Preparation of samples by extraction of particles from filter media for γ-ray spectrometry with high detection efficiency

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Abstract

The exposed filter media are usually compressed into disks for γ-ray spectrometry in atmospheric particulate radionuclide monitoring. A novel sample preparation process for γ-ray spectrometry by extraction of particles in filter media was proposed in order to raise detection efficiency. A device called a particle extractor was developed to extract the particles through a process of washing, spinning, flocculation and filtration. The process was validated by reference and real filter samples. The results showed that the detection efficiency of the rod sample in the well HPGe detector is 5.3 times that of the traditional sample in the coaxial detector.

Keywords Aerosol filter samples · γ-Ray spectrometry · Detection efficiency · Particle extraction

Introduction

The combination of aerosol sampling and γ-ray spectrometry is one of the most common and routine methods for monitoring atmospheric particulate radionuclides [1]. The sensitivity of the monitoring is often measured by the Minimum Detection Concentration (MDC) scale. For example, Ba-140 can be as low as 10 μBq m^{-3} with daily report by using ultrahigh-volume aerosol samplers with a flowrate of more than 500 m^3 h^{-1}, as well as a low-level γ-ray spectrometry [2, 3]. The filter media in the ultrahigh-volume aerosol samplers have to be designed to be as large as a typical area of about 0.2 m^2 to reduce filtration velocity, increase filtration efficiency, and to reduce pressure resistance and the power supple of blower or pump [4–6]. In order to avoid low γ-ray detection efficiency caused by the large size of the filter media, the exposed filter media is usually compressed into a disk by a hydraulic press [2, 5, 7]. These techniques have been applied in the radionuclide stations in the International Monitoring System (IMS) for the Comprehensive Nuclear-Test-Ban Treaty (CTBT) for two decades [8]. Recently, Hubbard et al. proposed that the baseline radionuclide sensitivity could be improved by 60% if the particle-pre-charging

technique was used to enhance aerosol sampling [9]. Miley et al. had previously investigated options for improving the Radionuclide Aerosol Sampler Analyzer (RASA) and the lowest possible MDC was still the major concern for the future radionuclide monitoring system [8].

Apart from the more advanced collection techniques, the sensitivity level of monitoring could also be lowered if the detection efficiency was improved by reducing the size of the sample for γ-ray spectrometry further. Although the traditional preparation of compression is convenient, it incorporates the redundant filter media into the sample for γ-ray spectrometry and thus it is impossible for the size of the sample to be small. If the redundant filter media was removed from the samples, the detection efficiency would be improved. The filter media most frequently used are made of polymeric fibres in ultrahigh-volume aerosol samplers (e.g. [10, 11]), so ashing was considered first, but unfortunately this can also cause loss of volatile radionuclides [12]. Microwave digestion [12] and the extraction-ashing-digestion process [13] have also been considered for the pre-treatment of the exposed filter media. Both of these methods could remove the filter media without a loss of volatile radionuclides, however, they are time-consuming and offer low efficiency because of the unnecessary decomposition of the polymeric filter media into small molecules. Particulate matter extraction methods for toxicological studies on atmospheric particulate matter have been well studied, and sonication in multiple solvents was applied as a key technique to deal with

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particulate matter on aluminium foil collection substrates and Teflon-coated glass microfiber filters [14, 15]. However, as illustrated later, sonication is not suitable for polypropylene fibrous filters in our study.

In this paper, we propose a novel process of extracting particles from the exposed filter media and incorporating the particles into the sample for γ-ray spectrometry. Firstly, a device called a particle extractor was developed to separate the particles and the filter media. The processes of washing, spinning, flocculation and filtration using the particle extractor was investigated and the recovery was validated by reference filter samples. The samples for γ-ray spectrometry were prepared by folding the final filter membrane with the particles, and the detection efficiency of the samples was determined using Cs-137 as reference radionuclide. Finally, the process was applied in atmospheric Be-7 monitoring.

Experimental

Process design

The particles captured in the fibrous filter media distribute on the whole profile of thickness so it would be difficult for them to be re-suspended by air, especially quantitatively as is required from the preparation of samples for γ-ray spectrometry. Thus, a much better alternative would be washing the filter media in liquid. When the exposed filter is in water, water molecular can break up the adherence of particles and the fibres. The effect can be enhanced by being stirred and surfactant. Next, the filter media needs to be spun in order to drain all of the suspension. Finally, the suspension is filtrated by a membrane filter media (Fig. 1). The final membrane filter media is different to the fibrous filter media in that it is much smaller and thinner, plus the particles can be separated from it very easily, if necessary.

