

Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry

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Abstract

We have developed techniques by sector-field inductively coupled plasma mass spectrometry (ICP-MS) for measuring the isotopic composition and concentration of uranium and thorium, focusing on the rare isotopes, ^{230}Th and ^{234}U . These isotopes have been widely used as tracers in earth sciences, e.g., chronology, paleoclimatology, archeology, hydrology, geochemistry, and oceanography. Measurements made on reference materials demonstrate that the analytical precision approximates counting statistics and that the accuracy of the measurement is within error of accepted values. Routine measurement times are 20 min for U and 10 min for Th. The sensitivities (ions counted/atoms introduced) are 2–3‰ for U and 1.5–2‰ for Th. Samples of 10–40 ng of ^{238}U (0.5–2.0 pg of ^{234}U) give measurement precisions of 1–2‰ (2σ) for $\delta^{234}\text{U}$ and U concentration ([U]). Only 0.4 pg of ^{230}Th are needed to achieve [^{230}Th] and $^{230}\text{Th}/^{232}\text{Th}$ data with errors less than 5‰ even for cases where $^{230}\text{Th}/^{232}\text{Th}$ is 10^{-5} or less. Our ICP-MS data, including uranium standards, thorium standards, ^{238}U – ^{234}U – ^{230}Th – ^{232}Th dating of speleothems and ^{230}Th – ^{232}Th in oceanic particulates, replicates measurements made by thermal ionization mass spectrometry (TIMS). Compared to TIMS, the ICP-MS method allows smaller sample size and higher sample throughput due to higher sensitivity, fewer sample preparation steps and shorter measurement times. However, mass biases, intensity biases, spectral interferences and instrumental blanks are significant and must be addressed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

U–Th systematics have important applications to various fields in the earth sciences. The ^{238}U – ^{234}U –

^{230}Th – ^{232}Th system has been utilized as an absolute chronometer with applications in paleoclimatology (Broecker and Thurber, 1965; Edwards et al., 1987; Winograd et al., 1992; Dorale et al., 1998), landscape evolution (Ford et al., 1972; Atkinson and Rowe, 1992), archeology (Schwarz, 1980), and human evolution (Swisher et al., 1996). ^{232}Th and ^{230}Th have been used as tracers for boundary scavenging, particle

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dynamics, and advection in the oceans (Anderson et al., 1983; Moran et al., 1997). Melting processes in the lithosphere have been constrained using U–Th–Pa data (Pickett and Murrell, 1997; Asmerom et al., 2000).

From the mid-1950s (Barnes et al., 1956) to the late 1980s, U-series measurements were made using α -counting methods. Measurement times of several days on samples containing $\sim 100 \mu\text{g } ^{238}\text{U}$ yielded precisions of ± 2 –4% based on counting statistics (Ivanovich and Harmon, 1992). The application of TIMS techniques in the 1980s greatly advanced analytical capabilities (Chen and Wasserburg, 1981; Chen et al., 1986; Edwards et al., 1986/87; Edwards, 1988). This method, with ionization efficiencies on the order of 1%, dramatically reduced the required sample sizes (10–100 ng U or Th) and provided high-precision data (± 1 –4%) in hours instead of days. Despite ongoing refinements in TIMS techniques (e.g., Cheng et al., 2000), certain limitations still exist, particularly those associated with ^{232}Th filament blanks and lower ionization efficiency for high Th loads. Sample preparation techniques are also labor intensive.

Quadrupole ICP-MS techniques have been widely used for trace and isotopic analyses (Montaser, 1998). However, the Gaussian peaks characteristic of these instruments restrict the analytical precision (2σ) to no better than $\sim 0.5\%$ for the measurement of the higher abundance uranium isotopes ($^{235}\text{U}/^{238}\text{U}$ ratio, Becker et al., 1999). Quadrupole ICP-MS measurements of a rare isotope of thorium (^{230}Th) have been performed on marine sediments with a precision of $\sim 5\%$ (2σ) (Shaw and Franco, 1991). Sector-field ICP-MS potentially provides an alternative technique for obtaining high-precision isotopic measurements (Walder et al., 1993; Halliday et al., 1995; Vanhaecke et al., 1996a; Quétel et al., 2000) and can provide advantages in the areas that TIMS and quadrupole ICP-MS are limited. The sector-field ICP-MS is capable of much higher precision measurements than the quadrupole ICP-MS because the magnetic sector entrance and exit slit designs result in flat-topped peaks. Luo et al. (1997) were the first to develop techniques for measuring natural uranium and thorium isotopic composition using a multi-collector sector-field ICP-MS (Fisons Plasma 54). Their analytical capabilities were broadly comparable to those of TIMS methods, except for analyses with very large thorium loads, in which

case the ICP-MS technique exhibited advantages. Subsequently, Hinrichs and Schnetger (1999) also developed uranium and thorium isotopic measurements by single collector ICP-MS. However, they focused on measurement of samples with much higher concentration than those of this study.

Here, we outline a technique for measuring uranium and thorium isotopic composition and concentrations using a sector-field ICP-MS equipped with a single electron multiplier, which can be operated in ion-counting or analogue mode (a Finnigan Element). As compared to multi-collector sector-field ICP instruments, the Finnigan Element is significantly less expensive and is designed to measure multiple low intensity ion beams as is generally necessary for uranium and thorium isotopic measurements (Chen et al., 1986; Edwards et al., 1986/87; Edwards et al., 1987; Edwards, 1988). As compared to TIMS sources, ICP-MS sources are inherently less stable. Multi-collector ICP-MS instruments solve this problem by using multiple Faraday cups to normalize out the instability (Luo et al., 1997). When beams are too small to measure on Faraday cups, calibration of electron multiplier(s)/Daly detector(s) is necessary. This is certainly possible, but does introduce errors (see the discussion in Cheng et al., 2000). Alternately, one can use a single multiplier and minimize the error introduced by source instability by employing rapid peak switching techniques (as is the case with the Element). This approach obviates many of the problems associated with multiplier calibration. The main issue then becomes the degree to which source instability remains a problem. Because of their extremely low natural abundances, ^{234}U and ^{230}Th measurements typically have errors due to counting statistics of 1% or higher. We will show that the error due to source instability is small compared to typical counting statistical errors, and that this approach is viable.

In this study, we also address a number of “front end” issues common to thorium and uranium measurements on any type of ICP-MS. First, it is necessary to maximize the efficiency of ionization and transmission. Taking advantage of a high efficiency nebulization system, such as the microconcentric nebulizer (MCN) (Vanhaecke et al., 1996b), the high-efficiency nebulizer (HEN) (Liu and Montaser, 1994), the direct injection high efficiency nebulizer (DIHEN) (Becker et al., 1999) or the multimicrospray nebulizer (MMSN)

(Huang et al., 2000), relatively stable ion beams and high sensitivities ($>1\%$) may be obtained. Using a supplemental electron source inside the skimmer can also improve ion transmission efficiency by 2–5 times (Praphairaksit and Houk, 2000). Second, unlike most TIMS systems, there is a significant instrumental memory blank from the residuum of previous samples for ICP-MS setups with an aqueous introduction system. Third, the background interpretation problems created by spectral interferences from organic compounds, coordination complexes, and isobars, as well as the additional signals produced by tails from major isotopes need to be overcome.

