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Preliminary study on aerosol particle addition calibration method for on-line quantitative analysis of airborne radioactive particles with ICP-MS

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An ambient aerosol concentration enrichment system coupled with ICP-MS for real-time monitoring of airborne radioactive particles is now under development. ICP-MS is very sensitive to sample introduction conditions, so it is necessary to develop an easy-use calibration method for on-line quantitative analysis in field application. In this paper, a calibration method using standard solution instead of monodisperse particles was established and validated preliminarily. First of all, four parameters for the method were determined experimentally, including: uptake flow rate and nebulisation efficiency of the Microconcentric nebuliser, nebulisation/transport efficiency of Aridus Desolvating Sample Introduction System, and Relative Sensitivity Factor between ¹⁵⁹Tb and ¹⁷⁴Yb. Then, monodisperse terbium nitrate particles were generated by a commercial Vibrating Orifice Aerosol Generator. Continuous aerosols of ytterbium nitrate droplets were nebulised from standard solution. They were mixed together, desolvated through the membrane dryer and introduced into ICP-MS for on-line analysis of terbium nitrate particles. The air sampled from nuclear environment was also introduced into ICP-MS to investigate the effect of flow rate on instrument responses. Finally, atom numbers of ¹⁵⁹Tb in discrete terbium nitrate particles were determined using the calibration method and compared to the calculated value. Results show that when air flow rate increase from 10 mL min⁻¹ to 100 mL min⁻¹, the ratio of ¹⁵⁹Tb ion count to ¹⁷⁴Yb ion intensity keeps constant although instrument sensitivity decreases by a factor of 25. The relative standard deviation of ¹⁵⁹Tb atom number measured is better than 18%. The discrepancy with the calculated value could be attributed to the over-estimation of atom number in the particles generated by VOAG because there was some liquid leakage in the VOAG.

Keywords: aerosol particle addition calibration method; on-line quantitative analysis; airborne radioactive particles; ICP-MS

1. Introduction

Commercial instruments for continuously monitoring alpha emitting radionuclides in airborne particles are now available. However, the result may be seriously interfered by radon progeny, filter background and aerosol dust, thus the spectrum analysis algorithm is

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often complex [1]. Several types of aerosol mass spectrometry (AMS) have been developed for on-line analysis of aerosol particles [2,3]. Two of them are now commercially available, including Aerodyne AMS and Aerosol Time-of-Flight Mass Spectrometry (TSI Inc.). However, they are mainly used for on-line analysis of organic species and fusible elements, but not suitable for refractory elements. It is also difficult to obtain quantitative results of species in the particle. For the purpose of personal health and environmental protection in nuclear environment, it is necessary to develop an on-line technique for fast, sensitive and accurate analysis of airborne radioactive particles.

As one of the most widely used MS, ICP-MS offers very low detection limit, high sensitivity, and fast analysis of inorganic components and isotopes. Solution nebulisation is the main sample introduction mode in which solution is nebulised into aerosol droplets and introduced into ICP. Off-line analysis of fg level plutonium in atmospheric particles has been reported [4]. However, the sampling procedure is time-consuming and the chemical process is complex. Since the 1990s, techniques using ICP-MS for on-line analysis of heavy metal and rare earth elements (REEs) in aerosol particles have been developed in laboratories [5–9]. Previous research shows that counting efficiency for particle concentration with ICP-MS is near 100%, and the detection limit for Pb, Zn and Tb could be down to sub-fg and fg level. It seems that ICP-MS has potential to be a powerful tool for on-line analysis of transuranium element in aerosol particles.