The first device considered for the process of extracting particles from the fibrous filter media was an ultrasonic cleaner [14–17]. However, our trials showed that although particles on membrane filter media can be detached quite easily, the particles in the polypropylene fibrous filter media only detached a little. These results are consistent with those in existing literature [14, 15]. We estimated that the organic fibres would absorb the ultrasonic energy by slight vibration, so the particles kept adhering to them. Then we tried manual washing and extracting, and found that the particles could

still be extracted, but the efficiency was very low, especially for manual spinning by squeezing. Next, household washing machines with washing and spinning capabilities were found to fulfil the functional requirements, however the commercial machines cannot be applied directly in this work because of the following reasons:

(1) There are numerous tiny gaps or orifices in the wells and bottom of the washing drum meaning that the particles will be trapped in them, resulting in the loss of particles.

(2) Household washing machines are designed to wash clothes under the design confinement that in the process of doing so they do not damage these items. Consequently, the agitation speed of these machines is as slow as 60 rpm approximately; the cleaning duration is as long as tens of minutes; the water consumption is as much as several litres. However, the extraction of particles with high levels of efficiency requires agitation with much higher speeds, and under a limited duration and with limited water.

These requirements obviously exceeded an adaption of a commercial washing machine, therefore a special device, called a particle extractor, was developed.

The particle extractor

The structure of the particle extractor is shown in Fig. 2. The main case consists of the upper drum and the water reservoir that are connected by a flange. The upper drum is connected with the upper bearing, the top plate, the agitator and the electric engine. The upper drum is fixed on an electric arm that can move vertically (not shown in Fig. 2), so that the upper drum can be opened for the addition of filter media and extraction reagents. In the water reservoir, the lower bearing supports the perforated drum, which can rotate on the bearing. The well of the perforated drum is full of holes, with a diameter of about 3 mm to allow for draining. The inner diameter of the water reservoir is 200 mm and its height is 250 mm.

When washing, the clutch is at the high position (as shown in the separate circle in Fig. 2), and the electric engine drives the top plate and the agitator in order to rotate. When spinning, the clutch is at the low position (as illustrated in the main diagram in Fig. 2), and the electric engine

Fig. 1 Schematic diagram of the process of extraction of particles in the fibrous filter media
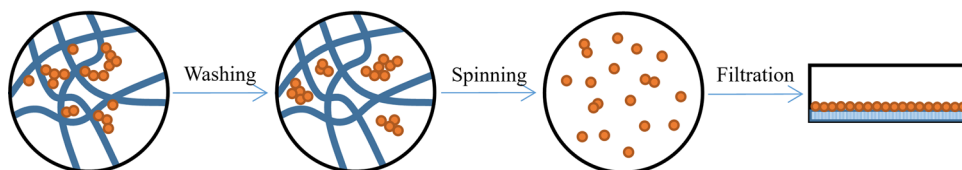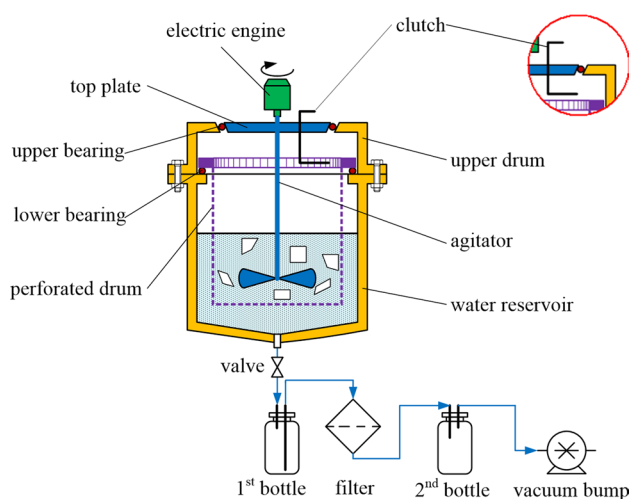
Fig. 2 Schematic diagram of the particle extractor. The clutch is at the low position for spinning in the main figure and at the high position for washing in the separate circle

drives rotation of the top plate, plus the agitator and the perforated drum.

