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气载、液载颗粒物直接进样ICP-MS技术及其在核工业中的应用

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摘要：颗粒物分析在核、环境、生命科学等领域具有重要价值，不经复杂化学处理直接将颗粒物引入高灵敏电感耦合等离子体质谱（ICP-MS）分析，具有分析速度快、可获取单颗粒特征信息、化学处理工作量小等优势。本文综述了气载、液载颗粒物直接进样ICP-MS分析技术，介绍了该技术在高效过滤器下游复杂基体气溶胶样品中的超痕量钚检测和悬浮液中单个氧化铒颗粒的高精度同位素分析中的应用，并从技术发展和分析应用角度进行了展望。

关键词：颗粒物；直接进样；电感耦合等离子体质谱（ICP-MS）；核工业；铀；钚
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Direct Introduction of Airborne and Suspension Particles into ICP-MS for On-line Elemental or Isotopic Analysis and Its Applications in Nuclear Field

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Abstract: Particle analysis is of great significance in nuclear, environmental, life science, etc. Direct introduction of airborne or suspension particles into highly sensitive inductively coupled plasma mass spectrometry (ICP-MS) for on-line elemental and isotopic analysis has advantages, such as simplifying chemical treatment, avoiding contamination and obtaining fingerprint information. This paper first reviewed this technology, including principle, calibration method, sample introduction method and ion detection method. Then, some studies on the principle and calibration method conducted by our group were introduced. Two cases of its application in nuclear field were presented: determination of ultra-trace plutonium concentration in aerosol samples with complicated matrix downstream of nuclear-grade filters, and precise measurement of erbium isotopes in suspended erbium oxide particles as uranium surrogates. Finally, further develop-

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ment and application of this technology were proposed.

Key words：particle；direct introduction；inductively coupled plasma mass spectrometry (ICP-MS)；nuclear field；uranium；plutonium

环境样品颗粒物分析技术在核保障、核法证、核环境监测等领域扮演着重要角色。目前，国内外已发展了基于SEM/EDX[1]、FT-TIMS[2-4]、SIMS[5-6]、LA-(MC)-ICP-MS[7-8]等的颗粒物分析技术，通常需要筛选定位、化学处理后进行分析测量。不经复杂化学处理直接将气载颗粒物（气溶胶）[9-14]、液载颗粒物（胶体[15-19]、悬浮液[20-21]）引入ICP-MS分析，具有分析速度快、可获取单颗粒特征信息、化学处理工作量小等优点。单颗粒ICP-MS（sp-ICP-MS）是一种颗粒物直接进样ICP-MS分析技术，在生态环境、医疗健康、工业生产等领域展示了强大的应用潜力[22-27]，并于2017年被ISO推荐为纳米粒子粒径分布和浓度的标准测量方法[28]。

自2000年以来，针对核工业领域的放射性废气和废水，本实验室将多种环境样品（气溶胶[29-30]、土壤[31-32]、水[33]）经化学处理后，采用ICP-MS测定超痕量钚。为加快时间响应，减少化学处理工作量以及可能引入的沾污，获取单颗粒携带的指纹信息，自2009年以来，本课题组开展了针对气载、液载颗粒物的sp-ICP-MS分析技术，先后对稀土/铀气溶胶单粒子元素含量[34-36]、过滤后气体中超痕量钚浓度[37-38]、悬浮液稀土单粒子同位素[39]进行在线检测分析；开展了气溶胶富集进样技术[40-41]、ICP等离子体数值模拟[42]和颗粒物进样等离子体参数实验诊断[43]、颗粒物蒸发凝结参数和模型[44-45]等研究。

