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A review on the mass spectrometric analysis of thorium

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Abstract: Mass spectrometric analysis of thorium is of great interest to geo-scientists and nuclear technologists. Though thorium is considered to be a mono-isotopic element for all practical purposes, the $^{230}\text{Th}/^{232}\text{Th}$ isotopic ratios provide useful information for various applications, e. g. dating of corals, build-up of ^{232}U during reactor irradiation, etc. Among the gamut of mass spectrometric techniques available for the isotopic analysis of different elements, thermal ionization mass spectrometry, inductively coupled plasma mass spectrometry and secondary ion mass spectrometry are more commonly used for Th analysis. The problems of blank contribution and poor ionization efficiency of thorium, which are more serious in thorium mass spectrometric analysis, are discussed. The present state of the Th mass spectrometry is highlighted, with the futuristic increased use of thorium in energy production, in focus. The need to prepare and make available the certified isotopic reference materials for $^{230}\text{Th}/^{232}\text{Th}$ isotope ratios is emphasized.

Keywords: Thorium, Th-230/Th-232, mass spectrometry, nuclear technology, geosciences.

1 Introduction

Thorium (Th) is an important primordial element in the actinide series and occurs as monazite (rare earth thorium-phosphate mineral with 3 to 9% of thorium oxide) in the igneous rocks in nature. There are a number of thorium isotopes, both natural and man-made, viz. ^{228}Th , ^{229}Th , ^{230}Th , ^{232}Th , ^{234}Th , which are encountered at different stages of the nuclear fuel cycle. All these isotopes of thorium are radioactive, with ^{232}Th being the longest-lived isotope with an alpha decay half-life of 1.40×10^{10} yr.

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^{230}Th ($t_{1/2} = 7.5 \times 10^4$ yr) is produced by the α -decay of ^{234}U and its abundance depends upon the amount of ^{234}U in the uranium sample and the time elapsed since the separation of uranium from thorium. ^{229}Th ($t_{1/2} = 7340$ yr) is the decay product of ^{233}U , which is produced by thermal neutron irradiation of ^{232}Th in a nuclear reactor. ^{228}Th ($t_{1/2} = 1.9$ yr) is the daughter product of ^{232}U which is produced by two successive (n, γ) reactions with ^{230}Th via the formation of ^{231}Pa , and by ($n, 2n$) reaction on ^{233}U . Thorium was considered a mono-isotopic element in the past. However, because of the significant abundance of ^{230}Th in deep-seawater, the Commission on Isotopic Abundances and Atomic Weights (CIAAW) of the International Union of Pure and Applied Chemistry (IUPAC), in 2013, recognized thorium as an element with two naturally-occurring isotopes, viz. ^{230}Th ($0.02 \pm 0.02\%$) and ^{232}Th ($99.98 \pm 0.02\%$) and recommended the average atomic weight of thorium as 232.0377(4) instead of 232.03806(2).

Thorium is a silvery white metal and is four times more abundant than uranium in the Earth's crust. Its potential as a nuclear fuel offers an alternative for safer and cleaner nuclear energy production, with simultaneous benefits of reduced volume and shorter life-time of the nuclear waste. Thorium-232, itself, is a fertile nuclide and leads to the formation of fissile nuclide ^{233}U , by neutron capture in a nuclear reactor. This $^{232}\text{Th}(n, \gamma)$ nuclear reaction is utilized to produce significant quantities of ^{233}U , with thorium as a blanket material in nuclear reactors. Thorium mixed with ^{233}U , enriched ^{235}U or plutonium (Pu) is an important nuclear fuel for the advanced heavy water reactor (AHWR) technology [1–4]. Use of thorium in nuclear reactors is the third stage of the Indian Nuclear Energy programme envisioned by its founder Homi J. Bhabha. Thorium dioxide fuel bundles are also used in the primary core for initial flux flattening to achieve full power operation in the first phase of pressurized heavy water reactor (PHWR) operation [2, 3]. Currently, attempts are underway to generate triply charged ions of ^{229}Th for the development of a nuclear frequency standard, by the utilization of nuclear transition in the isomeric state of ^{229}Th [5, 6]. The ion $^{229}\text{Th}^{3+}$ has a high ionization potential (27 eV) and a relatively simple electronic structure and is, therefore, the most suitable to determine the energy value of the isomeric state. One of the undesirable uses of thorium is in the

manufacture of the illicit drug methamphetamine, where thorium oxide is used as a catalyst to produce phenylacetone (P2P) which is a precursor of methamphetamine [7].

Isotope geologists use $^{230}\text{Th}/^{234}\text{U}$ daughter/parent nuclide pair for dating. Thorium isotope ratio measurements are also important to date corals by uranium-series disequilibrium method. These data are also important to understand sea level, radiocarbon calibration, rates of ocean and climate change, and timing of El Nino [8–10]. Thorium is highly insoluble in ocean, with residence times of about 20 yr in the ocean. This short residence time makes it very responsive to changes in the environment. The isotopes of Th are useful to study a wide variety of processes in the open ocean, including assessment of productivity and of ocean circulation. The behavior and uses of these isotopes in the near-shore and shelf environment are also important in spite of the preferential removal of Th from the oceans at their margins.

