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Application Note

Using Multicollector ICP-MS with a Desolvating Nebulizer Accessory for Stable and Radiogenic Isotope Ratio Measurements of Speleothem and Marine Coral Samples

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Introduction

Multicollector ICP-MS instruments are widely used in geochemistry for high precision isotope ratio measurements. Signal enhancement and/or interference reduction (ex. oxides and hydrides) is often necessary for useful measurement of low abundant isotopes and mass-limited samples.

This work will describe the setup and optimization of an advanced desolvating nebulizer accessory for multicollector ICP-MS. Important accessory benefits include inert wetted components for HF-containing samples, heated inert spray chamber and membrane desolvator for optimum sample transport efficiency, and new mass flow controllers with computer software control for Ar sweep and N_2 addition gases for ease of tuning.

The nebulizer accessory is especially applicable to multicollector ICP-MS analyses for uranium-thorium dating, as is commonly used for dating speleothem and marine coral calcite and aragonite samples. System setup parameters and dating measurements will be presented for representative sample types.

Instrumentation

The multicollector (MC) ICP-MS instrument used was a ThermoFisher Scientific Neptune, equipped with the Jet sampler and X interface skimmer cones but not with the high performance interface vacuum pump. The desolvating nebulizer system coupled to the Neptune was the Aridus3 (Teledyne CETAC Technologies); a CFlow-100 PFA nebulizer was connected to the PFA spray chamber of the Aridus3 and samples were self-aspirated in a manual mode.

A front view of the Aridus3 is depicted in Figure 1. The CFlow-100 PFA nebulizer and PFA spray chamber are on the left side of the Aridus3, behind a transparent door. Argon gas supply to the PFA nebulizer is from the host Neptune MC-ICP-MS and is under computer control from the Neptune software.

Figure 1. Aridus3 Front View at Ready Status

The Aridus3 was placed on the sample introduction bench of the Neptune MC-ICP-MS, as shown in Figure 2. A sample introduction line was connected between the outlet of the Aridus3 and the MC-ICP-MS torch.

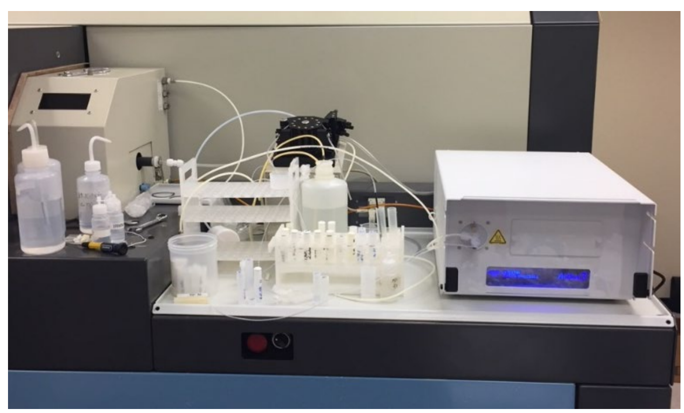

Figure 2. ThermoFisher Neptune MC-ICP-MS

An argon sweep gas supply and a nitrogen addition gas supply were connected to the back panel of the Aridus3, and both gas flows were set using mass flow controllers built into the Aridus3. An Aridus3 computer software program enabled setting of these gas flows as well as the temperature settings of the PFA spray chamber and the membrane desolvator oven module. A schematic of the Aridus3 gas flows is shown in Figure 3.