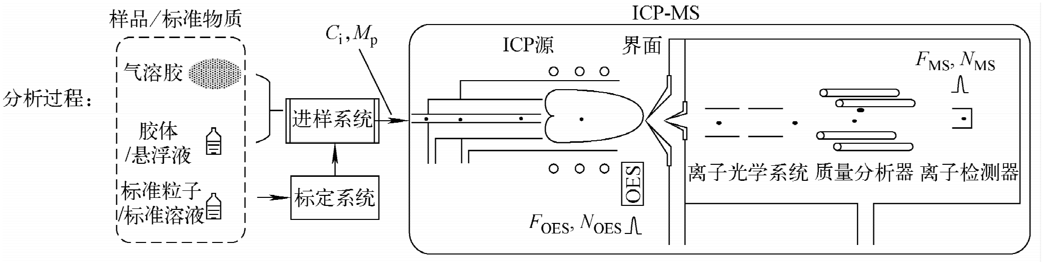
本文将简要介绍sp-ICP-MS技术原理，梳理关键技术、影响因素和注意事项，详细介绍本课题组在标定和进样方面开展的特色工作，展示该技术在纳米粒子超痕量核素检测、单粒子高精度同位素分析等方面的应用，并展望该技术的发展和应用方向。

1 sp-ICP-MS技术简介

1.1 分析原理

sp-ICP-MS技术的分析对象包括气溶胶、胶体、悬浮液等气载或液载颗粒物，分析过程包括进样、蒸发/原子化/电离、离子提取、离子传输调制、质量分析和离子检测，对应的物质形态、理化过程及影响参数示于图1。常见的ICP-MS仪器无需进行硬件改动便可用于单颗粒分析，只需针对特定样品选择合适的进样方式。

当颗粒进样浓度足够低时，在ICP源处可以观测到离散的特征发射光谱瞬态信号，持续时间为ms级[9,46-51]；MS离子检测器可以检测到离散的瞬态离子信号，脉冲宽度为数百



<table>
<tr><td>物质形态：</td><td colspan="2">颗粒物/液滴</td><td colspan="3">氩气载带的
颗粒物/液滴</td><td>干燥粒子</td><td colspan="2">原子团</td><td colspan="2">离子团</td><td colspan="2">瞬态离子信号</td></tr>
<tr><td>理化过程：</td><td colspan="4">采样/气溶胶化、载气置换、浓度富集、分离</td><td colspan="3">蒸发、原子化、电离</td><td colspan="2">离子提取</td><td>离子传输调制、质量过滤</td><td colspan="2">瞬态信号检测</td></tr>
<tr><td>影响参数：</td><td>M_p、C_p</td><td colspan="3">$f_{进样}$、$\eta_{进样}$</td><td colspan="3">$\eta_{蒸发}$、$\eta_{电离}$</td><td colspan="2">$\eta_{界面提取}$</td><td>$\eta_{离子传输}$</td><td>$\eta_{检测}$</td><td>N_{MS}、F_{MS}</td></tr>
<tr><td>分析应用：</td><td colspan="3">瞬态信号频率、强度</td><td colspan="6">数浓度、等效直径、粒径分布、元素含量分布、同位素比值</td><td colspan="3">环境、材料、食品、医药、工业、核</td></tr>
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图1 颗粒物直接进样ICP-MS技术的原理示意图

Fig. 1 Schematic of direct introduction of particles into ICP-MS for on-line elemental and isotopic analysis

μs[10,50,52-57]。特征发射光谱瞬态信号频率（F_{OES}，pulse/s）、瞬态离子信号频率（F_{MS}，pulse/s）与对应颗粒的数目进样通量（particle/s）之间应满足式（1）的关系：

$$F_{\text{MS}} = F_{\text{OES}} f_{\text{MS}} = C_{\text{i}} Q_{\text{载气}} f_{\text{ICP}} f_{\text{MS}} \qquad (1)$$

式中：C_{i} 是颗粒在 ICP 炬管进口处的数体积浓度；$Q_{\text{载气}}$是载气的体积流率；f_{ICP}是颗粒在 ICP 源中的传输效率；f_{MS}是离子团在 MS 中的传输效率。

瞬态离子信号强度（N_{MS}，count）与对应颗粒中目标元素的质量（m_{p}，kg）满足式（2）的关系：

$$N_{\text{MS}} = m_{\text{p}}\left(\frac{AN_{\text{Av}}}{M_{\text{M}}}\right)(\eta_{\text{蒸发}}\eta_{\text{电离}}\eta_{\text{界面提取}}\eta_{\text{离子传输}}\eta_{\text{检测}}) \qquad (2)$$

