A REVIEW ON THE MASS SPECTROMETRIC STUDIES OF AMERICIUM: PRESENT STATUS AND FUTURE PERSPECTIVE

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The manuscript reviews the various mass spectrometric techniques for analysis and chemical studies of Americium. These methods include thermal ionization mass spectrometry (TIMS), and inductively coupled plasma source mass spectrometry (ICPMS) for the determination of Am isotope ratios and concentration in nuclear fuel samples of interest in nuclear technology, and in complex biological and environmental samples. Ultra-sensitive mass spectrometric techniques of resonance-ionization mass spectrometry (RIMS), and accelerator-based mass spectrometry (AMS) are also discussed. The novel applications of electrospray ionization mass spectrometry (ESIMS) to understand the solution chemistry of Am and other actinides are presented. These studies are important in view of the world-wide efforts to develop novel complexing agents to separate lanthanides and minor actinides (Am, Np, and Cm) for partitioning and transmutation of minor actinides from the point of view of nuclear waste management. These mass spectrometry experiments are also of great interest to examine the covalent character of actinides with increasing atomic number. Studies on gas-phase chemistry of Am and its oxides with Knudsen effusion mass spectrometry (KEMS), Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS), and laser-based experiments with reflectron time-of-flight mass spectrometer (R-ToF) are highlighted. These studies are important to understand the fundamental chemistry of 5f electrons in actinides. Requirement of certified isotopic reference materials of Am to improve the accuracy of experimental nuclear data (e.g., the half-life of ^{243}Am) is emphasized. © 2016 Wiley Periodicals, Inc. Mass Spec Rev

Keywords: *americium; mass spectrometry; isotopic analysis; concentration determination; solution chemistry; gas phase chemistry; reference materials*

I. INTRODUCTION

Mass spectrometric analysis of Americium (Am), a trans-plutonium actinide, is challenging and interesting from the point of view of its associated radioactivity, and similarity to lanthanides in chemical behavior because of its electronic configuration. Am is not present in nature but is produced in nuclear-related activities (e.g., atmospheric weapons testing, nuclear power production, storage, and reprocessing of irradiated nuclear fuels, nuclear wastes, nuclear submarines), and is a long-lived component of minor actinides (MAs), which are of great concern for geological repositories. Am has a number of radioactive isotopes: ^{241}Am and ^{243}Am are the two important isotopes with α-decay half-lives of about 432.6 year and 7,370 year, respectively. ^{241}Am is produced from the β-decay of ^{241}Pu, which has a relatively short half-life of about 14.4 year, and the abundance of ^{241}Pu in Pu varies from 0.5% in research reactor-produced plutonium (Pu) to 20% in power-reactor produced Pu, and depends upon the burn-up of nuclear fuel, residence time of fuel in the reactor, and so on. ^{243}Am is produced by thermal neutron irradiation of enriched ^{242}Pu in a high-flux isotope nuclear reactor (HFIR), and is a useful isotope for various chemical studies of Am because of its longer half-life and, therefore, lower associated radioactivity compared to that of ^{241}Am.

Am, with an atomic number of 95, has an electronic configuration [Rn] $5f^7 7s^2$, which is similar to that of the lanthanide europium (Eu) (i.e., [Xe] $4f^7 6s^2$). However, the size of Am^{3+} (98 nm) is much closer to that of Nd^{3+} (98.3 nm) (Rubin, 1998). It is a common practice to use Eu as a surrogate to study and understand the chemistry of Am, because of the radio-toxicity of Am, and special α-containment infra-structure needed to work with Am. The first ionization potential of Am (5.97 eV) is near that of Pu (6.03 eV) (Rubin, 1998), and this closeness of ionization potentials leads to mutual isobaric interferences of ^{241}Pu and ^{241}Am at mass-to-charge ratio (m/z) of 241 in mass spectrometry. Americium can exist in various oxidation states (III–VI) in aqueous solutions, with Am(III) as its most stable-oxidation state. In acidic solutions, Am(III) can be oxidized to Am(IV). However, Am(IV) spontaneously reduces to Am(III) unless a complexing acid (e.g., phosphoric acid) is present to stabilize the Am(IV) species. Am(III) can be oxidized to Am(V) as AmO_2^+ with ozone or hypochlorite. More-powerful oxidizers [e.g., peroxydisulphate and Ag(II)] in non-reducing acids will oxidize Am(III) to Am(VI). Partitioning and transmutation (P&T) strategy, discussed in nuclear–fuel cycle, demands separation of Am, and other long-lived radioisotopes Np and Cm (commonly referred to as minor actinides) from lanthanides (Panak & Geist, 2013). Partitioning is of interest to reduce the volume and storage time of the nuclear waste and the associated heat load for safe disposal in a geological repository.

The most-common use of Am is in smoke detectors, as an ionization source, and several kilograms of Am are used each year for this purpose. The majority of these smoke detectors use a small quantity (about 0.25 μg) of ^{241}Am in the form of americium dioxide (AmO_2). This small quantity of ^{241}Am is equivalent to 30 kilo-Becquerel (kBq) of radioactivity. The

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radiation dose to the occupants of a house from a domestic smoke detector is very small and is not a health hazard, because this dose is very much less than that from natural background radiation due to cosmic rays, and from naturally occurring radioactive elements such as potassium, or radon. Americium (in combination with beryllium) is also used as a neutron source in non-destructive testing of machinery and equipment, and as a thickness gauge in the glass industry (http://www.world-nuclear.org/information-library/non-power-nuclear-applications/radioisotopes-research/smoke-detectors-and-americium.aspx). These Am-Be neutron sources are also employed as moisture-density gauges. Americium is used as a photon source in oil well-logging instruments. There are proposals to use ^{241}Am as a radioisotope thermoelectric generator (RTG) instead of ^{238}Pu in space–vehicles because of the availability of isotopically pure ^{241}Am from stored separated Pu samples (O'Brien et al., 2008; Robertson et al., 2014). Additionally, ^{241}Am^{16}O$_2$ is preferred in nano-satellites (1–10 kg range), due to its lower neutron dose compared to that from ^{238}Pu^{16}O$_2$, and this low neutron dose allows a reduction in the amount of shielding material (Robertson et al., 2014).

^{241}Am and other isotopes of Am are usually determined with α-spectrometry and γ-spectrometry. The various long-lived isotopes of Am and their properties are summarized in Table 1. A review (Vajda & Kim, 2010) discusses the various methods that can be used to separate and purify Am from various matrices to determine the isotopic composition and concentration of Am in various nuclear fuel samples, and environmental and biological samples. Mass spectrometric techniques are of interest due to their high sensitivity, selectivity, and high accuracy achievable to determine the abundances of various Am isotopes in different matrices. A number of reviews are available in the literature for the mass spectrometric analysis of long-lived radioactive nuclides (Myasoedov & Pavlotskaya, 1989; Becker, 2003; Leopold et al., 2008; Roos, 2008; Boulyga, 2011). However, no review is available till today on the mass spectrometric analysis of Am. The present review is written to bridge this gap, and highlight the potentials of various mass spectrometric techniques to undertake varieties of studies. In addition to the determination of isotopic composition and concentration, mass spectrometric analysis provides interesting information on the solution chemistry and gas-phase chemistry of Am and its compounds. These aspects are also discussed in the present review. It may be noted that, due to the radioactivity associated with various isotopes of Am, it is essential to have the infra-structure to handle the radio-isotopes with α-containments like a glove box enclosure for the ion-source of a mass spectrometer.