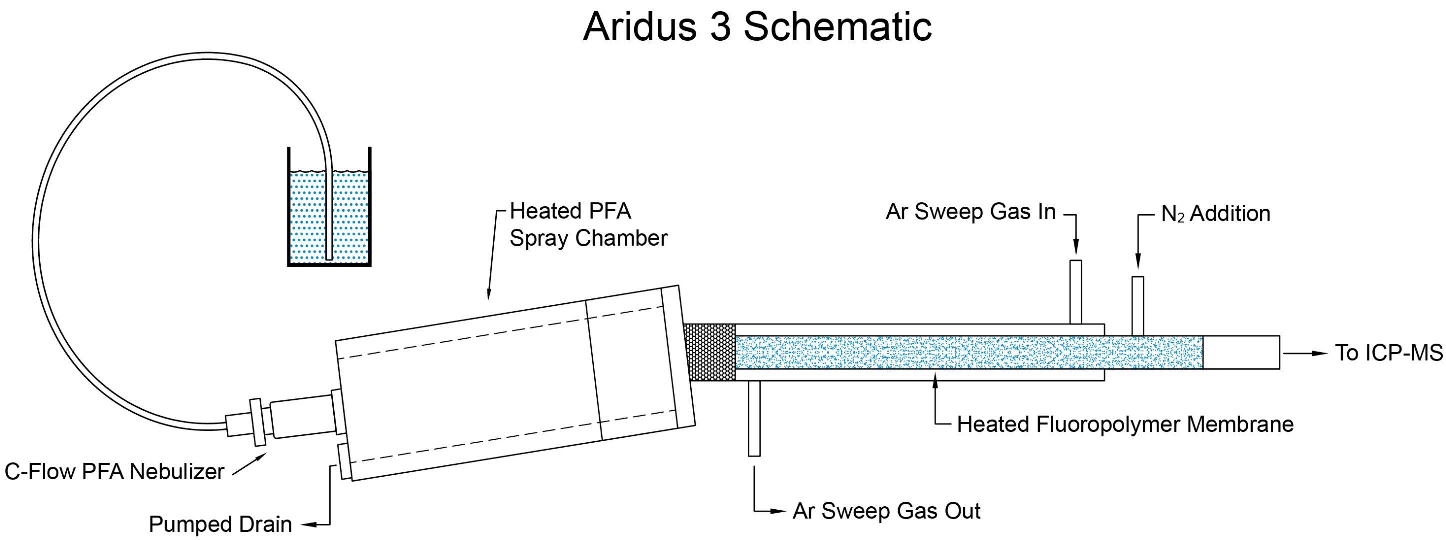

Figure 3. Aridus3 Schematic with Gas Flows

Neptune MC-ICP-MS and Aridus3 operating conditions were optimized using a 1 µg/L uranium standard; MC-ICP-MS operating conditions are listed in Table 1. A computer screen picture (Figure 4) of the Aridus3 software (AridusLink) shows argon and nitrogen gas flows and system temperature settings. The guard electrode was in place and the Jet type interface was sampler and skimmer cones only; the high performance interface vacuum pump was not in operation.

Table 1. Thermo Neptune MC-ICP-MS Conditions

Parameter	Value
ICP Power	1200 W
Coolant Gas	15.00 L/min
Auxiliary Gas	1.05 L/min
Sample Gas	0.97 L/min
Interface	Jet Type*
Extraction	-2000 V
Focus	-592.0 V
X-Defl.	8.46 V
Y-Defl.	0.02 V
Shape	193.00 V
Rot Quad 1	0.01 V
Source Offset	-10.00 V

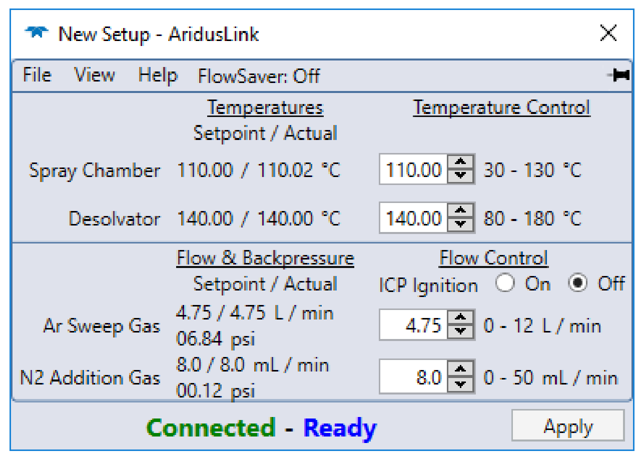

Figure 4. AridusLink Software Control Screen of System Temperatures and Gas Flows

Sample Types

Details of four sample types are:

1. Uranium-thorium analysis of cave moonmilk. Moonmilk is a cave deposit (speleothem) that has a toothpaste-like consistency (Figure 5). Mineral is calcite and sample was from the Grand Canyon (Arizona USA); sample mass used was 50 mg. The Thermo Neptune MC-ICPMS with the CETAC Aridus3 desolvating nebulizer was used for the analysis.
2. Uranium analysis of the uranium standard, NBL-112. The Thermo Neptune MC-ICPMS with the CETAC Aridus3 desolvating nebulizer was used for the analysis.
3. Uranium-thorium analysis of a marine isotope stage 5e coral from the Bahamas (Figure 6). Mineral is aragonite and sample powder mass used was 200 mg. The Thermo Neptune MC-ICPMS with the earlier version CETAC Aridus II desolvating nebulizer was used for the analysis.
4. Strontium analysis of standard NBS-987. NBS-987 was analyzed using the Thermo Neptune MC-ICP-MS with the CETAC Aridus3 desolvating nebulizer.

The results for a cave moonmilk are given in Table 2. Note that 8 cycles were run per block with an integration time of 20 seconds per cycle.

The results for the NBL-112 standard are given in Table 3; the standard solution was spiked with IRMM-3636.

A marine coral sample was previously analyzed, using the predecessor CETAC AridusII Desolvating Nebulizer System with the Thermo Neptune MC-ICP-MS. Results are for the coral sample are given in Table 4.

The last sample type measured was NBS-987 strontium standard; NBS-987 was introduced to the Aridus3 with Thermo Neptune MC-ICP-MS detection. Results are given in Table 5.

Figure 5. Example of calcite moonmilk coating cave walls.

Figure 6. Coral Reef on San Salvador, Bahamas

Table 2. Results for Cave Moonmilk (Tse'an Moria, Grand Canyon)

Parameter	Value
^{238}U concentration	0.6610 ± 0.0005 ppm
^{232}Th concentration	11.24 ± 0.05 ppb
^{230}Th/^{232}Th activity	4.0 ± 0.1
^{230}Th/^{238}U activity	0.02209 ± 0.00083
$\delta\ ^{234}U_{measured}$	297 ± 1 ‰
$\delta\ ^{234}U_{initial}$	299 ± 1 ‰
Uncorrected age	1871 ± 14 yr BP
Corrected age	1492 ± 202 yr BP

Table 3. Results for Uranium Standard NBL-112

Parameter	Value
^{235}U/^{233}U	12.516 ± 0.003, 2 σ standard error
^{234}U/^{238}U	0.000732011 ± 0.000004, 2 σ standard error
$\delta\ ^{234}U_{measured}$	38 ± 1 ‰

Table 4. Results for Marine Coral Sample

Parameter	Value
^{238}U concentration	2.463 ± 0.002 ppm
^{232}Th concentration	0.034 ± 0.006 ppb
^{230}Th/^{232}Th activity	171639 ± 29000
^{230}Th/^{238}U activity	0.76512 ± 0.00098
$\delta\ ^{234}U_{measured}$	104 ± 1 ‰
$\delta\ ^{234}U_{initial}$	148 ± 2 ‰
Uncorrected age	125219 ± 394 yr BP
Corrected age	125216 ± 394 yr BP

Table 5. Results for Sr Standard NBS-987

Parameter	Value
^{84}Sr/^{86}Sr	0.056484 ± 0.000003, 2 σ standard error
^{87}Sr/^{86}Sr	0.710243 ± 0.000007, 2 σ standard error

Summary

Using the CETAC AridusII and Aridus3 desolvating nebulizer enhances the signal by a factor of 4 making analyses easier and quicker. Note that the Neptune MC-ICP-MS was equipped with Jet sample and X interface skimmer cones but not with the high performance interface vacuum pump. Smaller samples can be analyzed, which can also reduce sample column chemistry time. The Aridus3 has a smaller footprint and can be operated remotely.

Reference on N_2 Addition

G.L Scheffler and D. Pozebon, Advantages, drawbacks, and applications of mixed Ar-N_2 sources in inductively coupled plasma – based techniques: an overview, Anal. Methods, 2014, 6, 6170-6182.

Acknowledgement

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