The technique using ICP-MS described above is still restricted in wide application of real-time monitoring of ambient aerosol, because sample flow rate is limited to be below 100 mL min^{-1} in order to maintain Ar-ICP. Several sampling interfaces coupled with Ar-ICP-MS have been introduced to convert carrier gas from air to argon-air by means of virtual impactor and Differential Mobility Analyzer [10,11]. Sioutas *et al.* [12–14] reported a Versatile Aerosol Concentration Enrichment Systems that could simultaneously concentrate ambient aerosol by a factor of 20~30. When these systems were coupled with aerosol mass spectrometry, the detection limit of instruments and time response can both be improved [15–17]. In our laboratory, an ambient aerosol concentration enrichment system coupled with Ar-ICP-MS is under development now. The system is a combination of aerosol particle condensation growth technique and concentration enrichment technique. The ambient aerosol of 1 L min^{-1} is sampled by a rotary pump and mixed with 10 L min^{-1} argon which is saturated by n-butanol vapour. The particles with size range from nanometer to micron can grow to several microns in a condenser under controlled operation conditions. Subsequently, the concentration of grown particle is enriched by a virtual impactor with cutoff diameter of $2.5 \mu\text{m}$. After desolvation process in a membrane dryer, the concentrated aerosol carried by 1 L min^{-1} argon-air (10:1) is introduced into Ar-ICP-MS for on-line analysis. The detection limit for species in the particles would be improved as particles concentration increases one order of magnitude in optimal condition. Nevertheless, it is necessary to investigate the influence of argon-air flow (100 mL min^{-1} air) because instrument is very sensitive to sample introduction conditions, such as flow rate and species.

When airborne radioactive particles with low concentration are introduced into ICP-MS, discrete signal pulses corresponding to individual particles can be observed. If standard particle sample is available, it would be simple to calibrate ICP-MS in real-time for on-line quantitative analysis. Unfortunately, this kind of standard particle is not commercially available. The monodisperse particles generated by a commercial Vibrating Orifice Aerosol Generator (VOAG) are often used as size standard for size calibration of instrument in aerosol measurement. Previous research has shown that the diameters

determined by optical microscope or Scanning Electronic Microscope are in good agreement with the calculated values [18,19]. In field application, it is unpractical to generate monodisperse particles by VOAG because the preparation process is troublesome, especially because the flow rate cannot match up with ICP-MS. So it is necessary to develop an easy-use method for instrument calibration in real-time. A calibration method using desolvated standard solution has been introduced for quantitative analysis of some solid samples during the development of Laser Ablation ICP-MS [20–22]. Results show that the measurement uncertainty of element concentration in samples could be better than 10% and the relative standard deviation could be a few percentage points. So it is worth while investigating whether a calibration method using standard solution could be used for on-line quantitative analysis of airborne particles with ICP-MS.

In this paper an aerosol particle addition calibration method was described in detail and validated preliminarily using artificially generated particles containing REEs. First of all, four key parameters were determined experimentally, including: uptake flow rate and nebulisation efficiency of the Microconcentric nebuliser (MCN), nebulisation/transport efficiency of Aridus, and Relative Sensitivity Factor (RSF) between ^{159}Tb and ^{174}Yb under different air flow rates. Then, monodisperse terbium nitrate particles were generated by VOAG. Continuous aerosols of ytterbium nitrate droplets were nebulised from standard solution. They were mixed together, desolvated through the membrane dryer and introduced into ICP-MS for on-line analysis of terbium nitrate particles. The air sampled from nuclear environment was also introduced into ICP-MS to investigate the effect of flow rate on instrument responses. Finally, ^{159}Tb atom numbers in discrete terbium nitrate particles were determined using the calibration method and compared to the calculated value.

2. Experimental

2.1 Instruments and reagents

Element ICP-MS was manufactured by Finnigan MAT Inc. (Now Thermo Fisher Inc.). Aridus Desolvating Sample Introduction System was manufactured by CETAC Technology. MCN (manufactured by Glass Expansion Inc.) is a MicroMist nebuliser in combination with Tracey cyclonic spray chamber. Model 3450 VOAG and Model 3936L Scanning Mobility Particle Sizer (SMPS) were both manufactured by TSI Inc.

Nitric acid and 2-propanol are both analytical-reagent grade. 18.2 MΩ cm deionised water was produced by a Milli-Q system (Millipore Inc.). Certified single element standard solutions of natural In, Tb, Yb, Tm ($1000\ \mu\text{g mL}^{-1}$) were bought from National Research Center of Certified Reference Materials (Beijing, China).