The first bottle downstream from the main case is arranged for the temporary storage of the suspension. Next, there is a stainless-steel filter with a membrane filter media which is used to collect the particles. The vacuum pump draws the suspension from the first bottle.

The purpose of the main case of the particle extractor is similar to that of household washing machines, however it has a number of distinctive features. The purpose of this work is focused on the collection of "dirty" particles, instead of the task of "cleaning" the filter media. The smooth inner well of the water reservoir and the drain outlet at the bottom help the machine to avoid the trapping or loss of particles during washing. The special electric engine can run at much higher speeds than washing machines are able to which increases the extraction efficiency. The size of the water reservoir is compact in order to avoid excessive water consumption. The flange between the upper drum and the water reservoir could cancel spillage of the suspension, although it would cause some inconvenience that can be accepted given that this is a special device.

The operational conditions of the particle extractor were investigated experimentally, including consideration of agitation profiles, extraction reagents, flocculants and membrane filter media. All experiments were conducted with the surrogate filter samples, which were made of blank polypropylene fibrous filter media (30 cm × 20 cm size), daubed with loess dust of a certain mass. The used loess dust had been dried, ground and sieved by mesh No. 500 (38 μm pore size). The surrogate filter samples were cut into small pieces with a size of 5 cm, prior to extraction. The operation of the particle extractor was similar to that of a household washing

machine. The flange was opened and the upper drum was lifted in order to add the filter pieces and extraction reagent. The clutch was switched to the high position and the agitator started with a programmed procedure for washing. Next, the valve was opened to allow drainage. As the suspension in the main case was all drawn out, the clutch was switched to the low position, and the electric engine drove the perforated drum to rotate at a high speed for spinning. Finally, the vacuum pump drove the suspension in the first bottle through the filter and all the particles were collected on the membrane filter media. The processes of washing, spinning and filtration was run individually or continuously as needed. The effects of the extraction of the particles were evaluated firstly by sight, and then by weigh.

Validation of the process of particle extraction

The process of particle extraction with definitive conditions was validated by the reference filter samples. We had developed a device and the corresponding process for producing the reference filter samples with filter media and soils [18]. Unfortunately, we had no reference soil containing suitable radionuclides which emit γ-ray. The diameter of reference soil particles are usually a few tens of micrometres, which is obviously larger than most of the atmospheric aerosols. As an adaptation, rare-earth oxides powder Dy_2O_3 with diameter of 0.2 μm (manufactured by Shanghai Naiou Nano Technology Co. Ltd, China) was used as surrogate of atmospheric particles to produce the reference filter samples as mentioned previously [18]. Because Dy_2O_3 is not radioactive, measurement by γ-ray spectrometry was adapted to measurement by mass spectrometry in this validation.

Preparation of the reference filter samples

The Dy_2O_3 powder of 0.5–1 g was dispersed by the Venturi tube into an aerosol that is filtrated by a blank polypropylene fibrous filter media (230 mm × 180 mm). The spike of Dy_2O_3 in a reference filter sample was weighed before and after exposure.

Pre-treatment of the reference filter samples

A reference filter sample was cut into 5 cm pieces and put in a 2 L beaker. 1 L of de-ionized water and 2 mL NF surfactant were added into the beaker, agitated and then kept still for wetting for a period of 10 min.

Washing

The filter sample pieces with surfactant solution were transferred into the main case of the particle extractor, and a further 2 L of de-ionized water and 1 mL surfactant were

supplemented. The clutch was switched to the high position and the agitation speed was set to 900 rpm. The washing run was for two periods. In one period, the agitator rotated 10 times and for 10 s each time; the direction of rotation changed each time; the agitator stood for 3 s when the direction changed.

Spinning

The valve was opened and the suspension was drained into the first bottle. The clutch was switched to the low position and the agitation speed was set to 1500 rpm. The spinning run duration was 1 min.

Repeat washing and spinning

The valve was closed. 3 L of de-ionized water and 1 mL of NF surfactant were added into the case. The above-mentioned washing and spinning were repeated once.

Flocculation and filtration

2.4 g $Al(NO_3)_3 \cdot 9H_2O$ were added into the first bottle with being agitation profilered. The suspension was left for 10 min for precipitation. A nylon filter membrane was installed into the filter. The vacuum pump was turned on for filtration.

