



Resolution of ^{176}Yb and ^{176}Lu interferences on ^{176}Hf to enable accurate $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio analysis using ICP-QQQ with MS/MS

Application note
Geology, environmental

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Introduction

Hafnium ^{176}Hf to ^{177}Hf isotope ratio analysis can provide insight into the different geological events and processes that a mineral underwent during its formation/metamorphosis; $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are also used for geochronology dating studies. Isotope geochronology is a dating technique in which the age of a rock or mineral is derived from differences in the abundance of two isotopes of an element. Changes in isotopic abundance may be caused by isotopic (mass) fractionation, or by radioactive decay; in each case, the ratio acts as a geological clock, allowing the time that the mineral was formed to be estimated. Hf has lower mobility than lead (Pb) in metamict minerals such as zircon, xenotime, euxenite etc., so Hf isotope ratios can offer an alternative to Pb/Pb or Pb/U ratios for dating these minerals.



Of the Hf isotopes of interest, ^{177}Hf is free from direct isobaric overlap from any other element and does not typically suffer from polyatomic interference from other co-existing elements. However, the second Hf isotope used in the isotope ratio calculation, ^{176}Hf , suffers isobaric overlap from ^{176}Lu and ^{176}Yb , as shown in Figure 1. In order to obtain accurate Hf ratios, it is therefore necessary to separate the ^{176}Hf signal from the overlapping Lu and Yb signals.

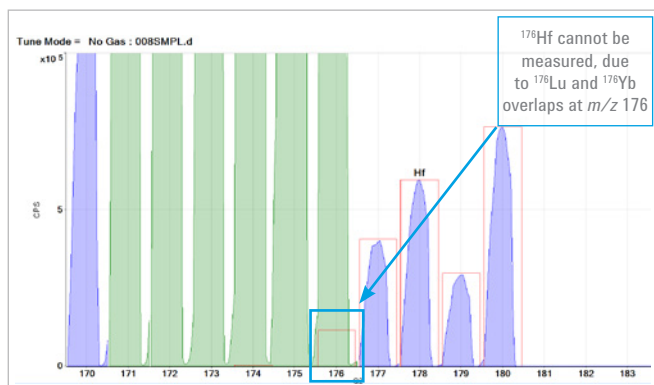


Figure 1. Hf (red peak template) in the presence of Lu and Yb matrix. The poor template fit for ^{176}Hf (highlighted in blue outline) is due to the contribution from ^{176}Lu and ^{176}Yb to the signal at m/z 176.

The mass resolution required to separate ^{176}Hf from the Lu and Yb isobaric interferences ($M/\Delta M$ of $\sim 140,000$ for ^{176}Lu and $>150,000$ for ^{176}Yb) is far beyond the capability of commercial High Resolution Sector Field ICP-MS (SF-ICP-MS), so sample preparation (chemical separation) is required prior to analysis. In cases where chemical separation cannot be performed, for example in-situ measurement by Laser Ablation (LA), the Lu/Yb overlaps mean that accurate Hf isotope ratio analysis is not possible, or must rely on mathematical corrections (and the errors they can introduce).

An alternative direct approach is “chemical” resolution within a collision/reaction cell (CRC), using specific gas phase ion-molecule reaction(s) that will either:

- React with the interfering ion to neutralize it or move it to a new mass.
- React with the analyte to create a new product ion at a different, non-interfered mass.

In this study, the second approach, known as “mass-shift”, was used. Hf reacts efficiently with ammonia cell gas to form Hf-ammonia cluster ions, while Lu and Yb

are relatively unreactive. However, ammonia will react with the other Hf isotopes and other co-existing ions present in a typical sample matrix. These other ions also form ammonia-adduct ions, creating new interferences that vary depending on the matrix composition. These ammonia-adduct ions would interfere with the original Hf isotope pattern, making Hf isotope analysis unreliable, so control over the reaction process is essential.

The solution to this problem is to use a tandem mass spectrometer, which has an additional mass filter before the CRC. This extra mass filter prevents all ions apart from the target mass from entering the CRC, so the reaction chemistry is precisely controlled and unwanted side-reactions are avoided. This double mass filter approach is only possible with a tandem MS (or MS/MS) configuration, which provides unprecedented control of the ion/molecule reaction chemistry used in CRC-ICP-MS methods.

