

Techniques for Measuring Uranium-series Nuclides: 1992-2002

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1. INTRODUCTION

Advances in geochemistry and geochronology are often closely linked to development of new technologies for improved measurement of elemental and isotopic abundance. At the beginning of the past decade, thermal ionization mass spectrometric (TIMS) methods were just beginning to be applied for long-lived uranium-series nuclide measurement (Edwards et al. 1987; Goldstein et al. 1989; Bard et al. 1990), with considerable advances in measurement speed, precision, and sensitivity over decay-counting methods. This opened up a vast number of applications in uranium-series geochronology and geochemistry of young sediments, volcanic rocks, and aqueous systems. Over the past decade there have continued to be advances in thermal ionization techniques, and the advent of alternative mass spectrometric methods, particularly multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), has continued to improve the quality of uranium-series studies.

So the past decade has been a particularly dynamic time for not only development of mass spectrometric techniques, but initiation of other methods related to long-lived uranium-series nuclide measurement. In the area of sample preparation, further development of microwave digestion methods had led to advances in speed and cost of analysis. In chemical separations, development of extraction chromatographic resins for isolating specific elements have simplified many separation problems and consequently improved analytical characteristics including sensitivity, speed of analysis, waste generation, and cost. With regard to instrumental analysis, advances in both decay-counting and mass spectrometry instrumentation have improved either measurement sensitivity or precision, speed of analysis, or analytical cost. One could argue that instrumental developments will continue to drive scientific breakthroughs in the application of uranium-series nuclides as tracers and chronometers in the earth and other sciences.

In this chapter we discuss improvements documented in the literature over the past decade in these areas and others. Chemical procedures, decay-counting spectroscopy, and mass spectrometric techniques published prior to 1992 were previously discussed by Lally (1992), Ivanovich and Murray (1992), and Chen et al. (1992). Because ICPMS methods were not discussed in preceding reviews and have become more commonly used in the past decade, we also include some theoretical discussion of ICPMS techniques and their variants. We also primarily focus our discussion of analytical developments on the longer-lived isotopes of uranium, thorium, protactinium, and radium in the uranium and thorium decay series, as these have been more widely applied in geochemistry and geochronology.

2. SAMPLE PREPARATION

2.1. Microwave digestion of solids

Sample digestion/dissolution is generally required for all forms of uranium-series analysis excluding gamma spectrometry, and for all sample matrices excluding the dissolved components of aqueous solutions. Development of microwave digestion techniques for solids predates the 1990's, and numerous reviews have documented use of these systems for sample digestion (e.g., Kuss 1992; Lamble and Hill 1998). Prior to the past decade, most of these digestion systems were closed system, in which both pressure and temperature increases in the vessel during the microwave process were used to aid the digestion process. In the past decade, systems with more precise temperature and pressure control have been developed to dissolve samples under more specifically predetermined conditions. These methods have been applied to measurement of elemental U and Th in geologic standards (e.g., Totland et al. 1992; Sen Gupta and Bertrand 1995), and excellent agreement has been obtained with consensus values for these elements using open vessel-hot plate or fusion digestions.

In addition, open system microwave processes where pressure is maintained at atmospheric have also been developed. These systems provide additional options for sample digestion and avoid safety issues with pressurized closed-system digestion. Along with open system methods, automated techniques for addition of acid solutions to reaction vessels have also been implemented, providing options for on-line elemental or isotopic analysis. The size range of samples to be digested has also been extended to 1 gram or greater through use of larger sample vessels in the open and closed system configurations, which also provides more suitability for uranium-series analysis. Although microwave methods have been mainly applied to determination of elemental concentrations, these techniques may provide distinct advantages for uranium-series isotopic analysis in terms of reduced acid requirements and improved speed of analysis. In addition, microwave energy may also promote more complete sample-tracer equilibration in isotope dilution analysis than would be achieved using only conventional digestion methods.

2.2. Tracer addition and tracer/sample equilibration

In most alpha and mass spectrometric methods for which sample preparation is extensive and chemical recoveries can vary considerably from sample to sample, precise elemental concentrations are determined by isotope dilution methods (e.g., Faure 1977). This method is based on the determination of the isotopic composition of an element in a mixture of a known quantity of a tracer with an unknown quantity of the normal element. The tracer is a solution containing a known concentration of a particular element or elements for which isotopic composition has been changed by enrichment of one or more of its isotopes.

In these situations, addition of a tracer of unique isotopic composition is required, and the nature of the tracers added depends on the measurement technique. For example, short-lived ^{232}U and ^{228}Th (with respective half-lives of 70 and 1.9 years) are commonly used as a tracer for alpha spectrometric analysis of U and Th, whereas longer-lived ^{236}U , ^{233}U and ^{229}Th (with half-lives of 23 million, 160 thousand and 7900 years, respectively) are commonly used for mass spectrometric isotope dilution analysis. For thorium and uranium, measurement of isotopic composition (i.e., $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$) can be combined with measurement of abundance, and in these cases the tracer must be of high-purity and appropriate corrections must be made for the low levels of natural U and Th isotopes that are inevitably present. For isotope dilution measurements only, it is also advantageous to have high-purity tracers to minimize errors associated with measurement

of the isotopic composition of the tracer. When a mixed spike (e.g., Wasserburg et al. 1981) is used, such as ^{233}U - ^{229}Th , the relative abundances of U-series isotopes can be determined more precisely, leading to improvements in dating precision. Normally, tracers are standardized by mixing them with either a gravimetric standard or a well-characterized secular equilibrium standard for which U-series isotope abundances are well known (e.g., Ludwig et al. 1992). Analysis of secular equilibrium rock standards such as Table Mountain Latite or TML (Williams et al. 1992) and Harwell Uraninite or HU-1 (e.g., Ludwig et al. 1992), ideally matching the matrix to be analysed, also allow one to evaluate U-series measurement accuracy.

Methods for preparing U-series tracer isotopes vary according to element, but generally involve nuclear reactions to provide the radioactive tracers of interest. Preparation of the tracer is particularly an issue for protactinium, since the only option for mass spectrometric measurement (^{233}Pa) has a short half-life (27 d) and must be replenished frequently (Pickett et al. 1994; Bourdon et al. 1999). ^{233}Pa can be prepared by milking a solution of ^{237}Np or by neutron activation of ^{232}Th . Both methods are somewhat limiting, as the ^{237}Np method involves handling of considerable alpha activity, and the ^{232}Th method requires frequent access to a nuclear reactor. For radium, enriched ^{228}Ra solutions can be prepared by milking a solution of ^{232}Th (Volpe et al. 1991; Cohen and O'Nions 1991). ^{229}Th is commonly prepared by milking a ^{233}U supply, whereas ^{233}U and ^{236}U can be prepared by neutron and alpha activation of ^{232}Th , respectively. These nuclear reactions are commonly followed by chemical separations to purify the element of interest.

Regardless of the tracers added, proper tracer-sample equilibration must be obtained for accurate isotope dilution analysis. For chemically unreactive elements such as Th and Pa, it is generally desirable to ensure tracer-sample equilibration with acids that have a high boiling point such as nitric and perchloric acids, for which tracer and sample are converted to the same chemical form upon increasing temperature and dry-down. Some laboratories have reported good results for Th (Stirling et al. 1995; Pietruszka et al. 2002) and Pa (Bourdon et al. 1999) using only nitric acid during dry-down, whereas earlier work has generally found perchloric acid to be necessary for accurate results for these elements (Goldstein et al. 1989; Pickett et al. 1994; Lundstrom et al. 1998). Other laboratories use boric acid rather than perchloric acid to eliminate fluorides and help promote complete equilibration. For more reactive elements such as U and Ra, such steps are less critical due to the tendency for these elements to chemically exchange between different compound forms, hence nitric or hydrochloric acid dry-downs are thought to be sufficient.

For precise measurement of isotopic composition by mass spectrometry, it is also common to use either a natural, known isotopic ratio to correct for instrumental mass fractionation (e.g., internal normalization) or to add a tracer for this purpose. For example for natural uranium samples, one can use the natural $^{238}\text{U}/^{235}\text{U}$ of 137.88 to correct for fractionation. Alternatively, one can use an added ^{233}U - ^{236}U double spike of ratio ~unity for the most precise fractionation correction and/or non-natural samples (e.g., Chen et al. 1986; Goldstein et al. 1989).

In contrast to thermal ionization methods, where the tracer added must be of the same element as the analyte, tracers of different elemental composition but similar ionization efficiency can be utilized for inductively coupled plasma mass spectrometry (ICPMS) analysis. Hence, for ICPMS work, uranium can be added to thorium or radium samples as a way of correcting for instrumental mass bias (e.g., Luo et al. 1997; Stirling et al. 2001; Pietruszka et al. 2002). The only drawback of this approach is that small inter-element (e.g., U vs. Th) biases may be present during ionization or detection that need to be considered and evaluated (e.g., Pietruszka et al. 2002).

3. CHEMICAL SEPARATIONS

Chemical separations to purify the element of interest are required for most forms of decay-counting excluding gross gamma spectrometry and for most mass spectrometric methods excluding some types of ICPMS analysis. This is mainly due to the necessity for removal of unwanted interferences in the mass or decay-energy spectrum of uranium-series elements. In many cases in mass spectrometry, chemical separations are also required to provide optimal ionization efficiency or measurement signal to noise ratio. While most standard separation methods of anion or cation exchange chemistry, solvent extraction, phase separation, and/or coprecipitation were developed prior to the last decade, recently developed extraction chromatography materials have improved many aspects of uranium-series analysis. Automated separation systems based on these materials and others have also been developed which further increase analytical throughput (e.g., Hollenbach et al. 1994).

3.1. Extraction chromatography resins/disks

Extraction chromatography resins consist of inert beads that are coated by an organic extractant that can be selective for concentration of any of a number of elements from aqueous solutions. These materials were largely developed and basic separation capabilities determined at Argonne National Laboratory by P. Horwitz and colleagues and have been applied for uranium-series measurement by investigators around the world. These materials have been applied in two geometric configurations: as extraction chromatography beds for standard gravimetric column chromatography, and as disks for more rapid extraction of elements from aqueous solutions (e.g., Joannon and Pin 2001).

One of the first bed materials was based on the extractant diamyl amyolphosphonate (DAAP; marketed under the name U-TEVA-Spec) and was designed for purification of the tetravalent actinides (U (IV), Th (IV), Pu (IV)) and hexavalent uranium (U(VI)). This material is characterized by high (>10-100) distribution coefficients for U and Th in significant (>3 M) concentrations of both nitric and hydrochloric acids, and so is useful for both U and Th purification (Horwitz et al. 1992; Goldstein et al. 1997; Eikenberg et al. 2001a).

An additional material based on the extractant octyl-phenyl-N,N-diisobutyl-carbamoylmethylphosphine oxide, or CMPO, (marketed under the name TRU-Spec) has also been widely utilized for separations of transuranic actinides (Horwitz et al. 1993a) but is also useful for uranium-series separations (e.g., Burnett and Yeh 1995; Luo et al. 1997; Bourdon et al. 1999; Layne and Sims 2000). This material has even greater distribution coefficients for the uranium-series elements U (>1000), Th (>10000), and Pa. As shown in Figure 1, use of this material allows for sequential separations of Ra, Th, U, and Pa from a single aliquot on a single column. Separations of protactinium using this material (Bourdon et al. 1999) provide an alternative to liquid-liquid extractions documented in Pickett et al. (1994).

Another material based on the crown ether extractant 4,4'(5')-bis(t-butyl-cyclohexano)-18 crown-6, marketed under the name Sr-Spec, is useful for separations involving divalent cations including Pb, Ba, and Ra (Horwitz et al. 1991). For ^{226}Ra analysis by TIMS, Ra-Ba separations are required because the presence of Ba drastically decreases the ionization efficiency of fg Ra samples from 10% to <1%. This material has been widely used for separations of Ra from Ba (e.g., Chabaux et al. 1994; Lundstrom et al. 1998; Rihs et al. 2000; Joannon and Pin 2001; Pietruszka et al. 2002) and is a complement or alternative to cation exchange separations for EDTA complexes of these elements (Volpe et al. 1991; Cohen and O'Nions 1991). Sr-Spec material would also be useful for ^{210}Pb analysis, since Pb has a greater distribution coefficient than Sr with this extractant.

Separation of U, Th, Pa, and Ra on a TRUTM Spec Resin Column**1. Sample Adjustment**

Sample Size: 0-2 g rock

Dissolve in 3-20 mL 10M HCl.

Add equal volume of 10M HCl + saturated H₃BO₃.

Equilibrate overnight.

2. Condition Column

Add 6 cv 0.01M HCl + 4 cv 10M HCl.

3. Radium Fraction

Load sample on column and save for Ra.

Add 1 cv 9M HCl (beaker wash) and save for Ra.

4. Thorium Fraction

Add 1 cv 4M HCl and 10 cv 1.2M HCl and save for Th.

5. Uranium and Protactinium Fraction

Add 10 cv (0.1M HCl + 0.05M HF) and save for U and Pa.

May pass U+Pa fraction through 2nd column of 0.5 mL Eichrom inert bead material to remove extractant.

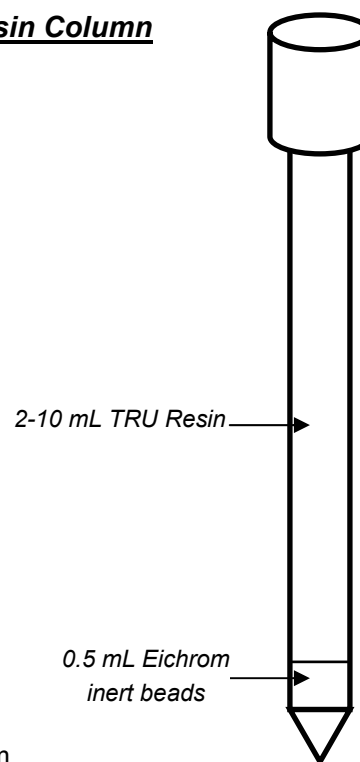


Figure 1. Schematic diagram showing a TRU-spec extraction chromatography method for separation of uranium, thorium, protactinium, and radium from a single rock aliquot. Further purification for each element is normally necessary for mass spectrometric analysis. Analysis of a single aliquot reduces sample size requirements and facilitates evaluation of uranium-series dating concordance for volcanic rocks and carbonates. For TIMS work where ionization is negatively influenced by the presence of residual extractant, inert beads are used to help remove dissolved extractant from the eluant.