Measurement

The particles in the filter membrane were transferred into a beaker and dissolved by hydrochloric acid, then the solution was diluted to a certain volume. The Dy concentration in the solution was measured using a quadrupole mass spectrometer. The working curve had been made by a concentration series of Dy solutions before measurement and Lu was used as the internal standard.

Preparation of samples for γ-ray spectrometry

After the particles were filtrated on the filter membrane, they could be separated from the membrane and then prepared as a sample for γ-ray spectrometry with very limited size. However, a more convenient and quicker alternative is to combine the membrane into the final sample, if the membrane was not expected to impact the detection efficiency significantly.

For a coaxial HPGe detector, we found a way to fold the membrane with a diameter of 200 mm to a square chip of 5 cm size as illustrated in Supplementary information. The square chip was put into a cylindrical box with a cover that can squeeze the chip in order to maintain its shape.

For a well HPGe detector, the membrane was folded into a strip with a width of 4 cm and then rolled into to a rod shape (See Supplementary information). The rod was inserted into a plastic tube with a 10 mm inner diameter and a length of 50 mm. The particles can also be separated from the membrane filter and added into the plastic tube. The tube can be inserted into the well of the HPGe detector for measurement.

Determination of the detection efficiencies

The detection efficiencies of the final samples were determined by spiking Cs-137 solution with certain activity in them. Three samples without particles were prepared, including the traditional filter media disk, the square chip and the rod in the plastic tube. A blank sheet of fibrous filter media measuring 450 mm × 450 mm was used and grids of 15 mm × 15 mm were drawn onto them. Cs-137 solution was dropped in the grids one-by-one and then the total spike mass was weighed. The spiked filer media was dried in the shade, folded and compressed into a disk in a die by a hydraulic press with a pressure of 25 MPa. The diameter of the disk was 70 mm and the thickness was measured to be 7.4 mm. The other two samples were prepared as follows: A certain Cs-137 was spiked on the filter membrane; the membrane was dried in the shade; the membrane was folded by the above-mentioned method.

Real samples contain particulate matters which would change the size of the samples for γ-ray spectrometry. As far as real samples are concerned, atmospheric aerosol concentration should be taken into consideration. The atmospheric aerosol concentration in China has tended to decrease in recent years because of the strict policies [19]. The PM_{10} concentration value in 2017 in the Beijing–Tianjing–Hebei Region of 113 µg m^{-3} is chosen as a typical value for the present research, since it is the highest value recorded within China. Given that the corresponding air pollution characteristic is rather close to that which occurs during the hot season, the ratio of PM_{10} to TSP (the Total Suspended Particles) of 0.61 [20] was selected to calculate the TSP value of 185 µg m^{-3}. The sample volume was set as 10,000 m^3 so the typical particle mass in real samples was about 2 g. Loess dust with a diameter of less than 72 µm was used as a surrogate for atmospheric aerosols.

The 2 g loess dust within a volume of 2 mL, can increase the thickness of the square chip sample (which has a 50 mm side length) by about 0.8 mm. This would have little additional effect on the detection efficiency of the blank square chip sample. However, for the rod sample in the plastic tube, the additional particles caused the rod to become too large to be inserted. The membrane filter media had to be removed and only the particles were used to be prepared as the fourth sample. The particles were weighed and inserted into a plastic

tube. Cs-137 solution was dropped in the plastic tube and the tube was dried in shade.

The detection efficiency can be calculated by the following equation:

$$\varepsilon = \frac{n}{A p_i K} \tag{1}$$

In this equation ε is the detection efficiency; n is the count rate of the net peak area, s^{-1} (cps); A is the activity of spiked Cs-137, Bq; p_i is the branch ratio of the γ-ray energy; K is the correction for decay.

Validation of the process by real samples

Atmospheric particulate was sampled by an ultrahigh-volume aerosol sampler in Xi'an, China as the methods had been showed in the other literature [21]. The exposed filter media was cut into pieces, and treated by the proposed process including washing, spinning, flocculation and filtration. The final nylon filter membranes with particulate were folded into square chips. The natural radionuclide Be-7 was measured by the coaxial HPGe detector [21] as the reference radionuclide for validation of the process.