Thorium is a refractory element with high first ionization potential (6.3 eV), which affects the Th^+ ion yield. Analysis of Th with any mass spectrometric technique demands the production of atomic or molecular ions of thorium. There are a number of mass spectrometric techniques which are used for Th analysis. These include thermal ionization mass spectrometry (TIMS), inductively coupled plasma source mass spectrometry (ICPMS), glow discharge mass spectrometry (GDMS), secondary ion mass spectrometry (SIMS), resonance ionization mass spectrometry (RIMS), and accelerator mass spectrometry (AMS). The high first ionization potential of thorium restricts the sensitivity of TIMS, but ICPMS and SIMS provide much higher ionization of Th, give higher precision and offer the capability to work with smaller samples. Generally, data on $n(^{230}\text{Th})/n(^{232}\text{Th})$ and $n(^{230}\text{Th})/n(^{234}\text{U})$ ratios are required in geo-sciences and nuclear technology. The concentration of Th is also needed for various applications. For example, the amounts of ^{230}Th in thorium and ^{232}Th in natural or enriched uranium used in nuclear reactors is required to calculate the amount of ^{232}U . This is because of ^{208}Tl progeny in the decay chain of ^{232}U , due to a high energy (2.8 MeV) gamma ray radiation, which governs the shielding requirements in future handling of the irradiated fuel [11].

A number of reviews are available in literature on the mass spectrometry of uranium and plutonium. But no comprehensive review on the mass spectrometry of thorium is available till today. This manuscript bridges this gap and gives the present state of art of the mass spectrometric analysis of thorium in nuclear technology and geo-sciences. It also highlights the precautions that need to be taken to confirm the absence of thorium blank in MS

analysis. Finally, the need of thorium spikes and isotopic reference materials of thorium is discussed.

2 Thermal ionization mass spectrometry (TIMS)

Thermal ionization mass spectrometry (TIMS) is a highly useful and well-recognized analytical tool for the determination of isotopic composition of different elements in the Periodic Table and it is commonly used to obtain isotopic abundances of different actinide elements associated with the nuclear fuel cycle. For thorium isotopic analysis by TIMS, a few challenges, like poor ionisation yield of Th^+ , low abundance of ^{230}Th (a few ppm), blank contribution from filament and reagents require special attention. High purity zone refined filament materials are to be used for sample loading. These filaments must be checked for the presence of thorium and out-gassed either in the mass spectrometer or in a separate degas unit, prior to sample loading. Special sample loading techniques like use of colloidal carbon loaded single or multiple filament assembly is necessary to enhance the yield of Th^+ ions. About 50 to 500 ng of thorium is required for TIMS analysis with single or triple filament loading. Also the abundance sensitivity (i. e., the contribution of major isotope at the minor isotope due to ions scattering) of the mass spectrometer must be determined and correction for the contribution of $^{232}\text{Th}^+$ at $^{230}\text{Th}^+$ must be made. Further, to achieve good precision in the isotope ratio data, $^{230}\text{Th}^+$ is usually measured with an ion counting system which uses a secondary electron multiplier (SEM) or a Daly detector on the axial channel. However, the use of SEM/Daly introduces additional parameters, i. e. gain calibration factor of SEM/Daly to Faraday cup and dead-time of SEM/Daly, and these factors must be considered in data processing. It is worth mentioning that present generation TIMS instruments available commercially are equipped with energy filters (e. g. wide aperture retarding potential WARP in PhoenixTM from IsotopX, retarding or repelling potential quadrupole RPQ in TRITONTM Plus from ThermoFisher) which give abundance sensitivity of a few ppb at ($M\pm 2$) mass with respect to M . These instruments are popularly known as high abundance sensitivity (HAS) mass spectrometers. Static multi-collector mode of data acquisition, with the axial ion counter for $^{230}\text{Th}^+$ and an off-axis Faraday cup for $^{232}\text{Th}^+$, is used to eliminate the time dependent fluctuations in the ion intensity. Gravimetrically prepared isotopic reference materials are required to deter-

mine the fractionation factor (mass bias) in TIMS analysis, when absolute isotope ratios are of interest.

For isotope dilution mass spectrometry (IDMS) of thorium, two isotopes, viz. ^{229}Th and ^{230}Th , can be used as spikes or tracers. ^{229}Th is a preferred spike isotope when data on both ^{230}Th and ^{232}Th are required. Alternatively, ^{230}Th can also be used as a spike. The equilibration of sample and spike isotopes is performed by repeated drying and re-dissolving. For the separation and purification of thorium from complex samples, ion-exchange resins (from BioRad or preferably Eichrom) must be checked for column blanks and co-elution of the organic matter in Th-fraction. During the TIMS analysis of spiked Th samples, sometimes, dynamic peak jumping mode with one Faraday cup is used to eliminate the uncertainty of changes in the gains of the Faraday cups and their inter-gain calibration, and also non-linearity over a wide range of intensity values. This is achieved by measurement of $^{229}\text{Th}/^{230}\text{Th}$ and $^{229}\text{Th}/^{232}\text{Th}$, independently at two different temperatures, from the same filament loading. However, this introduces another uncertainty due to differences in the isotope fractionation behaviour at two different temperatures of the filaments. An alternative way to eliminate uncertainty of gain changes of Faraday cups is to employ virtual amplifiers concept available in the Thermo TIMS instrument. A comparison of TIMS with other methodologies for the analysis of $^{232}\text{Th}/^{230}\text{Th}$ in volcanic rocks was presented by Rubin in 2001 [12].