In developing our technique, we first improved ion-source stability by installing a guard electrode (GE) sheath (Gray, 1986) around the torch. Second, we increased sensitivity by using a high-efficiency nebulization system, the CETAC MCN-6000. Third, we eliminated high background blanks from the residuum of previously analyzed samples. Fourth, we solved the problem of spectral interferences. Fifth, we determined a method to accurately correct for tails and electron multiplier biases. Finally, we duplicated measurements and compared U and Th analyses in standards and different environmental samples on both ICP-MS and TIMS to examine precision and accuracy of our methodology. All errors given in this paper are two standard deviations (2σ) unless otherwise noted.

2. Experimental

2.1. Instrumentation

Two Finnigan MAT-262-RPQ instruments were used for the TIMS analyses. Ion beams were measured on a multiplier behind a retarding potential quadrupole (RPQ). Measurement techniques are modifications of those presented in Edwards et al. (1986/1987), as described by Cheng et al. (2000). Samples were loaded onto triple zone-refined Re filaments in a double-filament configuration for U (Cheng et al., 2000), and on single, graphite-covered filaments for Th (Edwards, 1988).

ICP-MS analyses were made on a Finnigan Element, equipped with a double-focusing sector-field magnet in reversed Nier–Johnson geometry and a

single MasCom multiplier. The ICP-MS was operated at low resolution ($M/\Delta M=300$) and in electrostatic peak hopping mode (electric field jumping at fixed magnetic field). This means that the flatness of the peak top is 30–35% of the beam. Radio frequency (RF) power was set at 1250–1280 W. Argon flow rates were set at 13 l/min for the plasma gas, 0.95–0.98 l/min for the auxiliary gas and 0.4–0.5 l/min for the sample gas.

Although some wet introduction systems, like DIHEN (Becker et al., 1999) and MMSN (Huang et al., 2000), have the advantage of low memory blank, the interferences from oxides and hydrides are significant. We thus chose a dry sample introduction system, CETAC MCN-6000. The Sweep Ar flow was set at 4.0–4.3 l/min and no nitrogen was introduced. The temperatures of the spray chamber and desolvator were set at 75 and 160 °C, respectively. This system provided a 5- to 10-fold enhancement in sensitivity. Combined with a GE, a 10- to 30-fold increase in sensitivity relative to the unshielded micro-nebulization introduction system (CETAC MCN-100) was obtained. Over one million cps of ^{238}U was generated by a 0.4-ppb solution at a sample uptake rate of 30 $\mu\text{l}/\text{min}$. The sensitivity (combined ionization plus transmission efficiencies) was about 2.5–3% for U and 1.5–2% for Th.

2.2. Ion beam stability and data acquisition

The stable thermal-generated ion source of the TIMS method allows analysis by magnet-controlled peak jumping on a single multiplier, and the analytical precision basically follows counting statistics (Edwards, 1988). Scan cycles of 30–60 s are used for our U analyses and 20–40 s for Th analyses. Typically, 50–200 sets of data are measured for data reduction. In contrast to the stable TIMS source, the ICP-MS source generates a less stable ion beam and analytical error may therefore fall short of the statistically expected precision (e.g., Vanhaecke et al., 1996a). The instability is attributed to two major problems: (1) high-frequency ($>1\text{ s}^{-1}$) fluctuation of the plasma flame where ions are generated and (2) low-frequency ($<1\text{ s}^{-1}$) variation of sample introduction by the nebulization system.

In order to reduce the high-frequency fluctuation in the ICP-MS system, a concentric nickel GE in a glass cylinder, designed by B. Klaue of the University of

Michigan, was introduced to stabilize the ion beams. The device was installed to shield the torch, decrease RF power, and diminish arcing and local potential gradients in the plasma (Gray, 1986). After igniting the plasma, the GE was placed between the torch and the load coil. With the GE in place, a 0.5-cm length of the glass cylinder extended beyond the edge of the torch and reduced plasma flicker.

An inevitable, low-frequency variation of sample intensity was generated by the nebulization system. In the MCN-6000, the sample solution was aspirated by Sample Ar gas, misted through a microconcentric nebulizer into a spray chamber, then carried by Sweep Ar gas through a desolvator to create a dried aerosol. Finally, the aerosol was transported with the Sweep Ar gas into the torch. We found that the ion beam occasionally varied by a rate of 2–6%/min due to the unstable sample introduction rate. Since a single multiplier was used in the Element, we designed a short scan cycle of only 0.2 s to reduce the error from the beam drift. Measurement times were 20 min for U and 10 min for Th. Approximately, 8000 sets of U data (or 2000 sets of Th data) were measured for off-line processing. Using the combination of a GE and a fast data-acquisition method, we found that the analytical precision can be improved to approximate counting statistics (see Results and discussion).

2.3. Biases

Two types of multiplier biases exist, those correlating with mass and those correlating with beam intensity. Mass biases are offsets from true isotope ratios due to different isotopic masses (Cheng et al., 2000). Biases related to signal intensity fall into two categories. The first is due to the multiplier dead time, when a signal is under-counted. The second category is due to factors that are still poorly understood. This intensity bias is a small offset from the true ratio associated with beam intensity differences between isotopes, which we correct using an exponential function (Cheng et al., 2000). The detailed bias description and their corrections for TIMS are described by Cheng et al. (2000).

For the ICP-MS measurements, we measured $^{235}\text{U}/^{238}\text{U}$ ratios in a solution made by dissolving New Brunswick Laboratory Certified Reference Material 112A (NBL-112A, formerly National Bureau of

Standards Standard Reference Material 960) a high purity natural uranium standard. Dead time values ranged from 23 to 25 ns for the MasCom multiplier, MC-SEV-ICP. By measuring solutions with different U concentrations, we corrected for dead time with a precision of ± 0.5 –1 ns. We determined the magnitude of the intensity bias by measuring $\delta^{234}\text{U}$ of NBL-112A and comparing the measured value to the known value (Cheng et al., 2000). This bias may change over the course of several months, but no significant change larger than 1‰ was observed on the time scale of 4–5 weeks. Nevertheless, we routinely measured the intensity bias by analyzing NBL-112A prior to measuring samples. To correct for mass discrimination and mass bias, we normalized measured isotope ratios to the $^{236}\text{U}/^{233}\text{U}$ ratio of our spike solution using the exponential law (Russell et al., 1978):

$$R_t = R_m (M_i/M_j)^f \quad (1)$$

where R_t is a true isotope ratio, R_m is a measured ratio, M_i and M_j are the masses of isotopes i and j , respectively, and f is a mass fractionation factor.