However, there are some negative side-effects of these extractant materials, both in TIMS and ICPMS. For TIMS work, residual extractant in the eluant may negatively influence ionization behavior of uranium-series elements. This may occur by raising ionization temperature due to formation of refractory organic compounds on the filament, or by contributing to undesirable organic isobars in the mass spectrum. These effects can be minimized by using a lower bed of uncoated resin beads to help absorb the excess extractant (Pietruszka et al. 2002) and/or use of appropriate clean-up anion or cation exchange column chemistry. Similar effects have generally not been reported for ICPMS, presumably due to effective breakdown of the extractants at higher temperature in the ICP source, although in a few cases organic interferences in the ICPMS spectrum may be attributed to residual resins or extractants (Pietruszka et al. 2002). The presence of organic extractants in final ICPMS sample solutions may also contribute to significantly increased washout times between sample analysis.

4. INSTRUMENTAL ANALYSIS METHODS

4.1. Alpha spectrometry

Sources. It is well known that the optimal geometry for source preparation for alpha spectrometry is as an “infinitely thin” and uniform deposit on a flat surface. In practice,

“infinitely thin” can correspond to up to 100 μg of material deposited on a planchet of 1-2 cm in diameter. Both electrodeposition and co-precipitation (NdF_3) methods have traditionally been utilized for preparation of alpha spectrometric sources (e.g., Lally 1992).

However, during the past decade some innovative methods for preparation of radium, thorium, and uranium sources for aqueous samples have been reported (e.g., Surbeck 2000; Morvan et al. 2001; Eikenberg et al. 2001b). In these methods, radionuclides in water samples are adsorbed onto a thin layer (20 μm) of manganese oxide, followed by direct alpha counting of the oxide layer. As shown in Figure 2, energy resolution obtained from alpha counting of these materials can be nearly as good as for electroplated sources. Uranium adsorbing films (Surbeck 2000) have also been prepared utilizing a commercially available cation exchanger containing diphosphonate and sulfonate groups (Horwitz et al. 1993b). Energy resolution with these films is poorer than for the manganese oxide films, but is better than obtained with liquid scintillation alpha spectrometry (see below).

Instrumentation. Traditional methods of alpha and beta spectrometry instrumentation have changed little over the past decade. Alpha spectrometric methods typically rely on semi-conductor or lithium-drifted silicon detectors ($\text{Si}(\text{Li})$), or more historically gridded ion chambers, and these detection systems are still widely used in various types of uranium-series nuclide measurement for health, environmental, and

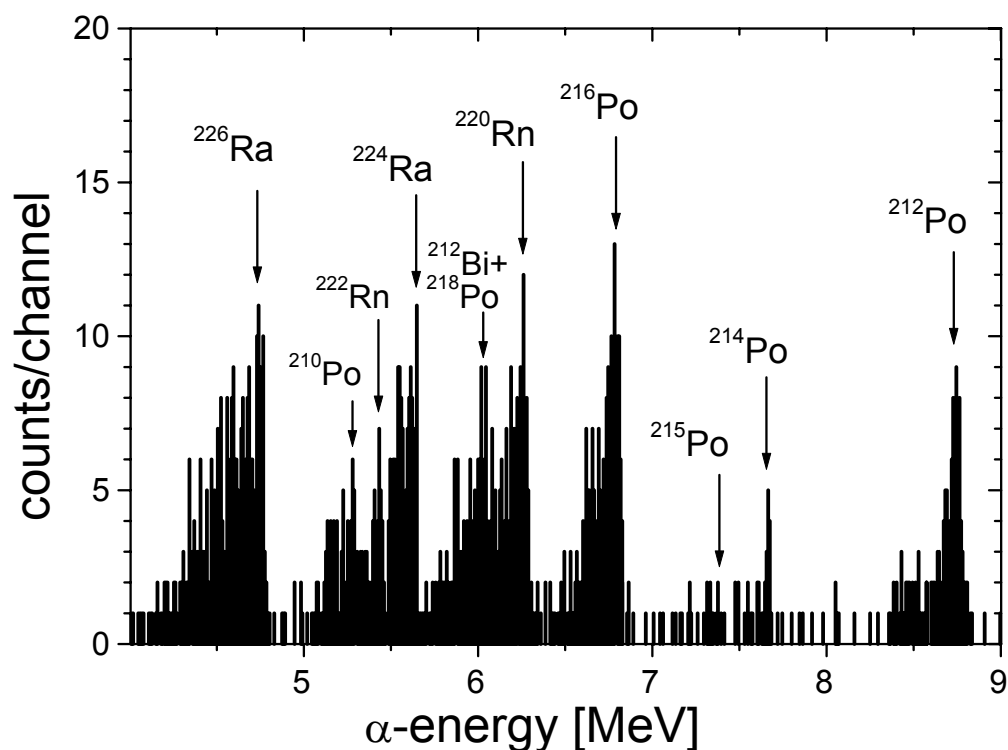


Figure 2. Alpha spectrum for a radium adsorbing manganese-oxide thin film exposed to a groundwater sample, after Surbeck (2000) and Eikenberg et al. (2001b). A 2×2 cm sheet is exposed to 0.1-1.0 L of sample for 2 days, capturing nearly all of the radium in the sample. These sample discs can be used directly for low-level alpha spectrometry without the need for further separation and preparation methods to produce planar sample sources. Energy resolution is nearly as good as for electroplated sources, and detection limits are typically 0.2 mBq/L (6 fg $^{226}\text{Ra}/\text{L}$) for ^{226}Ra and ^{224}Ra for a one-week counting period. These sensitivities are comparable to traditional methods of alpha spectrometry. [Used by permission of Elsevier Science, from Eikenberg et al. (2001), *J Environ Radioact*, Vol. 54, Fig. 4, p. 117]

geological applications. For many short-lived isotopes in the uranium and thorium decay series, traditional alpha spectrometry with semi-conductor detection is still either the method of choice or currently the only realistic alternative for low-level detection (e.g., Po-210 (Rubin et al. 1994) and Ac-227 (Martin et al. 1995)).

However, new techniques for detection of alpha-emitting isotopes via alpha liquid scintillation spectrometry have recently been developed (PERALS, or photon-electron rejecting alpha-liquid scintillation; e.g., Dacheux and Aupiais 1997). These methods combine chemical separation by liquid-liquid extraction with measurement of alpha activity by liquid scintillation. Scintillation detection is obtained because the organic extractant also contains an energy transfer reagent and a light-emitting fluor. A variety of combinations of aqueous phases and organic phases can be utilized, depending on the particular isotopes to be measured. For instrumentation, the method uses pulse shape discrimination to nearly eliminate the background from beta-emitting isotopes and to reduce background from gamma-ray activity. Detection limits comparable to alpha spectrometry are obtained, but with much less sample preparation for many matrices. Although isotope dilution is required for analysis of samples with complex matrices, aqueous solutions have more consistent recoveries, resulting in the option of direct analysis without tracer addition.

4.2. Gamma spectrometry

Over the past decade, traditional instrumentation for highest resolution gamma spectrometry has continued to rely on solid-state germanium detectors (e.g., Knoll 1989). Although there have been developments in the geometry of such detectors to improve counting efficiency, from extension of flat-planar detectors to larger sizes and to different geometries (e.g., well-type), their basic characteristics have not changed (El-Daoushy and Garcia-Tenorio 1995).

Minimization of background from cosmic rays or earth's natural radioactivity continues to be a major focus and relies on development of improved shielding or shielding materials (e.g., Semkow et al. 2002). Ground-level locations may use active rejection of cosmic-ray muons, either using NaI active shields, plastic scintillator, or proportional counters, and these anti-coincidence techniques provide reduced background. However, lowest backgrounds are achieved at deep-underground locations (e.g., Neder et al. 2000) for which cosmic rays are greatly reduced or not present.

Compton suppression gamma spectrometry has been applied for ^{228}Ra determination (James et al. 1998), but is particularly applicable for high-activity measurements where background is created by Compton scattering of gamma radiation originating from the sample itself. For low-activity measurements the Compton suppressor may act as a guard against cosmic radiation, although surrounding a Ge detector with the Compton suppressor may actually increase background from natural radioactivity present in the components of the suppressor.

In addition to instrumental improvements, various approaches have been used to improve the purity or geometry of sources of natural samples for gamma spectrometric measurement. For example, improvements in source preparation for ^{234}Th measurement in water and sediment samples by gamma spectrometry are discussed in Cochran and Masque (2003). It should be emphasized that one of the main advantages of gamma spectrometry is ease of use, since in many cases samples may be analyzed directly or with significantly reduced sample preparation compared to alpha, beta, or mass spectrometric techniques.

4.3. Thermal ionization mass spectrometry (TIMS)

The end of the 1980's saw the application of TIMS to U-series measurement (Chen et al. 1986; Edwards et al. 1987; Goldstein et al. 1989). This represented a major technological advance. Analysis time was reduced from one week to several hours, sample sizes for many carbonate or volcanic rock samples decreased from ~10-100 μg to 0.1-1 μg U or Th, measurement precision improved from percent to permil levels, and for the ^{238}U - ^{234}U - ^{230}Th decay series, the dating range was extended from 350,000 years to 500,000 years, compared with earlier alpha-spectrometric techniques. The first TIMS instruments utilized a single-collector and "peak jumping" analysis routines (e.g., Edwards et al. 1987; Goldstein et al. 1989; Bard et al. 1990). Despite the sequential measurement of isotopes, peak-tailing corrections, and limited dynamic range, analytical uncertainties of ~5‰ could be attained for U and Th. As a result, ^{230}Th -age uncertainties improved from $\pm 10,000$ to $\pm 2,000$ years in 120,000 year-old carbonate samples, and ^{230}Th -ages could be determined with uncertainties of $\pm 10,000$ years in 300,000 year-old samples. The improved precision and sensitivity opened up a vast number of applications in paleoclimatology and geochemistry.

Subsequently, a wide array of developments in TIMS methods for uranium-series measurement occurred during the past decade including initiation of methods for measurement of long-lived radium (Volpe et al. 1991; Cohen and O'Nions 1991) and protactinium isotopes (Pickett et al. 1994; Bourdon et al. 1999), development of improved sources or ionization methods for TIMS analysis, and introduction of commercially available multi-collector TIMS instruments designed specifically for uranium and thorium isotopic measurement.

Sources. The ionization efficiency in a TIMS source depends on a number of factors including the difference between filament work function and elemental ionization potential, as well as the temperature of the filament, elemental oxidation state and volatility, distribution of sample on the filament surface, etc. Ionization efficiency is defined as the number of atoms ionized in the source relative to the total number of atoms introduced to the instrument. In TIMS, transmission of ionized material through the mass spectrometer is normally assumed to be close to 100%, and ionization efficiency is given as the number of ions detected as a proportion of the number of atoms loaded onto the filament. Although effects of ionization potential, filament work function and temperature are theoretically given by the Saha-Langmuir equation (e.g., Wayne et al. 2002), in practice other chemical, physical, and geometrical effects often exert a more significant influence on ionization behavior and efficiency. In addition, evaporation and ionization of an element off the filament surface under vacuum causes an increasing depletion of the lighter isotopes over the heavier isotopes as progressively more of the sample is volatilized. This gives rise to a time-dependent instrumental mass fractionation, which varies with ionization method and may be corrected by either internal normalization or external standardization techniques.

Over the past decade, a number of improvements in source preparation have been utilized for uranium-series nuclide analysis by TIMS. These generally either involve methods to increase the work function of the filament material, addition of enhancers to optimize elemental volatility and oxidation state, geometrical improvements in filament configuration or sample loading, or instrumental improvements in source mechanism or design. Early TIMS uranium and thorium work utilized single Re filaments for analysis of small Th and U samples (ng or smaller; Chen et al. 1986; Edwards et al. 1987), and multiple filament assemblies for more effective ionization of larger samples (Goldstein et al. 1989). For single filament measurements of Th isotopes in low- ^{232}Th carbonate or water samples, ^{232}Th filament blanks can be significant and need to be carefully

controlled or monitored (Edwards et al. 1987). Samples for single filaments were typically loaded as dilute HCl or HNO₃ solutions between layers of colloidal graphite, called the graphite sandwich method. In this case, the graphite provides a reduced environment and samples are analyzed as the U⁺ and Th⁺ metal species at temperatures around 1700°C and 1900°C, respectively. Because ionization efficiency for this method is quite negatively correlated with sample size loaded, particularly for Th, triple filament configurations provide better ionization efficiency for larger U and Th samples (Goldstein et al. 1989). In multiple filament techniques for U and Th, the side filaments are used to control sample volatility at lower temperatures than the center, ionizing filament which is typically maintained at about 2100°C to produce U⁺ and Th⁺ metal species more efficiently. For U and Th, ionization efficiencies are typically a few epsilon to a few permil, but in exceptional cases, have been reported at the percent-level (e.g., Edwards et al. 1987; Esat 1995). More recently, Yokoyama et al. (2001) used a silicic acid-dilute phosphoric acid activator to measure ²³⁴U/²³⁸U by TIMS using UO₂⁺ ions. This approach yielded analytical uncertainties of 1‰ (2σ) on small samples of uranium (10-100 ng).

Radium samples for TIMS work can be prepared in a number of ways, due to the low ionization temperature for this element (~1300°C). For single filament analysis, samples can be loaded with a silica-gel mixture on single Re or Pt filaments, in either standard or reduced length (Delmore) configurations (Volpe et al. 1991). Alternatively, samples can be loaded onto the center W filament of a triple Ta-W-Ta filament assembly with a Ta-HF-H₃PO₄ activator solution (Cohen and O’Nions 1991). In this method, the side filaments are used to preheat the center filament and gently remove hydrocarbon interferences from the sample filament prior to Ra ionization. Lundstrom et al. (1998) modified these procedures slightly and used a TaCl₅ activator on single Re filaments.