TABLE 1. Properties and uses of long-lived Am isotopes

Property	^{241}Am	^{243}Am	^{242m}Am
Half-life	432.6 yr	7370 yr	141 yr (isomer) and 16 hr (g)
Main decay mode with energies	α-decay, 5.486 MeV followed by γ	α-decay, 5.28 MeV followed by γ	^{242m}Am decays to ^{242}Am (99.54%) and to ^{238}Np (0.46%) by α energy 5.64 MeV; ^{242}Am(g) decays by β^- and electron capture
Decay product (progeny)	^{237}Np (α-emitter)	^{239}Np (β^--emitter)	^{242}Am(g) decay products: ^{242}Cm (83%), ^{242}Pu (17%)
Production method	From β-decay of ^{241}Pu ($T_{1/2}$ = 14.4 yr)	By neutron irradiation of ^{242}Pu in a high flux reactor	-
Used for	Smoke detector, neutron source (along with Be), radioisotope thermoelectric generator (RTG)	Tracer in chemical recovery experiments, chemistry studies on Am	-
Specific power	114 Watts.kg^{-1}	-	-

II. DIFFERENT MASS SPECTROMETRIC TECHNIQUES USED FOR Am AND ITS COMPOUNDS

Mass spectrometric studies are required to obtain data on the isotopic composition and concentration of Am (Chartier, Aubert, & Pilier, 1999; Aggarwal et al., 2010), speciation and vapor pressure of various Am species in the gas phase (Gotcu-Freis et al., 2011), and stability constants of Am-complexes present in the solution (Panak & Geist, 2013), to provide interesting gas phase chemistry studies (Gibson, 2002; Gibson & Marcalo, 2006). A brief description of each mass spectrometric technique is given below with particular reference to its application for analysis of Am and its compounds.

A. Thermal Ionization Mass Spectrometry (TIMS) for Am

Thermal ionization mass spectrometry (TIMS) is a popular mass spectrometric technique for the determination of isotopic composition and concentration of various elements, including actinides, for various applications in biological, environmental, geological, and nuclear sciences (Burger et al., 2009). About 1 μL of the solution in dilute HNO$_3$ that contains about 100–500 ng of the element is loaded onto a high purity filament (rhenium, tantalum, tungsten, etc.), and dried with electric heating. The singly charged positive or negative ions are produced with the process of surface ionization with a single or a multiple filament assembly, and heated to appropriate temperatures governed by the vaporization characteristics and ionization potential (electron affinity for negative ions) of the element. TIMS requires the element to be available in pure chemical form to achieve good ionization efficiency, and this purity requirement necessitates elaborate chemical separation and purification steps prior to MS analysis. TIMS is generally free from polyatomic isobaric interferences, and does not suffer from any memory or carry-over effect as with inductively coupled plasma mass spectrometry (ICPMS) or gas-source mass spectrometry. There is an inherent limitation of isotope fractionation in TIMS that leads to preferential evaporation of the lighter isotope. As a consequence of this fractionation with an amplitude of 0.1–0.5% per mass unit in the actinides mass region, the observed atom ratio of the lighter to heavier isotope is more than the expected isotope ratio at the start of the analysis and this ratio decreases with time during analysis. This variation in the isotope ratio necessitates the optimization of analysis conditions with a certified reference material (CRM), and application of the mass fractionation correction factor to arrive at accurate isotope ratios. Unfortunately, no such isotopic reference material is available for Am so far. An alternative approach to circumvent this limitation is to employ total evaporation and ion current integration with a multi-collector detector system, as is popularly done for TIMS analysis of U and Pu. TIMS is a single-element analysis technique, and can be employed to determine the concentration of an element with isotope dilution mass spectrometry (IDMS), and is, therefore, applicable to elements with at least two stable or long-lived isotopes. In the case of Am analysis with TIMS, enriched ^{243}Am is used as a spike (tracer) to determine ^{241}Am with ID-TIMS. Am is separated and purified from Pu with anion-exchange or extraction chromatography to circumvent the isobaric interference of ^{241}Pu$^+$ at ^{241}Am$^+$. Because of the relatively high radioactivity of Am isotopes compared to that of U and Pu isotopes, special sample-loading procedures may be adopted to enhance ionization efficiency (number of ions produced to the atoms loaded on the filament) in TIMS. This enhanced ionization efficiency also allows one to analyze biological and environmental samples that contain small amounts of Am. A few such attempts to increase the ionization efficiency of Am reported in literature are discussed here (Zhou, 1987; Wayne et al., 2002; Burger et al., 2009).

The iridium granule technique was used to improve the ionization efficiency of Am (Zhou, 1987). The rhenium filament was loaded with a paste of pure iridium sponge mixed with a sucrose solution, and was heated with a slow increase of the current until the burning sucrose was smelled. The filament was heated to a temperature of about 1,520°C for an hour in vacuum. A porous iridium granule of 0.5 mm diameter was formed on the rhenium filament. An overall ionization efficiency of 3% was achieved with 0.3 ng of Am loaded on the Re filament, compared to a conventional ionization efficiency of 0.1–0.2%. A temperature restriction of 1,700 K was observed due to relatively low melting point of Ir (2,719 K) compared with that of Re (3,453 K) (Osterman & Antes, 2010) .

An efficiency of 0.16% for 0.17–0.29 pg Am cation-resin bead loads onto dimpled flat ribbon single Re filaments covered with carbon, in TIMS, was reported (Burger et al., 2009), in comparison to a total efficiency of 0.63% for 0.29 pg Am resin bead loaded into Re cavities with carbon additive. A higher efficiency with the carbon additive was due to the increased work function (5.36 vs. 4.96 eV) of the Re filament and could also be due to electron ionization (Wayne et al., 2002). The secondary electron multiplier (SEM) background count rates at ^{241}Am and ^{242}Am masses were between 1 and 0.01 counts per second (cps). The efficiencies and background count rates resulted in a detection limit of <0.1 fg (10^4–10^5 atoms) of $^{241-243}$Am with filament and cavity resin bead load techniques, respectively.

The introduction of a 10^{12} and 10^{13} Ω resistor for amplifiers with Faraday cups, in the future, instead of presently available 10^{11} Ω resistors, will significantly enhance the capability of TIMS to analyze much lower amounts of Am and other radioactive elements, without sacrifice in the precision and accuracy of isotope ratio data (Klaver et al., 2016; Trinquier & Komander, 2016).

TIMS is regularly used to determine the isotopic composition and concentration of Am in spent nuclear-fuel materials in nuclear technology (Chartier, Aubert, & Pilier, 1999). This use of TIMS is because the sample amount available is not a limitation, and the achievable accuracy of about 0.5%, in the absence of certified isotopic reference material, is acceptable. However, the determination of nuclear data [e.g., the half-life of ^{243}Am with relative activity method (Aggarwal, Parab, & Jain, 1980; Aggarwal et al., 2007)], which depends upon the determination of atom ratios and alpha activity ratios in synthetic mixtures of ^{241}Am and ^{243}Am, requires accuracy of better than 0.1%. TIMS has the potential to satisfy these accuracy requirements, if Am isotopic CRMs become available in future.

