0}}{k_0} \right), \quad [1]$$

where A is a ²³⁹Pu-specific activity and equals to 2.3×10^9 Bq/g; C_2 is the mass concentration of ²⁴²Pu working solution; Q_{up} is the liquid uptake rate of Aridus; η_a is the aerosol generation efficiency of Aridus and defined as the fraction of ²⁴²Pu in aerosol particles at the outlet to that in the solution uptake by the nebulizer (Su et al. 2011); Q_s is the real volume flow rate of gas sample and determined from the fitted curve of pressure versus time; $R_{9/2,0}$ and k_0 are the measured ²³⁹Pu/²⁴²Pu isotope ratio and the correction factor, respectively, when only ²⁴²Pu solution is nebulized and introduced into the torch; $\sum {}^{239}$ Pu/ $\sum {}^{242}$ Pu is the isotope ratio of the accumulated ²³⁹Pu ion count to the accumulated ²⁴²Pu ion count in the same integration time when 242 Pu solution and gas sample are both introduced; and k is the correction factor between 239 Pu and 242 Pu under the same condition.

Analysis by ELEMENT ICP-MS

Only one detector is installed in the ELEMENT ion detection system, so ion signals at different m/z values are collected in peak jump mode to obtain the atomic ratio. The natural uranium standard solution was weighed and diluted to obtain a working solution of $\sim 10^{-9}$ g/g. This solution was nebulized and k_0 was obtained by dividing the measured ²³⁵U/²³⁸U isotope ratio by the natural abundance ratio (7.252 × 10⁻³). Then, the ²⁴²Pu solution was nebulized to obtain the ²³⁹Pu/²⁴²Pu isotope ratio ($R_{9/2,0}$). After that both ²⁴²Pu solution and gas sample were introduced to obtain $\sum {}^{239}$ Pu/ $\sum {}^{242}$ Pu. It has been observed that the ion signal at m/z = 239 is weak, continuous, and nearly stable, while the ion signal at m/z = 242 is also stable under the same condition. So the measured 239 Pu/ 242 Pu isotope ratio $R_{9/2}$ is used instead of $\sum {}^{239}$ Pu/ $\sum {}^{242}$ Pu, and a simplified form of the Equation (1) is given as

$$C_{\rm s} = \frac{239AC_2 Q_{\rm up} \eta_{\rm a}}{242 Q_{\rm s}} \left(\frac{\overline{R_{9/2}}}{k} - \frac{R_{9/2,0}}{k_0} \right), \qquad [2]$$

where $\overline{R_{9/2}}$ is the average value of ²³⁹Pu/²⁴²Pu isotope ratios for six measurements. At last, uranium solution was nebulized instead of ²⁴²Pu solution to obtain *k* value while other introduction parameters remained the same.

TABLE 1 Detector arrangement of Nu MC-ICP-MS for gas direct introduction and solution nebulization

	H7 ~ H1, Ax, L1	IC0	IC1, IC2	IC3	L2
Gas sample direct introduction	~	242	~	239	\sim
Uranium solution nebulization	\sim	238	\sim	235	\sim

Analysis by Nu MC-ICP-MS

MC-ICP-MS is very suitable for highly precise determination of isotope ratios, as ion signals at different m/z values are collected simultaneously by multi-collectors. The measurement precision of isotope ratio is comparable with Thermal Ionization Mass Spectrometry, and is much better than single collector ICP-MS (Lu 2009). The detection system in Nu MC-ICP-MS used in this work has 10 faraday cup detectors and 4 ion counters.

The gas introduction system shown in Figure 2 was connected to the Nu torch. The measurement process was nearly the same as described in the previous section except that ion signals at m/z= 235, 238 and m/z = 239, 242 were collected simultaneously by IC0 and IC3, respectively, as shown in Table 1. Correction factor was introduced owing to the response difference between the two ion counters and mass discrimination effect.