Th is one of the most difficult elements to ionize in TIMS because of its strong electronegativity. The ionization efficiency decreases with increase in sample size because of decrease in the work function of the Re filament. A significant improvement in the ionization efficiency was reported by loading Th as ThF_4 , using a double rhenium filament assembly [13]. This improvement in the ionization was attributed to increase in the work function of Re because of change in the dipole moment of the metal-ion cloud (F^-) interface. An ionization efficiency of 2×10^{-4} was obtained with about 200 ng of Th loaded onto the filament. With evaporation and ionization filament temperatures of 1000 °C and 1950 °C, respectively, stable ion currents of Th^+ for 2–4 h with negligible isotope fractionation were obtained. A triple filament Re assembly, with boric acid as an activator, was used to analyze 50–100 ng of thorium [14]. The sample filament was heated to dull red at 2.0 A for 20 s before loading into the mass spectrometer. Th isotope ratios were analyzed by ^{229}Th bridge method, which involved peak jumping for ^{229}Th and ^{230}Th on the Daly detector at higher signal intensity ($> 1 \times 10^{-12}$ A) of ^{232}Th , followed by a second measurement with peak jumping of ^{232}Th and ^{229}Th at lower intensity of ^{232}Th

(2×10^{-13} A). Single filament assembly of high purity Re, outgassed and loaded with graphite, was used to analyze Th separated from coral samples [12]. ^{229}Th was used as a spike to determine ^{230}Th and ^{232}Th in the separated and purified fraction of thorium. About 50–100 ng of Th was analyzed with single filament assembly by loading Th onto a bed of carbon mixed with finely divided metallic Ir powder on Re filament. Stable Th^+ ion beam with a controlled carbon burn-off and an ionization efficiency of $6\text{--}8 \times 10^{-4}$ was achieved. An efficiency of 10^{-3} was achieved by sintering about 1–2 mg of Ir powder into a V-shaped Re filament during outgassing, followed by loading C and thorium [12].

Charge collection thermal ionization mass spectrometry was developed for determining low abundant isotope ^{230}Th , in view of its very low intensity [15]. In this method, instead of the commonly used high-value resistor with the Faraday cup, a capacitor was used. The capacitor accumulates the charge and gives rise to a time-varying voltage proportional to the ion-current. Thorium solution was loaded onto the out-gassed carburized zone-refined rhenium dimple filaments with thorium in between the two graphite layers. This was done to prevent the oxidation of rhenium filament and to improve the ionization efficiency of thorium in thermal ionization. The charge collection method when tested with filaments loaded with 15 pg of ^{230}Th , yielded Th^+ intensities up to 6×10^{-14} A over 1 h. The ionization efficiency of about 4% and analytical precision better than $\pm 0.6\%$ were achieved. The method was applied to thorium isotopic analysis in uraninite standard and a coral sample, with ^{229}Th as a tracer.

TIMS studies were reported on the formation of atomic (M^+) and molecular (MO^+) ions of thorium and uranium with different synthetic mixtures with Th/U amount ratios of 10, 1 and 0.1, and high purity rhenium double filament assembly with conventional sample loading technique of HNO_3 solution [16]. The intensity of ThO^+ was 10 times that of Th^+ at vaporization filament heating current of about 3.5 A, in spite of low ionization energy of Th (6.307 eV) compared to that of ThO (6.602 eV). This was explained on the basis of the combined effect of vaporization characteristics of thorium oxide from the rhenium filament and relative stabilities of the species in the vapor phase. The presence of Th on the filament during TIMS analysis of U was found to enhance the stability of the UO^+ ion. Because of the higher intensity, the ThO^+ ion was recommended for the isotopic analysis of Th, whereas both U^+ and UO^+ ions were considered useful for the TIMS analysis of U. The method was validated with TIMS determination of ^{232}U (2000 ppm) in a synthetic U sample, with Th/U amount ratio of 100, preceded by anion exchange separation of Th and U. The separation was car-

ried out using U-TEVA resin in an acid leached glass column, which was conditioned by washing with 4 M HNO₃. Loading of U and Th onto the resin was done using 4 M HNO₃. Thorium was eluted with 9 M HCl followed by 15 mL of 5 M HCl. U was then eluted with 0.1 M HNO₃. The separated fractions were converted into 1 M HNO₃ medium and were taken up for TIMS analysis. Chemical yield of more than 95% was achieved for both Th and U. The $n(^{232}\text{U})/n(^{233}\text{U})$ ratio obtained from the purified sample, after chemical separation, agreed with that obtained in pure U sample.