B. Inductively Coupled Plasma Mass Spectrometry (ICPMS) for Am

ICPMS is a popular mass spectrometric technique to determine concentrations and isotope ratios of Am and other actinide elements (Agarande et al., 2001; Truscott et al., 2001; Boulyga et al., 2003; Lee et al., 2003; Hang et al., 2004; Pointurier, Baglan, & Hemet, 2004; Wang, Chen, & Chiu, 2004; Epov et al., 2005; Lee et al., 2005; Varga, 2007; Varga et al., 2007a,b; Zheng & Yamada, 2008; Guerin et al., 2011; Krachler et al., 2014). In ICP, the M$^+$ ions are produced with generation of plasma (with Ar gas) at atmospheric pressure, and introduction of the sample into the spray chamber with a pneumatic nebulizer. The different elements present in the sample are atomized and ionized, and are introduced into the mass analyzer through sampler and skimmer cones, with the interface maintained at low pressure. ICPMS is thus a multi-element analysis technique because all the elements are ionized due to high temperature of the plasma. Various types of ICPMS instruments are available commercially. These are mass spectrometers with a quadrupole or time-of-flight mass analyzer, recently introduced triple-quadrupole mass spectrometer, single-collector magnetic sector-field (SF)-based high resolution, and multiple-collector (MC) high-resolution magnetic sector. Magnetic sector-based ICPMS mass spectrometers provide higher precision and accuracy as well as higher sensitivity, compared to Q-ICPMS or ToF-ICPMS systems. MC-ICPMS systems give the best precision and accuracy in isotope-ratio determinations, and are commonly used for various elements. However, matrix effects, instrumental mass-bias, spectroscopic and non-spectroscopic interferences, memory, or carry-over effect need to be checked, minimized, and corrected for. Various polyatomic interferences that arise from Hg, Tl, Pb, and Bi with S, Cl, and Ar are listed in Table 2 (Truscott et al., 2001; Varga, 2007). All these interferences can be resolved with a sector-field magnetic-sector ICPMS at a resolution of 4,000. The commonly encountered hydride interferences due to Pu isotopes (^{240}PuH$^+$ and ^{242}PuH$^+$) are eliminated with chemical purification and with a desolvation unit used for sample introduction in ICPMS. ICPMS has gained popularity compared to TIMS for ^{241}Am and other actinides determination in complex biological and environmental samples because of the less-stringent requirements of sample purity, ease of liquid sample introduction, and possibility to use either another element as internal standard for mass-bias correction, or employ an external calibration procedure. Additionally, elements with high ionization potential (>6 eV) difficult to analyze with TIMS, can also be efficiently ionized in an ICP source. Also, there is a possibility of hyphenation of ICPMS with a gas chromatograph, capillary electrophoresis, and so on for speciation applications. The mass bias in ICPMS is significantly higher than that observed in TIMS, but this mass bias remains constant with time in ICPMS.

ICPMS is quite popular for the determination of Am in biological and environmental samples, which contain Am at fg

TABLE 2. Polyatomic interferences in ICPMS analysis of Am

Interference at ^{241}Am (mass of polyatomic species)	Interference at ^{243}Am (mass of polyatomic species)
^{209}Bi^{32}S (240.95246) *[2310]*	^{209}Bi^{34}S (242.94826) *[2149]*
^{208}Pb^{33}S (240.94810) *[2217]*	^{208}Pb^{35}Cl (242.94549) *[2097]*
^{207}Pb^{34}S (240.94376) *[2132]*	^{207}Pb^{36}Ar (242.94344) *[2061]*
^{206}Pb^{35}Cl (240.94331) *[2124]*	^{206}Pb^{37}Cl (242.94036) *[2009]*
^{205}Tl^{36}Ar (240.94196) *[2099]*	^{205}Tl^{38}Ar (242.93714) *[1955]*
^{205}Tl^{36}S (240.94149) *[2092]*	^{203}Tl^{40}Ar (242.93472) *[1919]*
^{204}Pb^{37}Cl (240.93894) *[2045]*	-
^{204}Hg^{37}Cl (240.93938) *[2053]*	-
^{203}Ti^{38}Ar (240.93507) *[1980]*	-
^{201}Hg^{40}Ar (240.93267) *[1942]*	-

Adapted from Truscott et al. (2001) and Varga (2007).
Values in brackets [] in italics give the resolution of the mass spectrometer required to resolve the isobaric interference.

to pg levels. Extraction chromatography is generally used to separate and purify Am from bulk of other chemical constituents, prior to analysis by ICPMS.

C. Electrospray Ionization Mass Spectrometry (ESIMS) for Am

Electrospray ionization (an ESI source can be considered as a controlled-current electrolytic cell) is a fast, sensitive, and soft-ionization technique that allows the sample molecules to be transferred directly from solution to the gas phase. ESIMS allows direct and continuous introduction of the liquid samples; however, analytes must be charged before their transfer to the gas phase. Despite the short (milliseconds) time frame of electrospray ionization, a shift in the equilibrium can occur during the ionization process, and this shift can lead to changes in the gas-phase species in contrast to those present in the solution (McDonald et al., 2014). The technique offers the potential to determine the stoichiometry of complexes in solution, and to investigate their stability in the gas phase. ESIMS is now popular for speciation and metal–ligand equilibrium studies (Beuvier et al., 2015). Although ESIMS does not necessarily (faithfully) represent the various species present in a solution, it provides characterization of the stoichiometry of the metal–ligand complexes, and generates data to calculate the stability constants of various species. Use of a quadrupole ion-trap and collision-induced dissociation (CID) allows one to unravel the mechanism of formation of various species, and to elucidate the reasons for stability of those species. These studies are possible because variable-energy CID, also known as energy-resolved mass spectrometry (ERMS), provides information on structure and bonding (Di Marco & Bombi, 2006). It may be noted that a quantitative correlation of the gas-phase species observed in ESIMS with species present in the solution still remains a challenge (McDonald et al., 2014).

In electrospray, a fine aerosol of highly charged micro-droplets is created in a strong electric field. The sample solution passes through a highly charged capillary with a voltage in the range of 2–5 kV. The solution gets converted to a fine spray of highly charged droplets that evaporate due to the presence of the electric field with a stream of nitrogen. Because the spray capillary tip is very thin, the electric field at the capillary tip is very high (≈100 V/m). The ions (nano-droplets) are produced by the coulombic explosion of the shrinking charged droplets. ESIMS holds the potential to provide an insight into the solution chemistry of various complexing agents used in TALSPEAK (Trivalent Actinide–Lanthanide Separation with Phosphorous reagent Extraction from Aqueous Komplexes) (Lamouroux et al., 2006; Nash, 2015), SANEX (Selective ActiNide EXtraction), SANEX-DIAMEX (DIAMide EXtraction) (Muller et al., 2010) processes proposed to partition minor actinides (Am, Np, and Cm) and lanthanides in the framework of nuclear-waste processing.

D. Accelerator Mass Spectrometry (AMS) for Am

AMS, also known as high-energy mass spectrometry, offers high efficiency, high rejection of interferences, low susceptibility to matrix components, and large dynamic range to determine heavy radioactive isotopes (Litherland, 1980; Vogel et al., 1995; Fifield, 2008). AMS generates negative ions by Cs sputtering of the target that contains the element of interest. Negative ions are accelerated and reach the terminal maintained at a high voltage (0.5 MV or more), where they are stripped off their electrons by allowing these negative ions to pass through a thin carbon foil or with a gas stripper. The positive ions produced by stripping off electrons are further accelerated down the terminal, and are detected and measured with a suitable detector like an ionization chamber, Faraday cup, or time-of-flight system. There is an increasing interest to develop ultra-sensitive analytical techniques like AMS for bio-assay samples to determine long-lived heavy actinides.

A pilot study was performed with the compact AMS (0.5 MV, Tandy) at ETH, Zurich to determine the sensitivity and detection limit of AMS for ^{241}Am determination in synthetic samples that contained 0–20 fg of ^{241}Am (Christl et al., 2014). The samples were mixed with ^{243}Am tracer (about 4.96 pg) and were co-precipitated with titanium hydroxide (0.5 mg Ti) or ferric hydroxide (1 mg Fe). These precipitates were converted to oxide by heating at 650°C and were mixed homogeneously with 3–4 mg of Nb powder for AMS measurements. AmO^{-} ions were generated with Cs-ion sputtering of the sample, and Am^{+3} ions obtained by injecting negative molecular ions into a thin carbon stripper foil present in the 0.5 MV terminal were detected with an ionization chamber. Overall detection efficiencies in the range of 1.5×10^{-4} to 8×10^{-5} were obtained for various samples. The detection limit of 0.12 fg obtained for ^{241}Am in the synthetic samples demonstrated the high sensitivity of AMS required for bioassay samples.