2.4. Instrumental blank and spectral background

Using the MCN-6000 nebulization system, we found significant contamination from previous samples, ~ 0.1 –1% of the original sample beam. This remained a serious problem, even with long washout times (> 20 min). We solved this problem for uranium by running dilute HNO_3 through the system after measuring each sample, by physically washing the spray chamber and micro-nebulizer using dilute HNO_3 , and then by running dilute HNO_3 through the system again before aspirating the next sample solution. By using such a cleaning technique, the instrumental blank could be reduced to less than 0.1‰ of the original beam. The cleaning step took 10–15 min. For Th, we repeated the same procedure twice, but with dilute HF added to the HNO_3 .

There are two sources of background noise in the TIMS and ICP-MS systems. The first is the dark noise of the multiplier, which was generally lower than 0.05–0.1 counts per second (cps) on both instruments, but was occasionally higher than 0.1 cps. The dark noise was routinely measured and corrections were made during data processing. The second source of

background noise is spectral interference, including polyatomic interferences and the tails from the major isotopes, ^{238}U or ^{232}Th . For TIMS, polyatomic interferences from organics or complexes were generally insignificant. Regarding tails, the TIMS instrument is equipped with an RPQ energy filter so that the effect of the tail of the major isotopes was also generally insignificant. The abundance sensitivity was 2.0×10^{-8} at one atomic mass unit (amu) difference and 6.7×10^{-9} at 2 amu difference.

In the ICP-MS system, we have observed polyatomic interferences in samples with a relatively high concentration of organics (signals of 1–10 cps at masses 229–237). This caused a high noise/signal ratio of 5–20% for low [^{230}Th] analyses. To remove organic contamination, 2–3 drops of concentrated perchloric acid were added to the separated U and Th solutions after the last column separation step and dried at $\sim 150^\circ\text{C}$. For samples with particularly high organic content, e.g. speleothem with significant humus, an additional oxidation step was required. For uranium analysis, one possible isobaric interference on ^{233}U is from the hydride form of ^{232}Th , $^{232}\text{Th}^1\text{H}$. The $^{232}\text{Th}^1\text{H}^+ / ^{232}\text{Th}^+$ ratio was less than 4 ppm in the ICP-MS system. The ^{232}Th ion beam was usually less than 1×10^4 cps and never larger than 1×10^6 cps in the separated U fraction solution. We added appropriate amounts of spike solution to the samples so that the ^{233}U ion beam was $1\text{--}2 \times 10^5$ cps. Thus, the $^{232}\text{Th}^1\text{H}$ interference on ^{233}U is $<0.04\%$ and can be effectively neglected. The abundance sensitivity of the Element was calculated by measuring the tail of ^{238}U on solutions of NBL-112A and the tail of ^{232}Th on a solution made from the dissolution of high purity natural thorium metal obtained from Ames Laboratory (Ames Th standard, see Cheng et al., 2000). We also checked for possible matrix effects on the abundance sensitivity of the ICP-MS by using different nitric acid concentrations and by adding some Fe to the solutions (see below).

2.5. Reagents, standards and samples

SEASTAR ultrapure reagents were used and all chemical procedures were performed under clean room conditions. All bottles and beakers used in this study were cleaned following the processes described by Edwards (1988).

Three different U solutions, NBL-112A, Harwell uraninite (HU-1), and a speleothem carbonate (CAVE-1), were used. HU-1 has a $\delta^{234}\text{U}$ value of 0‰, NBL-112A a value of -37.0% (Cheng et al., 2000) and CAVE-1 a high value of 2453‰. For Th, we used our Ames ^{232}Th standard, with a low $^{230}\text{Th}/^{232}\text{Th}$ ratio of $0.6029 (\pm 0.0036) \times 10^{-6}$. Four other Th standards, Th-1, Th-2, Th-4 and Th-10, with $^{230}\text{Th}/^{232}\text{Th}$ ratios of 10^{-5} to 10^{-6} were made by mixing the Ames ^{232}Th standard with HU-1 (which has a $^{230}\text{Th}/^{232}\text{Th}$ ratio of 0.356).

We applied our ICP-MS technique to the U–Th dating of three stalagmites and also measured the Th isotopic composition and concentration of some particulate fractions of seawater samples. Aliquots of all samples were also measured by TIMS for comparison. The stalagmites were from two different locations (southeastern Missouri and northwestern Mexico) and have high $^{230}\text{Th}/^{232}\text{Th}$ ratios ($>10^{-4}$) (Dorale et al., in press). The seawater particulate samples were from the south Atlantic Ocean, collected during the 1996 International Oceanographic Commission Trace Metals Baseline Expedition (IOC-96) and included both surface and bottom waters (Moran et al., 2001). The $^{230}\text{Th}/^{232}\text{Th}$ of these samples ranged from 10^{-4} to 10^{-6} . Particulate ^{230}Th and ^{232}Th depth profiles at station 10 (IOC-96-ST10; 32°S , 42°W) were then made by ICP-MS.

2.6. Spiking and analysis

Samples were dissolved in 1% HNO_3 and spiked with a $^{233}\text{U}\text{--}^{236}\text{U}\text{--}^{229}\text{Th}$ tracer. Next U and Th were co-precipitated with ~ 6 mg of an Fe carrier, then separated to form a clean U fraction and a clean Th fraction using an anion exchange resin (BioRad 1-X8, 100–200 mesh, 0.6–1.0 ml column volume) (Edwards et al., 1987; Edwards, 1988). The isotopic compositions of U and Th in the solutions were measured by TIMS and ICP-MS. Four-fifths of each spiked speleothem solution was aliquoted for U and Th analysis by TIMS and the remaining one-fifth was used for ICP-MS analysis. Two-thirds of each dissolved filtered seawater particulate solution was used for Th analysis by TIMS and one-third for ICP-MS analysis.

The ^{238}U abundance sensitivity at low masses was analyzed on the ICP-MS using an unspiked standard

NBL-112A solution ($[^{238}\text{U}] = 40\text{--}60$ ppb). At the beginning of each day, the multiplier intensity bias value was obtained by correcting the measured $\delta^{234}\text{U}$ of NBL-112A to the accepted value of -37.0‰ (Cheng et al., 2000). Between measurements, we cleaned the MCN-6000 and made sure the background blank was $<0.1\text{‰}$ (including both the acid blank and any residual from previous analyses).