Protactinium samples for TIMS analysis are typically prepared by the graphite sandwich technique on single Re filaments (Pickett et al. 1994; Lundstrom et al. 1998), similar to methods for small Th and U samples (Chen et al. 1986; Edwards et al. 1987). An alternative method is to analyze protactinium with a silica-gel enhancer on tungsten filaments as the double-oxide at filament temperatures around 1400°C (Bourdon et al. 1999). For the graphite sandwich methods, identifying the appropriate amount of graphite is critical, since it is desirable to let uranium ionization complete prior to protactinium isotopic measurement to remove the ²³³U isobar produced from ²³³Pa decay from the ²³¹Pa/²³³Pa measurement. With too much graphite, uranium and protactinium ionization overlap, resulting in more complicated data reduction or rejection of data. However, it is desirable for some graphite to be present at the higher temperatures of Pa ionization (1900°C), so proper adjustment is a somewhat tricky aspect of these methods. The ²³³U isobar can also be minimized by ensuring a clean separation of Pa from U during ion exchange column chemistry, although some ²³³U isobar is inevitably present due to ²³³Pa decay between separation and analysis.

Carburization of rhenium filaments has been used to optimize Th and Pa ionization efficiency for TIMS analysis on single filaments (Esat 1995). ReC has a greater work function than Re metal, and elemental oxidation state is maintained in the reduced or metal state by the presence of carbon in the filament. Using this method and a mass spectrometer with improved ion optics, Esat (1995) was able to improve Th transmission and ionization efficiency by about a factor of 30 over conventional methods. Using more conventional mass spectrometry, Murrell et al. (personal communication) were able to improve ionization efficiency for Pa and Th by a factor of 5-10 over conventional graphite sandwich loads on Re filaments (Goldstein et al. 1989; Pickett et al. 1994). For Pa analysis, one drawback is that Pa and U ionization commonly overlap using this

procedure, and so a deconvolution procedure, where ^{238}U and ^{233}U peak intensities are approximately correlated and involving the isotopes ^{238}U , $^{233}\text{U} + ^{233}\text{Pa}$, and ^{231}Pa , should be applied to utilize more data and obtain accurate $^{231}\text{Pa}/^{233}\text{Pa}$ ratios.

Resonance ionization methods (RIMS) have also been explored for improving Th ionization efficiency for mass spectrometric measurement (Johnson and Fearey 1993). As shown in Figure 3, two lasers are required, a continuous resonant dye laser for resonance of thorium atoms, and a continuous UV argon laser for transition from resonance to ionization. Consequently, sophisticated laser instrumentation is required for these methods,

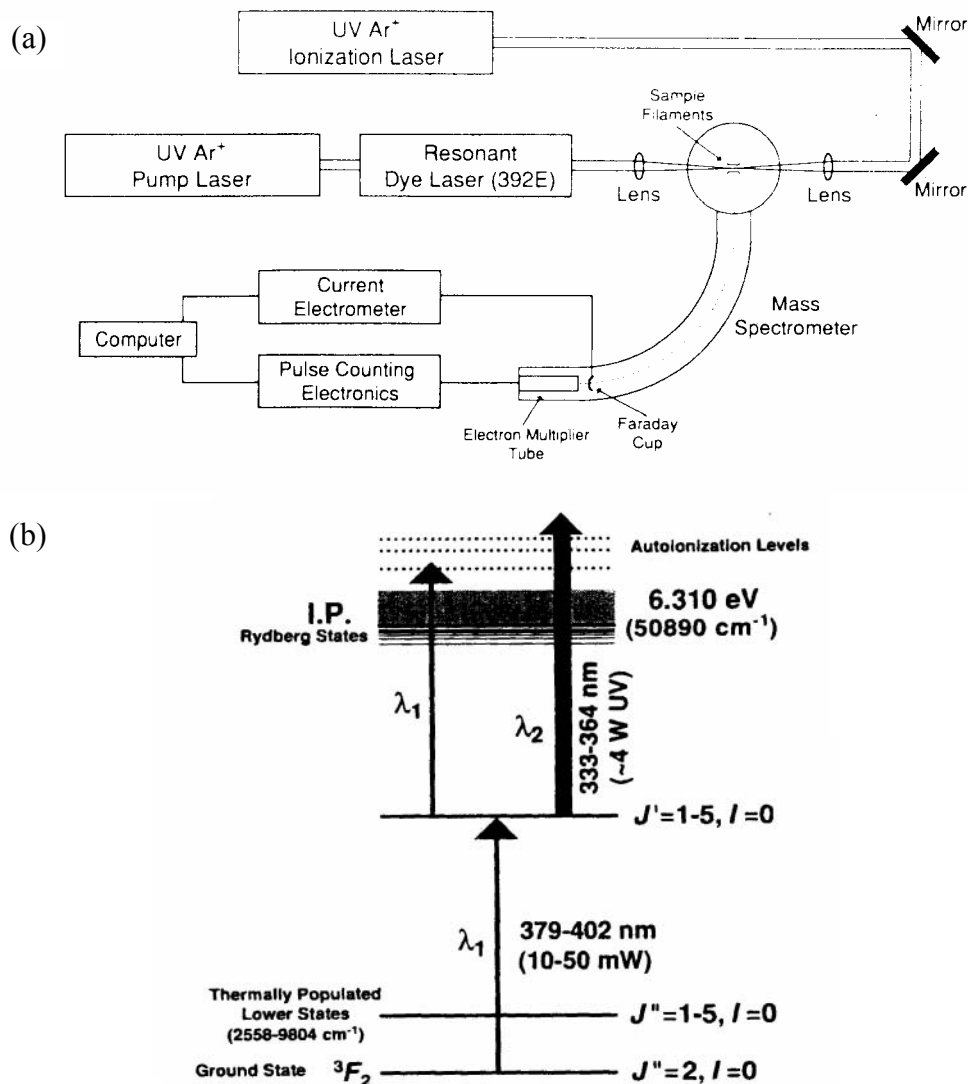


Figure 3. a) Simplified schematic of continuous wave resonance ionization mass spectrometry for thorium isotopic analysis, after Johnson and Fearey (1993). Two lasers are required for ionization, a narrow band laser for the resonant step and a high-powered ultraviolet Ar⁺ laser for the ionization step, and are coupled with a standard (NBS-1290) mass spectrometer. b) Thorium energy level diagram illustrating the two-step ionization process. Ionization/detection efficiency is improved by at least an order of magnitude (to 0.4%) relative to standard TIMS methods for large thorium samples. Internal precision is comparable to TIMS techniques (~0.5%), although a small bias of 2-4% is introduced due to differences in the transition strengths of ^{230}Th vs. ^{232}Th . However, the bias is reproducible and can be corrected using standards. [Used by permission of Elsevier Science, from Johnson and Fearey (1993), *Spectrochim Acta Part B*, Vol. 48, Figs. 1 & 2, p. 1066 & 1067]

and laser stability needs to be maintained over the measurement period for these methods to be utilized. However, ionization efficiency was increased by greater than an order of magnitude (to $\sim 0.4\%$) relative to standard TIMS techniques. Consequently, volcanic rock samples with as little 1-5 ng Th may potentially be analyzed using this method.

Ion guns or cavity sources have also been developed for improving elemental ionization for TIMS measurement (Duan et al. 1997; Wayne et al. 2002). As shown in Figure 4, one ion source is based on a tungsten crucible with a cavity (0.02 cm diameter, 1 cm depth) into which sample is loaded. The crucible is heated by electron

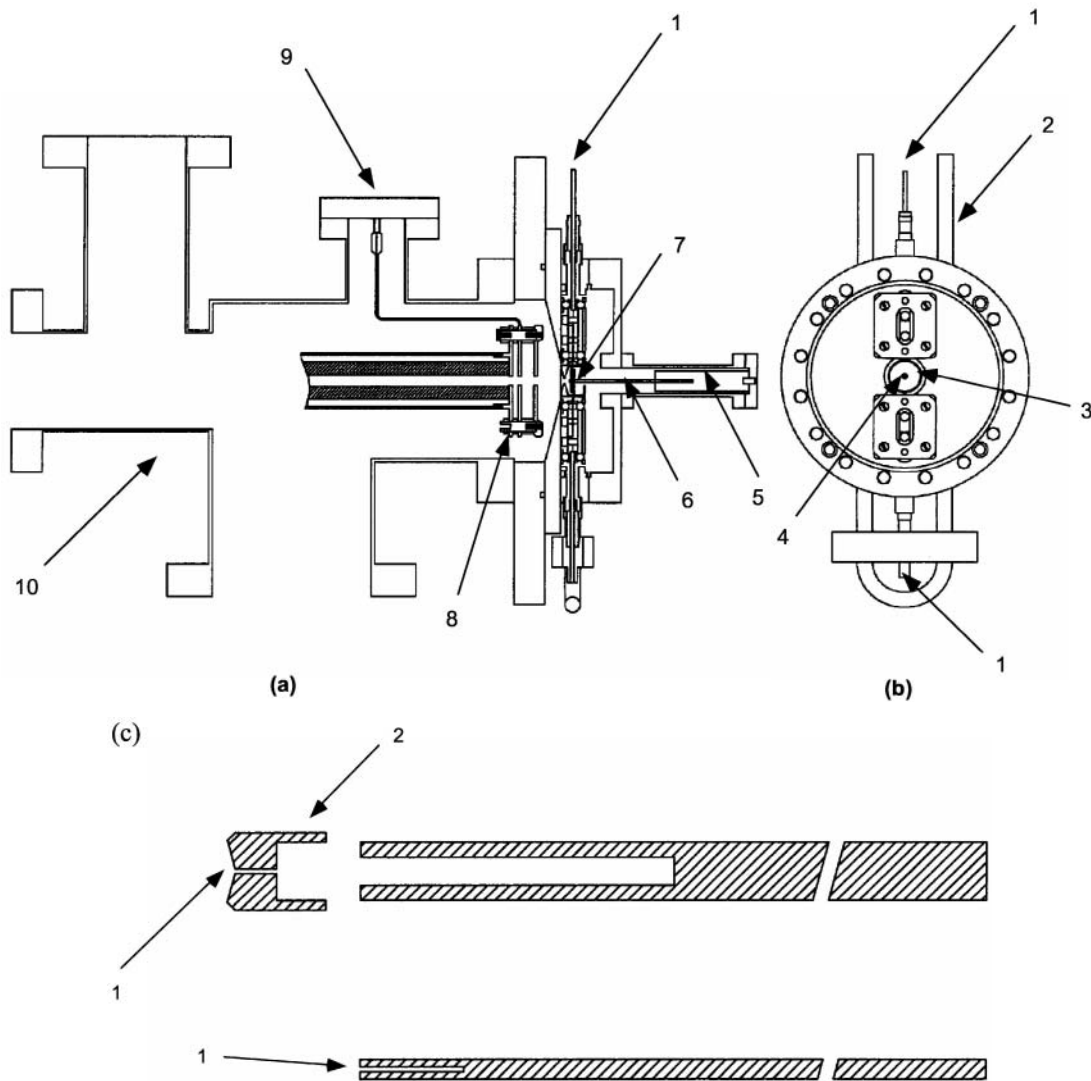


Figure 4. Schematic diagram of a cavity ionization source designed for TIMS or quadrupole mass spectrometry, after Duan et al. (1997). a) the ion source mounted on a mass spectrometer: 1, electrodes for power supply; 2, water or air cooling tubing; 3, electron bombardment shielding can; 4, the orifice of the shielding can; 5, crucible holder; 6, crucible; 7, electron bombarding filament; 8, ion lens; 9-10, quadrupole mass spectrometer; b) a coaxial view of the source, with same components as in a), c) tungsten crucibles used for the thermal ionization source. Top diagram illustrates a crucible for an isotope separator, bottom is the crucible for a quadrupole or magnetic sector spectrometer. 1, ionization channel; 2, crucible cap. Dimensions for the smaller thermal ionization crucible are 0.02 cm diameter and 1 cm depth. Ionization efficiency for many elements (ng to μg) is improved by at least an order of magnitude relative to standard filaments, although backgrounds can also be elevated relative to standard methods and need to be carefully evaluated. [Used by permission of Elsevier Science, from Duan et al. (1997), *Int J Mass Spectrom Ion Processes*, Vol. 161, Figs. 1 & 2, p. 29 & 30]

bombardment from a filament surrounding the crucible that can be modified to control the crucible temperature. Ionization efficiency for large samples (ng to ug) of many elements is enhanced by factors of 10-100 relative to standard TIMS sources due to the increased interaction of gaseous analyte atoms with the greater surface area of the crucible walls (Duan et al. 1997). Wayne et al. (2002) adapted this source to a time-of-flight mass spectrometer and obtained a maximum ionization efficiency of 1-3% for thorium samples of ~0.1-20 ng size, representing a factor of 10-30 improvement over conventional methods. However, blanks from the W cavity source are a particular issue for uranium analysis and also need to be carefully evaluated for thorium and other uranium-series measurements.

Detection systems. Prior to the past decade, most instruments used for uranium-series analysis were single-collector instruments, for which ion beams of the various isotopes are cycled onto a single low-intensity detector, usually with electronics operating in pulse counting mode (Chen et al. 1986; Edwards et al. 1987; Bard et al. 1990; Goldstein et al. 1989; Volpe et al. 1991; Pickett et al. 1994), in order to measure the low-intensity ion beams of ^{230}Th , ^{234}U , ^{231}Pa , ^{233}Pa , ^{226}Ra and ^{228}Ra . Daly detectors and discrete-dynode multipliers provide the best combination of linearity and dynamic range for isotope ratio measurement, although precise measurement (<1%) is usually limited to ratios below a few thousand (Cheng et al. 2000; Richter et al. 2001). Thus, the measurement of extremely large isotope ratios of uranium and thorium ($^{238}\text{U}/^{234}\text{U} = 20,000$ and $^{232}\text{Th}/^{230}\text{Th} = 200,000$) is problematic using single-collector instruments. A “bridge” isotope must instead be used (e.g., ^{235}U and ^{229}Th) and two isotope ratio measurements of about 100-1000 in magnitude are combined (e.g., $^{238}\text{U}/^{235}\text{U} \times ^{235}\text{U}/^{234}\text{U}$ and $^{232}\text{Th}/^{229}\text{Th} \times ^{229}\text{Th}/^{230}\text{Th}$) to yield the desired measurement (Chen et al. 1986; Goldstein et al. 1989).

An alternative to the bridge technique was recently reported for thorium analysis in silicate rocks for which both ^{230}Th and ^{232}Th are measured on a single ion-counting detector (Rubin 2001). With careful chemistry and mass spectrometry, $^{230}\text{Th}/^{232}\text{Th}$ ratios of igneous rocks can be measured with this technique with a precision that is similar to the bridge method. The disadvantage of this technique is that ^{230}Th ion-count rates are extremely low (around 10 cps) with normal silicate thorium ratios and are therefore subject to perturbations from background variation and low-level isobaric interferences in “normal” samples.