The Agilent 8800 and 8900 Triple Quadrupole ICP-MS (ICP-QQQ) instruments have an additional quadrupole mass filter (Q1), positioned in front of the CRC, with the capability of operating at unit mass resolution (MS/MS mode). In MS/MS operation, only a single mass-to-charge ratio (m/z) is transmitted through Q1, so the other Hf isotopes and any co-existing elements are rejected before they can enter the CRC. Unwanted side-reactions and potentially overlapping product ions are therefore eliminated. This method was used to measure Hf isotope ratios in a variety of samples containing Lu, Yb and mixed rare earth elements (REE). For this proof of concept, all work was performed using solution sample introduction, which allowed a greater flexibility to test interference removal. However, the same cell gas and MS/MS method can also be applied successfully to sample analysis using laser ablation (LA-ICP-QQQ).

Experimental

Instrumentation

The Agilent 8800* ICP-QQQ was configured with an SPS 4 autosampler and the standard sample introduction system consisting of a Micromist nebulizer (free aspiration), quartz spray chamber & torch, and Ni interface cones. Table 1 shows the key instrument parameters used for the analysis.

*The Agilent 8800 ICP-QQQ has been superseded by the 890 ICP-QQQ

Table 1. Instrument parameters

Parameter	Value
RF power	1550 W
Sampling depth	7.0 mm
Nebulizer gas	1.15 L/min
Spray chamber temp	2 °C
Ammonia (10% in He) cell gas	22% of full scale (~2.2 mL/min)
Octopole bias	-6.0 V
Energy discrimination	-8.0 V

Samples and sample preparation

Due to the reactivity of ammonia, its use as a cell gas leads to a complex population of product ions, even in a simple sample matrix. However, selection of the most appropriate adduct ion is relatively simple with ICP-QQQ, by performing a Product Ion Scan. Unique to the MS/MS mode of operation, a Product Ion Scan uses a fixed mass setting for Q1, combined with a Q2 scan across the selected mass range. To identify useful ^{176}Hf -ammonia product ions, Q1 was fixed to mass (m/z) 176 amu, and Q2 was scanned across the mass range from m/z 170 to m/z 260, while aspirating a solution of 5 $\mu\text{g/L}$ Hf. The resulting mass spectrum can be seen in Figure 2. Initially, the reaction product ion spectra may appear complex, but it should be noted that the use of a fixed mass setting for Q1 means that all these ammonia product ions are derived from the ^{176}Hf isotope. The most abundant ammonia adduct ion was $\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$, which occurs at $M + 82$ amu (m/z 258 for the ^{176}Hf isotope); this adduct was selected as the preferred mass transition.

It should be noted that the Hf adduct ion used is sensitive to CRC conditions, particularly the acceleration voltage applied from the Octopole Bias. This parameter was optimized to a lower value than is typically used, in order to favor the preferred transition and maximize the yield of the desired product ion. The cell gas flow rate was then re-optimized using the ICP-MS MassHunter autotune routines to further improve the product ion signal.

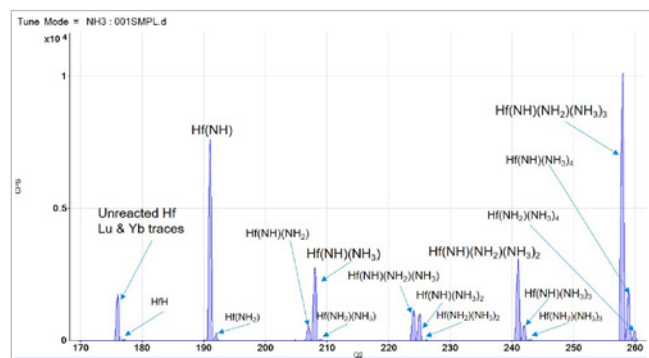


Figure 2. Product Ion Scan from m/z 170 to m/z 260 showing ammonia adduct reaction product ions formed from ^{176}Hf precursor ion (Q1 set to m/z 176)

A graphical representation of the ^{176}Hf transition can be seen in Figure 3; this schematic illustrates how Q1 (set to m/z 176) eliminates all ions apart from those at m/z 176, and Q2 (set to m/z 258) eliminates the unreacted ^{176}Lu and ^{176}Yb isotopes. The same mass transition is used for the other isotope of interest, ^{177}Hf , using Q1 and Q2 settings of m/z 177 and m/z 259, respectively.