AMS was also used recently to determine the ultra-trace amounts of ^{241}Am in sediment and soil samples (Kazi et al., 2014). A single-step DGA resin (normal: N,N,N′,N′-tetra-n-octyldiglycolamide) extraction chromatography column was used to separate Pu and ^{241}Am from the sediment samples. ^{243}Am was used as a spike to monitor the chemical separation yield, which was close to 100%. Pu and Am were both adsorbed onto the chromatography column from 8 M HNO_3 medium, and Am was eluted with 0.1 M HCl. Am was co-precipitated with 1 mL of 48% HF and 6 mg Nd. The micro-precipitate was centrifuged and dried for use as a sputter target in AMS with a terminal voltage of 0.85 MV. Am^{+3} ions were monitored with AMS, and Dy^{+2} was found to be the main m/z interference. ^{241}Am at a few Bq kg^{-1} (~30–50 fg kg^{-1}) was determined in soil and IAEA sediment reference materials (Table 3). A good agreement between the expected and measured ^{241}Am activity data demonstrated the capability of DGA extraction chromatography followed with AMS for accurate determination of ^{241}Am at ultra-trace levels. This method demonstrated the applicability of the DGA-based single-extraction chromatography column to determine Am in complex environmental samples. The approach offers the benefit to process simultaneously a number of samples with an automated solid-phase extraction set-up, and additionally eliminates the long counting times required in radiometric methods, with atom counting in AMS.

E. Resonance-Ionization Mass Spectrometry (RIMS) of Am

Resonance-ionization mass spectrometry is a photo-ionization process in which atoms in the gas phase are ionized with absorption of photons that energetically match the quantum selected states of the atoms. The atoms of a particular element can be excited and ionized selectively with a single color or multi-color lasers to circumvent isobaric interferences. Ultra-high sensitivity is achieved by tuning the lasers to specific energy states (Wendt et al., 1999; Wendt, Trautmann, & Bushaw, 2000; Wendt & Trautmann, 2005).

RIMS was used to determine the first ionization energy of Am as 5.9736(3) eV (Deissenberger et al., 1995). Due to the high sensitivity of RIMS (that arises from selective excitation and ionization), about 0.4 ng of ^{243}Am was sufficient for these measurements. An atomic beam of Am was excited in two steps with intersection of the two dye lasers exactly tuned to the resonance energies of Am (640.52 and 654.42 nm). A third laser (wavelength 578 ± 2 nm) was used for further excitation, and was tuned over the ionization threshold. The ions were accelerated to 2.9 keV. The third laser was scanned, and a sudden increase in the intensity of $^{243}Am^+$ ions measured with a channel plate detector after a time-of-flight mass spectrometer (drift length of 2 m) was used to determine the first ionization potential of Am. Although at one time, RIMS was considered to be a complementary analytical technique to AMS for ultra-sensitive analysis (Wendt, Trautmann, & Bushaw, 2000), it has, however, remained limited to a few laboratories only. One of the reasons for this limited usage of RIMS is the non-availability of any commercial RIMS instrument due to the sophisticated tunable lasers that are required, unlike the commercial availability of compact AMS systems (Christl et al., 2014), which can analyze many elements, including actinides.

TABLE 3. ^{241}Am determined by AMS in certified reference materials after separation with DGA extraction chromatography resin

Certified reference material (CRM)	Certified activity ($Bq\ kg^{-1}$)	Determined by AMS ($Bq\ kg^{-1}$)	95% confidence limit ($Bq\ kg^{-1}$)	Details of matrix
IAEA-384 sediment	7.1	6.4 ± 0.7	6.7 to 7.4	Fangataufa Lagoon sediment, almost 100% $CaCO_3$
IAEA-385 sediment	3.84	4.1 ± 0.36	3.74 to 4.01	Irish Sea sediment rich in silica, Ca, Al and Fe

Adapted from Tables 7 and 8, Kazi et al. (2014).

III. APPLICATIONS OF VARIOUS MASS SPECTROMETRIC TECHNIQUES FOR STUDIES WITH AMERICIUM

A. Isotopic Composition and Concentration of Am

Determination of isotopic composition of Am and concentration in irradiated nuclear fuels is required in nuclear technology for various reasons. For example, the experimental data on the isotopic composition and concentration of Am are important to develop and validate theoretically predictive ORIGEN (Oak Ridge Isotope Generation) code and neutronic code (Krachler et al., 2014). Additionally, experiments are underway to study the feasibility to burn plutonium in existing light-water reactors, and to reduce the production of other minor actinides (Am, Np, Cm). The determination of Am concentration is important to study the effectiveness of burning minor-actinides with test fuel samples (Guerin et al., 2011; Krachler et al., 2014).

In view of the specification limit of 0.25 wt% of Am in Pu-bearing nuclear fuels, ^{241}Am must be determined as a part of chemical quality assurance of nuclear fuels (Aggarwal et al., 2010). A number of radiometric techniques based on α- or γ-spectrometry can be used for this purpose. However, sometimes, IDMS with ^{243}Am as a spike is used to validate and calibrate these methods (Aggarwal et al., 2010).

Chartier et al. at CEA, France, in 1999, used isotope dilution-TIMS and isotope dilution-quadrupole-ICPMS to determine Am and Cm in mixed uranium-plutonium oxide (MOX) spent nuclear fuels. The sample-introduction systems in the two mass spectrometers were housed in special α-containment glove boxes for these measurements. Am/Cm were separated from U and Pu with an anion-exchange resin column (Dowex AG 1×4) in HNO_3 medium. Pure fractions of Am and Cm were obtained from separation with a high performance liquid chromatography (HPLC) method ($250 \times 4\ mm^2$ column, 5 μm particle size) with a strong cation-exchange silica-based stationary phase (Nucleosil SA) and 2-hydroxy-2-methylbutyric acid as complexing agent. The conditions used were 0.14 M HMB, pH = 4.1, and mobile-phase flow rate of 0.8 mL min^{-1} to yield retentions times of 7.7 min and 10.5 min for Cm and Am, respectively. For isotope dilution, enriched ^{243}Am (98.6%) was used as a tracer (spike). TIMS analysis of Am was carried out with 500 ng of Am loaded onto the two side filaments (tantalum) of a triple-filament assembly, with rhenium as ionization filament, and with total evaporation to take care of isotope fractionation effects. The mass bias in ICPMS was accounted for by analysis of the Am solution pre-calibrated with TIMS. Accuracy of better than 2.5% was achieved for ID-ICPMS analysis when compared to the data obtained with ID-TIMS. $^{241}Am/^{238}U$ ratios (in ppm) required for neutronics calculations were 1,207 and 1,872 with TIMS, and 1,230 and 1,917 with ICPMS, respectively, in the two spent fuel sample solutions. The advantages of ICPMS analysis in view of shorter analysis time and higher throughput compared to that with TIMS were recognized.

At JRC-ITU, Karlsruhe, Germany (Krachler et al., 2014), the dissolved solutions from two spent fuels MET 1–4 and 1–7 were used to determine the isotopic composition and concentration of Am with sector-field ICPMS. Because no reference material of Am is available commercially to check the validity of the methodology, ICP-OES based on an independent physico-chemical principle was also employed to compare the results of Am concentration (Krachler et al., 2014). The fuel samples were dissolved in a hot-cell at JRC-ITU in a mixture of 3 M HNO_3 and 0.2 M HF, and the solutions were diluted with 1 M HNO_3 (dilution factor of 9,000) for analysis with ICPMS. An in-house standard solution of ^{241}Am (5 μg kg^{-1}) was analyzed with SF-ICPMS that used ^{238}U as an internal standard for calibration. The amounts of ^{241}Am determined were about 7.8% and 16.6% higher than expected values, in the low- and medium-resolution modes, respectively, of ICPMS. This discrepancy was attributed to the (invalid) assumption of the same elemental sensitivity of ICPMS for all the actinides. The mass-bias correction factor with an exponential law function, based on intensities of ($^{232}Th^+ + ^{232}ThO^+$) and ($^{238}U^+ + ^{238}UO^+$) eliminated the discrepancy; the results agreed in low- and high-resolution modes, and the values were close to the expected concentration (Krachler et al., 2014). Table 4 presents the data on the isotopic composition and concentration of Am determined in two different test fuel samples. The results demonstrate the accuracy of SF-ICPMS and ICP-OES for Am concentration determination. Such studies highlight the potential of mass spectrometry to provide reliable experimental data to develop and verify theoretical computer codes for build-up and depletion of actinides for the safe and efficient nuclear power generation. Such studies also highlight the potential limitations and errors for application of this analytical technique to samples with unknown concentrations.