2.2 Principle

As shown in Figure 1, two-channel introduction mode was used. In one channel, terbium nitrate standard solutions ($V_{2\% \text{HNO}_3} : V_{2\text{-propanol}} = 1 : 1$) of two concentrations were sequentially feed into VOAG to generate monodisperse droplets. The droplets were carried by argon with high flow rate and desolvated partly in the transport process. Adjustable flow of monodisperse particle was sampled through the hole at the outlet of sampling chamber. In the other channel, continuous aerosol was nebulised from ytterbium nitrate standard solution (2% HNO_3) by MCN. The monodisperse particles and

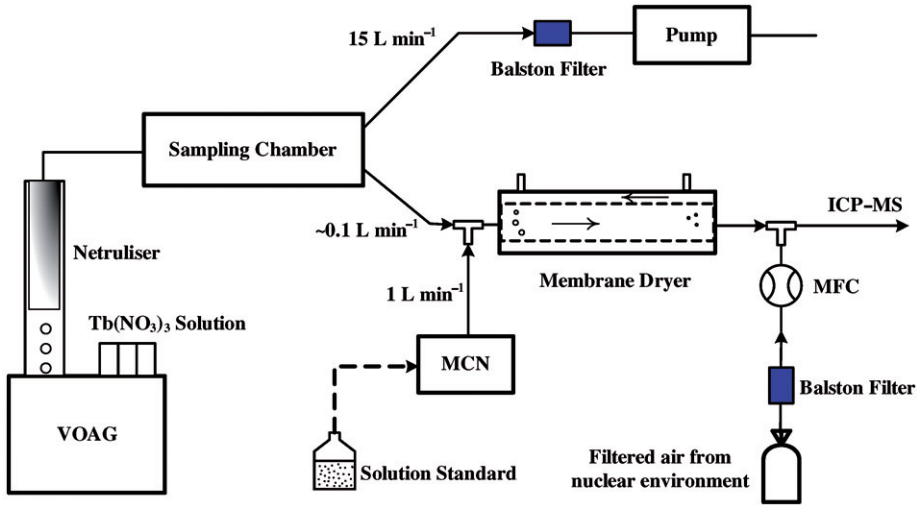


Figure 1. Schematic of the experiment for on-line quantitative analysis of REEs particles with ICP-MS.

continuous aerosol were mixed together at a tee connection and then introduced into Aridus for full desolvation. Nebuliser of Aridus was removed to avoid loss of particle, so it was used only as a membrane dryer. The air sampled from nuclear environment, in which methane and carbon monoxide of several percentage points were present while the main component was nitrogen, was filtered and introduced at the outlet of membrane dryer to investigate the influence of flow rate and species on instrument sensitivity.

The atom number of ^{174}Yb that reaches ICP per minute is:

$$N_{174} = Q_{\text{up}} \cdot C_{174,\text{st}} \cdot \eta_a \cdot \eta_{\text{trans}} \cdot N_A / M_{174} \quad (1)$$

where Q_{up} is uptake flow rate of MCN, $C_{174,\text{st}}$ is mass concentration of ^{174}Yb in standard solution, η_a is the ratio of element mass in particle reached the outlet of membrane dryer to that is uptaken by MCN,

$$\eta_a = \eta_{\text{MCN}} \cdot \eta_{\text{MD}} \quad (2)$$

where η_{MCN} is nebulisation efficiency of MCN, η_{MD} is particle transport efficiency in the membrane dryer, η_{trans} is particle transport efficiency from the outlet of membrane dryer to ICP, N_A is Avogadro number, M_{174} is atomic weight of ^{174}Yb .

Initial diameter of a droplet generated by VOAG is [23]:

$$D_d = \left(\frac{6Q_{\text{VOAG}}}{\pi f} \right)^{1/3} \quad (3)$$

Then atom number of ^{159}Tb in an individual particle can be calculated by:

$$N_{159,\text{c}} = \frac{\pi D_d^3 C_{\text{mv}}}{6} \frac{N_A}{M_{\text{Tb}(\text{NO}_3)_3}} = \frac{Q_{\text{VOAG}} C_{\text{mv}} N_A}{f M_{\text{Tb}(\text{NO}_3)_3}} \quad (4)$$

where Q_{VOAG} is liquid feed rate, f is vibrating frequency, C_{mv} is mass concentration (m/v) of terbium nitrate solution, $M_{\text{Tb}(\text{NO}_3)_3}$ is formula weight of terbium nitrate.