For the uranium isotopic measurements, a $^{233}\text{U}\text{--}^{236}\text{U}$ double-spike was used. Since the TIMS was equipped with an RPQ, tail contributions were insignificant and only ^{233}U , ^{234}U , ^{235}U and ^{236}U were measured. In contrast, tailing was a significant complication for the ICP-MS measurements, so we measured the half-mass positions as well as each mass of interest. From these data, $\delta^{234}\text{U}$ and $[^{238}\text{U}]$ were calculated using a half-life of $245,250 \pm 490$ years for ^{234}U (Cheng et al., 2000) and $4.4683 \pm 0.0048 \times$

10^9 years for ^{238}U (Jaffey et al., 1971). The measured atomic ratios were normalized to an internal standard with $^{236}\text{U}/^{233}\text{U} = 1.010572$.

On the ICP-MS system, the $\delta^{234}\text{U}$ value of NBL-112A was measured to examine within-run precision and reproducibility. Three standards, HU-1 (low $\delta^{234}\text{U}$), CAVE-1 (high $\delta^{234}\text{U}$), and NBL-112A (low $\delta^{234}\text{U}$) were measured sequentially to inspect possible blanks and accuracy. We then analyzed four NBL-112A solutions that were spiked with our $^{233}\text{U}\text{--}^{236}\text{U}$ tracer so that the ratio of $^{236}\text{U}/^{238}\text{U}$ of the mixture was 10^{-5} to 10^{-6} . This was to test the effectiveness of the tail correction for the ICP-MS, since the mixed isotopic composition of the solutions was known gravimetrically. These solutions were also good proxies for low $^{230}\text{Th}/^{232}\text{Th}$ samples.

To correct the baseline for ^{229}Th , the shape of the ^{232}Th tail between masses of 228.5–229.5 on the ICP-

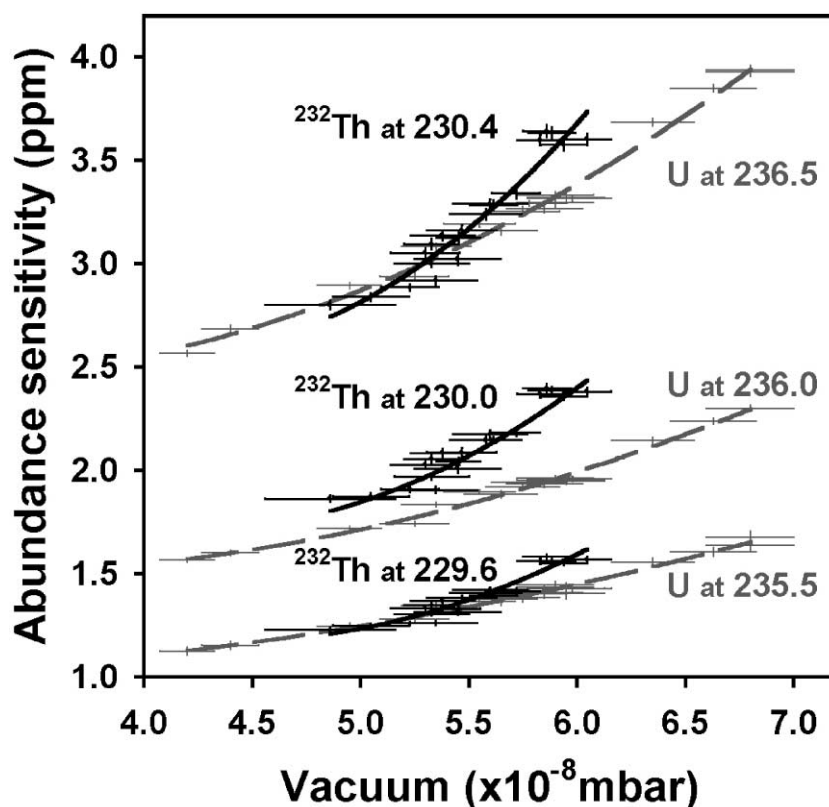


Fig. 1. The relationship between abundance sensitivity and vacuum condition for U (gray) and Th (black) on the ICP-MS. The ^{232}Th tail at mass 230 is 1.8–2.4 ppm and the U tail at mass 236 is 1.5–2.2 ppm, with the vacuum ranging from 4.8 to 6.0×10^{-8} mbar.

MS was obtained by measuring the unspiked Ames ^{232}Th standard ($[^{232}\text{Th}] = 60\text{--}100$ ppb). Since there is no ^{230}Th -free ^{232}Th standard available, the ^{232}Th tail at mass 230 (230t) could not be measured directly. To estimate 230t, we mixed a solution of Ames ^{232}Th standard with our ^{229}Th tracer so that the $^{229}\text{Th}/^{230}\text{Th}$ ratio the mixture was ~ 10 . The ion beams at masses between 228.5 and 230.5 were measured. Because the Th isotopic composition in this spiked solution was known, the true ^{230}Th ion beam intensity could be derived from the intensity of the ^{229}Th beam, which could be obtained by subtracting the ^{232}Th tail at mass 229 (229t) from the composite signal. The tail signal, 230t, was obtained by the difference between the composite signal at mass 230 and true ^{230}Th ion beam intensity. We then found that the ^{232}Th tail shape between masses 228.5 and 232.5 follows an exponential function (see below). During ICP-MS analyses, the signals at masses 228.6, 229.4, 229.6 and 230.4 were measured to correct for the ^{232}Th tail at masses 229 and 230. Because the TIMS instrument possesses

an RPQ, the ^{232}Th tail background at low masses is very small, and the signals at half masses were not measured during data acquisition. However, the ^{232}Th tail at masses 229 and 230 is still corrected based on the abundance sensitivity measured in advance.

Prior to the Th isotopic measurements each day, the multiplier intensity (1–2‰) bias and mass fractionation bias (plus mass bias, $\sim 0.3\text{--}0.5$) were obtained by correcting the measured $\delta^{234}\text{U}$ value of NBL-112A to -37.0‰ and $^{236}\text{U}/^{233}\text{U}$ to 1.010572. Consecutive measurements of spiked NBL-112A standard solutions revealed that the mass fractionation factor, f , varied only from 0.05 to 0.1, which corresponds to an error less than 0.1‰ for $[^{230}\text{Th}]$ and an error less than 0.2‰ for $[^{232}\text{Th}]$.