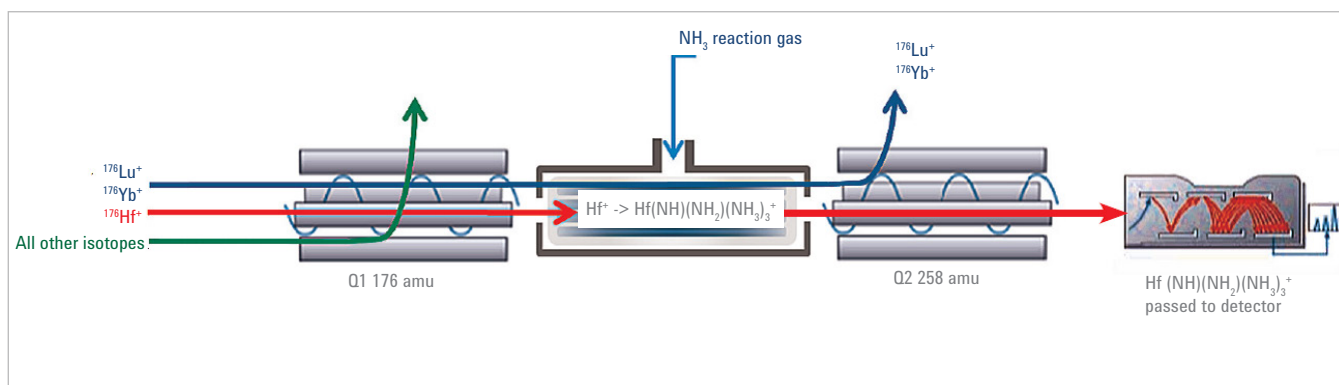


Figure 3. Schematic of the ^{176}Hf isotope reaction with ammonia cell gas in MS/MS mode.

To check that the Hf isotope pattern was maintained, a Neutral Gain Scan was performed where both Q1 and Q2 were scanned together, with a fixed mass difference of +82 amu applied to Q2. Figure 4 shows the resultant spectrum, confirming that the Hf-ammonia product ions match the overlay of the theoretical Hf isotopic abundances. Note that the higher mass Hf isotopes ($^{178}/^{179}/^{180}\text{Hf}$) are not of interest in the isotopic analysis and were not measured. This spectrum demonstrates the unique benefit of MS/MS mode, which ensures that inter-isotope overlaps cannot occur, as only one Hf isotope mass is present in the cell at any given time.

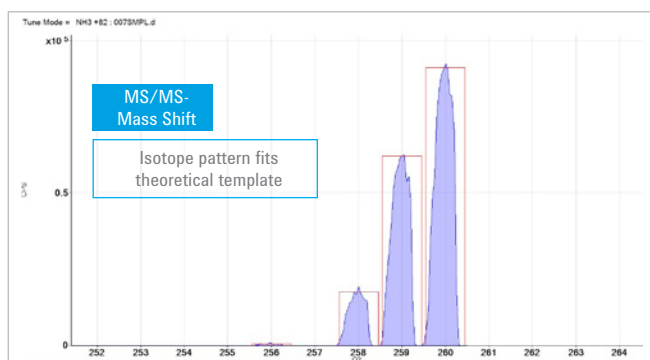


Figure 4. Neutral Gain Scan of the Hf isotopes as $\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$ clusters; theoretical Hf isotopic abundances are shown in red, confirming that the isotope ratios are preserved in the product ion spectrum

To simulate real-world sample analysis, several potential sources of interference were introduced to assess whether bias or new interferences were created. The test solutions included:

- Hf standard (5 ppb) – also used for Mass Bias Calibration
- 100 ppb Yb & 5 ppb Hf
- 100 ppb Lu & 5 ppb Hf
- 100 ppb Yb + Lu & 5 ppb Hf
- Mixed 100 ppb “REE¹” standard and 5 ppb Hf
- Mineral² sample with 100 ppb “REE¹” and 5 ppb Hf

1. Agilent Standard 8500-6944 containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, plus Sc, Y, Th.

2. Natural mineral sample containing approximately 500 ppm Ca, 120 ppm Mg, 15 ppm Na, 5 ppm K, 1500 ppm SO_4

Hf isotope ratio measurement

In order to provide comparative performance data, the ICP-QQQ was set to measure $^{176}/^{177}\text{Hf}$ isotope ratios in three separate acquisition modes:

1. No cell gas, “Single Quad” mode
 - “Base” ICP-MS data not utilizing any mechanism to reduce isobaric overlaps
2. NH_3 reaction gas, Single Quad Bandpass mode
 - Non-MS/MS operation, allowing a limited mass range “window” into the CRC
3. NH_3 reaction gas, MS/MS mode
 - Q1 operating as a mass filter with unit mass resolution, allowing only a single m/z into the CRC

Table 2 displays the Hf isotope ratio (IR) data for each of the test solutions in each instrument mode. It can be seen that there was a large positive deviation from the expected ratio (i.e. the ^{176}Hf signal was high relative to its theoretical abundance) in both of the Single Quad modes of operation (no gas mode and ammonia mode with bandpass filtering). This indicates that “Single Quad” operation did not resolve the Yb and Lu isobars at m/z 176, or stop the formation of new reaction product ion interferences.