式中：A 是目标核素的丰度，N_{Av}是阿佛加德罗常数，M_{M} 是元素的相对原子质量，$\eta_{\text{蒸发}}$、$\eta_{\text{电离}}$、$\eta_{\text{界面提取}}$、$\eta_{\text{离子传输}}$、$\eta_{\text{检测}}$分别是目标核素在蒸发、电离、界面离子提取、离子光学系统/质量分析器、离子检测器的传输/利用效率。若进样颗粒为球形纯颗粒，则 ρ_{p} 和 D_{p} 分别是球形颗粒的密度和直径。与文献[58-60]相比，式（2）考虑了蒸发、离子检测两个因素。

在常见的溶液雾化进样 ICP-MS 分析中，

$$I_{\text{s}} t_{\text{dwell}} = (C_{\text{液}}\ Q_{\text{液}}\ \eta_{\text{雾化}})\left(\frac{AN_{\text{Av}}}{M_{\text{M}}}\right)(\eta_{\text{蒸发}}\eta_{\text{电离}}\eta_{\text{界面提取}}\eta_{\text{离子传输}}\eta_{\text{检测}}) \qquad (3)$$

在气体直接进样 ICP-MS 分析中，

$$I_{\text{s}} t_{\text{dwell}} = (C_{\text{气}}\ Q_{\text{气}})\left(\frac{AN_{\text{Av}}}{M_{\text{M}}}\right)(\eta_{\text{电离}}\eta_{\text{界面提取}}\eta_{\text{离子传输}}\eta_{\text{检测}}) \qquad (4)$$

式中：I_{s} 是离子计数率（count/s），t_{dwell}是测量时间（s），$C_{\text{液}}$ 和 $Q_{\text{液}}$ 分别是液体中的元素浓度和液体进样速率，$\eta_{\text{雾化}}$ 是雾化进样系统的样品利用效率，$C_{\text{气}}$ 和 $Q_{\text{气}}$ 分别是气体中的元素浓度和气体进样速率。式（2）～（4）构成了 sp-ICP-MS 技术的原理基础。

1.2　关键技术

1.2.1　标定方法　标定方法是 sp-ICP-MS 技术的关键，已报道的方法有标准粒子法、标准溶液单分散液滴法、标准溶液连续雾化法[26]和标准气体发生法[13]。标准粒子法是选择分析特性（粒径、热物理参数等）与待测粒子相似的标准粒子，其成分和粒径已知，可直接比较仪器对两者的响应。目前，许多国家的计量部门推出了认证纳米粒子参考物质（Au、Ag、TiO_2、聚苯乙烯、SiO_2、Al_2O_3 等）[26]，此外，英国 BBI 和美国 NanoComposix 等公司销售的 Au[18,55,61]、Ag[55,62]、SiO_2[46,54,63]单分散粒子经准确表征（SEM、TEM 等）后可作为测试参考物质使用。该方法的优点是简单直接，缺点是标准粒子种类有限。标准气体法将气态的金属羟基配合物（$Cr(CO)_6$、$Mo(CO)_6$、$W(CO)_6$）[12-14]直接引入 ICP-MS 后，根据式（4）标定，但金属种类有限。

标准溶液单分散液滴法是利用标准溶液和专门的发生器产生粒径均一（单分散好）、元素含量可控的液滴用于 sp-ICP-MS 标定。可以利用压电陶瓷激励毛细管产生单分散微米级液滴，如振动孔气溶胶发生器[9,34,36]、单分散干燥微颗粒注射器[64]和单分散微液滴发生器[55]；还可以利用电分级原理选择单分散纳米级粒子，如差分迁移率谱仪[11]、离子迁移率谱仪[65]。由于需要专门的发生器，该方法使用存在不便。标准溶液连续雾化法利用超声雾化去溶[13-14]、微量雾化[62,66-69]、微量雾化去溶[35-38]、高效超微量雾化去溶[70-72]等进样系统，产生连续稳定、多分散、微米级液滴用于标定。为了改善稳定性，避免溶剂干扰，通常需要将雾化液滴去溶，粒径减小至亚微米级[36]。该方法的优点是标准溶液种类丰富且易获得，无需专门的单分散颗粒物发生器，可直接利用 ICP-MS 现有的雾化进样系统。