Different spiking methods and data acquisition Schemes were chosen for samples with various $^{230}\text{Th}/^{232}\text{Th}$ ratios. Natural samples can be divided into three groups with different ranges of $^{230}\text{Th}/^{232}\text{Th}$ ratios. For samples with low $^{230}\text{Th}/^{232}\text{Th}$ ratios ($10^{-5}\text{--}10^{-6}$), but relatively high Th concentrations,

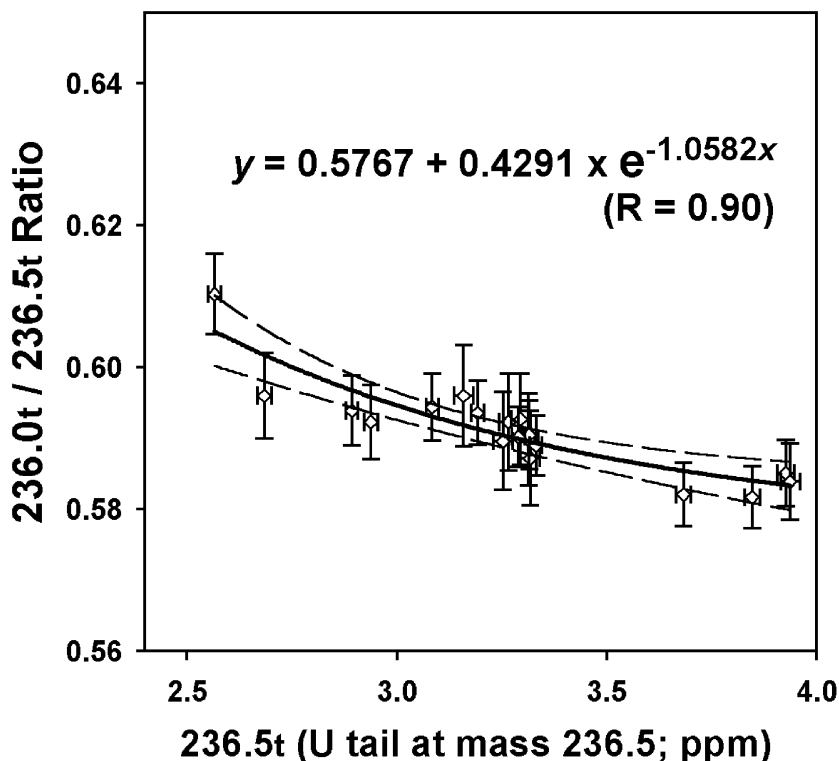


Fig. 2. Tail correction for ^{236}U in U analyses on the ICP-MS using an empirical relationship between 236.0t/236.5t and 236.5t.

e.g. volcanic rocks, two aliquots of the sample were spiked with appropriate amounts of the ^{229}Th solutions and $[^{230}\text{Th}]$ and $[^{232}\text{Th}]$ were measured separately. The four prepared Th standard solutions with low $^{230}\text{Th}/^{232}\text{Th}$ ratios were used to check precision and reproducibility for this group measured on ICP-MS. For samples with low $^{230}\text{Th}/^{232}\text{Th}$ ratios (10^{-4} – 10^{-6}) and low $[^{230}\text{Th}]$ (e.g., seawaters, seawater particulates and cave waters), we added an appropriate amount of ^{229}Th spike to a single aliquot. $[^{230}\text{Th}]$ and $[^{232}\text{Th}]$ were then measured in a single run. A single aliquot was also spiked for samples with high $^{230}\text{Th}/^{232}\text{Th}$ ratios ($>10^{-4}$), e.g. corals and speleothems.

3. Results and discussion

3.1. Uranium tailing

The abundance sensitivity of ^{238}U was approximately 5.4 ppm at mass 237 (237t), 1.6 ppm at 236

(236t), 1 ppm at 235 (235t), 0.4 ppm at 234 (234t) and 0.2 ppm at 233 (233t). The degree of tailing also depended on vacuum conditions (Fig. 1). The log-mean of the counts recorded at the half-masses was used to correct baselines for ^{233}U , ^{234}U and ^{235}U . Since the peak created by ^{235}U makes a significant contribution to the baseline over the mass interval 235.5–236.5 (in addition to the tail from ^{238}U), the signal at mass 236.5 (236.5t) was used to estimate the tail at mass 236 by an empirical formula (Fig. 2). This combination of tails causes the shape of the baseline to deviate from the exponential function that characterizes the rest of the baseline. The shape of the tail was not effected by varying concentrations of HNO_3 used to dissolve the samples (from 0.5% to 2%) or by the addition of Fe (from 100 ppb to 100 ppm) to the sample solutions.

3.2. Uranium standard measurements

The results of continuously duplicated measurements of NBL-112A under the same operational

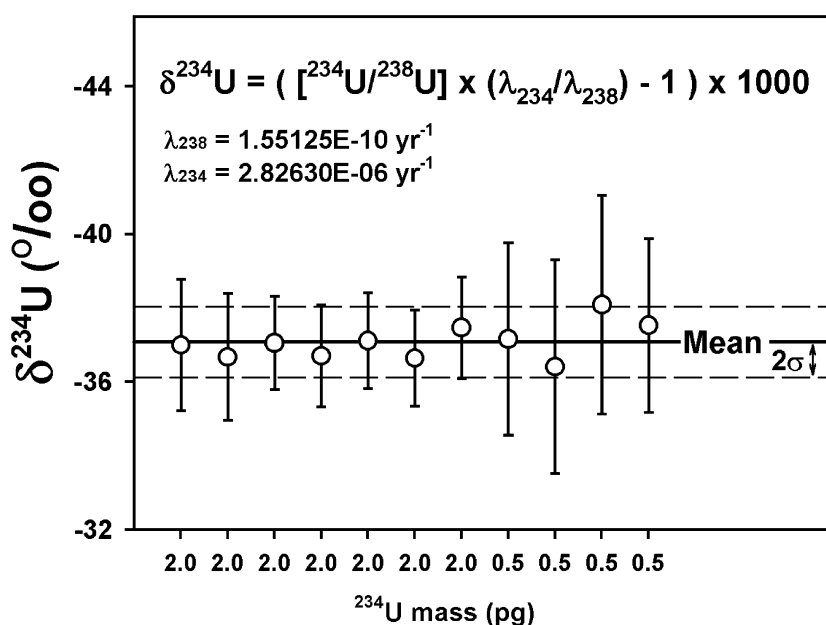


Fig. 3. Duplicate measurements of $\delta^{234}\text{U}$ on NBL-112A using the same intensity bias value obtained from the first measurement. The mean of the other 10 measurements is $-37.1 \pm 1.0\text{‰}$. The between-run error is similar to the within-run statistical errors indicating that the ion beam generated from the plasma is stable and the precision basically follows counting statistics.

conditions are shown in Fig. 3. A sample size of 36 ng ^{238}U allowed an internal precision (within-run) of $\pm 1\%$, close to the error expected from counting statistics. The mean of 10 duplicates is $-37.1 \pm 1.0\%$, and shows no significant difference from the data measured by TIMS ($-37.0 \pm 0.6\%$). The external error, 1.0%, is smaller than any individual errors (1.2–2.4%), which indicates that the reproducibility of the U isotopic measurements basically follows counting statistics and the internal error is an accurate measure of the true uncertainty.