A double-focusing magnetic sector TIMS was initially used for thorium isotope measurements in silicate rocks to provide adequate abundance sensitivity (Goldstein et al. 1989). However in the late 1980's, commercially available multi-collector instruments became available that provide more options for uranium-series analysis. These instruments generally consist of an array of Faraday cups situated after the magnet, with a Faraday cup and/or low level counting system (Daly knob or electron multiplier) located after an electrostatic analyzer (ESA) or retarding potential filter (e.g., Palacz et al. 1992; Cohen et al. 1992; Rubin 2001). The energy filter improves abundance sensitivity. Abundance sensitivity is defined as the peak tailing contribution from one mass to an adjacent mass and is normally determined by measuring the contribution of mass 238 to mass 237 using a pure U standard solution. By using an energy filter, abundance sensitivity is typically <0.5 ppm at one amu, enabling the measurement of low abundance ^{230}Th in the presence of high-abundance ^{232}Th , typical of silicate rocks. Without an energy filter, abundance sensitivity is about an order of magnitude worse (~5 ppm at one amu), and in silicate rocks, the ^{230}Th peak may be of the same order of magnitude to the contribution from ^{232}Th tailing. Tailing corrections based on mathematical subtraction can be made (McDermott et al. 1993), but these can also be difficult to determine

precisely. With an energy filter, more time can also be spent measuring peak count rates rather than counting backgrounds, increasing the efficiency of the analysis. An energy filter may also be desirable to enhance the abundance sensitivity on ^{234}U in the presence of peak tailing from ^{238}U .

The first multiple-collector TIMS instruments permitted simultaneous measurement of the U-series isotopes in static or multi-static mode. The main advantage of these techniques is that multi-collection permits simultaneous collection of the major and minor isotope beams, improving the efficiency of data collection. In addition, greater variations in ion beam intensity can be accommodated than with single-collector techniques. In static collection, the main disadvantage is that the Faraday-ion counting gain must be stable during the course of the analysis and must be measured either during or before analysis. In multi-static modes of collection for uranium, the gain can be obtained during analysis by switching the ^{235}U beam between Faraday and ion-counting detectors, and so $^{234}\text{U}/^{238}\text{U}$ ratios with extremely high precision can be obtained. This, coupled with high abundance sensitivity capabilities, permits reduced analysis times, smaller sample sizes and analytical precisions of up to 1-2‰ for the U-Th isotopes for carbonates (e.g., Stirling et al. 1995). Analysis is possible on high- ^{232}Th silicate rocks, as well as low- ^{232}Th carbonate samples.

Despite the application of multiple-collector arrays to TIMS U-series measurement, it is usually still necessary to cycle the low-level Th isotopes (^{230}Th , ^{229}Th and carbonate ^{232}Th) through a single low-level detector, so that measurement precision is still limited by beam intensity fluctuations and poor data acquisition efficiency. To overcome these limitations, Esat (1995) applied charge-collection TIMS (CC-TIMS) to thorium isotope measurement. In “charge-collection” mode, a Faraday collector is still utilized, but the usual high-value feed-back resistor ($10^{11}\ \Omega$) in the electrometer amplifier is replaced with a 20 pico-Farad air-core capacitor (Fig. 5). Provided that the ion beam is stable, charge builds up on the capacitor with time in a linear fashion and is displayed in analogue mode as a monotonic increase in voltage and the rate of voltage accumulation is related to the ion current. This technique allows the measurement range to be extended below $10^{-14}\ \text{A}$, while preserving the advantages of Faraday cup arrays, allowing all low-level ion currents to be monitored simultaneously, in multiple channels. Charge collection achieves very high levels of precision; the uncertainty in $^{229}\text{Th}/^{230}\text{Th}$ is routinely 0.6‰ for sample sizes corresponding to 30 pg of ^{230}Th .

In static collection for untraced thorium samples, the gain is typically measured during the warm-up stage of analysis for which the ^{232}Th beam is switched between Faraday and ion-counting detectors, and variations in this gain during a run have sometimes been noted (Rubin 2001). In multi-static collection for traced Th analysis, ^{229}Th can be switched between Faraday and ion-counting detectors to provide an in-run measurement of Faraday-ion counting gain. This method can therefore provide very high precision results, similar to uranium analysis by this technique.

Accuracy for all thorium measurements by TIMS is limited by the absence of an appropriate normalization isotope ratio for internal correction of instrumental mass fractionation. However, external mass fractionation correction factors may be obtained via analysis of suitable thorium standards, such as the UC-Santa Cruz and IRMM standards (Raptis et al. 1998) for $^{230}\text{Th}/^{232}\text{Th}$, and these corrections are usually small but significant (< few ‰/amu). For very high precision analysis, the inability to perform an internal mass fractionation correction is probably the major limitation of all of the methods for thorium isotope analysis discussed above. For this reason, MC-ICPMS techniques where various methods for external mass fractionation correction are available, provide improved accuracy and precision for Th isotope determinations (Luo et al. 1997; Pietruszka et al. 2002).

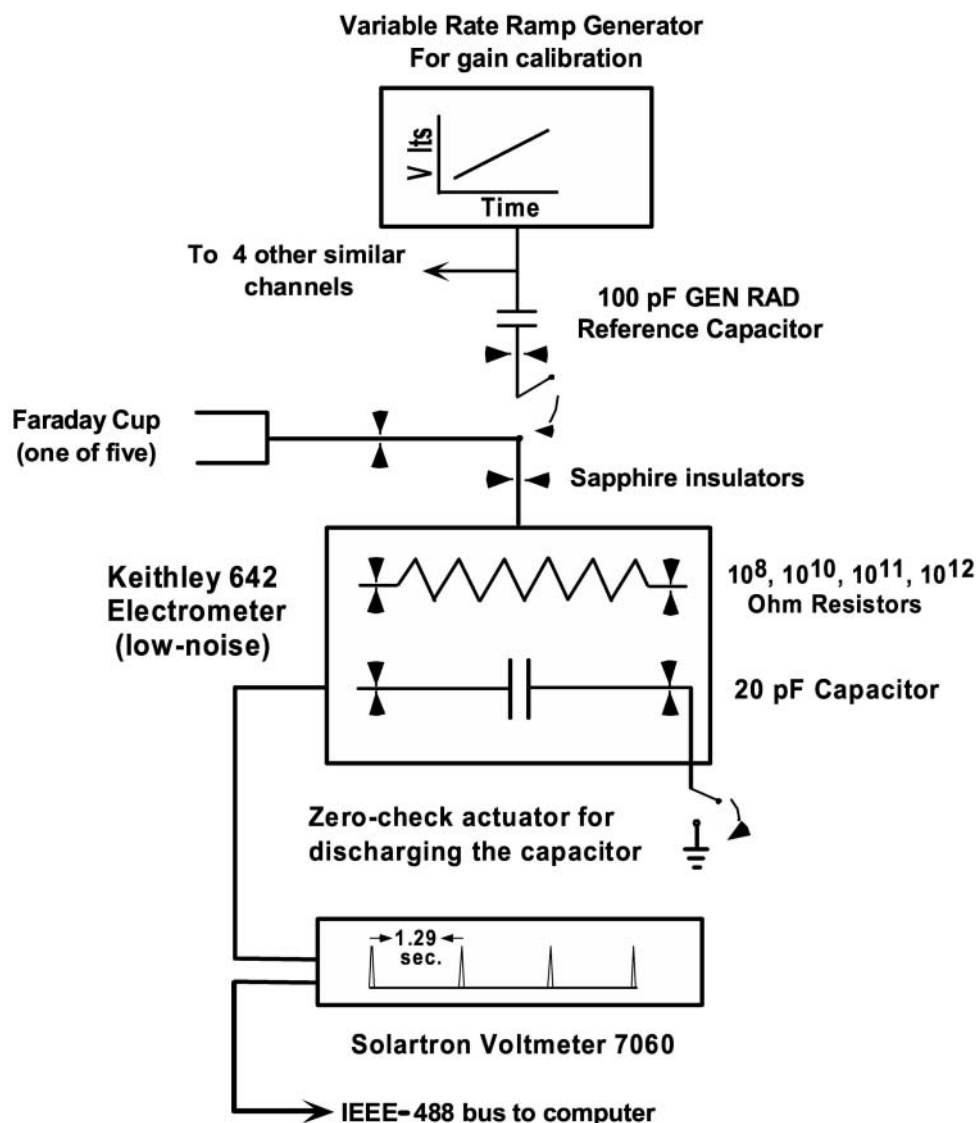


Figure 5. Schematic diagram of one of the five channels of a charge-collection system for thermal ionization mass spectrometry of thorium, after Esat (1995). In “charge-collection” mode, a Faraday collector is still utilized, but the usual high-value feed-back resistor ($10^{11} \Omega$) in the electrometer amplifier is replaced with a 20 pico-Farad air-core capacitor. Charge builds up on the capacitor with time and is displayed in analogue mode as a monotonic increase in voltage, with the rate of voltage accumulation related to the ion current. This technique allows the measurement range to be extended below 10^{-14} A, while preserving the advantages of Faraday cup arrays, allowing all low-level ion currents to be monitored simultaneously, in multiple channels. Charge collection achieves very high levels of precision; the uncertainty in $^{229}\text{Th}/^{230}\text{Th}$ is routinely 0.6% for sample sizes corresponding to 30 pg of ^{230}Th . [Used by permission of Elsevier Science, from Esat (1995), *Int J Mass Spectrom Ion Processes*, Vol. 148, Fig. 1, p. 163]

4.4. Secondary ion mass spectrometry (SIMS)

SIMS has also been successfully applied for thorium isotopic measurement during the past decade. This technique has been applied for both chemically separated thorium samples (England et al. 1992; Bourdon et al. 1994; Layne and Sims, 2000), as well as in-situ analysis of minerals with high thorium content such as zircons (Reid et al. 1997).

Although detailed methods depend on the instrument used, sources and ionization method are the major difference between SIMS and TIMS methods. SIMS methods

employ either primary Ar^+ or O^- beams which bombard spectrographically pure carbon plachets containing precipitated thorium sample. Ion separation is similar to TIMS methods, obtained with either large radius magnetic sectors and/or electrostatic analyzers, which can provide adequate abundance sensitivity for measurement of ^{230}Th in the presence of a large ^{232}Th beam (<0.1 ppm for a change in one mass unit at mass 232). Ion detection is similar to TIMS methods, with sequential or simultaneous collection of ^{232}Th on a Faraday cup and ^{230}Th on an axial electron multiplier, and the use of standards to determine the Faraday-multiplier gain. The main advantage of SIMS techniques for chemically separated samples is that ionization efficiency for Th (~2%) is substantially greater than for TIMS methods. Hence sample size requirements for Th analysis in volcanic rocks are substantially lower with SIMS work (10 ng or less), while overall measurement reproducibility is comparable to TIMS methods (0.5 to 1%). However, the main disadvantage of SIMS is equipment cost, as commercially available SIMS instrumentation is considerably more expensive than TIMS instruments.

4.5. ICPMS and MC-ICPMS

Inductively coupled plasma mass spectrometry (ICPMS) techniques have been widely applied for uranium-series nuclide measurement during the past decade. The major strengths of ICPMS are five-fold. First, the high ~6000 K temperature attained in the plasma source produces efficient ionization (>90%) of nearly all elements (Gray 1985; Jarvis et al. 1992). This includes those with high first ionization potentials that are difficult to ionize by TIMS, thorium being just one example. Second, in contrast to TIMS, ionization efficiency is not a function of load size and signal intensity can be increased simply by using a more concentrated solution. Third, the mass discrimination of the plasma source, although large, is essentially constant during an analysis and can be reliably corrected at high levels of precision (Walder and Freedman 1992, Walder et al. 1993; Halliday et al. 1995; 1998). Fourth, the mass discrimination is widely considered to be independent of the chemical properties of the element, and to a first order, is a function of mass only with relatively minor inter-element biases during ionization and/or detection. Therefore, two elements with overlapping mass ranges can be admixed, and the mass bias in the isotopic composition of one can be used to correct for mass discrimination in the isotopic composition of the other (e.g., Halliday et al. 1995; Luo et al. 1997; Marechal et al. 1999; Rehkamper and Halliday 1999). Fifth, sample throughput is typically faster than can be achieved using TIMS. Less sample preparation may be required in certain applications such as direct analysis of aqueous solutions, although care must be taken to eliminate matrix effects. Matrix effects refer to the influence of the major element composition on measured isotopic composition, due to mass discrimination, isobaric interferences, or other phenomena in the source region.

Techniques in “conventional” ICPMS are comprised of quadrupole ICPMS (Q-ICPMS), high-resolution sector-field ICPMS (HR-ICPMS) and time-of-flight ICPMS (TOF-ICPMS). For low-level ion counting, all are equipped with a single detector, typically an electron multiplier operating in pulse counting mode. These techniques share the same ICP source but utilize different methods of ion separation and focusing (quadrupole, magnetic sector, and time-of-flight). Further comparisons between these methods are discussed in Section 5.

Multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combines sector-field ICPMS with a multiple collector detector system and has recently emerged as an alternative to TIMS for precise U-Th isotope measurement. The full potential of MC-ICPMS has yet to be realized. Yet despite this, its performance in high precision isotope measurement already challenges and, in some cases, surpasses that ever achieved by TIMS (e.g., Lee and Halliday 1995; Blichert-Toft and Albarède 1997).

The first isotopic measurements of U using MC-ICPMS were published by Walder and Freedman (1992) and Taylor et al. (1995). This work was followed by a series of combined U and Th isotopic studies at the University of Michigan using a VG Elemental Plasma 54, the first commercially available MC-ICPMS instrument (Fig. 6). The results of these studies demonstrated that uncertainties of $\sim 1\%$ ($2\sigma_M$) were achievable for $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{238}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ in both standard reference materials and natural samples containing $\sim 200\text{--}600$ ng of U and silicate Th (Luo et al. 1997; Stirling et al. 2000 and Stirling et al. 2001). This is competitive with even the highest quality data acquired by TIMS.