使用标准溶液单分散液滴法或标准溶液连续雾化法时，若样品颗粒及基体简单，可将其与标准溶液液滴交替进样；若基体复杂，仪器响应波动大，可将样品颗粒与标准溶液混合稀释进样，但此时较高的基线信号不利于检测弱信号[73]。若基体效应严重或需要进行超痕量分析时，可考虑使用目标核素的稀释剂标准溶液将其与样品颗粒同时进样，即在线同位素稀释法[35,38,74-75]。

1.2.2　进样方法　用于颗粒物直接分析的雾化进样系统按雾化效率 $\eta_{\text{雾化}}$高低大致可分为三类：1）中低效（1%～20%）的商用微量雾化进样系统[36,66,76-80]；2）中高效（20%～90%）的商用微量雾化去溶进样系统[36,66,76,81]；3）高效（>90%）、超微量雾化进样系统[71-72]和单液滴发生器[55,73,79]等。样品基体[36,66,80]和雾室（Scott≈PTFE<PP<glass）[81-82]对雾化效率均有影响。近年来，有报道采用离子交换树脂去除离子[83]、

电喷雾扫描电迁移率谱仪[84]等进样技术。

气载颗粒物直接进样的条件比较苛刻，因为ICP源处于常压环境且对进样条件相对敏感。当空气直接进样流量为100 mL/min时，ICP-MS灵敏度约下降至无空气进样时的1/30；若进一步增大空气流量，ICP源不稳定甚至会熄灭[36]。一种解决方式是将颗粒物经专门的进样装置[11,12,40,65]处理后以气载状态引入ICP源，这些进样装置具有气固分离、载气置换、浓度富集、标准在线加入等功能，能够在增大进样流量的同时缓解基体效应，最终实现加快时间响应、改善灵敏度。另一种解决方式是将气载颗粒物通过颗粒-液体收集器[85-88]高效收集到液体中，可溶性组分溶解到液体中，难溶性组分形成悬浮液，然后进样分析。前一种方法能够使颗粒始终保持气载状态，有利于测量粒度分布等原始信息，但系统通常较复杂，不利于获得较高的传输效率；后一种方法相对简单，能够区分可溶性和难溶性组分，关键是颗粒收集效率和后续进样时的样品利用效率。

1.2.3 离子检测方法 离子检测技术的发展及应用大大推动了sp-ICP-MS相关原理研究、分析应用和仪器研发。在早期研究中，为克服ICP-MS仪器对快信号的检测能力不足，Nomizu等[9-10,89]从二次电子倍增器处提取信号并进行模拟处理和数字处理（时间分辨达20 μs），观测到瞬态离子信号波形，获得了信号宽度、强度与粒径的关系，比较了峰面积法和峰高法。目前，Perkin Elmer[52,63,90]、Agilent[91]、Thermo Fisher[53]等公司生产的ICP-Q MS或ICP-SF-MS，在TRA或single particle模式下的时间分辨可达10～100 μs，配合使用定制的数据采集单元可获得5 μs的时间分辨[92]。此外，还报道了时间分辨为33 μs的ICP-TOF-MS原型仪器[93]。一种简单有效的瞬态信号检测方法是利用数字示波器观测二次电子倍增器处提取的信号，时间分辨可达μs级[54-55,57]，并深入研究了中心通道气流对信号宽度和强度的影响。研究和分析实践表明：时间分辨为数百μs时，能够获得较好的检出限[52,63,90,94]。

颗粒物中的元素组成和同位素比值是其指纹信息，具有重要的分析价值。对脉冲宽度仅为数百μs的单颗粒瞬态离子信号，时间分辨为ms级的sp-ICP-Q MS难以跳峰监测多个m/z处的离子信号，故无法进行单颗粒多元素分析。若时间分辨改善至数十μs，不仅有利于克服分子离子干扰（如进样SiO_2时克服$^{14}N_2^+$对^{28}Si的干扰[63]），还可以实现双质量数离子测量[90]，但测量不同步会导致比值存在偏差，计算得到的颗粒物质量分布也会有较大偏差。由于磁场扫描速度较慢，sp-ICP-SF-MS通过电场扫描获得较高的时间分辨（100 μs级），但比sp-ICP-Q MS慢，难以用于多元素分析。MC-ICP-MS通过多个离子检测器同时接收不同m/z处的信号，可实现高精度同位素分析[95]，本课题组采用MC-ICP-MS对悬浮液中氧化铒颗粒的同位素组成进行了高精度分析[39]。由于离子检测器的空间布放限制，MC-ICP-MS只能同时接收质荷比邻近的离子信号，故其在单颗粒多元素分析中的应用受到局限。ICP-TOF-MS能够接收同一推斥信号脉冲中的所有m/z离子[96]，因此是单颗粒多元素分析的理想手段[93,97]。