The calculations of $\delta^{234}\text{U}$ and $[^{238}\text{U}]$ of the three standards from data measured by ICP-MS and by TIMS were not significantly different (Table 1). For example, the $\delta^{234}\text{U}$ and $[^{238}\text{U}]$ data for CAVE-1 are $2455.0 \pm 3.6\%$ and 1530.6 ± 2.2 ppm by ICP-MS and $2452.5 \pm 3.5\%$ and 1530.1 ± 2.0 ppm by TIMS. After analyzing CAVE-1 (with high $\delta^{234}\text{U}$), the ICP-MS still measured the correct $\delta^{234}\text{U}$ and $[^{238}\text{U}]$ values for NBL-112A. This illustrates that after physically cleaning the introduction system between runs, the instrumental blanks are insignificant and no contamination was introduced from the preceding sample. It also shows that the background for each isotope was effectively subtracted from the signal.

3.3. Mixtures of NBL-112A and ^{233}U – ^{236}U tracer

The results of the measurement of mixtures of NBL-112A and ^{233}U – ^{236}U spike with $^{236}\text{U}/^{238}\text{U}$ ratios of 10^{-5} to 10^{-6} are shown in Fig. 4. The U tail contributed about 1.6 ppm at mass 236. Even for the case where $^{236}\text{U}/^{238}\text{U} \cong 10^{-6}$, where the ^{236}U beam is only 80% of the U tail ($^{236}\text{U}/236\text{t}=0.8$), the correct value of $\delta^{234}\text{U}$ could still be obtained. The external errors of four sets of $\delta^{234}\text{U}$ measurements were all less than the individual counting errors. This

indicates that the precision indeed follows counting statistics in our ICP-MS system. In addition, the measured $^{236}\text{U}/^{238}\text{U}$ ratios are the same as the theoretical values within error. This indicates once more that the tailing can be corrected effectively and suggests that our ICP-MS system can be used to analyze Th for samples with $^{230}\text{Th}/^{232}\text{Th}$ ratios as low as 10^{-5} – 10^{-6} .

3.4. Uranium in speleothems

The $[^{238}\text{U}]$ and $\delta^{234}\text{U}$ data of three speleothem sub-samples measured by ICP-MS and by TIMS are listed in Table 2. The calcite sub-samples weighed between 200 and 300 mg. Although only one-fifth of the sample (corresponding to 40–60 mg of calcite) was aliquoted for ICP-MS analysis, the precision (1–2%) obtained is comparable to that of TIMS analyses, which utilized the other four-fifths. The two data sets are all consistent within error and provide further evidence that high precision isotopic measurements can be achieved by ICP-MS.

3.5. ^{232}Th tailing

The abundance sensitivity of ^{232}Th is more sensitive to vacuum conditions than that of ^{238}U (Fig. 1). The ^{232}Th tail between masses 228.5–229.5 follows an exponential function. Therefore, the log-mean of the tail at masses 228.6 (228.6t, ~ 0.6 ppm) and 229.4 (229.4t, ~ 1.1 ppm) was used to calculate the baseline at mass 229 (229t, ~ 0.8 ppm). The ratio of the calculated 230t to the log-mean of the tail at masses 229.6 and 230.4 (229.6t and 230.4t) is one (1.002 ± 0.008) regardless of pressure (Fig. 5). This indicates that the shape of ^{232}Th tail at this interval is exponential and the log-mean of 229.6t and 230.4t is an appropriate baseline calculation. Solutions with varying HNO_3 (from 0.5% to 2%) and Fe (from 100 ppb to 30 ppm) concentrations showed no matrix effect on the tail measurements.

3.6. Thorium standard measurements

The data for four Th standards, with $^{230}\text{Th}/^{232}\text{Th}$ ratios of 10^{-5} to 10^{-6} , from both ICP-MS and TIMS measurements, are all consistent within error, even when the $^{230}\text{Th}/230\text{t}$ ratio is ~ 1 (Table 3). Only 0.4–

Table 1
Measurements of uranium standards on ICP-MS and TIMS

Standard	Method	$\delta^{234}\text{U}$ (‰)	^{238}U (ppb)
HU-1	TIMS	-0.1 ± 0.6	953.7 ± 1.1
	ICP-MS	0.4 ± 1.4	953.6 ± 1.3
CAVE-1	TIMS	$2,452.5 \pm 3.5$	$1,530.1 \pm 2.0$
	ICP-MS	$2,455.0 \pm 3.6$	$1,530.6 \pm 2.2$
NBL-112A	TIMS	-37.0 ± 0.6	$7,032.0 \pm 7.0$
	ICP-MS	-37.1 ± 1.2	$7,029.9 \pm 5.3$

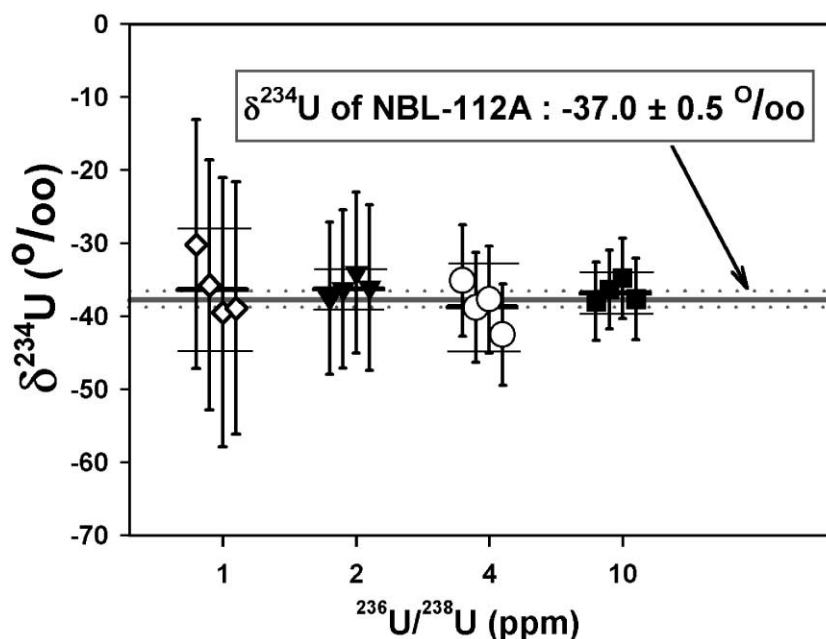


Fig. 4. Measurements of $\delta^{234}\text{U}$ on NBL-112A, spiked with ^{233}U and ^{236}U so that $^{236}\text{U}/^{238}\text{U}$ ranges from 1 to 10 ppm. The data for $^{236}\text{U}/^{238}\text{U}$ of 10 ppm (cubes; $^{236}\text{U}/^{236}\text{t}=8.0$), 4 ppm (circles; $^{236}\text{U}/^{236}\text{t}=2.4$), 2 ppm (triangles; $^{236}\text{U}/^{236}\text{t}=1.6$) and 1 ppm (diamonds; $^{236}\text{U}/^{236}\text{t}=0.8$) are all consistent with the true value (determined by TIMS, gray lines).