The weakness of MC-ICPMS lies in the inefficiency by which ions are transferred from the plasma source into the mass spectrometer. Therefore, despite very high ionization efficiencies for nearly all elements, the overall sensitivity (defined as ionization plus transmission efficiencies) of first generation MC-ICPMS instruments is of the order of one to a few permil for the U-series nuclides. For most, this is comparable to what can be attained using TIMS.

Several second-generation MC-ICPMS instruments have been developed since this initial work. With one exception, all are double-focusing instruments, and in contrast to the Plasma 54, all are equipped with fast laminated magnets to allow rapid switching between masses. Some have variable mass resolution (400 to 10,000). While moderate to high mass resolution is critical for some elements to avoid spectral interferences, these are not considered to be problematic in the U-Th mass range and the standard resolution of 400 normally suffices for U-series measurements. All second-generation instruments have benefited from design improvements at the interface between the plasma source and the mass spectrometer, resulting in significantly enhanced sensitivities of up to an order of magnitude compared with the Plasma 54. This has allowed precise data to be acquired

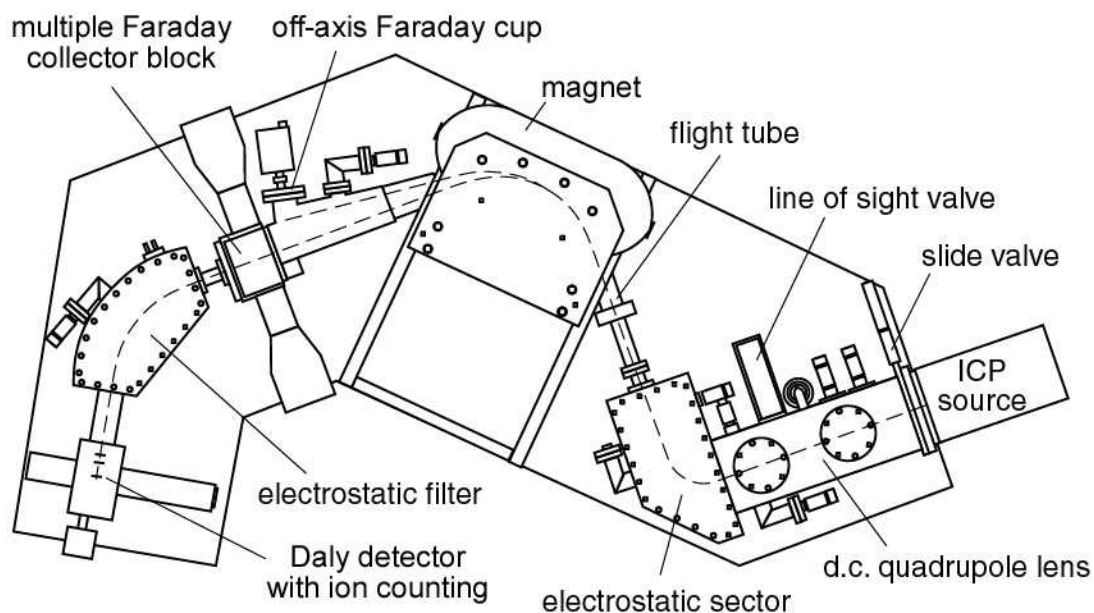


Figure 6. Schematic outline of the first commercially available multiple collector ICPMS, the “Plasma 54,” after Halliday et al. (1995). This instrument uses Nier-Johnson double-focusing and is equipped with eight independently adjustable Faraday collectors. The axial collector can be wound down to provide access to a Daly detector equipped with ion counting capabilities and a second-stage energy filter for high abundance sensitivity measurements. The sample may be introduced to the plasma source by either solution aspiration or laser ablation.

on smaller sample sizes with U and Th contents at the 100-10 ng level (e.g., Nakai et al. 2001; Turner et al. 2001; Robinson et al. 2002). Multiple-collector ICPMS is thus fast becoming a widely accepted means for obtaining high-quality data for the U-series isotope systems. The following discussion mainly focuses on features of MC-ICPMS analysis, although both MC-ICPMS and ICPMS methods share basic characteristics in source and general design.

Sources/sample introduction. Solution aspiration. In both ICPMS and MC-ICPMS, the standard means of sample introduction is to aspirate the chemically separated analyte into the plasma source as an aerosol. It is usual to first dissolve the sample in a solution of dilute acid. For U-Th analysis, solutions of dilute HNO₃ are normally used for sample introduction, although it may be desirable to add a trace amount of HF to the thorium fraction to prevent precipitation. Molecular interferences and/or memory effects may also determine the acid medium for sample introduction. Conventional glass aspiration systems use a Meinhard cross-flow nebulizer to aspirate the sample into droplets, coupled to a cooled spray chamber, which removes the larger droplets and excess solution by condensation. Solution uptake rates are typically ~500 µl/min. Conventional aspiration produces a “wet” plasma containing some polyatomic oxides and hydrides, which may create molecular interferences that require correction. Such interferences can often be reduced to negligible proportions by injecting the sample as a “dry” aerosol using a micro-concentric nebulizer or MCN (with solution uptake rates of 50 to 150 µl/min; Vanhaecke et al. 1996) coupled to a heated spray chamber and membrane desolvator. Molecular interferences can also be controlled by chemically separating the analyte from the sample matrix so that only pure solutions are introduced to the system. As an added benefit, desolvating nebulization systems are highly efficient, typically resulting in significantly better sample utilization compared with conventional nebulizers. Other high-efficiency systems are available (e.g., Liu and Montaser 1994; Becker et al. 1999; Huang et al. 2000; McLean et al. 2001), but in general, all are wet nebulizers and as such, are still prone to hydride and oxide interference formation. Between sample runs, the nebulizer must be flushed with a cleaning solution, typically dilute acid in order to minimize sample memory effects.

Laser ablation. A laser ablation system can be used in place of solution nebulization as the sample introduction system. During laser ablation sampling, the high-energy laser beam produces a micro-plasma from the sample and nebulizer gas that ablates the sample surface. The sample is enclosed by an optical cell, through which the laser beam may pass undisturbed. Typically, the cell is mounted on a stage that can be rotated or moved in the x, y and z directions by computer control, and several samples can be loaded simultaneously to minimize sample changeover time. Sample preparation is very easy; provided the sample fits into the sample chamber, and sits a minimum distance below the top of the sample cell, all that is required is to attach the sample to a mount with an adhesive. Polishing of the sample surface may also be desirable to enhance any surface textures and to promote stable ion beams. During ablation, it is usual to view the sample and pit morphology with transmitted (plane or polarized) or reflected light using a binocular microscope or an on-line video camera and monitor. Laser ablation sampling for U-series isotopic analysis has been used in both conventional ICPMS and MC-ICPMS (e.g., Becker et al. 2000; Stirling et al. 2000; Guillon and Günther 2002).

Ion extraction. The aspirated or laser ablated sample is transported from the sample introduction system into the center of the torch by a ~1 l/min flow of Ar carrier gas where it is immediately dissociated and ionized by energy transfer with the hot ~6000 K temperature of the surrounding Ar plasma. Ionization efficiencies are >95% for U and Th (Jarvis et al., 1992). For laser ablation sampling, helium may be employed as the carrier

gas instead of Ar because ablation in a pure He atmosphere has been found to significantly enhance sensitivity for some elements (e.g., Eggins et al. 1998; Günther and Heinrich 1999; Horn et al. 2000).

For most instrument configurations, the ions are then accelerated into a rotary-pumped “expansion chamber” situated between the first water-cooled Ni “sample” cone and second Ni “skimmer” cone by a large accelerating voltage of up to 10,000 volts. The expansion chamber is held at a vacuum of ~ 1 mbar, enabling the ions to undergo supersonic expansion and a small proportion (several permil) are extracted behind the skimmer cone. It is during this extraction process that most of the sample is lost. Ion sampling in this interface region is associated with the preferential extraction of heavy isotopes over lighter ones. This is generally ascribed to steady-state “space-charge effects,” in which heavy isotopes are less deflected from the optical axis than lighter ones, and creates an essentially constant instrumental mass bias that is largely a function of mass alone. The MC-ICPMS mass bias is large— ~ 0.5 to 1% per a.m.u in the mass range of the U-Th isotopes—and is in stark contrast to TIMS, where instrumental bias is approximately an order of magnitude smaller but time-dependent due to the progressive evaporation of the sample from the filament surface. Once behind the skimmer cone, the ions are optically focused onto the entrance slit into the mass analyzer by a series of ion lenses. This transfer lens region is held at a vacuum of $\sim 10^{-5}$ to 10^{-8} mbar by turbo-molecular pumps.

Ion focusing. Collision/reaction cells. Collision or reaction cells are commonly employed to convert molecular interferences into either neutral species or species that are different from the analyte mass, which enables the analyte ions to emerge from the cell free of interferences. The analyte ions can then be directed into the mass analyzer (quadrupole or sector) for normal mass separation. Single-focusing instruments often utilize a quadrupole or hexapole collision cell/reaction cell, positioned between the mass spectrometer interface and the magnetic sector analyzer. As analyte ions are directed into the collision/reaction cell, they collide with a “collision gas” fed into the cell. Energy is transferred during collision-induced reactions, which thermalizes or cools the sample ions, reducing their energy spread, and dissociates molecular ions creating potential interference masses. In Q-ICPMS, the application of a collision/reaction cell has been found to significantly enhance ion transmission, sensitivity and measurement precision, compared to Q-ICPMS without a collision cell (e.g., Becker and Dietze 2000). Collision/reaction cells have also been utilized in MC-ICPMS, most notably with the second-generation Micromass IsoProbe.

Nier Johnson double focusing. Most MC-ICPMS instruments utilize double-focusing with Nier Johnson geometry, in which ions passing through the mass spectrometer entrance slit are energy- then direction-focussed. The ICP sector magnet provides double dispersion and direction-focusing and is similar to that used in TIMS. Energy-focusing is combined with the magnet because the ion beams produced during plasma ionization show a large ion energy spread, significantly larger than the range of kinetic energies produced during thermal ionization. This must be compensated for to prevent a blurring of the image, which occurs because an ion beam passing through a magnetic field is deflected by an amount dependent on its ion energy as well as its mass and charge. Normally energy-focusing is achieved using an electrostatic analyzer. The double-focusing configuration provides the “flat-topped” peak shapes that are a requisite in high-precision isotope measurement. Nier Johnson (or reversed Nier Johnson) geometry is also used in double-focusing sector field HR-ICPMS.

The quadrupole mass analyzer utilized by Q-ICPMS is comprised of quadrupole rods with combined DC and RF potentials that can be set to allow analyte ions with a specific

mass-to-charge ratio access to the detector. All other ions will collide with the quadrupole rods and will not reach the detector. In TOF-ICPMS, the analyte ions are accelerated into the flight tube with the same kinetic energy, so that ions of a different mass will also have different velocities. The lightest ions will arrive at the detector first. The entire mass spectrum will reach the detector within 50 μ s, providing \sim 20,000 spectra/s.

Ion detection. Only moderately high precision (0.5-10%) can normally be obtained using conventional ICPMS instruments and “peak-hopping” because the ionization conditions in the plasma source are highly unstable. This causes short-term fluctuations in ion beam intensity at the 1-second level (referred to as “plasma flicker”) upon which longer period intensity oscillations may be superimposed due to irregularities in nebuliser uptake and sample introduction rates. MC-ICPMS instruments alleviate these difficulties by the simultaneous collection of ion beams in multiple detectors. Isotope ratios are monitored instead of ion beam intensities (as is often the approach in TIMS and ICPMS), in order to cancel out plasma source instability, thereby increasing measurement precision dramatically. High levels of precision have also been reported for HR-ICPMS instruments employing fast electrostatic mass scanning (by adjusting the acceleration voltage while keeping the magnetic field constant) to smooth out signal fluctuations due to plasma flicker (e.g., Quétel et al. 2000a; Choi et al. 2001; Shen et al. 2002).

All MC-ICPMS instruments are equipped with a multiple Faraday collector array oriented perpendicular to the optic axis, enabling the simultaneous “static” or “multi-static” measurement of up to twelve ion beams. Most instruments use Faraday cups mounted on motorized detector carriers that can be adjusted independently to alter the mass dispersion and obtain coincident ion beams, as is the approach adopted for MC-TIMS measurement. However, some instruments instead employ a fixed collector array and zoom optics to achieve the required mass dispersion and peak coincidences (e.g., Belshaw et al. 1998).

For low-level ion detection, the first-generation Plasma 54 instrument is equipped with a single Daly detector behind a second stage ESA for the sequential measurement of low-level isotopes at high abundance sensitivity. The second-generation instruments are each equipped with multiple ion-counting channels, one operating at high abundance sensitivity, for the simultaneous measurement of multiple low-level ion beams (Figs. 7-9). This feature may greatly improve the precision and sensitivity of radium and protactinium isotope measurement, where both tracer and analyte isotopes are typically measured on low-level ion detectors.