Results and discussion

Operational conditions of the particle extractor

Agitation profiles

The agitation speed for washing had been designed deliberately to be as fast a speed as possible. However, the centrifugal force caused by the high agitation speed drove the extraction reagent to flow up along the well of the water reservoir, even passing the lower bearing. Limited by the phenomenon, the speed of washing was set at 900 rpm. The speed for effective spinning was tested to be 1500 rpm.

In household washing machines, agitation is distinctive in that the rotational direction changes frequently and periodically. This is a very effective way to increase turbulent intensity, which helps liquid move between the inside and outside of the fabric [22]. This agitation profile was inherited by the particle extractor. A frequency-converter was applied in our particle extractor for controlling speed and changing direction. The acceleration time of the rotation of the extraction reagent in the particle extractor was assessed to be approximately 7 s.

The agitation profile was designed to rotate in one direction for a while and then to rotate in the reverse direction. The duration of rotation in one direction was 10 s, then it was kept still for 3 s when the direction changed in order to protect the electric engine. A washing period for washing was set to be 10 s of rotation, repeated ten times, making the total duration period 127 s.

Extraction reagents

A number of extraction reagents were tested including pure chloroform, chloroform ethanol solution and two surfactant (aqueous) solutions. The solubility of loess dust in those reagents was tested prior to the experiments conducted on the surrogate filter samples. The results revealed that loess dust dissolved in ethanol and water and caused a 5–6% loss of recoveries, whereas it barely dissolved at all in pure chloroform (Table 1). This would be taken into consideration during analysis of the following experiments.

As chloroform was tested for extraction, the residue of the filter pieces was visually inspected after each period of washing. After the first period, the majority of the particles were washed out of the filter media and the filter media also disintegrated to some degree. After the second period of washing, some parts of the filter media seemed to dissolve in chloroform, and there was a layer of oil liquid on the surface of the chloroform in the particle extractor. After the third period, the filter media seemed to have mostly disintegrated and some particles were mixed with the residues of the filter media. The residue of the filter media was kept in the perforated drum, so some particles would be also retained there. The quantitative results demonstrated that the recovery rate was about 50% (No. 1–3 in Table 2).

It was anticipated that the filter media could disintegrate because of the strong solvency of chloroform, thus ethanol was added to weaken the solvency of the extraction reagent. The volume ratios of chloroform to ethanol, 3:1, 2:1 and 1:1, were tested and the optimum ratio was 1:1. At this ratio the particles could be extracted well and the structure of the filter media was also preserved. The recoveries of loess dust in the surrogate filter samples by chloroform ethanol solution were about 90% (No. 4–6 in Table 2).

The chloroform ethanol solution showed good recovery of the particle in the surrogate filter samples, but chloroform and ethanol are both volatile and slightly toxic, and therefore are not suitable for routine use. Next, two commercial surfactants,

Table 1 Loss of recoveries due to solubility of loess dust in the reagents

Reagents	Spiked loess/g	Recovered loess/g	Recovery/%
Chloroform	0.4324	0.4293	99.3
Chloroform ethanol solution	0.4586	0.4354	94.7
Surfactant solution	0.4200	0.3951	94.1

Table 2 Recoveries of loess dust by the various extraction reagents

No.	Reagents	Spiked loess/g	Recovered loess/g	Recovery/%
1	Chloroform	0.7651	0.4173	54.5
2		0.7828	0.3709	47.4
3		0.7264	0.4069	56.0
Mean		–	–	52.6
4	Chloroform ethanol solution	0.6252	0.5715	91.4
5		0.5632	0.5203	92.4
6		0.7655	0.6816	89.0
Mean		–	–	90.9
7	LYL surfactant solution	0.7343	0.5508	75.0
8		0.8229	0.6295	76.5
9		0.6141	0.4975	81.0
Mean		–	–	77.5
10	NF surfactant solution	0.8094	0.7244	89.3
11		0.8136	0.7010	86.2
12		1.5516	1.4086	90.8
Mean		–	–	88.8

LYL and NF, were tested. 2–4 mL surfactants were added into 3 L of water in a beaker and then were mixed. The sample pieces were soaked in the solutions for several minutes before being added into the main case of the particle extractor. This was because the wetting of the surrogate filter samples in the surfactant solutions was slower than in the organic solvents. Both surfactant solutions showed good recovery rates for the surrogate filter samples (No. 7–9 and No. 10–12 in Table 2, respectively), while the NF surfactant solution showed improved recoveries of 86–90%. Given that these recovery percentages are close to those of the chloroform ethanol solution, the NF surfactant solution was chosen as the extraction reagent in the following studies.