RESULTS AND DISCUSSION

Plutonium Concentration Monitored by CPC and the Filter Sampling Method

The particle number in the filtered gas was monitored by CPC during the filtration process and no increase in particle number was observed. However, particles below 10 nm could not be detected because of the instrument response limit. Plutonium activity concentration monitored in the filter sample shows that the average concentration is comparable to the background value. According to these results, it seems that the HEPA filter operates normally and no obvious penetration has occurred.

Plutonium Concentration Determined Directly by the Technique Established in this Paper

Comparing with normal air, the matrix effect is more serious when the gas sample is introduced into ICP-MS. Thus, the gas flow rate is limited to 15 ml/min to avoid acute decrease of instrument sensitivity. The liquid uptake rate of Aridus (Q_{up}) determined experimentally is 0.119 g/min (RSD = 3.8%). The aerosol generation efficiency (η_a) is 30% when the sweep gas flow rate is optimized to be 2.8 L/min. When ELEMENT is used, k_0 and k are 0.994 (RSD = 0.32%) and 1.025 (RSD = 0.94%), respectively. When Nu is used, k_0 and k are 1.056 (RSD =

	ELEMENT ICP-MS		Nu MC-ICP-MS		
No.	Q _s (ml/min)	C _s (Bq/m ³)	Q _s (ml/min)	C _s (Bq/m ³)	
SO	7.6	Not detected	24.5	5.7×10^{-3}	
	5.3	1.7×10^{-2}	8.2	1.1×10^{-2}	
S1	7.6	2.4×10^{-2}	11.7	2.7×10^{-2}	
	Mean	2.0×10^{-2}	Mean	1.9×10^{-2}	
	5.6	2.4×10^{-2}	4.9	1.4×10^{-2}	
S2	7.6	4.4×10^{-2}	9.6	2.6×10^{-2}	
	Mean	3.4×10^{-2}	Mean	2.0×10^{-2}	
	5.3	2.1×10^{-2}	7.4	9.3×10^{-3}	
S 3	7.4	2.9×10^{-2}	10.0	1.6×10^{-2}	
	Mean	$2.5 imes 10^{-2}$	Mean	1.3×10^{-2}	

 TABLE 2

 Comparison of ²³⁹Pu concentration in four aerosol samples determined by ELEMENT and Nu

0.14%) and 1.070 (RSD = 0.19%), respectively. The ²³⁹Pu/²⁴²Pu isotope ratio in the ²⁴²Pu solution was determined by ELEMENT and Nu. After correction, the average values are 1.20×10^{-3} ($\sigma = 6.8 \times 10^{-5}$) and 1.264×10^{-3} ($\sigma = 6.4 \times 10^{-6}$), respectively. Value of 3σ is used instead of $(\frac{R_{9/2}}{k} - \frac{R_{9/2.0}}{k_0})$ in Equation (2) to calculate the DL for plutonium concentration. Assuming Q_s is 7.6 ml/min, the results show that DL for ELEMENT and Nu are 5.0×10^{-3} Bq/m³ and 5.5×10^{-4} Bq/m³, respectively.

As shown in Table 2, plutonium in sample S0 could not be detected by ELEMENT because of its relatively poor DL. Concentrations in samples S1 ~ S3 are in the range of 2.0 × 10^{-2} Bq/m³ ~ 3.4 × 10^{-2} Bq/m³. The results with Nu reveal that the concentration in sample S0 is of the order of 10^{-3} Bq/m³ while concentrations in samples S1 ~ S3 are in the range of 1.3×10^{-2} Bq/m³ ~ 2.0×10^{-2} Bq/m³. The plutonium concentrations in samples S1 ~ S3 are much higher than the blank value, which indicates that some plutonium particles have penetrated the six-stage HEPA filter system. The penetrated particles might not also be collected by the filter sample because its collection efficiency is comparable with that of the HEPA filter.