Previous research has shown that $\text{Tb}(\text{NO}_3)_3$ and Y_2O_3 particles could be ionised fully in ICP when their physical diameter is smaller than $3\ \mu\text{m}$ [9,24,25]. Peak jump mode between $m/z = 159$ and 174 is used to determine the ion count of $^{159}\text{Tb}^+$ ($n_{159,m}$) in single pulse corresponding to discrete particle and intensity of $^{174}\text{Yb}^+$ ($n_{174,m}$) from continuous aerosol. There is a relationship between them:

$$\frac{n_{159,m}}{n_{174,m}} = k_{159/174} \frac{N_{159}}{N_{174}} \quad (5)$$

where N_{159} is the real atom number in $\text{Tb}(\text{NO}_3)_3$ particle. $k_{159/174}$ is RSF between ^{159}Tb and ^{174}Yb , and can be defined as:

$$k_{159/174} = \frac{R_{159/174,m}}{R_{159/174,t}} \quad (6)$$

where $R_{159/174,t}$ and $R_{159/174,m}$ are the true value and the measured value of element ratio respectively in the solution.

Then

$$N_{159,m} = \frac{Q_{\text{up}} C_{174,\text{st}} \eta_{\text{MCN}} \eta_{\text{MD}} \eta_{\text{trans}} N_{\text{A}} n_{159,m}}{M_{174} k_{159/174} n_{174,m}} \quad (7)$$

The $N_{159,m}$ obtained was compared with $N_{159,c}$ to validate the method described above.

2.3 Measurement of four parameters

2.3.1 Q_{up} and η_{MCN} of MCN

MCN was used as sample introduction system coupled with ICP-MS. Q_{up} is determined by weighing the mass decrement of solution after a period of sample introduction. When ytterbium nitrate standard solution was nebulised, the drain was pumped and collected into a drain bottle. After a few minutes, the mass decrement of the standard solution and the drain were both weighed. The drain was also nebulised and introduced into ICP-MS subsequently to measure the intensity of $^{174}\text{Yb}^+$, so

$$Q_{\text{up}} = \frac{\Delta m_0}{\Delta t} \quad (8)$$

and

$$\eta_{\text{MCN}} = 1 - \frac{\Delta m_1}{\Delta m_0} R_{\text{MCN},174} \quad (9)$$

where Δt is sample introduction time, Δm_0 is the mass decrement of standard solution, Δm_1 is the mass increment of the drain, $R_{\text{MCN},174}$ is the ratio of $^{174}\text{Yb}^+$ intensity in drain to that in standard solution.

2.3.2 Nebulisation/transport efficiency of Aridus and particle size distribution at the outlet

When Aridus is used as solution introduction system, there are three processes that could cause the loss of analyte: the drain, the transport process in tube and membrane, and the diffusion through membrane. The memory effect of Aridus is very slight, so analyte loss in

the tube and membrane can be ignored. It is very difficult to quantify the analyte loss through membrane. The nebulisation efficiency of Aridus is much higher than that of MCN. We can assume that the nebulisation efficiency of Aridus is 1, then transport efficiency (η_{MD}) in Equation (2) can be replaced by nebulisation/transport efficiency ($\eta_{MD,0}$). Filter collection method was used to determine $\eta_{MD,0}$.

(1) Particle size distribution at the outlet of Aridus

Determination of the particle size distribution at the outlet of Aridus is significant for estimation of η_{trans} based on empirical formula and selection of appropriate filter film for particles collection.

2% HNO₃ blank solution, indium nitrate solutions of 1 $\mu\text{g g}^{-1}$ and 50 $\mu\text{g g}^{-1}$ were nebulised sequentially. Flow at the outlet was divided into two parts by a 'Y' type tube connection. Particle size distribution in one channel was scanned by SMPS and flow in the other channel was released to the atmosphere.