Multiple-collection techniques. Uranium. Table 1 shows a typical protocol used by multi-collector instruments (equipped with one ion counting channel) both in MC-TIMS, MC-ICPMS and LA-MC-ICPMS (e.g., Cohen et al. 1992; Stirling et al. 1995; Luo et al. 1997; Stirling et al. 2000; Pietruszka et al. 2002). A first sequence monitors the atomic ratios between ^{234}U , ^{235}U and ^{238}U by aligning Faraday collectors for masses ^{235}U (10^{-13} A) and ^{238}U (10^{-11} A), while the low intensity ^{234}U ion beam (10^{-15} to 10^{-16} A) is measured simultaneously in the low-level detector. A second sequence shifts all masses to monitor ^{235}U in the ion counting channel relative to ^{238}U . A comparison of the two sequential $^{235}\text{U}/^{238}\text{U}$ measurements using different collector configurations provides an estimate of the drift in the relative gain between the ion counter and Faraday cup, for which the ^{234}U ion beam intensity must be corrected at the end of each two-sequence cycle. In TIMS, where the ion beams are relatively stable, either ^{235}U ion beam intensities, or more precisely $^{235}\text{U}/^{238}\text{U}$ ratios, can be used to monitor the gain. A second correction is also applied at the cycle level: Using empirically derived linear, power or exponential laws (e.g., Russell 1978; Wasserburg et al. 1981; Hart and Zindler 1989; Habfast 1998), all ratios are corrected for instrumental mass fractionation using $^{238}\text{U}/^{235}\text{U}$ normalized to the assumed “true” value of 137.88 (Steiger and Jäger 1977) for natural

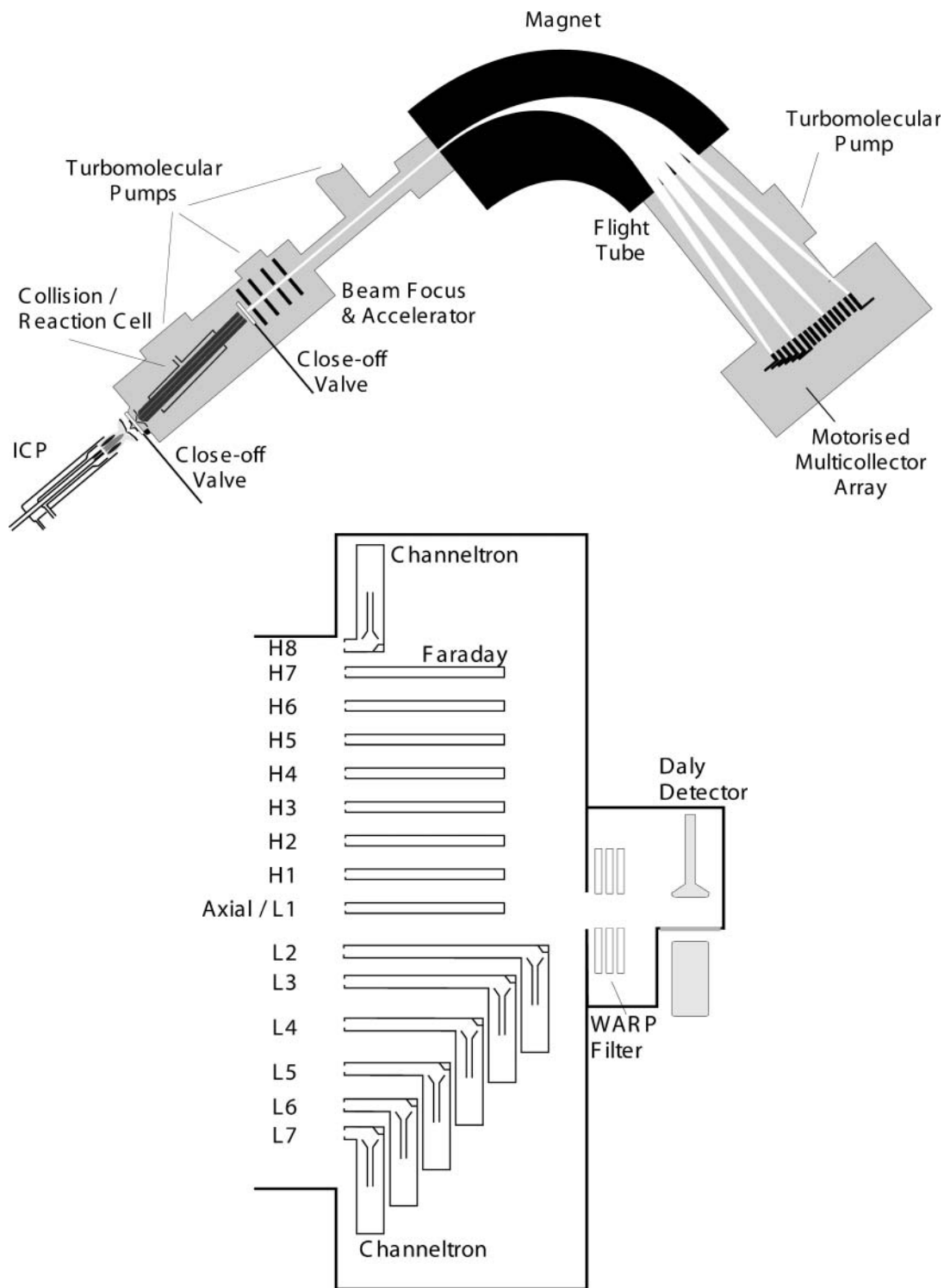


Figure 7. Schematic outline of a second-generation MC-ICPMS instrument (Micromass IsoProbe 2) (top) and its collector array (bottom). This instrument is single focusing and utilizes a collision cell to minimize the energy spread of ions entering the magnet. A schematic of the collector array also illustrates one possible configuration for multi-collection for either TIMS or MC-ICPMS, with a motorized multiple-collector array of moveable Faraday cups on the high mass side and moveable channeltrons for ion counting on the low mass side. The axial position is occupied by a removable Faraday, with a Daly detector located behind the retarding potential filter for high abundance sensitivity measurements. [Used with permission of Micromass.]

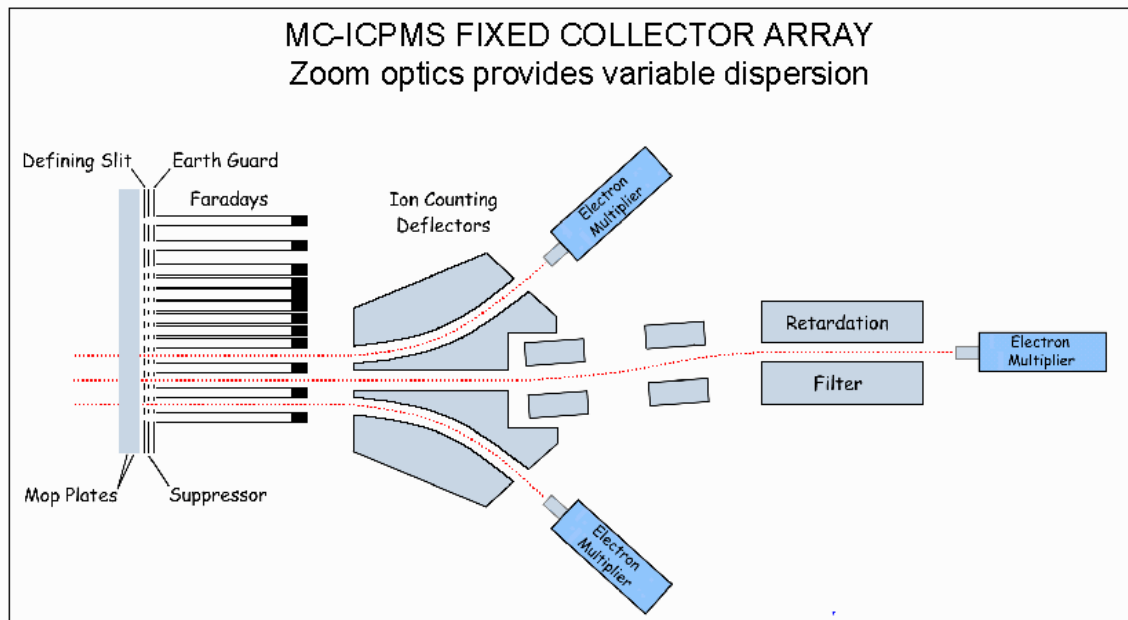
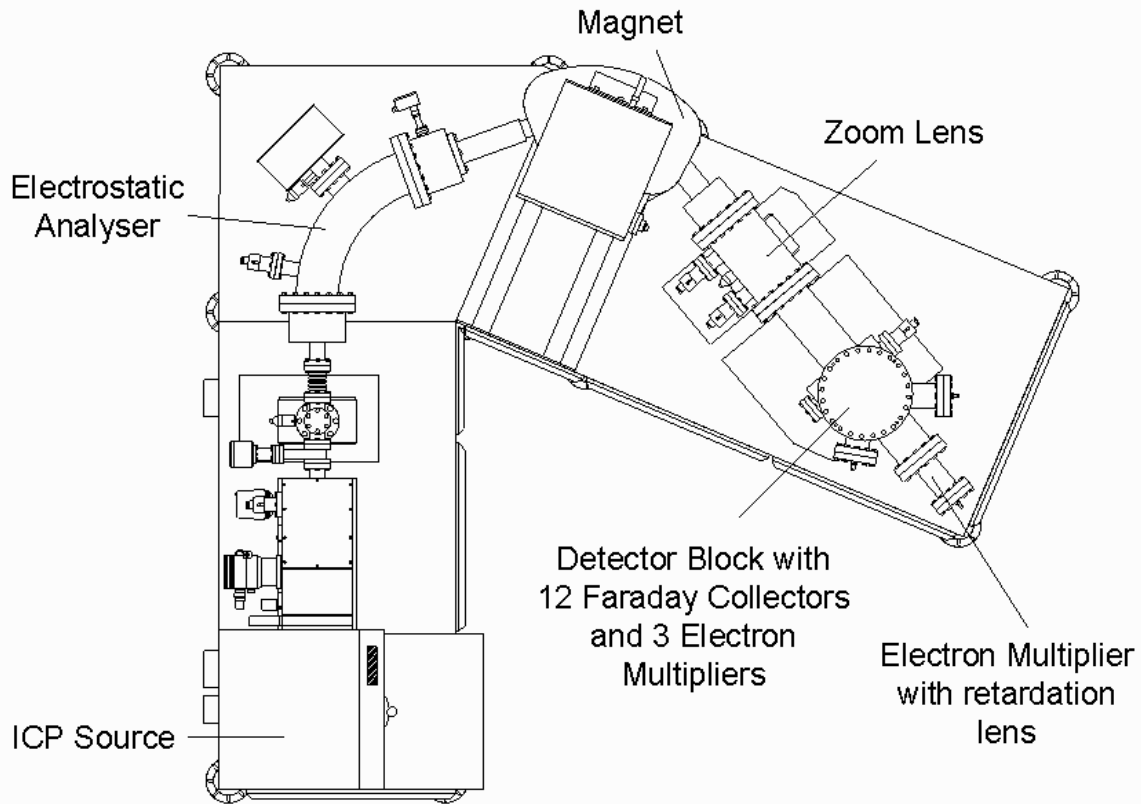


Figure 8. Schematic outline of a second-generation MC-ICPMS instrument (Nu Instruments Nu Plasma), equipped with a multiple-Faraday collector block for the simultaneous measurement of up to 12 ion beams, and three electron multipliers (one operating at high-abundance sensitivity) for simultaneous low-intensity isotope measurement. This instrument uses zoom optics to obtain the required mass dispersion and peak coincidences in place of motorized detector carriers. [Used with permission of Nu Instruments Ltd.]

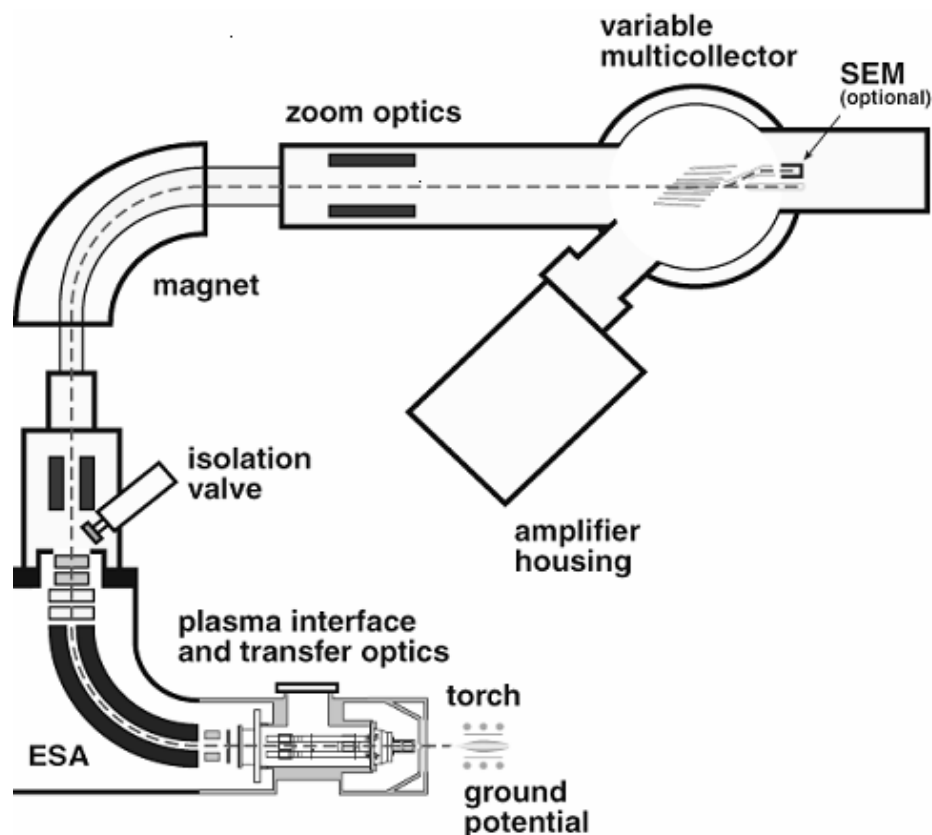


Figure 9. Schematic diagram showing a second-generation MC-ICPMS instrument (ThermoFinnigan Neptune). This instrument utilizes double-focusing and is equipped with a motorized multiple-Faraday collector block with two channels that can be operated in high-resolution mode. Optional multiple-ion counting channels are also available for the simultaneous measurement of low-intensity ion beams. [Used with permission of Thermo Finnigan.]

samples. This practice of normalizing the measured ratio to an invariant ratio of the same element is referred to as “internal normalization”. The large instrumental mass fractionations inherent to MC-ICPMS (up to 1% per amu in the mass range of the U-Th isotopes for all signal intensities) necessitates careful control and monitoring of the correction factors. Applying a mass fractionation correction at the cycle level also allows the small but time dependent TIMS correction to be reliably made.

For solution nebulization MC-ICPMS and MC-TIMS, typical runs consist of up to 100 ratios collected over ~30 minutes to 1 hour. This includes time for background measurement (typically monitored at half mass on either side of the peak) and peak centering, but excludes filament warm-up time for TIMS and nebulizer cleaning for MC-ICPMS. Sample sizes of ~1000-10 ng of total U for TIMS and MC-ICPMS are required to attain 2σ measurement uncertainties of a permil or better on $^{234}\text{U}/^{238}\text{U}$ (e.g., Stirling et al. 1995; Luo et al. 1997; Yokoyama et al. 2001; Robinson et al. 2002). Smaller samples containing only 1 ng-levels of ^{238}U have been measured by laser ablation MC-ICPMS, over shorter acquisition times of ~10 minutes, yielding $^{234}\text{U}/^{238}\text{U}$ measurements at 100 μm scale resolution, with 2σ uncertainties of $\pm 3\text{-}4\%$ (Stirling et al. 2000).