3 Inductively coupled plasma mass spectrometry (ICPMS)

MC-ICPMS is quite popular for the isotopic analysis of thorium. The magnetic sector based instruments are more popular compared to quadrupole based ICPMS, because of the flat-topped peak shapes with the former compared to Gaussian peak shape with the latter. The use of ICP as an ion source offers relatively high ionization efficiency of Th, has less stringent requirements on sample purity, and allows rapid analysis. In ICPMS, the Th solution in dilute HNO₃ is introduced into the argon plasma with a pneumatic nebulizer and the atomic ions generated are introduced into the mass analyzer through sampling and skimmer cones, which are pumped differentially. The ions of different masses of an element can be detected and measured simultaneously, in the static multi-collection mode, with a multi-Faraday cup system. An ion counting system which consists of a Daly detector or a secondary

electron multiplier is incorporated in the commercially available MC-ICPMS instruments. This ion counting system can be used to measure a low abundant isotope, e. g. ²³⁰Th (3–8 ppm) in the case of thorium in volcanic rocks. Standard-sample-standard (SSB) bracketing approach is employed to take care of the drift in the ion intensity. In the early stages of the work with Th isotope ratios, uranium was used as a proxy to correct for mass bias and also as a bracketing standard. However, this is not correct because of small differences in the transmission through sampler and skimmer cones of thorium isotopes with lower masses compared to uranium isotopes with heavier masses.

MC-ICPMS was used to determine ²³⁰Th/²³²Th isotope ratios in river water samples and silicate minerals [17]. Static multi-collection mode was used for data acquisition to reduce the consumption of the sample, that allows a minimum of material to be analysed. But the disadvantage is that the inter-cup gain and abundance sensitivity cannot be assessed during the course of the mass spectrometric analysis. Because the collector configuration of the MC-ICPMS from Nu Instrument is such that thorium isotopes cannot be analysed in static mode with the “zoom” optics configured for a single mass spacing, the “zoom” optics were set to achieve a 0.667 mass spacing between ²³²Th and ²³⁰Th. A precision of 1% at the 95% confidence level was achieved for the determination of thorium isotope ratios in low-concentration geological materials.

MC-ICPMS studies were performed with thorium standards and in ocean particulates [18]. The results showed that only 0.4 pg of ²³⁰Th is required to determine ²³⁰Th/²³²Th isotope ratios with errors less than 5 times those of TIMS, even for cases where ²³⁰Th/²³²Th is 10⁻⁵ or less. Compared to TIMS, the ICP-MS method allowed

Table 1: Various isotopes of thorium encountered at various stages of nuclear fuel cycle. TS^b

Th-isotope	Half-life	Decay mode	Method of production	Remarks
²²⁸ Th	1.9 yr	A	α-decay of ²³² U	Used as a tracer in radiochemistry experiments
²²⁹ Th	7340 yr	A	α-decay of ²³³ U	Used as a spike in IDMS and IDAS; determination required in nuclear forensics; its nuclear isomer useful in nuclear frequency standard due to its remarkably low excitation energy of (7.6±0.5) eV
²³⁰ Th	7.5 × 10 ⁴ yr	A	α-decay of ²³⁴ U	Used as a spike in IDMS and IDAS; determination required in nuclear forensics and in geo-chronology for ocean sediments
²³² Th	1.4 × 10 ¹⁰ yr	A	Naturally occurring (monazite)	Useful to convert into ²³³ U fissile isotope; will give ²³² U by double beta decay
²³⁴ Th	24.1 d	β	α-decay of ²³⁸ U	Extracted from natural U; used as a tracer in radiochemistry experiments, e. g. solvent extraction

TS^b Please mention Table 1 in the text.

Table 2: Comparison of TIMS and ICPMS for thorium analysis.

Parameter	TIMS	ICPMS	Remarks
Ionization efficiency	0.005 to 0.05%	0.2%–0.3%	Lower sample amount needed in ICPMS
Memory/carry-over effect	No memory effect	Memory effect needs to be monitored	Wash out needed in ICPMS after each sample injection
Time of analysis	About 2–3 h	About 1–20 min	High throughput possible with ICPMS
Isobaric interferences	Isobaric interference from $^{232}\text{U}^+$	Molecular isobaric interferences exist	Molecular isobaric interferences need to be checked in ICPMS
Sample introduction	Single or multiple filament with graphite loading	Thorium solution in dilute HNO_3 medium	Laborious sample loading in TIMS; blank from filament to be controlled in TIMS
Spike isotope needed	Spike isotope required for concentration determination	Concentration can be determined without spike addition	Rhodium or another element can be added as an internal standard for analysis by ICPMS
Instruments available commercially	MC-TIMS: TritonPlus with RPQ from ThermoFisher, Germany; Phoenix with WARP filter from Isotopx, UK	MC-ICPMS: NeptunePlus from ThermoFisher, Germany; NuPlasma from Nu Instruments, UK	MC-ICPMS is more expensive than MC-TIMS

smaller sample size and higher sample throughput due to higher sensitivity, fewer sample preparation steps and shorter measurement times. However, the memory effect that basically does not exist with the TIMS method must be removed before each sample measurement or the accuracy of the measurements may be compromised.