(2) Selection of filter and on-line determination of total collection efficiency with ICP-MS

HB1 polypropylene filter and 3M filter were selected because they have low resistance, high collection efficiency and low REEs background. When the filter was mounted to the outlet of Aridus, the pressure in Aridus would slightly increase. So the value of $\eta_{MD,0}$ determined under this condition might deviate slightly from that under normal conditions.

The total collection efficiency of filter for HB1 was:

$$\eta_{\text{filter}} = 1 - R_{\text{HB1},115} \quad (10)$$

and for 3M:

$$\eta_{\text{filter}} = 1 - R_{\text{3M},115} \quad (11)$$

where $R_{\text{HB1},115}$ and $R_{\text{3M},115}$ are ratios of $^{115}\text{In}^+$ intensity in downstream to that in upstream for HB1 and 3M filters, respectively.

(3) $\eta_{MD,0}$ of Aridus

Ytterbium nitrate standard solution was nebulised by Aridus. The desolvated particles were collected by the filter at the outlet. The mass decrement of standard solution after a period was weighed. A known quantity of ^{169}Tm was added onto the filter to indicate recovery rate in the whole chemical process (ashing, dissolution and transfer). A series of standard solutions of natural ytterbium and thulium were prepared. The concentrations of ^{169}Tm and ^{174}Yb were measured with external calibration method using ICP-MS. Assume that recoveries for ^{169}Tm and ^{174}Yb were the same, then

$$\eta_{MD,0} = \frac{C_{174} \cdot M_t}{C_{174,0} \cdot \Delta M_{st} \cdot \eta_{\text{filter}} \cdot \eta_{\text{recovery}}} \quad (12)$$

where C_{174} is the concentration of ^{174}Yb in solution, M_t is the quantity of solution after chemical process for filter, $C_{174,0}$ is the concentration of ^{174}Yb in ytterbium nitrate standard solution, ΔM_{st} is the mass decrement of standard solution, η_{recovery} is the recovery rate of ^{169}Tm in the whole chemical process.

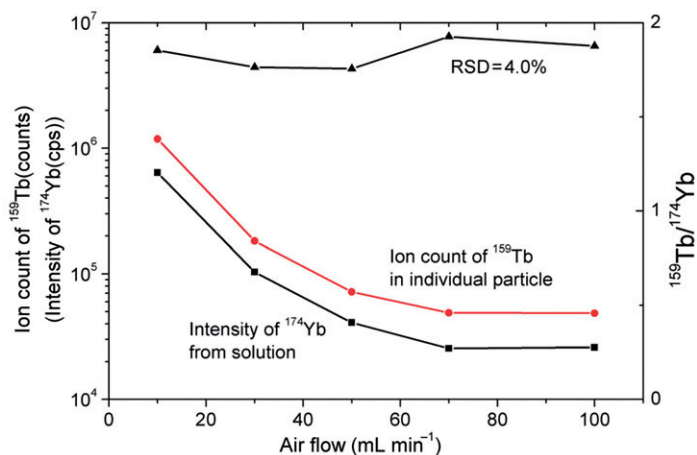


Figure 2. Effect of air flow rate on ion count of ^{159}Tb in individual particles and intensity of ^{174}Yb from continuous aerosol.

2.3.3 RSF between ^{159}Tb and ^{174}Yb

The terbium nitrate standard solution and ytterbium nitrate standard solution were mixed to prepare a synthetic standard solution. It was nebulised by Aridus and introduced into ICP-MS to determine $^{159}\text{Tb}/^{174}\text{Yb}$ ratios under different air flow rates. Thus, $k_{159/174}$ can be obtained by Equation (6).

3. Result and discussion

3.1 Effect of air flow rate on instrument response for discrete Tb particle and continuous aerosol of Yb particles

Figure 2 shows that instrument sensitivity decreases by a factor of 25 when air flow increases from 10 mL min^{-1} to 100 mL min^{-1} . Even so, the count of $^{159}\text{Tb}^+$ from discrete particle and the intensity of $^{174}\text{Yb}^+$ from continuous aerosol vary synchronously and $n_{159,m}/n_{174,m}$ keeps constant. It means that aerosol particle addition calibration method could be dependable and practical. It also indicates that the sampling system described above can be well coupled with ICP-MS for real-time monitoring of ambient aerosol.

