Element XR HR-ICP-MS with Jet Interface in dry plasma: exceptional detection sensitivity and improved abundance sensitivity

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Introduction

The Thermo Scientific™ Jet Interface™ option for the Thermo Scientific Element™ Series HR-ICP-MS sets a new standard for sensitivity in elemental analysis and ensures outstanding long-term signal stability.[1,2] The Jet Interface includes: a high-capacity pump, the Jet sample cone, and the X skimmer cone (Figure 1).

Here we focus on the exceptional detection sensitivity that can be obtained in dry plasma conditions with a Thermo Scientific™ Element XR™ HR-ICP-MS equipped with the Jet Interface. Dry plasma conditions are achieved by coupling the Element XR instrument to a desolvating nebulizer system. We also report improved abundance sensitivity in dry plasma compared to the previously documented[3] abundance sensitivity in wet plasma.

Our new data show that in dry plasma the Element XR HR-ICP-MS equipped with the Jet Interface can typically achieve:

- Sensitivity 30 to 50 times higher than the specified sensitivity in wet plasma without the Jet Interface[4].
- Abundance sensitivity (determined at mass 238 ± 1 amu in low resolution mode, LR = 300) better than 7 ppm at both the low and the high mass side of the 238 peak.

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Experimental

Analytical set-up and tuning (detection sensitivity experiments)

An Element XR HR-ICP-MS equipped with the Jet Interface was coupled in different experiments to two desolvating nebulizers from Elemental Scientific Instruments™ (ESI): the Apex 2Q™ and Apex Omega™. For comparison, a dataset was collected in wet plasma conditions (i.e., using the standard sample introduction system and not the desolvating nebulizer system). Table 1 details the operating conditions and acquisition parameters of the mass spectrometer and sample introduction system.

The Apex 2Q improves sensitivity by increasing the sample transport efficiency. Liquid samples are nebulized with the PFA Microflow nebulizer into a heated cyclonic spray chamber and Peltier cooled condenser. The Apex Omega is a high-performance desolvating system with self-aspirating PFA nebulizer and quartz spray chamber.

Figure 1. The Jet Interface includes the Jet sample cone and the X skimmer cone, as well as a high-capacity dry pump (not shown) which replaces the standard interface pump of the Element HR-ICP-MS.

Table 1. Operating conditions and acquisition parameters (detection sensitivity experiments)

Experiment	Wet Plasma 1 (WP1)	Dry Plasma 1 (DP1)	Dry Plasma 2 (DP2)	Dry Plasma 3 (DP3)	Dry Plasma 4 (DP4)
Sample introduction	Twinnabar™-type quartz cyclonic spray chamber; 200 µL/min MicroMist™ nebulizer, self-aspirating; 2.2 mm I.D. quartz standard injector tube	Apex 2Q desolvating system; 100 µL/min PFA APEX nebulizer; 2.2 mm I.D. quartz standard injector tube	Apex 2Q desolvating system; 100 µL/min PFA APEX nebulizer; 1.8 mm I.D. push-fit sapphire injector tube	Apex 2Q desolvating system; 100 µL/min PFA APEX nebulizer; 1.8 mm I.D. push-fit sapphire injector tube	Apex Omega desolvating system; 100 µL/min PFA APEX nebulizer; 1.8 mm I.D. push-fit sapphire injector tube
Cones	Ni Jet sample cone and Ni X skimmer cone				
RF power	1,100 W	1,050 W	1,050 W	1,200 W	1,065 W
Ar AUX gas	0.85 L/min	0.85 L/min	0.85 L/min	0.85 L/min	0.75 L/min
Ar sample gas (Element XR)	1.20 L/min	1.19 L/min	1.09 L/min	1.10 L/min	1.16 L/min
Ar sweep gas (desolvator)	N/A	0.21 L/min	0.24 L/min	0.25 L/min	4.00 L/min
N_2 (desolvator)	N/A	0.3 mL/min	0.3 mL/min	0.3 mL/min	4.6 mL/min
Detection mode	Triple: automatic switch between SEM (Analog and Counting mode) and Faraday cup (Faraday mode) in less than 1 ms				
Sample type	Thermo Scientific™ 1 ppb Tune solution, 5% HNO_3				
Isotopes monitored	10 isotopes in mass range 7–238 measured in Low Resolution (R = 300), ^{45}Sc and ^{59}Co measured in Medium Resolution (R = 4,000); Figure 3				
Detection sensitivity (LR)	4.3×10^6 cps/ppb ^{115}In	2.7×10^7 cps/ppb ^{115}In	2.9×10^7 cps/ppb ^{115}In	4.7×10^7 cps/ppb ^{115}In	5.3×10^7 cps/ppb ^{115}In
Transmission: ^{59}Co(MR) / ^{59}Co(LR)	10%	11%	12%	11%	8%
$^{238}UO/^{238}U$	0.08	0.09	0.09	0.10	0.06

In the Apex Omega, the combination of a multistage Peltier-cooled desolvating system in series with a helical membrane desolvator simultaneously maximizes sensitivity and minimizes oxides. Both desolvating systems integrate mass flow controllers for Nitrogen and Argon gas flows (the latter is referred to as "Ar sweep gas").