$^{230}\text{Th}/^{232}\text{Th}$ isotope ratios were determined in volcanic rocks and other Th isotope standards with ThermoFisher Neptune MC-ICPMS [19]. It was proved conclusively that the use of uranium isotopic standards to correct for linearity, ion transmission and mass bias differences in thorium leads to 2%–3% lower $^{230}\text{Th}/^{232}\text{Th}$ isotope ratios and, therefore, should be abandoned. This study utilized UCSC ThA reference material for normalization of the isotope ratio data obtained on Th. Detailed studies were performed to show that the linearity differences between decadal differences in count rates can be of the order of two percent; ion transmission of RPQ filter for Th and U differs by up to 3%–4%; and that mass bias fractionation factor (f) is significantly different for U and Th ($f_{\text{U}}/f_{\text{Th}} = 0.76$). This study also stressed the need to make available well characterized isotopic reference materials for the $^{230}\text{Th}/^{232}\text{Th}$ isotope ratios.

The memory effect of Th needs to be monitored and adequate washing must be done [20]. In a recent study on the dating of young corals, the memory effect was alleviated by flushing the system prior to analysis of a new sample, for 15 min, with 5% aqua-regia followed by 2% HNO_3 to prevent any cross contamination or “memory”

Table 3: $^{232}\text{Th}/^{230}\text{Th}$ isotope ratios in various samples.

Sample type	$^{232}\text{Th}/^{230}\text{Th}$ ratio
Marine corals	About 10 to 500
Igneous rocks	> 150 000
Natural thorium	> 10^6

effect [10]. Because TIMS and ICPMS are the two commonly used mass spectrometric techniques for thorium analysis, a comparison of their salient features is given in Table 2. Table 3 gives the $^{232}\text{Th}/^{230}\text{Th}$ isotope ratios expected in various samples.

4 Secondary ion mass spectrometry (SIMS)

Secondary ion mass spectrometry is a useful mass spectrometric technique for the direct analysis of solid samples, e. g. rocks. This involves the generation of secondary ions by sputtering the sample with primary ions of caesium or oxygen and generating positive or negative secondary ions, respectively. This technique offers the potential to perform surface analysis, micro analysis, and depth profiling with variation in the energy and intensity of the primary ion beam.

SIMS, with a high-resolution and high-transmission ion microprobe (Cameca IMS 1270), was used to determine $^{232}\text{Th}/^{230}\text{Th}$ ratios in volcanic basaltic rocks [21]. The separated and purified Th fraction from the rock samples was mounted on a planchet of spectrographically pure carbon. The distribution of Th solution into the carbon was achieved by slight heating of the planchet during deposition and this integration of thorium with carbon prevented charging problems during SIMS analysis. The sample was bombarded with 100–250 nA of O^- primary ions produced in a duoplasmatron source. An ionization efficiency of about 2% was achieved, which is much higher than that in TIMS and ICPMS. The Th^+ ions were monitored at a resolving power of about 2000, and ^{230}Th was measured with an SEM and ^{232}Th with a Faraday cup. The results obtained on $n(^{230}\text{Th})/n(^{232}\text{Th})$ ratios in reference materials and rock materials characterized by other mass spectrometric techniques give excellent agreement. The method appears promising because of low sample size requirement, simple sample preparation and rapid analysis for achieving a reproducibility of better than 1%. However, because of hydride formation in SIMS, the amount of ^{229}Th spike to be added for IDMS has to be restricted and the contribution of $^{229}\text{ThH}^+$ (about 1% of $^{229}\text{Th}^+$) must be accounted for by the determination of ThH^+/Th^+ from $^{232}\text{Th}^+$ and $^{232}\text{ThH}^+$ peaks in the same sample. Further, the use of ThO^+ instead of Th^+ is worthy of future investigations.

Time-of-flight SIMS was used to determine thorium electrodeposited on stainless steel disks and to establish a correlation of SIMS data with those from alpha spectrometry [22]. Primary ion beam of 25 keV Bi^+ ions, with an intensity of 1 pA, was employed and the mass spectra of secondary ions were recorded in both the positive and the negative ion modes. Intensities of various ions of thorium including atomic, and molecular – viz., oxide, hydroxide and oxy-hydroxide etc., were measured. These ions were $^{232}\text{Th}^+$, ThO^+ , ThOH^+ , ThO_2H^+ , $\text{Th}_2\text{O}_4\text{H}^+$, ThO_2^- , ThO_3H^- , ThH_3O_3^- . The measured intensities of $^{232}\text{ThO}^+$, $^{232}\text{ThOH}^+$, $^{232}\text{ThO}_2\text{H}^+$ indicated the presence of oxidized forms of thorium in the upper layers of the surface and linear correlations between alpha spectrometry and SIMS data were obtained.

5 Accelerator mass spectrometry (AMS)

Accelerator mass spectrometry was used for the determination of ultra-trace amounts of Th in high purity Cu used

for detectors and shielding materials in rare-event physics GERDA neutrino experiment [23]. AMS involved the generation of negative ions by sputtering with ionized Cs ions. For Th determination in Cu, ThCu^- (m/z 295) ions were generated and used. These negative ions were injected into the tandem accelerator with a terminal voltage of about 10 MV. The positive ions were generated by stripping of several electrons from the negative ions, by a carbon stripper foil in the high voltage terminal, and Th^{9+} ions were used for detection with a time-of-flight system and a silicon surface barrier detector. The lowest Th concentration determined was $(1.5 \pm 0.6) \times 10^{-11}$ g/g which corresponds to (59 ± 24) $\mu\text{Bq/kg}$.