3.2 Q_{up} and η_{MCN} of MCN

A ytterbium nitrate standard solution with about 20 ng g^{-1} ^{174}Yb was sampled continuously by MCN for about 15 min. Results show that Q_{up} is $(82.1 \pm 1.1)\text{ mg min}^{-1}$, $\Delta m_1/\Delta m_0$ is $73.0\% \pm 1.0\%$, $R_{MCN,174}$ is 1.21 ± 0.01 . Then η_{MCN} calculated is 11.4% with Equation (9). This value is consistent with the values reported in the literature [26,27].

3.3 Characterisation of Aridus

3.3.1 Particle size distribution at the outlet

Droplets nebulised from solution are desolvated efficiently in the membrane dryer, the size distributions are all lognormal and the mode diameters are below 100 nm as

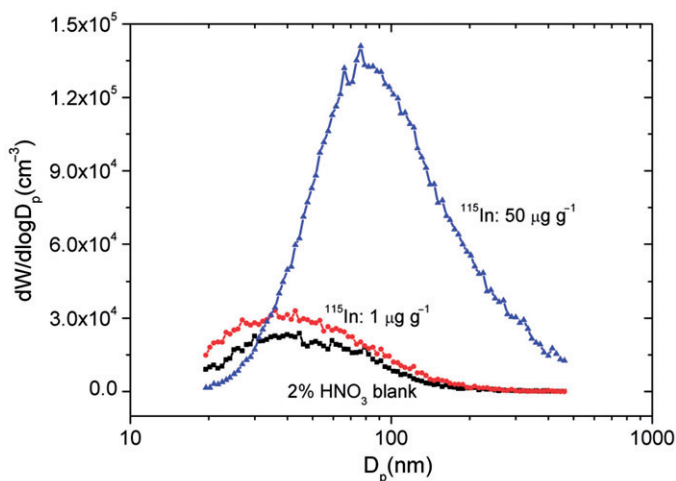


Figure 3. Size distributions of particle at the outlet of Aridus desolvating sample introduction system.

shown in Figure 3. The distribution tends towards larger diameter as solution concentration increases. Since concentration of ytterbium nitrate solution used is much lower than $1 \mu\text{g g}^{-1}$, the distribution is similar to that from 2% HNO_3 . Loss mechanism of nanoparticles in the tube under laminar flow is mainly diffusion loss [28]. Therefore η_{trans} in Equation (7) should be higher than 99.9%.

3.3.2 $\eta_{\text{MD},0}$ of Aridus

Total collection efficiencies of HB1 and 3M filters were 98.7% and 99.4%, respectively. Recovery in whole chemical process was $(92.6 \pm 1.9)\%$. The dependence of $\eta_{\text{MD},0}$ on flow rate of sweep gas is shown in Figure 4. $\eta_{\text{MD},0}$ increases as the flow rate of sweep gas increases. The difference between HB1 and 3M filters is due to their resistances difference.

3.4 Determination of ^{159}Tb atom number in individual particle

The sweep gas of membrane dryer was fixed at 2 L min^{-1} . When only terbium nitrate particles were introduced, the signal pulses observed were almost the same compared with that when both terbium nitrate particles and ytterbium nitrate droplets were simultaneously introduced. It indicates that coagulation of terbium nitrate particles and ytterbium nitrate droplets was not serious. The values of ^{159}Tb atom number measured in particles of two diameters are summarised in Table 1. The relative standard deviation of $N_{159,m}$ is better than 18%; however, the value is only about 40% of the calculated value.

It was observed in the experiment that liquid leaks through drain valve of VOAG since it has been operated for nearly nine years. Therefore the conditions used in our experiment were different from nominal conditions presented in the instruction manual of VOAG [23]. The Q_{VOAG} in Equation (4) would be $0.492 \text{ mL min}^{-1}$, which was 64% higher than nominal value. A factor of 1.64 might be used to correct $N_{159,m}/N_{159,c}$ ratio, as advised by technical engineer from TSI Inc.