As Table 1 illustrates about ~ 6% loess dust dissolved in the surfactant solutions and the average recovery of loess in the surrogate filter samples was 88.8% (Table 2), therefore only approximately 5% of loess dust was lost. Given that the water reservoir of the particle extractor, the tubing and the first bottle was always carefully cleaned, this 5% loss is likely to be due to the particles attached on the fibre of the filter media.

Flocculation

During the trial tests, it was discovered that the filter membrane was easily clogged by the small particles and the filtration velocity could decline sharply. Flocculants were considered because they can accelerate the precipitation of tiny particles, and form flocculent precipitant to reduce filtration resistance [23]. After all the suspension drained from the case of the particle extractor into the first bottle in Fig. 2, some solid reagent $Al(NO_3)_3 \cdot 9H_2O$ was added into the bottle as flocculant. The solution in the bottle was agitated until the solid powder dissolved and then it was kept still for 10 min before filtration. The amounts of 0.2, 0.4, 0.6 and 1 g per 1 L of water were tested and the results showed that 0.4 g per litre of water can flocculate well. The filtrate became clearer after the flocculant had been added. This implies that the flocculant should agglomerate the tiny particles in the suspension and increase the filtration efficiency of loess. However, it is difficult to measure the effect by weighing the product because the flocculate colloid could interfere with the weight of the loess.

Filter membranes

The common commercial micropore filter membranes are made from mixed celluloses, PTFE or nylon. The mixed cellulose membranes are hydrophilic; the PTFE membranes are hydrophobic or oleophylic; and the nylon membranes can be both hydrophilic and oleophylic. The tensile strength of the nylon membranes is also proven to be the best among the three by manual trial. Consequently, the nylon micropore membrane was chosen for filtration.

The size of the pores in the membranes was also a concern. Generally, the smaller the pore diameter is, the higher the rate of filtration efficiency. However, filtration resistance levels also increase as the pore diameter reduces. The low limit of the pore diameter of the sheet filter membranes was about 0.1 μm, as we discovered. The filter membranes with a pore diameter of less than 0.1 μm, was used for ultra-filtration and nano-filtration. They are usually prepared to be hollow fibres rather than sheets, since hollow fibres can run under higher pressure forces. Nevertheless, hollow fibre was not suitable for the preparation of samples for γ-ray spectrometry because the residue is difficult to be separated.

Finally, nylon sheet filter membrane with a pore size of 0.1 μm (manufactured by Yibo Filter Media Ltd Co, China) was selected in this study.

Validation of the process of particle extraction

The measured Dy amounts in the reference filter samples are illustrated in Table 3. The average recovery rate is 87.5%, which is consistent with the recovery rates of the surrogate filter samples, which had a mean of 88.7% for No. 10–12 in Table 1. However, if about 6% dissolution of loess in the surfactant solutions and Dy_2O_3 is insoluble was taken into consideration, recovery of Dy_2O_3 powder would be 7% less than that of loess in filter media. There would be two possible reasons for this fact. The first is that Dy_2O_3 powder is so small at a size of 0.2 μm that it could attach onto the fibre of the filter media more easily than loess dust. The second is that a small part of Dy_2O_3 powder would have a size smaller than the pore size of 0.1 μm in the filter membrane, so they pass through the filter membrane. Nevertheless, an average recovery rate of 87.5% demonstrates that the process can extract the particles effectively from the fibrous filter media and transfer the particles on the filter membrane.

Detection efficiencies of samples for γ-ray spectrometry

The measured detection efficiencies are shown in Table 4. For the coaxial detector, the detection efficiency of the square chip sample is 6.33%, twice that of the traditional disk sample (3.07%). The detection efficiency of the rod sample in the well HPGe detector is 16.2%, 2.5 folds of the square chip sample, and 5.3 folds of the traditional disk sample. The detection efficiency of the particles sample in

the well detector is 19.0%, which is slightly higher than the 16.2% of the blank membrane filter in the well detector, which should benefit from the reduced length of the sample, at 25 mm. Given that MDC is about inversely proportional to the detection efficiency [21], the results also demonstrate that MDC using the rod sample and the well detector is only 19% compared to the traditional sample and the coaxial detector.