0.5 pg ^{230}Th is needed to obtain a precision of 4 ‰. For $^{230}\text{Th}/^{232}\text{Th} > 6$ ppm, the precision is essentially equivalent to counting statistics. For $^{230}\text{Th}/^{232}\text{Th} < 6$ ppm, errors from tail corrections are also significant. The differences for $[^{230}\text{Th}]$ and $[^{232}\text{Th}]$ between measured data on ICP-MS and those on TIMS or gravimetrically determined values are all less than 2.5 ‰ and 1.0 ‰ (all values are less than counting statistics errors). This indicates the ICP-MS technique can be applied to low $^{230}\text{Th}/^{232}\text{Th}$ analyses.

3.7. Thorium in speleothems and ^{230}Th dating

The measured $[^{230}\text{Th}]$, $[^{232}\text{Th}]$ and $^{230}\text{Th}/^{232}\text{Th}$ ratios of three stalagmites are shown in Table 2. The ICP-MS and TIMS data are consistent within error. However, because of the relatively high ionization–transmission efficiency in the ICP-MS method, samples with only 0.7–1.0 pg ^{230}Th could be measured to a precision of 3 ‰. Comparable precision by TIMS required four times the sample size. For speleothems

Table 2
Speleothem uranium and thorium isotopic measurements by ICP-MS and TIMS

Sample I.D.	Method	Sample size (mg)	^{238}U (ppb)	$\delta^{234}\text{U}$ (‰)	^{230}Th (ppt)	^{232}Th (ppt)	$^{230}\text{Th}/^{232}\text{Th}$ (atomic)	Age (corrected) ^a
CC\DBL-L-27.5	TIMS	240	812.2 ± 1.3	3,031.9 ± 3.4	16.27 ± 0.04	2,938 ± 20	0.00559 ± 0.00004	37,710 ± 150
	ICP-MS	60	811.7 ± 1.6	3,037.7 ± 5.8	16.35 ± 0.05	2,895 ± 17	0.00570 ± 0.00004	37,890 ± 180
CC\DBL-L-75.2	TIMS	240	796.4 ± 1.5	2,509.0 ± 4.6	16.13 ± 0.05	401 ± 75	0.041 ± 0.008	45,000 ± 200
	ICP-MS	60	796.7 ± 1.6	2,506.0 ± 5.5	16.20 ± 0.06	396 ± 16	0.041 ± 0.002	45,260 ± 230
VA2-1-BR	TIMS	160	987.7 ± 1.7	427.0 ± 1.8	20.67 ± 0.14	340 ± 44	0.061 ± 0.008	198,160 ± 3420
	ICP-MS	40	988.0 ± 1.8	427.4 ± 2.8	20.65 ± 0.08	331 ± 25	0.063 ± 0.005	197,300 ± 2300

^a Ages are for corrected for initial ^{230}Th using a $^{230}\text{Th}/^{232}\text{Th}$ value of 4.4 ± 4.4 ppm. The correction is < 25 years for all three samples.

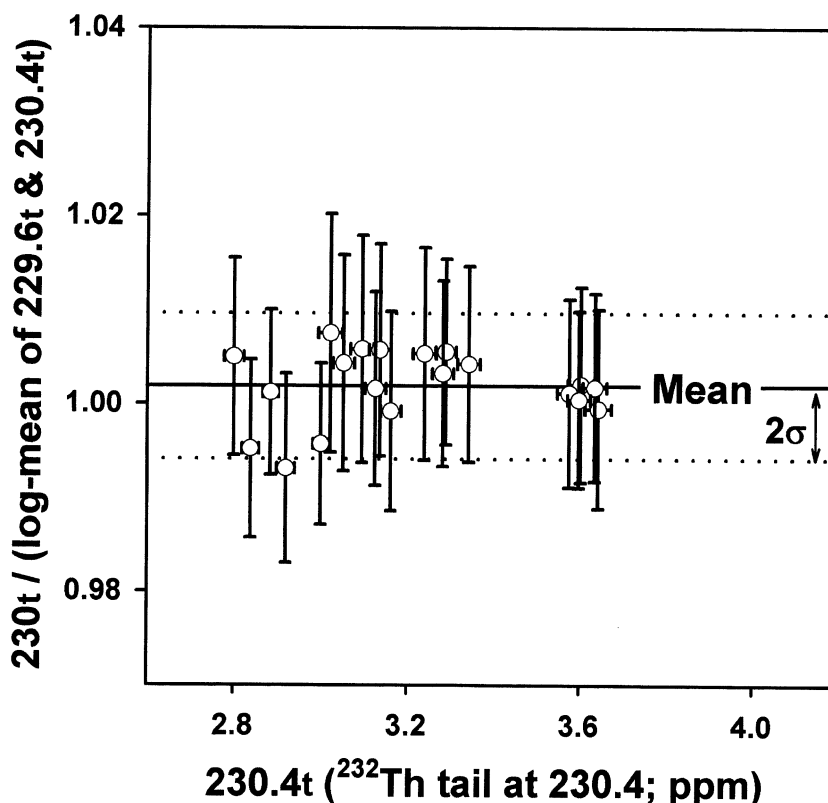


Fig. 5. The relationship between the ratio of ^{230}t to the log-mean of $^{229.6}\text{t}$ and $^{230.4}\text{t}$ vs. $^{230.4}\text{t}$. The mean of the ratios is 1.002 ± 0.008 , indicating that the ^{232}Th tail at this mass interval is an exponential function.

with low ^{232}Th , the ICP-MS method offers an additional advantage over the TIMS method because the ^{232}Th filament blank, a source of significant uncertainty in most TIMS analysis, is trivial for the ICP-MS method. Based on the results of the Th and U analyses in Table 2, it is clear that the ICP-MS technique can be effectively applied to ^{230}Th dating in speleothems. Furthermore, the smaller sample size requirements of the ICP-MS technique has significant practical implications for the high-resolution dating of speleothems. For speleothems containing >0.1 ppm ^{238}U , age errors $<0.5\%$ are possible for sub-samples that are 10–200 mg in size.