6 Resonance ionization mass spectrometry (RIMS)

Resonance ionization mass spectrometry offers the potential to provide much higher ionization efficiency (10^{-2} to 10^{-3} ion per atom) for refractory element like thorium using continuous wave (cw) laser excitation. A two-color, two photon ionization process, near the ionization threshold was reported for thorium [24]. The auto-ionizing structures above the ionization threshold provide high ionization efficiency, because of their higher cross-sections compared to continuum photo-ionization. A XeCl excimer laser was used to pump two dye lasers with output energies of 1–3 mJ in 15 ns pulses. The dye laser beams were overlapped in space and counter-propagated through the source region of a time-of-flight mass spectrometer (TOFMS). It was recommended that with a multi-photon process to ionize thorium, it is preferable to tune the ionizing laser in resonance with an autoionizing state to increase the ionization efficiency.

7 Electrospray ionization mass spectrometry (ESI-MS) of thorium complexes

ESI-MS was used to identify the complexes of the tetradentate N,N' -diethyl- N,N' -ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen, L) ligand (containing hard-soft donor atoms – viz., O and N, respectively) with thorium, uranium and europium [25]. Et-Tol-DAPhen is a promising efficient ligand in the GANEX (Group Actinide EXtraction) process for the group separation of actinides from fission products in the highly acidic liquid

waste solutions. The ESI-MS spectra were obtained in the positive ion mode with an ion trap mass spectrometer and collision-induced dissociation (CID) was done with helium. The results obtained for the complexation process at different metal-to-ligand $[M]/[L]$ ratios, in acetonitrile medium, were compared with those from the theoretical calculations based on density functional theory (DFT). The different species observed for Th were $[\text{ThL}_2(\text{NO}_3)_2]^{2+}$ of m/z 680 at low $[M]/[L]$ ratios; and the 1 : 2 species $[\text{ThL}_2(\text{NO}_3)_3]^{3+}$ of m/z 433 and a new 1 : 1 species $[\text{ThL}(\text{NO}_3)_3]^+$ of m/z 920 at the high $[M]/[L]$ ratios. The MS/MS results of the CID experiments showed that the coordination moieties remained intact, which supported the strong coordination of Et-Tol-DAPhen ligands with metal ions. Natural bond orbital (NBO), molecular electrostatic potential (MEP), electron localization function (ELF), atoms in molecules (AIM) and molecular orbital (MO) analyses showed more covalent character of the metal–ligand bonds of the actinides complexes and the stable cationic M–L complexes in acetonitrile were found to be in good agreement with the ESI-MS results.

8 Typical examples of thorium concentration determination

Isotope-dilution ICPMS, with ^{229}Th as a spike (tracer), was used to determine pg amounts of thorium and uranium in Cu (used for detector material) and Pb (used as a shielding material) in support of the Majorana Demonstrator neutrinoless double beta decay experiment (with ^{76}Ge) at Sanford Underground Research Facility (SURF), Lead, South Dakota, USA. This was essential to ascertain the radiochemical purity of Cu and Pb [26]. Ion exchange separation was performed using AG 1X4, 200–400 mesh, anion exchange resin in HNO_3 medium to remove bulk of Cu and Pb from the dissolved sample solutions. Thorium was eluted from the column with 0.1 M HCl. All the necessary precautions were taken to minimize Th blank. Thorium was analyzed with a quadrupole based ICPMS instrument. Detection limits of 0.0084 pg $^{232}\text{Th}/\text{g}$ (0.034 mBq $^{232}\text{Th}/\text{kg}$) and 0.23 pg $^{232}\text{Th}/\text{g}$ (0.94 mBq $^{232}\text{Th}/\text{kg}$) were achieved for copper and lead samples, respectively. Efforts are continued to develop new ion sources with improved ionization efficiencies. Two positive-ion sources – viz., a hot-cavity surface ionization source (HCSIS) and a hot-cavity resonant ionization laser ion source (RILIS) were used in an attempt to evaluate the ionization efficiency of Th [27]. For the HCSIS, the dominant ion beam observed was of ThO^+ and ionization efficiencies of 2%–4% were

obtained with W and Re cavities, respectively. It will be of interest to investigate charge exchange cell to convert positive atomic ions into negative ions [27].

Pulsed glow discharge time-of-flight mass spectrometer (PGD-TOFMS) was used to determine Th in various rocks and minerals [28]. Secondary cathode (Ta, Al) was used to analyse electrically non-conducting samples. Relative sensitivity factor for Th, with Zr or Pb as internal standard, was determined with an aim to quantify the obtained peak intensity. Standard addition approach was also used for quantification. PGD-TOFMS method offers the advantage of direct analysis of solids and thus eliminates the blank problems associated with sample dissolution and purification. A detection limit of 0.5 ppm of Th was obtained.