The difference of detection efficiencies between the square chip sample and the traditional disk results from the geometry of the samples, i.e. it is the effect of the removal of the filter media. The dramatic increase in the detection efficiency of the rod sample can also be attributed to the well detector. It is well known that the detection efficiency in the well detector is much higher than that of the coaxial detector because of the large solid angle. The traditional disk sample is too large to be put into the well, so it has to be measured by a coaxial detector. Extracting particles from the filter media provides an opportunity to use the well detector to lower the MDC.

Validation of the process by real samples

The obtained Be-7 concentrations are in a range of 0.65–1.59 mBq m^{-3} as illustrated in Table 5. These concentrations are consistent with the reported local Be-7 concentrations of 0.95–16.64 mBq m^{-3} in 2002–2003 [24], although they are closer to the lower historical values. It requires further detailed research. The results show that the proposed process can be applied in atmospheric radionuclides monitoring while the recovery of the certain radionuclide need be determined individually.

Table 3 Recoveries of the Dy in the reference filter samples

No.	Spiked Dy/g	Recovered Dy/g	Recovery/%
1	0.6983	0.5841	83.6
2	0.6996	0.6385	91.4
Mean	–	–	87.5

Table 5 Atmospheric Be-7 concentrations in the present paper

No.	Air volume/m^3	Be-7 activity/Bq	Be-7 concentration/ (mBq m^{-3})
1	9607	6.26	0.65
2	11,545	18.35	1.59
3	8527	6.01	0.70

Table 4 The detection efficiencies of the various samples with spiked Cs-137

Sample matrix[a]	Sample shape	Sample size/mm	Detector	Cs-137 spike/Bq	Count rate/s^{-1}	Detection efficiency/%
FF	Disk	$\varphi 70 \times 7.4$	Coaxial	561.5	14.65	3.07
MF	Square chip	$50 \times 50 \times 1$	Coaxial	619.6	33.34	6.33
MF	Rod	$\varphi 10 \times 40$	Well	619.6	85.15	16.2
P	Rod	$\varphi 10 \times 25$	Well	636.1	103.0	19.0

[a]*FF* fibrous filter media, *MF* membrane filter media, *P* particles

Actually, it should be expected that radionuclides would dissolve in the solution to some degree during the extraction process. This would result in radionuclide loss. In principle, the soluble radionuclides, such as iodine and cesium, can be precipitated by adding the corresponding precipitants (e.g. [25, 26]), and these operations can be easily inserted before the present process of flocculation. The other operations such as washing, spinning, flocculation and filtration show no difference among radionuclides. Since the precipitants are distinct for the various radionuclides, the details of precipitation and other possible operations require further investigation in certain applications.

Conclusions

In relation to the sensitivity of the atmospheric particulate radionuclides monitoring, a novel sample preparation process for γ-ray spectrometry by extracting particles from filter samples was proposed to increase the detection efficiency. A device called a particle extractor was developed to extract the particles through a process of washing, spinning, flocculation and filtration. The main part of the particle extractor resembles household washing machines, but the new design results in lower levels of particle loss and a higher agitation speed. A nylon micropore filter membrane with a pore size of 0.1 μm was chosen for the filtration. Four extraction reagents were tested through the use of surrogate filter samples including chloroform, chloroform ethanol solution and two surfactant solutions. The NF surfactant solution was eventually selected because its recovery of 88% is close to the best one (90.9% by chloroform ethanol solution), but it is safer and more convenient to use. Flocculant of $Al(NO_3)_3 \cdot 9H_2O$ was applied in order to reduce filtration resistance and increase filtration efficiency. The extraction process was validated by the reference filter samples with a recovery rate of 87.5%. The samples with particles for γ-ray spectrometry were prepared by folding the final filter membrane. The detection efficiency of the samples was determined by spiking Cs-137. The results showed that the detection efficiency of the square chip sample by coaxial HPGe detector is twice of that of the traditional disk sample, while the detection efficiency of the rod sample in the well HPGe detector is 4.3 times higher. With the help of the process of extracting particles from the filter media, the MDC with the well detector can be lowered to 19% of the traditional one. The process was also validated by atmospheric Be-7 monitoring.

The results in this paper have proven that the detection efficiency can be significantly improved if the particles are separated from the filter media. This technique can be improved further in certain applications.

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