2 sp-ICP-MS 应用

2.1 原理研究

早期研究观察到单颗粒进样时散射光脉冲-OES特征发射光谱脉冲[98]、OES特征发射光谱脉冲-MS瞬态离子信号之间一一对应的关系[50]。为检验进样单颗粒与MS离子信号之间的对应关系，本课题组用振荡床发生氩气载带的、数浓度较低、大小为数百nm的稀土气溶胶粒子，一路（气流量为$Q_{载气}$）直接引入ICP-MS（Element 1型，Finnigan MAT公司产品），用于检测瞬态离子信号频率值$F_{\rm MS}$；另一路平行引入凝结核粒子计数器（3010型CPC，TSI公司产品，对大于20 nm粒子的计数效率为1[99]）测量浓度$C_{\rm i}$；对$F_{\rm MS}/Q_{载气} \sim C_{\rm i}$数据点进行线性拟合，得到斜率值1.09±0.08，截距值0.01±0.01，由式(1)可知，$f_{\rm ICP} \cdot f_{\rm MS} = 1.09 \pm 0.08$，据此判断ICP-MS对进样粒子的计数效率接近100%[34]。$f_{\rm ICP} \cdot f_{\rm MS}$略大于1，可能是$Q_{载气}$值偏小所致。用振动孔气溶胶发生器（3450型VOAG，TSI公司产品）产生单分散硝酸铽液滴，粒径大小和单分散性分别用激光粒度仪（8810型，中科院安徽光机所研制）和级联撞击器（Nano-MOUDI 125A型，MSP公司产

品）进行在线和离线检验，将这些液滴直接引入 ICP-MS 并测定单个液滴中^{159}Tb 的离子计数，再与液滴中 Tb 原子数目的计算值比较，即得仪器对不同大小颗粒的探测效率。结果表明：当硝酸铽粒子的物理直径在 0.4～2.5 μm（对应 Tb 质量为 10～10^4 fg）时，仪器响应为线性，探测效率为 2×10^{-5}[34]。

汇总文献报道的 sp-ICP-MS 对单个 Au 等颗粒的标定曲线，结果示于图 2。可知：1）不同仪器对不同元素颗粒的标定曲线斜率值差异较大，主要取决于仪器对相应元素的灵敏度，如 Agilent 7500 系列的四极杆 ICP-MS 对 Au 的探测效率为 1.5×10^{-5} 级[26,100-101]，ICP-SF-MS 的灵敏度通常较高[34,53,73]，而 ICP-TOF-MS 的探测效率略差[93]。2）对小颗粒的检测能力（标定曲线低端）受仪器灵敏度、本底和基体的制约，粒径检测下限通常为数十至数百 nm，且与元素有关[102]。3）对大颗粒的检测能力受不完全电离[51]和离子检测器饱和等因素的影响，导致离子计数偏离线性，文献报道 SiO_2 颗粒[63,80]、ZrO_2 胶体颗粒[17]、UO_2 胶体颗粒[19]、硝酸铽液滴[34]的粒径检测上限为 1～5 μm，Au 颗粒的粒径检测上限约为 200 nm[18,61]。