The concentration uncertainties indicate that a systematic error exists. This is mainly attributed to unrepresentative sampling, particle loss during storage, and measurement uncertainty. The sampling bias might not be serious, as nanoparticles below 100 nm can flow with the carrier gas quite well because of its small inertia. In the measurement, the transport losses due to diffusion loss in tubes could be ignored. Ultrasonic vibration has been utilized during the measurement to eliminate the deposited and adhered particles in the sampler; however the effect is not noticeable because of the ultra-trace concentration.

At present, the particle loss in the sampler due to diffusion deposition and possible electrostatic adherence with the inner surface could not be well characterized. Efforts have been made to investigate the fraction of the deposited and adhered particles through conventional chemical techniques. After gas direct analysis, 1 liter of deionized water was injected into the sampler to wash out the particles. The liquid was baked softly by infrared lamp to obtain an enriched liquid of several milliliters. ²⁴²Pu ID-ICP-MS was used to determine ²³⁹Pu amount in this liquid. The result shows that ²³⁹Pu amount in the liquid is of the order of 20 fg, which is a little higher than the blank value. Meanwhile, the amount of the plutonium particles suspended in the gas is calculated from the direct analysis results. These two values roughly agree with each other. Hence, it is still impossible to distinguish the fraction of the lost particles.

In order to overcome the limit of the air flow directly introduced into the torch, an Ambient Aerosol Concentration Enrichment System (AACES) coupled with ICP-MS has been developed and tested preliminarily (Su et al. 2009b). The principle of AACES is the combination of particle condensation growth technique and aerosol aerodynamic enrichment technique. It consists of a saturator, a condenser, and a Slit Virtual Impactor (SVI). About 1 L/min of ambient aerosol is introduced into the inlet of AACES and mixed with 10 L/min clean argon saturated by n-butanol vapor. The mixture is supersaturated in the condenser, which is cooled by a circulator so that the particles are activated and grow to several microns. A prototype of SVI with $D_{50} = 2 \ \mu m$ has been designed and manufactured to concentrate the grown particles. Preliminary results demonstrate that ICP-MS could work properly when AACES is used as an ambient aerosol sample introduction interface. Considering the sample loss in the AACES and the sensitivity fluctuation of mass spectrometer, the total enrichment factor for the studied element in artificially generated aerosol particles is 5.5. After optimization of the AACES and miniaturization of ICP-MS unit, these techniques would serve as a powerful real-time monitor for radioactive aerosol and heavy metal containing atmospheric aerosol.

1204

Q _s (ml/min)	<i>R</i> _{9/2,0}	$\overline{R_{9/2}}$	<i>t</i> (s)	$N_{239,p}$ (atom)	$D_{\rm p}$ (m)
5.6	1.26×10^{-3}	1.96×10^{-3}	1	2.14×10^{3}	5.4×10^{-9}
7.6	1.26×10^{-3}	2.96×10^{-3}	1	5.37×10^{3}	$7.4 imes 10^{-9}$

 TABLE 3

 Estimated sizes of the penetrated plutonium nanoparticles based on single particle detection method

Preliminary Investigation on the Size of Penetrated Plutonium Particles

Degueldre and Favarger (2003, 2004) and Degueldre et al. (2006) have developed single particle ICP-MS for on-line rapid analysis of single colloidal particle in water. The water is nebulized and the colloidal particles are introduced into the torch. An ion cluster is generated due to the ionization of colloidal particle in the plasma. The induced transient signal pulses can be detected and measured for a selected m/z by mass spectrometer. The recorded peak intensity is determined as a function of the particle size and the fraction of the studied element in the colloidal particle. Meanwhile, the frequency of the ion clusters is directly proportional to the concentration of particles in the suspension. The results show that the detectable mass in the particles is down to 10^{-14} g level, while the detectable particle size is of the order of 10^{-8} m. Recently similar techniques using ICP-MS have been proposed for highly sensitive detection of gold nanoparticles (Ag-NP) in bio-analytical applications (Scheffer et al. 2008, Hu et al. 2009).