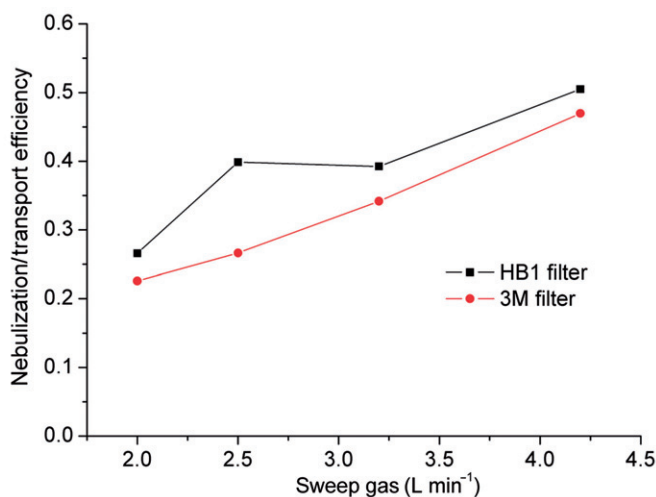


Figure 4. Dependence of nebulisation/transport efficiency of Aridus on flow rate of sweep gas.

Table 1. Summary of measured atom number of ¹⁵⁹Tb in individual particles under different air flows while sweep gas was fixed at 2 L min⁻¹.

$C_{174,st}(\text{ng g}^{-1})$	Air flow (mL min ⁻¹)	$n_{174,m}(\text{cps})$	$n_{159,m}(\text{count})$	$k_{159/174}$	$N_{159,m}(\text{atom})$
(A) particle I 15.869	10	6.39×10^5	1.18×10^6	1.35	3.18×10^9
	30	1.03×10^5	1.82×10^5	1.49	2.74×10^9
	50	4.09×10^4	7.18×10^4	1.65	2.46×10^9
	70	2.54×10^4	4.90×10^4	1.50	2.97×10^9
	100	2.59×10^4	4.86×10^4	1.50	2.89×10^9
Avg(atom)					2.85×10^9
RSD					9.4%
$N_{159,c}/\text{atom}$					6.94×10^9
$N_{159,m}/N_{159,c}$					0.41
(B) particle II 3.208	20	3.58×10^4	3.00×10^3	1.48	2.65×10^7
	20	2.89×10^4	1.93×10^3	1.48	2.11×10^7
	20	1.12×10^4	1.06×10^2	1.48	2.99×10^7
	Avg(atom)				
RSD					17.2%
$N_{159,c}(\text{atom})$					6.94×10^7
$N_{159,m}/N_{159,c}$					0.37

It is difficult to quantify η_{MD} without disturbing the normal operation condition. η_{MD} obtained is a little lower than the real value under normal operation condition. Inner pressure rises when the filter is mounted to the outlet of membrane dryer. Thus, more analyte would diffuse through the membrane and be carried away by sweep gas. The analyte loss may increase by a few percentage points. Besides, $k_{159/174}$ determined off-line

might be a little different from that in the process of on-line analysis, although the operation parameters were nearly the same.

4. Conclusions

When air flow increases from 10 mL min^{-1} to 100 mL min^{-1} , ratio of ^{159}Tb ion count to ^{174}Yb ion intensity keeps constant even though instrument sensitivity decreases by a factor of 25. It means that aerosol particle addition calibration method could be dependable. The method has been established and validated preliminarily in this paper. Thus, the uptake flow rate and nebulisation efficiency of MCN were determined accurately. The dependence of nebulisation/transport efficiency on flow rate of sweep gas in Aridus was determined by the filter collection method. The atom number of Tb in individual particles was determined. The relative standard deviation is better than 18%. The discrepancy with the calculated value could be attributed to the over-estimation of atom number in the particles generated by VOAG because there was some liquid leakage in the VOAG. Results show that the aerosol particle addition method would be practical for real-time monitoring of airborne radioactive particles using ICP-MS.

Further research is still needed to validate the method accuracy. Off-line analysis using ICP-MS would be an alternative way to determine the average mass in monodisperse particles generated by VOAG. Besides, isotope dilution method is preferred because sensitivity differences among isotopes are less than elements.

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