Laser-ablation isotope-dilution sector-field ICPMS was used to determine Pu and ^{241}Am in *Sphagnum* moss by Boulyga et al., because these species retain actinides and thus act as biological indicators of actinides atmospheric contamination from global fall-out or accidental nuclear release. About 1–2 g of the moss sample was mixed with ^{243}Am tracer. The sample was ashed in a muffle furnace at 600°C for 20 hr, cooled, and leached with 6 M HCl. The concentrations of ^{241}Am measured were close to the limit of quantification (LOQ) of the method, and were in the range of 2.8–4.1 Bq kg^{-1}, which corresponds to 22–32 fg g^{-1}, with an estimated uncertainty of 30–35%. These studies demonstrate the potential of LA-ICPMS to analyze moss samples.

^{241}Am along with other actinides (Np, U, Pu, and Th) was determined in urine samples, for bioassay, with on-line coupling the extraction chromatography column to a Q-ICPMS (Hang et al., 2004). The TRU extractant resin, which consists of carbamoylmethylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP), was used as a stationary phase. Sample injection and matrix clean-up on the column was done with 3 M HNO_3. This procedure also allowed the pre-concentration of actinides on the resin column. A gradient elution with a mixture of 2 M HCl and oxalic acid was used to sequentially elute the five actinides. The various actinides were determined within 30 min, and a detection limit of 3.7 pg (0.15 Bq) was obtained for ^{241}Am in urine. The approach demonstrates a quick and easy method for bioassay (i.e., analysis of urine samples) to determine actinides, with an extraction-chromatography column coupled on-line to a Q-ICPMS. This ICPMS-based method also holds potential for speciation studies (e.g., with the correlation of elemental oxidation states and elution times in chromatography) (Krupp et al., 2005).

Several researchers have demonstrated the applicability of Q-ICPMS and SF-ICPMS to analyze ^{241}Am in various kinds of samples; for example, urine, sediments, lung, liver, and so on. The first step in all these determinations is pre-concentration and separation of Am, which can be done with several approaches (Warwick, Croudace, & Carpenter, 1996). The majority of researchers have used a calcium fluoride co-precipitation method, which was followed with pre-concentration and separation with TRU resin. Table 5 summarizes the results reported by various researchers. It can be seen that absolute detection limits of fg g^{-1} are possible with ICPMS to determine ^{241}Am. These

TABLE 4. Isotopic composition and concentration of Am determined with sector field ICPMS in irradiated fuel samples

Isotopic composition of Am (weight %)				
Am-isotope	Fuel sample (MET 1-4)	Calculated by ORIGEN-2	Fuel sample (MET 1-7)	Calculated by ORIGEN-2
^{241}Am	43.1%	44.1%	41.6%	40.6%
^{242}Am	1.8%	2.1%	0.9%	1.0%
^{243}Am	55.0%	53.8%	57.5%	58.4%

Concentration of Am (μg. g^{-1})		
Fuel sample and composition	SF-ICPMS	ICP-OES
MET 1-4 63.9% U, 19.5% Pu, about 9% Zr, 2% REE, 2% MA (0.6% Am), 1% Mo	51.7 ± 0.26	53.9 ± 1.4
MET 1-7 61.4% U, 15.1% Pu, about 9% Zr, 5% REE, 5% MA (1.6% Am), 1% Mo	233 ± 12	227 ± 7

Adapted from Tables 3 and 4, Krachler et al. (2014).

data demonstrate the future potential of Q-ICPMS and SF-ICPMS instruments to analyze Am in complex biological and environmental samples.

A detection limit of 0.05 fg (6×10^{-6} Bq) was reported for ^{241}Am with a single-collector double-focusing ICPMS system (Pointurier, Baglan, & Hemet, 2004). This detection limit was better than the best detection limits of conventionally used radiometric techniques; that is, α-spectrometry (about 10^{-4} Bq) and γ-spectrometry (10^{-3} Bq).

ICPMS was used to determine the age, and Be/Am amount ratios of two sealed Am-Be neutron sources that were dismantled in a hot-cell at the Idaho National Laboratory, USA (Sommers et al., 2009). The samples were dissolved in 2 M HCl and diluted with 8 M HNO_3 to separate Pu from U and Am with TEVA extraction chromatography resin with automated gas-pressurized extraction chromatography (GPEC). Two quadrupole-based ICPMS systems (VG PQ3 and PerkinElmer DRC II) equipped with a glove box or a radiological hood were used to handle the radioactive solutions. A peak-jumping mode was used for data acquisition for Am, Np, and Be. ^{241}Am and its progeny ^{237}Np were determined to calculate the age (i.e., time since purification) of the sources. The Be/Am ratios of $6.3 \pm 52\%$ (1σ) and $9.81 \pm 3.5\%$ (1σ), and the ages of 25.0 year ± 2.1 months and 25.4 year ± 0.6 months were obtained for the two sources (Sommers et al., 2009). The determined age agreed with the expected age from the date of purchase of each source. Such studies are useful for nuclear-forensics applications and to demonstrate the capability of ICPMS to discriminate various Am-Be sources of different origins.

B. Solution Chemistry of Am

The solution chemistry of Am(III) is of great interest from the point of view of nuclear waste management. Previously, lanthanides [e.g., Eu(III)] were used as a surrogate to study the extraction behavior of Am(III) because of their similar electronic configuration, and the special facilities required to handle α-radioactive Am isotopes. This approach is not acceptable now, because partitioning and transmutation (P&T) of minor actinides (Am, Cm, Np) from spent nuclear fuels (SNF) demands the separation of Am from various lanthanides. This separation is required because of large concentration (50×) of lanthanides (some of these lanthanides are neutron poisons) and thus do not allow efficient burning of minor actinides with fast neutrons in a nuclear reactor. Therefore, a good separation is desirable for P&T approach. Further, there is a great deal of interest to develop solvents and diluents of CHON (carbon, hydrogen, oxygen, and nitrogen group) class, so that these organic compounds can be completely incinerated without any increase in the secondary waste volume, and, thus, easy to manage and dispose of (Retegan et al., 2009). Another important attribute of the CHON class of complexants is the elimination of pollution by S and other elements upon incineration. New extraction solvents should have good solubility in organic diluents, should be able to extract Am(III) at higher acidities (1–2 M HNO_3), give a good separation factor between actinides and lanthanides (>100 or more), extraction kinetics should be fast, stripping back of the extracted actinides should be easy and simple, and should have good radiation stability.