2.2　标定方法

本课题组用市售的雾化去溶进样系统（Aridus I, CETAC 公司产品）产生连续稳定的标定用气溶胶，对发生器雾化效率及输出气溶胶的特性开展大量表征工作。用扫描迁移率气溶胶谱仪（3936L 型 SMPS，TSI 公司产品）测量不同浓度标准溶液雾化时输出气溶胶的粒度谱，发现进样溶液浓度低于 1 μg/g 时，输出气溶胶小于200 nm，其粒度谱与2％HNO_3空白溶液相似。基于两种滤膜，采用滤膜收集法测定不同吹扫气流量下的雾化效率 $\eta_{雾化}$。结果表明，当吹扫气流量从 2.0 L/min 升至 4.2 L/min 时，$\eta_{雾化}$值从 20％增至 50％。与常规的雾化进样系统相比，雾化去溶进样系统在样品利用效率和缓解水基体影响方面有优势，但 $\eta_{雾化}$ 对吹扫气流量 $Q_{吹扫气}$ 敏感，实际分析时的吹扫气流量往往偏离标定时的吹扫气流量，由 $Q_{吹扫气}\sim\eta_{雾化}$ 曲线内插得到的 $\eta_{雾化}$ 值用于计算会引入一定误差。

为克服气溶胶、悬浮液直接进样时严重的基体效应，发展了气溶胶在线加入/稀释法。用 VOAG 发生单分散硝酸铽液滴作为待测颗粒，用 Aridus 发生连续稳定的硝酸镱气溶胶作为标定气溶胶，两者混合并加入不同流量的洁净空气以模拟基体效应，然后一起引入 ICP-MS 仪器进行分析。实验观察到，当空气流量从 0 增大到 100 mL/min 时，^{174}Yb离子计数率（I_{174}，指示仪器灵敏度）下降至先前的约 1/30，^{159}Tb 离子计数（N_{159}）同步变化，两者的比值保持稳定。N_{159} 和 I_{174} 是测量值，t_{dwell} 是设定值，C_{174} 是配制值，$Q_{液}$ 由称重法得到，$\eta_{雾化}$ 由滤膜收集法测定，考虑两核素灵敏度的相似性，根据式（2）和式（3）可以测定硝酸铽液滴中铽的质量 $m_{159,\mathrm{m}}$。在灵敏度下降数十倍的不利情况下，$m_{159,\mathrm{m}}$的测量精度达到 17％，比计算值 $m_{159,\mathrm{c}}$ 偏大 37％，误差主要来自 $\eta_{雾化}$ 和 $m_{159,\mathrm{c}}$。

为进一步检验上述方法，采用^{233}U气溶胶在线加入法对单分散天然铀液滴中的^{238}U含量

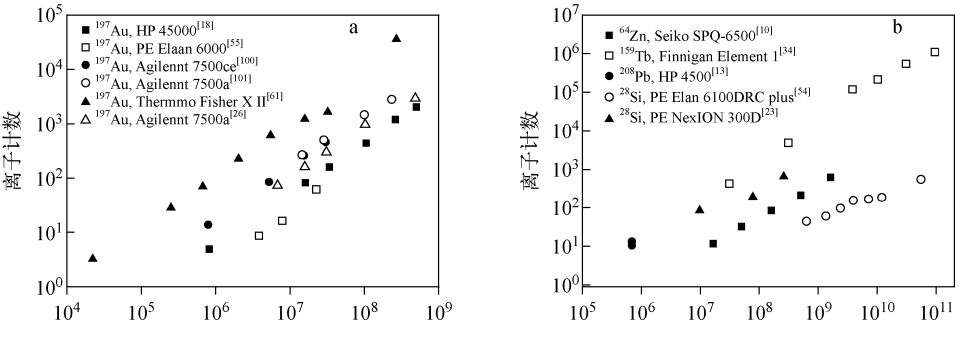

图 2　sp-ICP-MS 对 Au 粒子（a）和其他单粒子（b）的标定曲线文献值

Fig. 2　Calibration curves of single particle ICP-MS for Au particles (a) and other types of particles (b) retrieved from literatures

进行定量分析[35]。采用以下措施改善方法的准确性：对发生器进行简化改造，吹扫气流量在2.5、2.8 L/min时，发生器的雾化效率实测值分别为5.54%和5.59%；考虑吹扫气流量和引入氮气对^{233}U、^{238}U质量歧视的影响。结果表明，单颗粒中^{238}U原子个数测量值的精度达5.6%，比计算值偏大19%。通过以上措施，单个液滴中待测核素的质量测量值的准确度改善显著，但仍高于计算值（由VOAG工作参数和标准溶液浓度计算得到），因此推测计算值可能偏低。