By contrast, MS/MS mode with NH_3 cell gas gave consistent, accurate Hf IR data in all the sample matrices.

To visualize and further investigate the potential overlaps that could have caused the poor Hf isotope ratio performance in Single Quad mode, a mass scan of the mineral sample was performed using Single Quadrupole Bandpass mode with NH_3 reaction gas. The spectrum can be observed in Figure 5. The measured Hf isotopic pattern (far right of the spectrum) does not match the theoretical abundance template, showing that the Hf isotopes suffer overlap from new cell-formed cluster ions, due to the lack of control over the reaction processes. In a complex sample matrix, numerous cell-formed interferences are created, precluding the accurate analysis of many target product ions.

Table 2. ^{176/177}Hf isotope ratio (IR) data measured in samples containing various sources of interferences, using three different ICP-QQQ operating modes. The “deviation” is the error in the measured ratio relative to the true ratio of 0.282796.

Sample	No gas Single Quad		NH ₃ Single Quad bandpass		NH ₃ MS/MS	
	IR	Deviation	IR	Deviation	IR	Deviation
Hf 5 ppb	0.27981	0.989	0.28252	0.999	0.28196	0.997
Hf 5 ppb, Yb 100 ppb	15.25251	53.935	0.30461	1.077	0.28370	1.003
Hf 5 ppb, Lu 100 ppb	3.18739	11.271	1.06062	3.750	0.28051	0.992
Hf 5 ppb, Yb, Lu 100 ppb	18.51262	65.463	1.06267	3.758	0.28099	0.994
Hf 5 ppb, REE mix 100 ppb	15.26995	53.996	0.64603	2.284	0.28139	0.995
Hf 5 ppb, Mineral REE mix 100 ppb	16.16150	57.149	0.63479	2.245	0.28230	0.998