As no increase in particle number above 10 nm is observed in filtered gas by CPC, the penetrated plutonium particles would be below 10 nm. Single particle detection method with ELE-MENT has been developed in our laboratory (Su et al. 2009a, 2010a). It is utilized to detect single plutonium nanoparticle in this work. Ion signal at m/z = 239 is recorded in time scan mode, which includes an integration window of $10 \sim 1000$ ms, followed by a standby period of 1 ms. No discrete signal pulse is observed, which indicates that the plutonium nanoparticles are continuously introduced. Assuming that the signal within each integration time is attributed to only one particle, it is feasible to obtain the upper limit of the particle mass. The atom number of ²³⁹Pu is calculated by the following equation:

$$N_{239,p} = \frac{N_{\rm A} C_2 Q_{\rm up} \eta_{\rm a} t}{242} \left(\frac{\overline{R_{9/2}}}{k} - \frac{R_{9/2,0}}{k_0} \right), \qquad [3]$$

The equivalent physical diameter of plutonium particles assuming the form of 239 PuO₂ is determined by

$$D_{\rm p} = \left(\frac{6N_{239,\rm p}M_{\rm PuO_2}}{\pi N_{\rm A}\rho_{\rm PuO_2}}\right)^{1/3},$$
 [4]

where N_A is the Avogadro constant and *t* is the integration time at m/z = 239; M_{PuO2} is the mole mass of ²³⁹PuO₂ and equals to 271 g/mol; ρ_{PuO2} is the density of ²³⁹PuO₂ and equals 11.64 g/cm³ (Dean 1999). The integration time at m/z = 239 should be long enough to improve the measurement precision for a weak signal. As shown in Table 3, the equivalent physical diameter of the penetrated plutonium nanoparticles would be below 10 nm if it were assumed to be in the form of ²³⁹PuO₂.

Clement (1995) summarized that the aerosol penetration rate through capillaries is linearly related to the Standard Leak Rate (SLR) when no particle sampling or deposition losses occur. Experimental results show that particle penetration falls sharply at SLR of 10^{-4} Pa m³/s. As the leak rate of the whole filtration system in this work is less than 10^{-8} Pa m³/s, plutonium penetration through the contract surface between the filter unit and steel holder could be excluded. There might be two penetrating approaches for the plutonium nanoparticles: (i) direct penetration of plutonium particles from upstream flow through the six-stage HEPA filter; and (ii) release from α recoil of the plutonium particles captured by the filter. At present, it is unable to apply thermal rebound model to predict the penetration probability of plutonium nanoparticles through HEPA filter, for the accurate values of K_p and $\sigma_{p,s}$ are unavailable.

CONCLUSION

Through on-line monitoring of particle number concentration above 10 nm by CPC and off-line monitoring of ²³⁹Pu activity concentration by ²⁴²Pu ID-ICP-MS, it is confirmed that HEPA filter works properly during field operation. Direct introduction and rapid determination of ultra-trace plutonium aerosol in downstream of the HEPA filter have been conducted using EL-EMENT ICP-MS and Nu MC-ICP-MS. The results show that the DLs of ELEMENT and Nu for plutonium are 5.0×10^{-3} Bq/m³ and 5.5 \times 10⁻⁴ Bq/m³, respectively. Concentrations in the filtered gas are of the order of 10^{-2} Bg/m³ while the blank value is 5.7×10^{-3} Bq/m³. Some plutonium nanoparticles have penetrated the six-stage HEPA filter and the plutonium concentrations after filtration are nearly stable at different sampling periods. These phenomena could not be observed by traditional on-line and off-line monitoring methods. The size of penetrated plutonium nanoparticles was investigated with single particle detection method using ELEMENT. Preliminary results indicate that the plutonium nanoparticle would be below 10 nm assuming the form of 239 PuO₂.

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