Isotope dilution measurements using a ^{233}U and/or ^{236}U spike tracer can be performed separately, or combined with the isotopic composition run. Spike tracers can be measured on an ion counting channel, or alternatively, it may be preferable to concentrate the tracer (provided the spike corrections are small) and measure it on a

Table 1. Examples of collector configurations for U-series measurements using a multiple-Faraday array coupled to a single ion counter.

		Far-1	IC	Far-2	Far-3	Far-4	Far-5
URANIUM							
<i>Uranium Multi-Static, Internal Normalization using MC-TIMS or MC-ICPMS</i>							
Sample	S1	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
	S2		²³⁵ U			²³⁸ U	
<i>Uranium Static, External Standardization using MC-ICPMS</i>							
Standard	S1	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
Sample	S1	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
Standard	S1	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
THORIUM							
<i>Thorium Static, External Standardization (no internal mass fractionation correction) using TIMS Faraday-Ion Counter gain determined at the start of the session</i>							
Sample	S1		²³⁰ Th		²³² Th		
<i>Thorium Multi-Static, Traced analysis using TIMS Faraday-Ion Counter gain determined during analysis</i>							
Sample	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
	S2		(²²⁹ Th)			²³² Th	
<i>Thorium Multi-Static, External Normalization using MC-ICPMS</i>							
Sample	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
	S2	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
<i>Thorium Static, External Standardization using MC-ICPMS</i>							
Standard	S1	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
Sample	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
Standard	S1	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
	<i>or</i>						
Standard	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
Sample	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
Standard	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
<i>Thorium Multi-Static, External Standardization using MC-ICPMS</i>							
Standard	S1		²³⁰ Th		²³² Th		
	S2		(²²⁹ Th)			²³² Th	
Sample	S1		²³⁰ Th		²³² Th		
	S2		(²²⁹ Th)			²³² Th	
Standard	S1		²³⁰ Th		²³² Th		
	S2		(²²⁹ Th)			²³² Th	
URANIUM-THORIUM							
<i>U-Th Multi-Static, Internal Normalization using MC-ICPMS or LA-MC-ICPMS</i>							
Sample	S1	(²²⁹ Th)	²³⁰ Th		²³² Th		
	S2	(²³³ U)	²³⁴ U	²³⁵ U	(²³⁶ U)		²³⁸ U
	S3		²³⁵ U		²³⁸ U		

Notes: S1 through S3 refer to respective sequences 1 through 3 in a single cycle of data acquisition. Internal normalization protocols for uranium monitor ²³⁵U sequentially in a Faraday collector and in the ion counter (IC). The ion counter to Faraday relative gain is then determined by comparing (²³⁸U/²³⁵U)_{Faraday} with (²³⁸U)_{Faraday}/⁽²³⁵U)_{IC}. Internal normalization also corrects each ratio for instrumental mass fractionation at the end of each cycle using (²³⁸U/²³⁵U)_{Faraday} normalized to the true value of 137.88. For traced Th analysis by TIMS, the ion counter to Faraday relative gain can be determined by comparing (²²⁹Th/²³²Th)_{Faraday} with (²²⁹Th)_{IC}/⁽²³²Th)_{Faraday}. External standardization corrects for the ion counter/Faraday gain based on normalization to bracketing measurements for well-characterized standards. The mass fractionation correction may also be applied using sample-standard bracketing, or alternatively, may be applied at the cycle level, as is the approach for internal normalization protocols. Spike tracers, ²³³U or ²³⁶U and ²²⁹Th, shown in parentheses, can also be monitored during combined isotopic composition and isotope dilution runs. During LA-MC-ICPMS, ²³⁰Th and ²³²Th are monitored during the same sequence as ²³⁸U (monitored on a high-mass Faraday collector; not shown) to obtain reliable measurements of ²³⁰Th/²³⁸U and ²³²Th/²³⁸U without isotope dilution.

Faraday collector, simultaneously with ^{238}U , ^{235}U and ^{234}U during the first sequence. This shortens the analysis routine, consuming less sample. Ion beam intensities are typically larger in MC-ICPMS than in TIMS due to the ease with which signal size can be increased by introducing a more concentrated solution. While this yields more precise data, non-linearity of the low-level detector response and uncertainties in its dead-time correction become more important for larger beam intensities, and must be carefully monitored (Cheng et al. 2000; Richter et al. 2001).

In MC-ICPMS, external standardization procedures have also been implemented (Table 1), whereby sample–standard bracketing is used to cancel out the drift in the Faraday to ion counter gain (Stirling et al. 2000; Robinson et al. 2002). In this case, U isotopic composition is determined as a static measurement in one cycle only, by normalizing mass fractionation-corrected ratios for the unknown sample to those determined on a well-constrained standard. It may also be desirable to monitor instrumental mass fractionation using external standardization techniques. A typical approach is to analyze the standard before and after the sample so that drift in the Faraday to ion counter gain can be cancelled out by linear interpolation. External standardization protocols have two main advantages. First, data acquisition times are shorter than those for multi-static protocols, so that less sample is consumed. Second, ion beam intensities are not restricted by the necessity to keep ^{235}U ion counts below 1,000,000 cps. The main disadvantages of external standardization are also two-fold. First, it is not possible to correct for short-term non-linear perturbations in the Faraday to ion counter gain, which may ultimately limit the precision and accuracy of the measurement. Second, matrix differences between the sample and standard may compromise the reliability of the mass bias correction, although during solution nebulization, these may not be significant at the permil-levels of precision attainable in U-Th isotopic measurement. Matrix-dependent effects during laser ablation MC-ICPMS, on the other hand, can be extremely large and at the 10 to 100% level (e.g., Stirling et al. 2000). External standardization was tested for solution nebulization measurements by Luo et al. (1997) using a Plasma 54 instrument, but was found to create greater variability in the data than observed for multi-static protocols, which was presumed to be due to non-linear short-term variability in the gain correction. For this reason, internal monitoring of the gain at the cycle level is often considered preferable, particularly for U where sample size is generally not limited. Nevertheless, provided the gain is stable, and care is taken to matrix-match the bracketing standard with the sample, external standardization can yield results that are of comparable precision and accuracy to those determined using internal normalization techniques (e.g., Robinson et al. 2002).

Thorium. Multiple-collector measurement protocols by TIMS for thorium isotopic analysis typically involve the simultaneous measurement of ^{232}Th and ^{230}Th (for silicate rocks), or ^{229}Th and ^{230}Th , then ^{229}Th and ^{232}Th (for low- ^{232}Th samples), using an axial ion counter and off-axis Faraday collector (Table 1). Various methods are used to correct for the relative gain between the low-level and Faraday detectors and 2σ -uncertainties of 1-5% are typically obtained (Palacz et al. 1992; Cohen et al. 1992; McDermott et al. 1993; Rubin 2001). Charge-collection TIMS protocols enable ^{229}Th , ^{230}Th and ^{232}Th to be monitored simultaneously on a multiple-Faraday array and can achieve measurement uncertainties at the sub-permil level (Esat et al. 1995; Stirling et al. 1995).

However, thorium has only two naturally occurring long-lived isotopes, and all Th measurements by TIMS are limited by the absence of a well-constrained isotope ratio that can be used for internal normalization purposes to correct for instrumental mass fractionation. In this regard, one of the most important advantages of MC-ICPMS over MC-TIMS is the ability to admix two elements with overlapping mass ranges and use the

instrumental mass discrimination factor determined for one to calculate mass fractionation corrections for the other. This approach, referred to as external normalization, relies on the mass fractionation factor being independent of the chemical properties of the analyte, but means that U chemically separated from the same sample can be admixed with the Th fraction, allowing all thorium ratios to be corrected for mass fractionation using $^{238}\text{U}/^{235}\text{U}$ normalized to the 137.88 true value. A two-sequence multi-static routine can then be utilized (Table 1), in which thorium isotopic composition is measured in one sequence, and uranium isotopic composition in the other (Luo et al. 1997; Stirling et al. 2001; Pietruszka et al. 2002). The U sequence provides both the mass fractionation and Faraday-ion counter gain corrections, the latter of which can be determined by monitoring ^{234}U in the ion counter and comparing the fractionation-corrected $^{234}\text{U}/^{238}\text{U}$ to the true ratio determined earlier from the U run. For isotope dilution runs, the protocols can be modified to include ^{229}Th measurement, either in an ion counter or Faraday cup. As is the case for U, 100 thorium ratios can be collected over 30 minutes to one hour, although Th measurement is normally significantly faster by MC-ICPMS than by MC-TIMS because thermal ionization often requires very long warm-up times of up to several hours. Very precise and accurate data can be acquired using these MC-ICPMS protocols; measurement precision is $\sim 1\%$ on $^{230}\text{Th}/^{232}\text{Th}$ and can be better than 1% on $^{230}\text{Th}/^{238}\text{U}$. Typical sample sizes are $\sim 10\text{-}100$ ng of total Th for silicate rocks and 10 pg-levels of ^{230}Th for low- ^{232}Th measurements. For TIMS, Th ionization efficiency is a function of load size. Therefore TIMS, with lower overall background count rates, may be best suited for small Th samples, whereas MC-ICPMS, with significantly greater ionization efficiency, may provide significantly improved results for large Th samples. In MC-ICPMS, thorium isotopic composition can be measured at the same time as U in a combined U-Th analysis. Although this consumes more Th than a two-sequence routine, analytical precision is comparable and accuracy may be better when Th and U are monitored simultaneously (Stirling et al. 2001).

External standardization was applied to silicate Th isotopic measurement using MC-ICPMS by Nakai et al. (2001). These authors determined Faraday-ion counter gain and mass fractionation corrections for thorium based on bracketing measurements for standard solutions of natural uranium. The advantage of this approach is that Th isotopic compositions can be acquired on small samples (~ 10 ng of ^{232}Th) as a single static measurement over a short 10-15 minute analysis period. However, because instrumental mass fractionation (and Faraday-ion counter gain) can vary between solution runs, as a function of both time and solvent loading, it is advantageous to check the veracity of the instrument calibrations using additional, matrix-matched Th standards if using techniques in external standardization. Turner et al. (2001) determined $^{230}\text{Th}/^{232}\text{Th}$ to a precision of 1% or better on ng levels of silicate thorium, and Robinson et al. (2002) obtained measurement uncertainties at the 1‰-level on ~ 250 ng of carbonate thorium using bracketing measurements for a well-characterized Th standard.

Without isotope dilution, the simultaneous measurement of U and Th is essential in LA-MC-ICPMS, although large (10-100% level) elemental, matrix-dependent fractionation effects can still be observed between U and Th (e.g., Stirling et al. 2000). As a result, Th/U ratios can be systematically lower, and apparent ^{238}U - ^{234}U - ^{230}Th -ages systematically younger than the true values. The source of this U-Th fractionation appears to be incomplete vaporization and ionization of laser-generated particles within the plasma (Günther 2002; Guillong and Günther 2002) and the effect becomes increasingly problematic for larger particle sizes.

Radium and Protactinium. TIMS protocols for both radium and protactinium currently involve cycling the isotopes ^{226}Ra and ^{228}Ra (tracer or normal), and ^{231}Pa and

^{233}Pa (tracer), through a single low-intensity detector (Cohen and O’Nions 1991; Volpe et al. 1991; Pickett et al. 1994; Bourdon et al. 1999). These two-isotope TIMS methods do not permit internal correction for instrumental mass fractionation, which is generally thought to be small relative to overall measurement precision (5-10%). MC-ICPMS techniques can provide more precise corrections for mass fractionation utilizing external normalization. For example, multiple-collector measurement protocols using MC-ICPMS for ~ 100 fg load sizes of silicate radium have been reported by Pietruszka et al. (2002). Natural uranium was admixed to the Ra sample fractions to allow instrumental mass fractionation to be monitored using $^{238}\text{U}/^{235}\text{U}$, and the isotopes ^{226}Ra and ^{228}Ra were cycled through a single Daly detector. Using this approach analytical precision to $\sim 3\%$ on $^{226}\text{Ra}/^{230}\text{Th}$ was obtained. However, unlike uranium and thorium, overall collection efficiency for MC-ICPMS of 0.5% is still lower than typically achieved by TIMS (1-10%).

5. COMPARISON OF ANALYTICAL METHODS FOR U-SERIES NUCLIDES

A variety of parameters for various analytical methods for uranium, thorium, radium, and protactinium isotopes are summarized in Table 2. Estimated detection limits for various techniques are also presented in Figure 10. Alpha spectrometric methods are the traditional method of measurement for these isotopes, and still provide one of the more cost effective methods of analysis. Hence they are well suited for many applications where higher detection limits and lower precision are acceptable and analytical cost is paramount (e.g., environmental monitoring). They are also in many cases the only option for analysis of very short-lived isotopes of the uranium and thorium decay series. However, for the longer-lived isotopes in terms of basic parameters including sample size requirements, detection limit, analytical precision, and time of analysis, alpha spectrometry currently lags behind other methods based on atom counting. Gamma spectrometry also continues to be a viable option for measurement of beta-emitting uranium-series nuclides with short half-lives, such as Pb-210, Ac-227, Ra-228, and Th-234 (Fig. 10). Although this method has higher detection limits than other techniques, it generally has simpler and faster sample preparation compared to alpha, beta, or mass spectrometry.

TIMS methods emerged in the late 1980’s and early 1990’s as an alternative to decay counting techniques. Order of magnitude improvements in sample size requirements, analytical precision, and time of analysis were achieved for uranium, thorium, protactinium, and radium analysis, with a corresponding penalty in terms of analytical cost and throughput. Although analysis times are smaller for TIMS, sample throughput is normally lower than for decay counting, for which chemical separations are not as extensive, clean laboratory chemistry space may not be required, and multiple counters can be operated simultaneously at less cost. However application of TIMS methods has led to many scientific breakthroughs in uranium-series geochronology and geochemistry.

In the past three years, MC-ICPMS has emerged as an alternative to TIMS for precise measurement of the U-series isotopes with comparable or better precision. U-Th isotopes can now be routinely measured at the sub-permil level. Previously, this had only been demonstrated using charge-collection TIMS applied to thorium isotope measurement. Data collection efficiency, sample size requirements, and detection limits can also be greatly improved over TIMS. For the ^{238}U - ^{234}U - ^{230}Th system applied to carbonate samples, this has extended the dating range beyond 600,000 years, and ^{230}Th -age uncertainties of ± 2000 years are now attainable on 300,000 year-old samples (e.g., Stirling et al. 2001).