3.8. Thorium in oceanic particulates

Thorium isotopic compositions and concentrations in particulate fractions of seawaters analyzed by ICP-MS and TIMS are shown in Table 4. There are no

significant differences between the ^{230}Th (0.3–5.5 fg/l), ^{232}Th (12–80 pg/l) and $^{230}\text{Th}/^{232}\text{Th}$ (7–100 ppm) data that were measured by the two methods. For deep seawater particulate ^{230}Th of 2–5 fg/l, measurement precisions of 2–3% can be achieved on samples with 10–25 fg ^{230}Th by ICP-MS, comparable to that obtained for samples containing at least 20–50 fg ^{230}Th necessary for TIMS analysis. For a surface seawater particulate ^{230}Th of 0.3–0.4 fg/l, precisions of 6–10% were obtained on samples with 1.4–2 fg ^{230}Th by ICP-MS analysis, similar to that for samples of 3–4 fg measured by TIMS. The results reveal that only 4–5 l of surface seawater or 0.5 l of deep seawater is needed to obtain a precision better than 10% for ^{230}Th in the particulate fraction. For the reported range of seawater ^{230}Th concentrations of 1–20 fg/l (Moran et al., 1997; Edmonds et al., 1998), less than 1 l of seawater is required to obtain a measurement precision of 2–10%.

Table 3
Measurements of four thorium standards on ICP-MS and TIMS

Standard	$^{230}\text{Th}^a/^{230}\text{t}$	^{230}Th used in ICP run (pg)	Method	$[^{230}\text{Th}]$ (fmol/g)	$[^{232}\text{Th}]$ (pmol/g)	$^{230}\text{Th}/^{232}\text{Th}$ (atomic; ppm)
Th-10	10	0.4	TIMS	$2.888 \pm 3.1\%$	$178.9 \pm 1.4\%$	$16.14 \pm 3.4\%$
			ICP-MS	$2.890 \pm 4.7\%$	$179.0 \pm 1.2\%$	$16.15 \pm 4.8\%$
			gravimetric	$2.882 \pm 2.2\%$	$178.7 \pm 0.8\%$	$16.13 \pm 2.3\%$
Th-4	4	0.5	TIMS	$1.393 \pm 4.9\%$	$211.3 \pm 1.1\%$	$6.592 \pm 5.0\%$
			ICP-MS	$1.390 \pm 4.9\%$	$211.2 \pm 1.3\%$	$6.581 \pm 5.1\%$
			gravimetric	$1.389 \pm 2.5\%$	$211.2 \pm 0.8\%$	$6.577 \pm 2.5\%$
Th-2	2	0.4	TIMS	$0.744 \pm 4.0\%$	$203.8 \pm 1.5\%$	$3.651 \pm 4.3\%$
			ICP-MS	$0.744 \pm 8.5\%$	$203.5 \pm 1.3\%$	$3.657 \pm 8.6\%$
			gravimetric	$0.743 \pm 2.8\%$	$203.6 \pm 0.8\%$	$3.651 \pm 2.8\%$
Th-1	1	0.4	TIMS	$0.527 \pm 4.7\%$	$238.8 \pm 1.2\%$	$2.210 \pm 4.9\%$
			ICP-MS	$0.532 \pm 15\%$	$238.9 \pm 1.5\%$	$2.228 \pm 15\%$
			gravimetric	$0.530 \pm 3.2\%$	$238.7 \pm 0.8\%$	$2.222 \pm 3.3\%$

^a The ratio of ^{230}Th to ^{232}Th tail at mass 230 (230t) in ICP-MS measurement.

3.9. Advantages and disadvantages of ICP-MS

The ICP-MS technique offers several advantages compared to the TIMS technique. Because of more consistent and often higher sensitivity (e.g., 1‰ for TIMS and 2–3‰ for ICP-MS), ICP-MS analyses require samples only 1/3–1/2 as large as samples for TIMS. Measurement times (10–20 min) are only 1/10–1/5 of those for TIMS (2–3 h), so significantly higher throughput can be achieved. Mass discrimination can be corrected and the ^{232}Th blank is low. Fewer chemistry steps are needed and the ICP-MS

method may involve easier instrumental operation. Disadvantages include the plasma-generated ion source, which is less stable than the thermal source in TIMS. The ICP-MS technique has significant spectral interferences (polyatomic complexes and isobars), which are generally trivial in TIMS. For example, interfering species can be diminished during filament preheating using the TIMS method; however, in the low-resolution ICP-MS system, a separation process is required or these interferences may affect the analysis. The problem of the memory effect or instrumental blank exists on the ICP-MS, a problem

Table 4
Particulate fraction of seawater thorium isotopic measured by ICP-MS and TIMS

Sample I.D.	Seawater filtered (l)	Method	Fraction of sample	^{230}Th used (fg)	^{230}Th (fg/l)	^{232}Th (pg/l)	$^{230}\text{Th}/^{232}\text{Th}$ (ppm)
IOC-96-ST6-40m	14.8	TIMS	2/3	2.9	0.321 ± 0.018	38.36 ± 0.50	8.43 ± 0.47
		ICP-MS	1/3	1.4	0.323 ± 0.026	38.65 ± 0.37	8.42 ± 0.69
IOC-96-ST8-50m	14.0	TIMS	2/3	2.9	0.345 ± 0.022	12.20 ± 0.13	28.5 ± 1.8
		ICP-MS	1/3	1.4	0.342 ± 0.017	12.22 ± 0.15	28.2 ± 1.5
IOC-96-ST10-400m	14.8	TIMS	2/3	4.4	0.480 ± 0.030	26.80 ± 0.21	18.1 ± 1.1
		ICP-MS	1/3	2.2	0.478 ± 0.024	26.92 ± 0.33	17.9 ± 0.9
IOC-96-ST6-4550m	13.3	TIMS	2/3	20	2.249 ± 0.060	82.09 ± 0.93	27.63 ± 0.80
		ICP-MS	1/3	10	2.263 ± 0.056	82.09 ± 0.71	27.81 ± 0.70
IOC-96-ST8-5155m	13.5	TIMS	2/3	29	3.263 ± 0.071	32.55 ± 0.28	101.1 ± 2.3
		ICP-MS	1/3	15	3.296 ± 0.063	32.67 ± 0.32	101.8 ± 2.2
IOC-96-RFZ-5220m	13.5	TIMS	2/3	49	5.48 ± 0.10	62.16 ± 0.68	89.0 ± 1.9
		ICP-MS	1/3	25	5.62 ± 0.11	63.43 ± 0.73	89.3 ± 2.1

Locations: ST6 (8°S, 45°W); ST8 (16.3°S, 25°W); ST10 (33°S, 40°W); RFZ: (0.5°S, 20°W).

that basically does not exist with the TIMS method. This memory effect must be removed before each sample measurement or the accuracy of the measurements may be compromised.

4. Conclusions

After addressing the problems with instrumental blanks, biases and interferences, high-precision and high-sensitivity measurements of uranium and thorium isotopic compositions and concentrations can be made on an ICP-MS. This technique allows reduced sample size, higher sample throughput, and the ability to analyze samples with low Th concentrations.

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