2.3 分析应用

2.3.1 高效过滤器下游复杂基体气溶胶样品中的超痕量钚检测 钚材料在爆炸、燃烧或事故条件下会产生钚气溶胶，国内外对其形成机理、源项特征、净化、取样监测等开展了大量研究[103-104]。由于吸入后会造成内照射危害，钚气溶胶必须经核级高效过滤器净化，经检测达标后才能排放。采用大流量取样-化学处理-ICP-MS测量方法[29-30]对钚气溶胶进行监测，虽然能获得极低的检出限，但取样时间长、化学处理工作量大、易受沾污。钚气溶胶α连续监测仪[105]受氡子体干扰、粉尘自吸收、滤膜取样效率等因素限制，应用场景受限。

颗粒物直接进样ICP-MS在线分析技术不仅适用于单颗粒，也可应用于连续气溶胶。本课题组[37]报道了采用^{242}Pu气溶胶在线加入法，用Element ICP-MS对高效过滤器下游复杂基体气溶胶样品进行直接进样快速分析。该方法对^{239}Pu的检出限为1.4×10^{-3} Bq/m^3，主要制约因素是严重的基体效应和^{239}Pu/^{242}Pu比值的测量精度，样品中^{239}Pu浓度在3.1×10^{-3}～1.2×10^{-2} Bq/m^{3}之间，比辐射防护规定的导出空气浓度限值（0.2 Bq/m^3，PuO_2形式吸入时）[106]低。为改善检测效果，使用灵敏度和测量精度更好的MC-ICP-MS（Nu Plasma型，Nu公司产品）对后续相似样品中的超痕量钚进行检测[38]，估算出穿透^{239}Pu粒子的大小约为10 nm。文献[107-109]报道过类似的穿透现象，推测是由钚α衰变引起的反冲或溅射所致。

2.3.2 悬浮液中单颗粒的高精度同位素分析

对反应堆回路水和放射性废水中的悬浮液粒子进行检测和同位素分析，可以快速判断燃料组件是否破损及严重程度，评估燃料组件类型、反应堆堆型和燃耗深度等，这些信息对于核安全与核保障具有重要价值[110]。胶体粒子会增强核素迁移[111]，对它们进行同位素分析能够甄别核素来源、研究迁移行为，对核环境现场研究有重要意义。

针对上述需求，课题组发展了单颗粒直接进样MC-ICP-MS高精度同位素分析技术。由于天然铒的丰度范围可以覆盖从天然铀到高浓铀的丰度值范围，因此使用天然丰度的氧化铒纳米颗粒作为铀颗粒模拟样品，将它们分散到超纯水中制成悬浮液，雾化进样至MC-ICP-MS，同时接收m/z 162、164、166、167、168和170处的离子流，单次积分时间为200 ms，采用单点法和线性回归法分别计算铒同位素比值。结果表明，线性回归法得到的比值精度和准确度好于单点法，如^{170}Er/^{166}Er、^{168}Er/^{166}Er、^{167}Er/^{166}Er比值的精度为0.1%～0.24%，低丰度的^{164}Er/^{166}Er（真值4.78×10^{-2}）、^{162}Er/^{166}Er（真值4.15×10^{-3}）比值精度为2%～6%；^{170}Er/^{166}Er、^{167}Er/^{166}Er、^{164}Er/^{166}Er比值的相对偏差小于0.6%，^{162}Er/^{166}Er比值的相对偏差为−36%。该技术具有快速筛选、灵敏检测和同位素分析等优点，可以作为一种快速、灵敏的筛选技术。

3 展望

从技术发展角度看，需重点改善标定曲线的斜率（仪器灵敏度）、质量/粒径检测下限和上限。例如，更换提取效率更高的界面[92]可以显著提高仪器灵敏度，优化分析条件（中心通道气流、采样深度等[54]）有利于数微米颗粒的完全电离，采用联用技术（离子交换树脂等[83]）去除基体和溶解态元素的影响，发展弱信号鉴别和提取技术[60,94,112]。

从分析应用角度看，需大力拓展技术的应用场景，如生态环境、食品医疗卫生、工业生产等。分析实际样品时应注意基体效应影响[26,75]，采用合适的标定方法。此外，还应通过评估、检验等方式提高技术的标准化和数据质量[67,78]。

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