ICPMS was used to determine ^{232}Th along with ^{238}U and ^{40}K (naturally occurring radionuclides) in marine sediments from five potential sites along the Gulf of Thailand, for future setting up of nuclear and thermal power plants and heavy industry [29]. These studies were performed to establish baseline data for future environmental monitoring because the marine sediments act both as sink and source of radionuclides. The sediment samples were oven-dried, ashed in a muffle furnace and the ashed residues were digested using microwave in acid mixture prior to analysis with Q-ICPMS. Rhodium was used as an internal standard for ICPMS analysis. The concentration data were converted into radioactivity and it was established that the radiological health hazards to the people living nearby sampling areas and to those who handle the marine sediments are within limits recommended by the UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation).

Ores (apatite and black schist) and mill tailing samples were analysed by Q-ICPMS for naturally occurring radionuclides including ^{232}Th in Finland [30]. A comparison of the ICPMS results was carried out with those from other analytical techniques – viz., X-ray fluorescence, gamma ray spectrometry and alpha-particle spectrometry. Sample digestion with HNO_3 was found to be the best method for sample dissolution and good agreement was observed in the data obtained by different analytical techniques.

Q-ICPMS was used for thorium colloid analysis in water by a single particle mode [31]. The flash of ions due to the ionization of thorium colloidal particle in the plasma torch was detected and measured in a time scan for either $^{232}\text{Th}^+$ or $^{232}\text{Th}^{16}\text{O}^+$. The peaks were analyzed as a function of the particle size or fraction of the element in the colloid phase. The frequency of the flashes was directly proportional to the concentration of particles in the colloidal suspension. The analysis of $^{232}\text{Th}^+$ allowed the detection

of colloid with sensitivity down to a size of about 80 nm (about 10 fg).

9 Inter-laboratory, inter-comparison experiments

The results of an international inter-laboratory experiment performed for the determination of $n(^{230}\text{Th})/n(^{232}\text{Th})$ ratios with MC-ICPMS were published in 2008 [32]. Five synthetic Th isotopic reference materials (UCSC Th “A”, OU Th “U”, WUN, IRMM-CRM-35, IRMM-CRM-36) and six rock reference materials (UCSC Table Mountain Latite TML, Icelandic ATHO, USGS BCR-2, USGS W-2, USGS BHVO-2, LV 18) were analyzed by researchers from six different laboratories and three different manufacturers of MC-ICPMS. Three researchers used ThermoFisher Neptune, two researchers used Nu Plasma HR and one researcher used GV Isoprobe. Both the linear and exponential fits were used to correct for the tailing of ^{232}Th at ^{230}Th . Researchers from two laboratories used U isotopic reference materials for mass fractionation and SEM/Faraday gain calibration. The data reported by various researchers were normalized to a value of 5.856×10^{-6} of $n(^{230}\text{Th})/n(^{232}\text{Th})$ in UCSC Th “A”. The data reported by researchers from different laboratories on synthetic and rock reference materials agreed within the reported uncertainties, and consensus values were arrived at for the rock reference materials. The $n(^{230}\text{Th})/n(^{232}\text{Th})$ values reported using U normalization were lower due to differences in the mass bias and mass dependent transmissions of U and Th MC-ICPMS. Also, a need was expressed for commercial availability of a certified gravimetrically prepared reference material with $n(^{230}\text{Th})/n(^{232}\text{Th})$ ratio of 5×10^{-6} . This is because the two IRMM CRMs have the extreme $n(^{230}\text{Th})/n(^{232}\text{Th})$ values of 11.380×10^{-6} and 3.047×10^{-6} , and are not an optimum selection for the volcanic rock samples [32].

Another inter-laboratory, inter-comparison experiment was organized in 2007, under the aegis of GEOTRACES, for the inter-calibration of ^{230}Th and ^{232}Th in sea water, suspended particles or sediments, because the long-lived radio-nuclides serve as useful tracers in the ocean research, and provide an insight into the changes that have occurred in the past as well as give information about the rates of different processes in modern ocean. Researchers from 19 laboratories participated in this experiment [33–35]. Most of the laboratories used $\text{Fe}(\text{OH})_3$, MnO_2 or $\text{Mg}(\text{OH})_2$ as a carrier for pre-concentration of thorium. The precipitate was dissolved and the solution was subjected to anion exchange separation proce-

dures with HNO_3 and HCl . ^{230}Th and ^{232}Th were determined by various mass spectrometric techniques – viz., MC-TIMS, SC-ICPMS, MC-ICPMS, and AMS. Contamination from sample containers, laboratory-ware and reagents was observed to be a serious problem for ^{232}Th . Yield monitors were found to equilibrate with dissolved Th in seawater in less than one day. No detectable loss of dissolved Th was observed in samples of filtered seawater acidified to a pH between 1.7 and 1.8, during storage for up to 3 years. It was concluded that the Bermuda Atlantic Time Series (BATS) station will serve as a GEOTRACES baseline station for future inter-calibration of ^{232}Th and ^{230}Th concentrations in seawater.