After the limited success of lipophilic bistriazinyl pyridines (BTP), new compounds [i.e., lipophilic bistriazinyl bipyridines

TABLE 5. Detection limits achieved for determination of ^{241}Am with various mass spectrometric techniques in different matrices

No.	Detection limit (DL)/ Quantitation limit (QL)	MS technique used	Matrix and separation methods	[Reference], Year
1.	1.2 fg g^{-1} , 0.6 fg (DL)	SF-ICPMS	Sediment, human liver and lung, extraction with 0.1M ammonium hydrogen oxalate	[Truscott et al], 2001
2.	1.6 pg (QL)	SF-ICPMS	Sediments (isotope dilution), precipitation and extraction chromatography with TRU resin	[Agarande et al], 2001
3.	3.6 fg.g^{-1} (QL)	LA-SF-ICPMS	Moss samples	[Boulyga et al], 2003
4.	0.05 fg, 6μBq (DL)	SF-ICPMS	Standard	[Pointurier et al], 2004
5.	3.7 pg /0.15 Bq (DL)	Q-ICPMS	Urine, TRU resin	[Hang et al], 2004
6.	0.9 to 8 fg.g^{-1} (DL)	Q-ICPMS	Urine, flow injection /extraction chromatography	[Epov et al], 2005
7.	0.86 fg.g^{-1} / 0.11 mBq.g^{-1} (DL)	SF-ICPMS	IAEA-384, 385 sediments, IAEA-308 seaweed; Isotope dilution with ^{243}Am, CaF_2 precipitation and TRU resin	[Varga et al], 2007
8.	0.32 fg.g^{-1} / 0.041 mBq.g^{-1} (DL)	SF-ICPMS	Sediment IAEA-368, isotope dilution, CaF_2 precipitation and TRU resin	[Zheng & Yamada], 2008
9.	2 pg (DL)	Q-ICPMS	Sediment, dissolved in 0.6M $LiBO_2$ + 9M HCl, separation & purification by TEVA and DGA resin columns	[Guerin et al], 2011
10.	11 fg / 1.4 mBq (DL)	AMS	IAEA-384 and 385 sediments, DGA resin	[Kazi et al], 2014
11.	0.12 fg (DL)	AMS	Synthetic sample	[Christl et al], 2014

(BTBPs)] were synthesized at Reading University, United Kingdom, to form 1:2 complexes with BTBPs rather than the 1:3 complexes formed by BTP. This 1:2 complex formation was advantageous from the solvent radiolytic degradation point of view, because a decrease in concentration would have a smaller effect on distribution ratios with BTBPs than with BTPs. Nitrogen polydentate BTBP extractants [i.e., 6,6′-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridines] were investigated because they act as a tetradentate to metal ions, and have good selectivity for trivalent actinides over lanthanides. Despite some drawbacks such as its limited solubility in 1-octanol-based diluents and its slow kinetics, CyMe4-BTBP was selected as the European reference molecule to develop a SANEX (Selective ActiNide EXtraction) process to separate minor actinides [Am(III), Cm(III)] from the lanthanides produced in fission (Retegan et al., 2009).

The stoichiometry of the compounds in the extraction of Am with $CyMe_4$-BTBP [6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-(1,2,4) triazin-3-yl)-(2,2′) bipyridine], and C5-BTBP [6,6′-bis(5,6-dipentyl-(1,2,4)triazin-3-yl)-(2,2′) bipyridine] with molecular weights 594.8 and 534.7 g mol^{-1}, respectively, in three diluents (cyclohexanone, nitrobenzene, and octanol) was studied with ESI (Retegan et al., 2009). An ion-trap mass spectrometer was used so that collision-induced dissociation (CID) studies could be performed for MS^n experiments. Twenty microliter of the organic phase after solvent extraction, diluted 100- to 300-times with acetonitrile/water (80:20 or 50:50 v/v in case of nitrobenzene) was injected into ESIMS at a flow rate of 70 $\mu L\ hr^{-1}$. It should be noted that 20 µL of the organic phase diluted 100–300 times undoubtedly dramatically affects the solution speciation, and hence most of the inferences about solution speciation derived from ESI-MS are qualitative at best. The positive-ion mass spectra were recorded after optimization of the sample cone voltage at 30 V. Energy-resolved experiments were also conducted with changes in the cone voltage to study the kinetic stability of different ions in the Am-BTBP complexes. The $CyMe_4$-BTBP complex was observed to be more resistant to fragmentation than the C5-BTBP complex because of the higher cone voltage required to fragment the former. The stoichiometry of the complex $L_2Am(NO_3)_3$, where L denotes the BTBP extractant, was not affected by the change in the diluents and of the substituent on the BTBP moiety. The metal-ligand species $L_2Am(NO_3)_3$ present in the solution phase was converted into $[L_2Am]^{3+}$ and $[L_2Am(NO_3)]^{2+}$ in the gaseous phase, as observed in the ESI mass spectra, where L denotes the BTBP extractant. The absence of a $[L_2Am(NO_3)_2]^+$ peak in the mass spectra suggested that one or two nitrates are in the outer-coordination sphere. If all the nitrate ions were in the outer-coordination sphere, then a single, high-intensity $[L_2Am]^{3+}$ peak would have been observed in the ESIMS. In contrast, a very low intensity $[L_2Am]^{3+}$ peak was seen to suggest that at least one nitrate is bonded to the Am ions. Furthermore, from the MS^2 studies on these species in the gas phase, it was proposed that one nitrate is directly coordinated to the metal ion, with the two other anions in the outer-coordination sphere (Retegan et al., 2009). The dissociation route of $[(C5\text{-}BTBP)_2Am(NO_3)]^{2+}$ highlighted the presence of a labile hydrogen atom on the C in the alpha position of the triazynyl ring, which is a fragility point of C5-BTBP. The non-covalent forces that hold the complexes together were electrostatic interactions. Recently, the separation factor between Am(III) and Eu(III) is shown (Ekberg et al., 2015) to increase with decreasing relative permittivity of the diluents and also by decreasing solubility of $CyMe_4$-BTBP to support the direct bonding of NO_3^- to Am(III) to lead to the formation of a $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ complex. This behavior of separation factor is because the inner coordination sphere bonding of nitrate ion reduces the charge density of the complex, to make the Am-complex more stable and soluble in the solvents with low relative permittivity compared to corresponding lanthanides complexes with outer-sphere coordination (Ekberg et al., 2015).

Researchers at the French Atomic Energy Commission have also developed (Berthon et al., 2010) an alternate DIAMEX-SANEX process to separate Am(III) with a mixture of a diamide DMDOHEMA (N,N′- dimethyl-N,N′-dioctylhexylethoxymalonamide) and a dialkyl phosphoric acid HDEHP (di-n-ethyl-2hexylphosphoric acid) dissolved in a suitable aliphatic diluent. In this process, the lanthanides and trivalent actinides are co-extracted with the diamide, and the actinides are stripped from the organic phase. ESIMS studies were performed with a homogeneous phase obtained with solutions of DMDOHEMA, HDEHP, HNO_3, ^{241}Am, and ethanol. The mass spectra showed that the different mixed complex species of the type $D_xAmA_2(NO_3)$ or D_xAmA_3 ($x \leq 5$), (D stands for DMDOHEMA, and A for the anion of HDEHP) were formed, and these mixed species were more stable thermodynamically than the unit complexes; those data are consistent with the synergistic extraction behavior at an aqueous solution acidity of about 1 $mol\ L^{-1}$ HNO_3. Different species observed in the ESI mass spectrum are listed in Table 6. Table 7 gives the molecular structures of the compounds used to separate lanthanides and actinides. It must be noted that the gaseous-species observed in ESIMS do not always represent the solution-phase species because of artefacts in the ionization in ESIMS (McDonald et al., 2014), and therefore, the ESIMS data should be interpreted with caution to correlate with the solution chemistry.

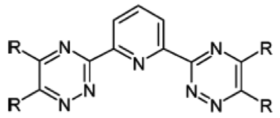
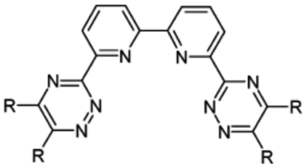
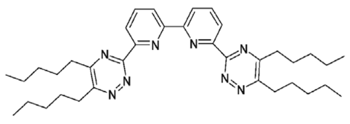
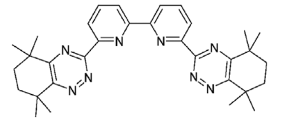
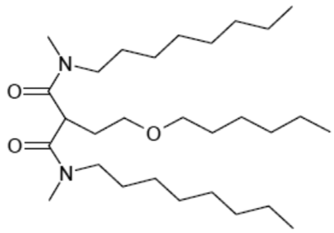
ESIMS with negative ions was recently used to study the complex formation of adenosine triphosphate (ATP) with Am (Mostapha et al., 2014). Americium was purified from iron with 0.5 HDEHP, and from Np and Pu with an anion-exchange resin. About 100 µL of the ^{241}Am solution diluted in 500 µL

TABLE 6. Various species observed in the positive ion ESIMS of Am with DMDOHEMA and HDEHP (D stands for DMDOHEMA and A denotes the anion $DEHP^-$)

Species	m/z value
$[D_2AmA_2]^+$	1847.9
$[D_2AmA(NO_3)]^+$	1588.4
$[DAmA(NO_3)]^+$	1106.8
$[DAmA_2]^+$	1366.1
$[D_3AmA]^{2+}$	1005.1 (Highest intensity)
$[D_2AmA]^{2+}$	763.8 (Second high intensity)
$[D_2Am(NO_3)_2]^+$	1330.2
$[D_3Am(NO_3)]^{2+}$	875.8
$[D_2Am(NO_3)]^{2+}$	634.2
$[D_5Am]^{3+}$	884.2
$[D_4Am]^{3+}$	724.1
$[D_3Am]^{3+}$	563.3

Adapted from Berthon et al. (2010).