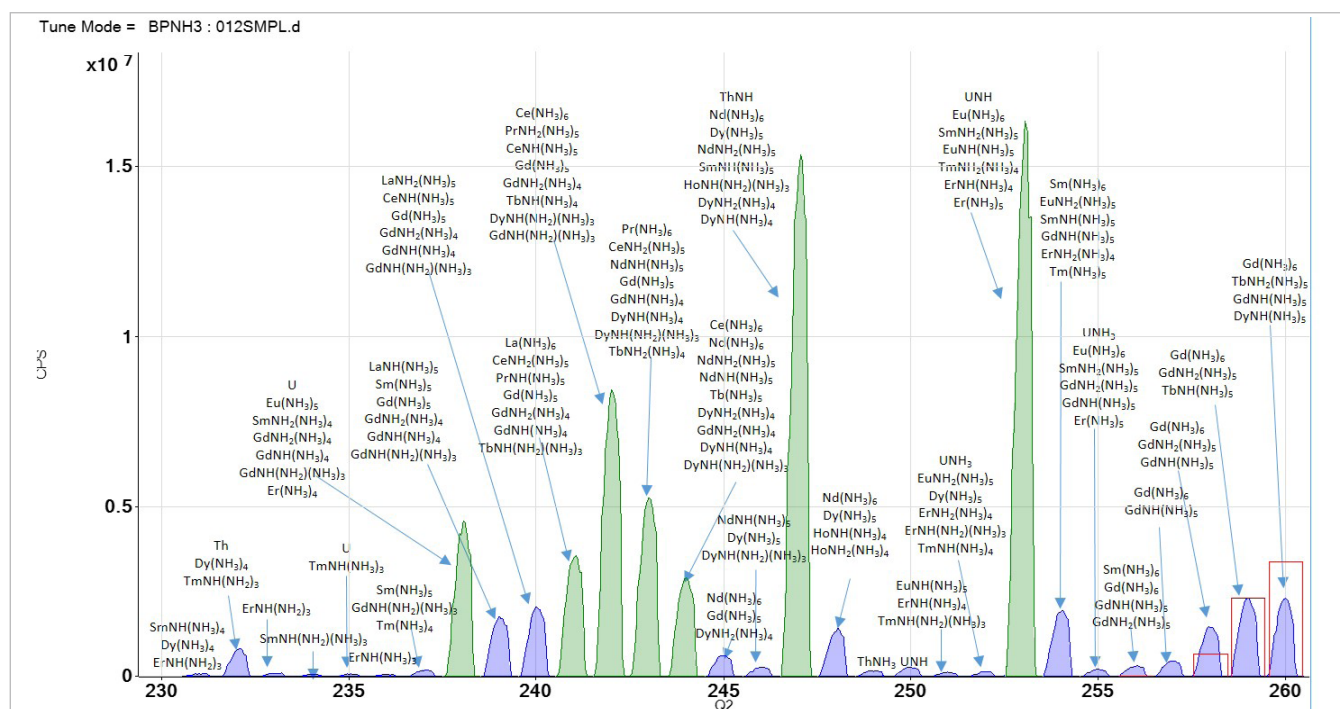


Figure 5. Mass spectrum of the mineral sample acquired under Single Quad Bandpass mode using ammonia as the reaction gas. The poor fit of the measured Hf isotopic pattern (far right) illustrates the interferences that occur in Single Quad mode. Some examples of cell-formed ammonia cluster ions are shown.

Many matrix elements and other analytes can react with ammonia to produce higher order reaction products, so MS/MS mode is essential to remove these precursor ions before they enter the cell and form new interferences.

The 8800 and 8900 ICP-QQQ use an additional quadrupole mass filter, operating at unit mass resolution and positioned before the CRC, to control which ions enter the reaction cell. This ensures unprecedented levels of control over the reaction processes that occur within the cell. MS/MS mode can quickly switch between on-mass measurement and off-mass

measurement within a single acquisition, supporting multi-element analysis in each gas mode. Figure 6 shows the Hf isotopes measured using off-mass mode ($Q2=Q1 + 82$ amu) and the other masses measured on-mass ($Q1=Q2$). The small, residual peaks for unreacted Th and U can be seen, along with ThO and UO. Most of the Th and U would have reacted with ammonia cell gas, forming adduct species that are not measured in MS/MS on-mass mode. Any undesired side reactions are eliminated before they can proceed, so the underlying analyte isotope ratios are preserved in the product ion spectrum.

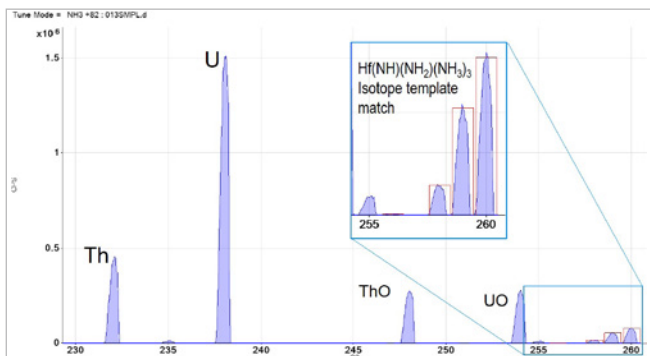


Figure 6. Mass spectrum of the mineral sample measured using NH_3 mass-shift mode for Hf and on-mass mode for all other isotopes. The Hf isotopic pattern illustrates that all of the interferences that occurred in Single Quad mode (shown in Figure 5) have been resolved.

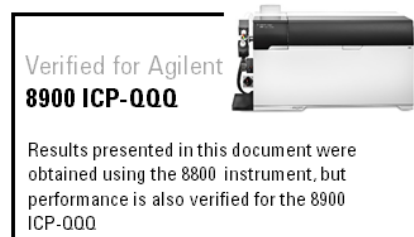
Conclusions

The MS/MS capabilities of Agilent's ICP-QQQ measured Hf isotope ratios with excellent accuracy—even in samples containing high levels of co-existing and potentially interfering matrix elements.

The isobaric overlaps from ^{176}Lu and ^{176}Yb on ^{176}Hf were eliminated using NH_3 as the reaction gas. The reaction chemistry was controlled in the cell by operating the first quadrupole mass filter at unit mass resolution set to m/z 176. This excluded all ions apart from those at m/z 176 (^{176}Lu , ^{176}Yb and ^{176}Hf). Since only Hf reacts readily with NH_3 , ^{176}Hf was free to be measured via its most appropriate cluster ion at m/z 258, effectively avoiding the isobaric overlaps from Lu and Yb. Together with the corresponding ammonia cluster ion formed from the ^{177}Hf isotope, this method allowed accurate Hf isotope analysis to be performed in a range of complex synthetic sample matrices.

In summary:

- Chemical resolution using a reaction gas offers a powerful alternative to mass resolution, allowing access to isobars beyond the maximum resolution available with commercial High Resolution SF-ICP-MS.
- Control over the reaction processes is essential to avoid new, unexpected interferences forming from the sample matrix and other coexisting elements and isotopes.
- MS/MS technology affords unprecedented control over the reaction processes, greatly simplifying methodology regardless of the process or sample matrix.
- Crucially, MS/MS operation allows access to higher order reaction product (cluster) ions, while still preserving the analyte's original isotopic information.



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