10 Burn-up determination

Burn-up determination, expressed in terms of atom% fissions, requires the determination of stable fission product isotopes of Nd (i. e. $^{145}\text{Nd} + ^{146}\text{Nd}$ or ^{148}Nd) or ^{139}La to determine the total number of fissions, by mass spectrometry. The nuclides that undergo fission are ^{233}U produced from ^{232}Th , along with ^{235}U or ^{239}Pu initially mixed with thoria. Isotope dilution TIMS is commonly used for the determination of Th, U and stable fission product, after their separation from other fission products employing a suitable anion exchange procedure. As an example, ^{230}Th was used as a spike for determination of Th by ID-TIMS. The ^{230}Th spike was calibrated with ID-TIMS using a natural thorium chemical assay standard [36]. Burn-up values determined with stable $^{145}\text{Nd} + ^{146}\text{Nd}$ as well as ^{139}La burn-up monitors agreed well with each other. In another study, ^{229}Th spike calibrated with ID-TIMS was used to determine the burn-up of irradiated thoria sample employing ^{148}Nd as a burn-up monitor [37]. Thorium was analysed as ThO^+ in TIMS because of its higher intensity compared to that of Th^+ . Mass spectrometry provides the most reliable data on burn-up of irradiated fuels. These experimental burn-up values are highly useful to reactor physicists to develop and improve the computer codes [38].

11 Half-life determination

TIMS was used to re-determine ^{230}Th half-life as $75\,690 \pm 230$ yr (2σ), which is about 4‰ higher than previously reported data [39]. ^{230}Th ages calculated with the new half-life are generally older than those calculated with the previously used half-life data. For dating materials older than 350 ka in laboratories that rely solely on gravimetric standardization procedures, use of new decay constant and

its higher precision will considerably reduce the errors in age arising from uncertainty in the decay constant [40]. This was further improved, in terms of precision, recently in 2013 to $75\,584 \pm 110$ yr by the same group using MC-ICPMS [41].

12 Nuclear forensics

Nuclear forensics has now matured into an interdisciplinary science and various international laboratories are actively pursuing the development of procedures and techniques for the same. ^{234}U - ^{230}Th is the most useful radio-chronometer to determine the age of highly enriched U material [42, 43]. This involves the isotope dilution mass spectrometric determination of progeny ^{230}Th , present in the interdicted U enriched material, and the data are used to determine the time elapsed after the last chemical separation. The first radio-chronometry standard, CRM 125-A with about 4% enriched in ^{235}U is now available. It is a fuel grade UO_2 pellet assay, isotopic, and radio-chronometry standard from the New Brunswick Laboratory, USA [44].

13 Critical discussion

Contamination with natural Th from reagents, laboratory-ware, working environment of the laboratory is quite common at picogram to nanogram levels. This must be checked to rule out the possibility of any erroneous data. One of the ways to confirm this is to run each experiment in duplicate, with all the precautions to control the Th blank. This variable Th blank was observed by many researchers working with thorium as well as in the inter-laboratory inter-comparison exercise. The resins from Eichrom industries were observed to give lower Th blanks compared to those from BioRad. Note that significant variability in Th blanks is observed between lots of resins from the same supplier. High purity rhenium filaments used in TIMS analysis must be checked, out-gassed and stored with care. The absence of memory or carry-over effect in ICPMS must be verified, particularly, in analyses of blind (unknown) samples. These are essential aspects of Th mass spectrometric analysis because solutions with nanogram or lower amounts of Th are processed and used at different stages of separation and analysis. In addition, abundance sensitivity, SEM (or Daly) to Faraday cup gain factor, instrumental mass bias, mass dependent transmission of ions through energy filters (RPQ or WARP) and linearity must be checked periodically.

The ^{229}Th and ^{230}Th spikes should be made available to all the researchers without any restrictions. There is a strong need to prepare and characterize the isotopic reference materials of Th for geo-science and for nuclear technology applications. These reference materials will be highly useful in TIMS to find out the mass bias, and in ICPMS, for standard-sample bracketing (SSB) approach. The assumption of Th and U, having exactly the same behaviour in TIMS and ICPMS, needs to be experimentally checked and most likely, may not be true. Future investigations are necessary to enhance the ionization yield of Th in different mass spectrometric techniques to improve the sensitivity to fulfil the needs of various studies, e. g. nuclear forensics, sea water analysis, etc. MC-TIMS, MC-ICPMS and SIMS will continue to be the main mass spectrometric techniques for Th analysis in various samples. ESIMS will play an important role for speciation studies in solutions. Ultrasensitive techniques of RIMS and AMS are valuable for determination of extremely small amounts (fg or less) of Th in materials used in exotic physics experiments (e. g., neutrino detection, dark matter). The author recommends that the researchers from nuclear and geo-sciences laboratories must not remain in isolation, but interact to share the benefits of research by each of them. Finally, the depletion of economically accessible uranium resources, less production of long-lived heavy actinide isotopes, and the inherent proliferation resistance of thorium fuel will encourage researchers and technologies to employ thorium based fuels in nuclear reactor technology, including the accelerator driven sub-critical systems (ADS), with an increased demand on Th analysis by mass spectrometry in various matrices.

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