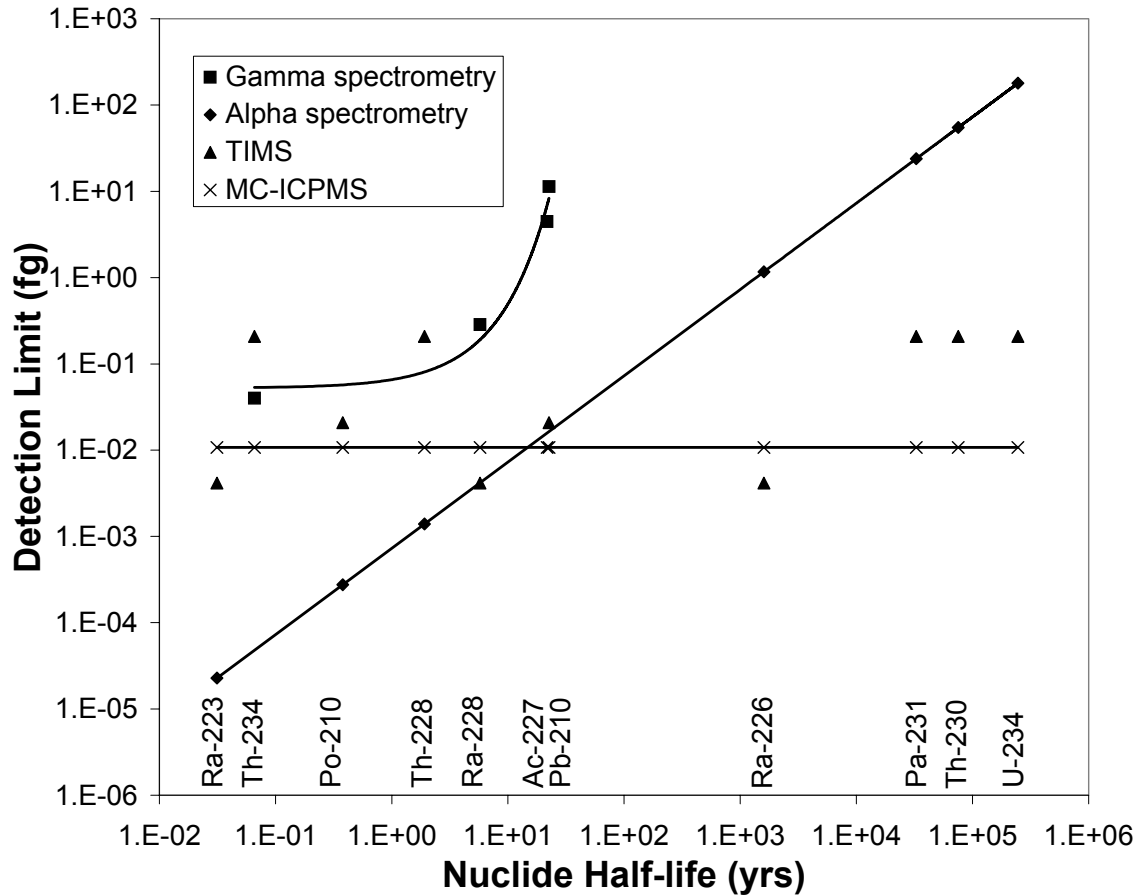


Figure 10. Estimates of detection limits as a function of uranium-series nuclide half-life for various decay and atom counting techniques. Gamma spectrometry has the highest detection limits but also is the simplest and least expensive method of uranium-series analysis in terms of sample preparation. Alpha spectrometry has higher detection limits for longer-lived nuclides but provides optimal detection for short-lived (<10 yr half-life) nuclides. TMS sensitivities vary with element analyzed and ionization efficiency, but TMS provides improved detection limits (~0.1 fg) for longer lived nuclides. MC-ICPMS detection limits are relatively element independent (~0.01 fg). Detection limits are generally lower than for TMS due to improved signal collection utilization (ion multi-collection) and ionization/collection efficiency, although for some elements (e.g., radium) TMS would provide optimal detection. Detection limits are based on counting statistics only (three times the standard deviation of the background) and are estimated for situations where interferences or isobars are absent. In cases of longer-lived nuclides (^{235}U , ^{238}U , ^{232}Th), detection limits are blank limited. Parameters used for each method are: 1) Gamma spectrometry: 7 day count period, 3% detector collection efficiency, 10 count per day background; 2) Alpha spectrometry: 7 day count period, 30% detector collection efficiency, 1 count per day background; 3) TMS: ionization/collection efficiency ranges from 0.1 to 5%, 1 count per second background, 60 min total measurement period with 10% collection utilization 4) MC-ICPMS: ionization/collection efficiency is 0.5%, 1 count per second background, 20 min total measurement period with 50% collection utilization.

Conventional ICPMS has been widely applied to U-series isotope measurement over the past decade (e.g., Shaw and Francois 1991; Heumann et al. 1998; Becker et al. 1999; Hinrichs and Schnetger 1999; Platzner et al. 1999; Becker et al. 2000; Becker and Dietze 2000; Halicz et al. 2000; Quetel et al. 2000a; Quetel et al. 2000b; Choi et al. 2001; McLean et al. 2001; Shen et al. 2002). Isotope ratio measurements are based on the successive “peak-jumping” measurement of isotopes as they are cycled through a single electron multiplier. Using Q-ICPMS, analytical precision (2σ) approaches 3-10% for

Table 2. Comparison of analytical methods for U-series nuclides

		Alpha Spec.	TIMS	MC-TIMS	ICPMS	MC-ICPMS	LA-ICPMS	LA-MC-ICPMS	SIMS
Sample Size	U Th (silicates) Pa Ra	1-100 µg 1-100 µg 10-50 pg 10-20 pg	100-2000 ng 100-2000 ng 30-1000 fg 1-1000 fg	10-1000 ng 10-1000 ng ---- ----	10-450 ng 10-600 ng 10-1000 fg 20-1000 fg	10-450 ng 10-600 ng ---- 10-3600 fg	1 ng 1 ng ---- ----	1 ng 1 ng ---- ----	---- 10-100 ng ---- ----
Precision (2σ)	²³⁸ U ²³⁵ U/ ²³⁸ U ²³⁴ U/ ²³⁸ U ²³² Th ²³⁰ Th/ ²³² Th ²³¹ Pa/ ²³⁵ U ²²⁶ Ra	2-10% 2-10% 2-10% 2-10% 2-10% 2-10% 2-10%	0.1% 0.5% 0.5% 0.3% 0.5% 0.3-1.0% 0.5-1.5%	0.1% 0.1% 0.1-0.2% 0.3% 0.1-0.4% ---- ----	0.1-5% 0.5% 0.1-10% 0.5-5% 0.5-10% 1-5% 2-6%	<0.1% 0.01% 0.05-0.2% <0.1% 0.1-0.3% ---- 0.3%	5% 4% 1-2% 10% 1-12% ---- ----	<0.2% <0.2% 0.4% ---- 0.8% ---- ----	---- ---- ---- ---- 0.5-1.0% ---- ----
Meas. Time	U Th Pa Ra	1-28 day 1-28 day 1-28 day 1-28 day	4 hrs 4 hrs 3 hrs 3 hrs	1-2 hrs 2 hrs ---- ----	1-10 min 1-10 min 3 min 3 min	15-30 min 15-60 min ---- 30 min	1-5 min 1-5 min ---- ----	5-10 min 5-10 min ---- ----	---- 1 hr ---- ----
Detector Type	U, Th, Pa, Ra	Semiconductor	Single ion counter	Multiple-Faraday + single or multiple-ion counters	Single ion counter	Multiple-Faraday + single or multiple-ion counters	Single ion counter	Multiple-Faraday + single or multiple-ion counters	Multiple-Faraday + single ion counter

	Alpha Spec.	TIMS	MC-TIMS	ICPMS	MC-ICPMS	LA-ICPMS	LA-MC-ICPMS	SIMS
Sensitivity (Collection Efficiency)	U	0.01-1% load size dependent	0.01-1% load size dependent	0.01-1% nebulizer & instrument dependent (HR > Q)	0.01-1% nebulizer & instrument dependent (1 st < 2 nd)	0.01-0.1% matrix & instrument dependent (HR > Q)	0.1% matrix & instrument dependent (1 st < 2 nd)	----
	Th	0.01-1% load size dependent	0.01-1% load size dependent	0.01-1% nebulizer & instrument dependent (HR > Q)	0.01-1% nebulizer & instrument dependent (1 st < 2 nd)	0.01-0.1% matrix & instrument dependent (HR > Q)	0.01-0.1% matrix & instrument dependent (1 st < 2 nd)	2%
	Pa	0.1-1.0%	0.1-1.0%	0.1% nebulizer & instrument dependent (HR > Q)	----	----	----	----
	Ra	1-10%	1-10%	0.01-1% nebulizer & instrument dependent (HR > Q)	0.5% nebulizer & instrument dependent (1 st < 2 nd)	----	----	----
Instrumental Mass Fractionation	U	<0.3%/AMU Time-dependent	<0.3%/AMU Time-dependent	<0.5%/AMU Time-independent	<1%/AMU Time-independent	<0.5%/AMU Time-independent	<1%/AMU Time-independent	<0.1%/AMU
	Th	<0.3%/AMU Time-dependent	<0.3%/AMU Time-dependent	<0.5%/AMU Time-independent	<1%/AMU Time-independent	<0.5%/AMU Time-independent	<1%/AMU Time-independent	<0.1%/AMU
	Pa	<0.3%/AMU Time-dependent	<0.3%/AMU Time-dependent	<0.5%/AMU Time-independent	----	----	----	----
	Ra	<0.3%/AMU Time-dependent	<0.3%/AMU Time-dependent	----	<1%/AMU Time-independent	----	----	----

Notes: HR = High Resolution HR-ICPMS, Q = Quadrupole Q-ICPMS, 1st = First generation MC-ICPMS, 2nd = Second generation MC-ICPMS.

various isotope ratios and is limited by instability of the plasma during sequential peak measurement and difficulties in obtaining reliable peak shapes. In general, higher precision measurements to the permil-level can be obtained from HR-ICPMS because the magnetic sector design produces flat-topped peak shapes, significantly higher sensitivities and lower instrumental background, resulting in higher signal-to-noise ratios and lower detection limits. Low abundance sensitivity (at the ~5 ppm level) can affect the accuracy of $^{230}\text{Th}/^{232}\text{Th}$ measurements on silicate samples, and accuracy is typically monitored using a well-characterized matrix-matched standard, and corrected by employing a tailing correction (e.g., Shen et al. 2002). Corrections for instrumental mass fractionation are normally obtained using external standardization procedures, although internal normalization has also been applied (e.g., Shen et al. 2002). HR-ICPMS instruments can be operated in high-resolution mode (normal mass resolution $M/\Delta M$ is 300) in order to resolve molecular interferences and/or to improve abundance sensitivity (e.g., Hinrichs and Schnetger 1999), but this results in a decrease in sensitivity and in precision. Techniques in Q-ICPMS can rival those of HR-ICPMS if collision cells are installed (e.g., Becker and Dietze 2000). TOF-ICPMS allows measurements of up to 20,000 spectra per second but to date, has not been extensively applied to the U-series systems.

None of the above-mentioned ICPMS techniques can rival MC-TIMS and MC-ICPMS in terms of analytical precision, but the advantage of conventional ICPMS lies in the speed and ease with which data can be acquired. Analysis times are typically less than 10 minutes, and results can be obtained on solid, liquid or gas samples directly, without chemical preparation. Direct analysis will, however, give rise to high levels of molecular ion formation (e.g., $^{207}\text{Pb}^{16}\text{O}^{12}\text{C}^+$ or $^{203}\text{Tl}^{16}\text{O}_2^+$ on $^{235}\text{U}^+$) and matrix effects, which limit precision and are difficult to correct.

SIMS techniques have occupied somewhat of a narrower niche in uranium-series analysis, but have significantly improved Th isotope analysis relative to TIMS for chemically separated samples. The major improvement relative to TIMS is an improvement by about an order of magnitude in efficiency or sample size requirements for silicates. For uranium and/or thorium rich minerals such as carbonates and zircons, both SIMS and laser-ablation MC-ICPMS have been used for the direct *in situ* analysis of U and Th isotopes (Reid et al. 1997; Stirling et al. 2000) on very small (pg to ng levels of total U and Th) samples, at 10-100 μm scale resolution.

6. FUTURE DEVELOPMENTS

MC-ICPMS instruments have only recently been applied for uranium-series analysis, and so there is much potential for further development of measurement techniques using their unique capabilities. Second-generation instruments are now equipped with multi-collecting ion counting capabilities, and such capabilities are also available for TIMS instruments. In particular, application of low-level multi-collection to uranium, thorium, radium, and protactinium analysis may greatly improve analytical sensitivity for these measurements, thereby extending analysis to materials with lower U and Th concentrations such as mineral separates for internal mineral isochron dating applications. Low-level multi-collection may also significantly improve many aspects of direct uranium and thorium analysis of minerals using laser-ablation techniques. Finally, multi-collection ion counting may extend the range of analytes to uranium-series isotopes with shorter half-lives, such as lead-210 and actinium-227.

For both TIMS and MC-ICPMS, improvements in sources are likely to play a major role in enhancing measurement sensitivity. This includes further development of cavity sources for TIMS and newer ICP sources and nebulizers with reduced isobaric

interferences or background. With regard to measurement sensitivity, one of the current weaknesses of MC-ICPMS lies in the inefficiency by which ions are transferred from the plasma source into the mass spectrometer. The challenge of future instrumentation will be to improve the overall sensitivity in this “interface” region, resulting in additional improvements in detection limits for many elements. However, continued application of MC-ICPMS techniques should almost certainly lead to enhanced analytical throughput and decreased analytical costs. For example, it may be possible to reduce costly and time-intensive chemical separations for many types of uranium-series analysis, with particular emphasis on aqueous systems. This may lead to larger uranium-series data sets than are now possible, improving both the quality and quantity of uranium-series applications and studies in geochemistry and geochronology.

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