TABLE 7. Molecular structures of the compounds used to separate lanthanides and actinides

S.No.	Complexing agent	Molecular structure
1.	Bistriazinyl pyridine (BTP)	
2.	Bistriazinyl bipyridine (BTBP)	
3.	C5-BTBP [6,6'-bis(5,6-dipentyl-(1,2,4)triazin-3-yl)-(2,2')bipyridine]	
4.	CyMe₄-BTBP [6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-(1,2,4) triazin-3-yl)-(2,2')bipyridine]	
5.	DMDOHEMA [N,N'-dimethyl-N,N'-dioctylhexylethoxy-malonamide]	

of 0.025 M HNO_3 ([Am] about 5.5 mM, pH 3.55 adjusted with 1 M NaOH) was added to a solution of ATP in water with an Am:ATP molar ratio of 1:3. An ESI mass spectrum was recorded with a quadrupole ion-trap mass spectrometer, at an Am:ATP molar ratio of 1:3, at a pH of 3.55, and sample flow rate of 120 μL hr^{-1} (Mostapha et al., 2014). The different ions observed were $[Am(NaHATP)_2(NaH_2ATP)]^{2-}$ at a m/z ratio of 911.2 (1:3 complex), $[Am(NaHATP)(HATP)]^{2-}$ at m/z 635.7 (1:2 complex), and $[Am(NaHATP)_2]-$ at m/z 1,294.6 (1:2 complex). This study showed that Am forms a soluble complex with an excess of ATP, and was observed to form an insoluble complex, before 1:1 stoichiometry.

There are only a few studies reported of Am-complexes with ESIMS, due to the challenges associated with Am radiotoxicity. It is believed that with renewed interest in the use of nuclear energy to meet the ever-increasing demand of electricity, and thrust in the development of new extractants to partition minor actinides, researchers at a few more international laboratories will venture into ESIMS studies of complexes of Am and other actinides to understand the various chemical aspects.

C. Gas-Phase Chemistry of Am

Organo-metallic gas-phase chemistry studies on trans-plutonium actinides are challenging due to the associated radioactivity, and because this radioactivity requires materials to be suitably handled with instruments enclosed in α-containment glove boxes. The gas phase chemistry is interesting because there are no perturbing factors like solvation (in solution chemistry) or lattice neighbors (in solid-state chemistry). The reactivity of any metal ion with any organic reagent or species can, therefore, be directly related to the electronic configuration of the metal ion and thermo-chemistry aspects or energetics. Also, it is possible to generate easily the low-valent species (M^{2+}, M^{3+}, etc.) in the gas phase compared to that in the condensed phase. The studies for different lanthanides and actinides in the gas phase, over the last two decades, are reviewed in a few publications (Gibson, 2002; Gibson & Marcalo, 2006).

Laser ablation with prompt reaction and detection (LAPRD) was employed on actinides gas phase chemistry by Gibson (1998a). In these experiments, a 2 mJ output pulsed laser (XeCl, $\lambda = 308$ nm) was focused onto the americium oxide-containing Cu target. The ablated ions travel a distance of about 3 cm long reaction zone, which contains a reagent for product formation. After a 35-μsec delay of the laser pulse, the product ions formed as well as the unreacted ions are injected orthogonally into a reflectron ToF mass spectrometer for measurement. The LAPRD experiments were done with different actinide-containing targets: pure Am, Am + Np, and Am-Tb-Tm. Seven alkene reactants were used for studies. These reactants showed M^+-induced dehydrogenation in the order: ethene < *trans*-2-butene < 1-butene < benzene < cyclohexene < 1,3,5,7-cyclooctatetrene (COT) < 1,5-cyclooctadiene (COD). Am^+ was inert for the linear and cyclic C_6 alkenes, whereas dehydrogenation products $[Am\text{-}C_8H_8]^+$ and $[Am\text{-}C_8H_6]^+$ were observed with COD and COT. The yields of these products were lower than with the preceding actinide. The data showed that 5f electrons of Am^+ do not substantially participate in C–H or C–C activation. This poor participation is because the ground-state Am^+ has an electronic configuration of $[Rn]5f^77s^1$, and this electronic configuration must be excited to $[Rn]5f^66d^17s^1$ with an activation energy of 245 kJ mol^{-1}. The results of these studies showed that the 5f electrons are ineffective at forming σ-bonds in the C-An-H intermediate.

Gibson (1998b) employed metal polymer co-ablation (MPCA) with a pulsed laser, and a reflectron time-of-flight mass spectrometer (R-TOFMS) to study the organo-metallic gas phase chemistry of Am. $^{243}AmO_2$ was dispersed in a polyimide organic matrix, and the mixture was co-ablated into vacuum. A XeCl excimer laser (λ 308 nm) with a target irradiance of 10^8 W cm^{-2} or a pulsed coumarin-503 (C503) dye laser (λ 488 nm) with a target irradiance of 10^7 W cm^{-2} was used for ablation. These studies were undertaken to investigate the expected trend of decrease in covalency with increase in the atomic number across actinide series, in organo-actinide bonding, due to the contraction of the 5f electrons, and finally transition into fully ionic bonding like that in lanthanides. In the case of Am, a quasi-lanthanide-like behavior is expected. Polyimide poly-{*N,N′*-(1,4-phenylene)-3,3′,4,4′-benzophenonetetracarboxylic imide/amic acid, $[-C_{23}H_{10}O_5N_2-]_n$ (Aldrich no. 18464-0) was used for ablation because it produces fragment radicals (e.g., C_nH_n, C_nH_x [x odd], CN), closed-shell ligand L species (e.g., alkynes and nitriles) with high intensities and fullerenes. An electron ionization source was also incorporated in the ion source to study the neutrals generated with laser ablation. The intensity of $AmCN^+$ was much higher than that of AmC_2H^+, in comparison to that with U, Np, and Pu, where the intensities of these two ions were comparable. The abundance of AmO^+ peak was observed to be quite small due to the low dissociation energy (550 kJ mol^{-1}) of AmO. The intensities of other species were in the order $AmC_2^+ < AmC_2H^+ < AmCN^+$. These observations, along with the very high electron affinity of [CN] (372 kJ mol^{-1}) compared to that of $[C_2H]$ (282 kJ mol^{-1}), suggested that the bond in $AmCN^+$ is more ionic than that in lower actinides. A high-intensity peak at m/z of C_{110}^+ was conclusively assigned to an $Am^{2+}\text{-}C_{90}^-$ fullerene species. These results were corroborated by interpretations and the studies performed previously by Gibson on lower actinides and various lanthanides.

Santos et al. (2003) reported the studies on the gas phase thermochemistry of Am oxides with FTICR mass spectrometry. ^{243}Am-Pt alloy (2% Am) was prepared by melting in an arc-melting furnace. The FT-ICR system equipped with a three Tesla magnet and fundamental wavelength (1,064 nm) Nd-YAG laser was used. The Am^+/AmO^+ ions were produced with laser desorption ionization (LDI) of the oxide layer on the sample surface or by reaction of Am^+ with $C_2H_4O_2$ or O_2. Argon gas (10^{-5} torr) was introduced into the mass spectrometer either through pulsed valves or a leak valve for collisional thermalization of the reactant ions. Reactions of Am^+ performed with the oxidants N_2O, C_2H_4O, H_2O, O_2, CO_2, and NO led to the formation of AmO^+ with all reagents except NO. Similar reactions of AmO^+ showed that AmO^+ reacted only with C_2H_4O to form AmO_2^+. The ionization energies of AmO (5.9 ± 0.2 eV) and AmO_2 (7.23 ± 0.15 eV) were determined, and bond-dissociation energies of Am^+-O (560 ± 30) kJ/mol and OAm^+-O (390 ± 40) kJ/mol were estimated. Such studies are very important to fundamentally understand the periodic chemical behavior of the actinides and to unravel the nature of 5f electrons.

Vapor pressure is an important thermophysical property of nuclear fuel to predict the behavior under normal operational and accidental conditions in a nuclear reactor. Such studies are important for Am and its compounds due to the P&T concept for minor actinides. Knudsen Effusion Mass Spectrometry (KEMS) was used (Gotcu-Freis et al., 2011) to study the vaporization behavior of americium dioxide (AmO_2) up to 2,200 K. Various species produced during vaporization at high temperature were identified, and their vapor pressures, ionization energies, and bond-dissociation energies were determined. The vapors were generated in tungsten and iridium Knudsen cells. About 30 mg of the sample, annealed in air up to about 1,200 K for a few hours to obtain $AmO_{2.00}$, was used for vapor-pressure measurements. The temperature of the Knudsen cell was increased at a rate of 10 K/min. The ion currents of Am^+, AmO^+, and AmO_2^+ were measured at various fixed temperatures, with variation of electron ionization energies (2 eV to about 40 eV). It was found that about 49% of $AmO_{2(g)}$ dissociates into AmO, and 33% into Am metal, with a final composition of the vapor phase as approximately 18% Am, 35% AmO, and 47% AmO_2. These vapor phase composition studies are the first studies done with pure americium dioxide sample with high-temperature mass spectrometry, and the total vapor pressures measured were slightly lower than those reported previously (Ackermann et al., 1966). These studies also showed a different vaporization behavior of AmO_2 compared to Np and Pu oxides, in that only dioxide was the major species with small amounts of monoxide and no metallic vapor. These results emphasize the importance to generate gas-phase data from the various compounds of each actinide (e.g., Am) and not from any homologs or other actinide compounds.

IV. CERTIFIED REFERENCE MATERIALS FOR Am

Despite the recognized need, no certified isotopic reference material (CRM) of Am (e.g., for $^{243}Am/^{241}Am$ isotope ratio) is commercially available till now. Also, no chemical assay reference material of Am is available to calibrate an ^{243}Am spike used in isotope-dilution mass spectrometry. Researchers assume that the atomization and ionization behavior of Am is similar to that of Pu in TIMS and ICPMS and this assumption is not true. The international laboratories (e.g., IRMM, NBL, NIST, etc.) with infrastructure, access to ^{243}Am, and with experience to prepare and characterize the reference materials, should adventure into the preparation and characterization of such reference materials for Am. With the increased dependence on nuclear energy, and extended burn-up of the irradiated fuels, the amount of ^{241}Am produced will further increase, and, therefore, the mass spectrometric methodologies (TIMS, ICPMS, etc.) for accurate determination of Am, will be in greater demand in future. Additionally, these reference materials will help to improve the accuracy of nuclear data (e.g., the α-decay half-life of ^{243}Am) with the relative activity method.

V. CONCLUSIONS AND FUTURE PERSPECTIVES

Certified reference materials of Am (for isotopic and chemical assay) are essential to understand the ion-source chemistry in TIMS, and to study the effect of various parameters in Am analysis with ICPMS. TIMS and ICPMS are the two complementary analytical techniques that will find more applications for Am analysis in spent fuels, nuclear forensics, and in environmental and biological samples. The popularity of electrospray ionization with a quadrupole ion-trap mass spectrometer to perform collision-induced dissociation, by inorganic mass spectrometrists, will unravel new aspects of solution and gas-phase chemistry of Am and its complexes with novel complexing agents and diluents. Quantitaive correlation of the gas-phase species observed with ESIMS to those actually present in the solution is still in its infancy and must be done with great caution. Studies of Am complexes with various soft complexing agents are needed to confirm a slight enhancement of covalency (i.e., somewhat softer character of actinides ions compared to lanthanide ions) in actinide metal-ligand bonds compared to that in lanthanides. The results will be further interpreted and supported by various theoretical models based on density functional theory (DFT), and so on. There is, however, no substitute to quality experimental data. AMS, because of its ability of atom counting, will play an important role for ultra-trace determination of Am in various complex environmental and biological matrices. The AMS method must be evaluated for ^{241}Am and ^{243}Am determination in building materials (e.g., cement, concrete, etc.) because the EPA-approved method of alpha spectrometry depends on a minimum of 4 hr of spectrum recording, in addition to the usual difficulties of poor energy resolution and interferences from close-lying alpha energies of ^{238}Pu and ^{228}Th (www.epa.gov). TIMS and SIMS will be highly useful to experimentally determine the transmutation of Am dispersed in an inert magnesia matrix, in a fast reactor (Lamontagne et al., 2013). For studies on trans-plutonium actinides, international collaborations in terms of availability of actinide isotopes, α-containment facilities, glove-box enclosed instruments, human-resources, and expertise is the best route to generate world-wide useful and reliable data for safe and efficient use of nuclear energy. This collaboration assumes particular significance for radioactive samples in view of the security and safety issues associated with the transport of such samples to another laboratory for analysis, and with the costs involved in shipping these samples.

ABBREVIATIONS

AMS	accelerator based mass spectrometry
BTBP	bis triazinyl bipyridines
CHON	carbon hydrogen oxygen nitrogen
CID	collision induced dissociation
COD	cyclo octa diene
COT	cyclo octa tetrene
CMPO	carbamoyl methyl phosphine oxide
CRM	certified reference material
DFT	density functional theory
DGA	di glycol amide
DIAMEX	diamide extraction
DMDOHEMA	dimethyl dioctyl hexyl ethoxy malonamide
DRC	dynamic reaction cell
ERMS	energy resolved mass spectrometry
ESIMS	electrospray ionization mass spectrometry
FTICR-MS	fourier-transform ion cyclotron resonance mass spectrometry
GPEC	gas-pressurized extraction chromatography
HDEHP	diethyl hexyl phosphoric acid
HFIR	high flux isotope reactor
HMB	hydroxy methyl butyric acid
HPLC	high performance liquid chromatography
IAEA	international atomic energy agency
ICPMS	inductively coupled plasma-source mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectroscopy
IDMS	isotope dilution mass spectrometry
IRMM	institute of reference materials and measurements
KEMS	knudsen effusion mass spectrometry
LA-ICPMS	laser ablation-inductively coupled plasma mass spectrometry
LAPRD	laser ablation with prompt reaction and detection
LOQ	limit of quantification
MAs	minor actinides
MC	multiple collector
MOX	mixed oxide
MPCA	metal polymer co-ablation
NBL	new brunswick laboratories
NIST	national institute of standards and technology
ORIGEN	oak ridge isotope generation
P&T	partitioning and transmutation
RIMS	resonance-ionization mass spectrometry
RTG	radioisotope thermoelectric generator
R-ToF	reflectron time-of-flight
SANEX	selective actinide extraction
SEM	secondary electron multiplier
SF	sector field
SNF	spent nuclear fuel

TALSPEAK	trivalent actinide-lanthanide separation with phosphorous reagent extraction from aqueous komplexes
TBP	tributyl phosphate
TEVA	tetravalent actinides
TIMS	thermal ionization mass spectrometry
TRU	transuranites

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