The multi-element Thermo Scientific™ 1 ppb Element Tune-up Solution™ was used for tuning and analysis. Plasma conditions were initially tuned to maximise signal stability and sensitivity for a non-oxide forming analyte (e.g., ^{115}In) while monitoring oxide formation (e.g., $^{238}U^{16}O/^{238}U$). This involved a coarse tuning of the Ar sweep gas and N_2 gas flows. A finer, iterative tuning of both gas flows was subsequently performed to reduce the oxides while maintaining the In sensitivity. As a result, the signal intensity of the oxide forming analyte increases relative to the signal intensity of the non-oxide forming analyte. The formation of oxides is primarily influenced by the proximity of the plasma relative to the cones and the tuning of the Ar sample gas, Ar sweep gas and N_2 gas flows.

With the Jet interface option, optimal sensitivity and signal stability are achieved (in both wet and dry plasma conditions) with a RF power of ~1,100 W) and a relatively retracted position of the torch compared to tuning with the standard interface.

Using a push-fit injector (instead of an injector with a ball-joint connector) to connect the sample gas line from the desolvating unit allowed the best signal stability (experiments DP2–DP4).

Analytical set-up and tuning (abundance sensitivity experiments)

For the abundance sensitivity experiment (DP5), the Element XR system equipped with the Jet Interface was coupled to an Apex Omega desolvating nebulizer system. Table 2 details the operating conditions and acquisition parameters.

The single collector detection system of the Element XR HR-ICP-MS incorporates a single high performance, discrete dynode, dual mode secondary electron multiplier (SEM) with a linear dynamic range of over nine orders of magnitude (Figure 2). An additional Faraday cup extends the linear dynamic range to over 10^{12} cps. The Element XR HR-ICP-MS also features an abundance sensitivity "filter lens" that acts as an energy filter. A positive voltage can be applied to the filter lens to create an energy barrier: only ions with high energy pass this barrier, reach the exit slit, and continue towards the detector.

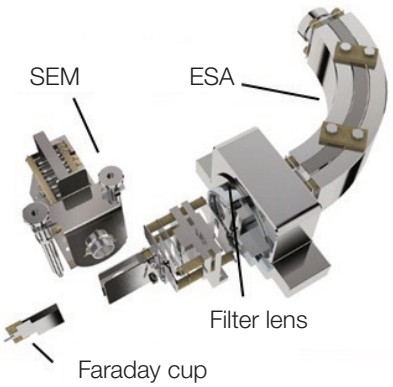

Figure 2. Element XR Electrostatic Scanning Analyzer (ESA) and detection system (SEM and Faraday)

Table 2. Operating conditions and acquisition parameters (abundance sensitivity experiments)

Experiment	Dry Plasma 5 (DP5)
Sample introduction	Apex Omega desolvating system; 100 µL/min PFA APEX nebulizer; 1.8 mm I.D. push-fit sapphire injector tube
Cones	Ni Jet sample cone; Ni X skimmer cone
RF power	1,100 W
Ar sample gas (Element XR)	1.10 L/min
Ar sweep gas (desolvator)	3.75 L/min
N_2 (desolvator)	3.7 mL/min
Detection mode	Triple
Sample type	Thermo Scientific 1 ppb U solution, 2% HNO_3
Isotopes monitored	6 isotopes in the mass range 234–239 measured in LR
Detection sensitivity (LR, determined on Tune solution)	2.0×10^7 cps/ppb ^7Li 7.0×10^7 cps/ppb ^{115}In 4.5×10^7 cps/ppb ^{238}U
$^{238}UO/^{238}U$	0.02

Results and discussion

Detection sensitivity

The sensitivity for twelve isotopes measured in LR and MR during experiments WP1 and DP1-4 is plotted in Figure 3. Consistent with previously reported data,[2] experiment WP1 shows that with the Jet Interface the sensitivity is improved across the mass range compared to the standard interface (i.e., the 4.3×10^6 cps/ppb ^{115}In sensitivity in WP1 is four times the sensitivity specified for the Element HR-ICP-MS with standard interface). In dry plasma experiments DP1-DP3, the sensitivity per ppb ^{115}In ranged from ~27×10^6 to ~47×10^6 cps. Such a range can be ascribed to differences in the actual sample flow rate and joint tuning of the Element HR-ICP-MS and desolvating unit parameters. The highest sensitivity was obtained employing the Apex Omega desolvating nebulizer system (experiment DP4, Table 1; see also experiment DP5, Table 2). The different detection sensitivity between DP4 and DP5 (respectively, ~5×10^7 and ~7×10^7 cps/ppb ^{115}In) is to be related to differently tuned Ar and N_2 gas flows.

In general, in all experiments with the Jet Interface, the improvement in sensitivity in dry plasma across the mass range compared to wet plasma ranged from a minimum of 6–8 times to over one order of magnitude (Figure 3).

Abundance sensitivity

Abundance sensitivity can be defined as the intensity of a given isotope at spectral peak maximum, relative to the intensity of that isotope at 1 amu lower and at 1 amu higher than the mass position corresponding to peak maximum.

For experiment DP5, six isotopes in the mass range 234–239 were measured in LR while aspirating a 1 ppb U solution. Three samples were measured for ~6 minutes each, with the filter lens voltage respectively set to 0, 11, and 13 V. The intensities measured for each isotope and the calculated abundance sensitivities (for the ratios 237/238 and 239/238) are presented in Table 3. Mass scans across the same range were collected and are shown in Figure 4.

The use of a desolvating system prevents ^{238}UH formation at mass 239, which typically occurs in wet plasma conditions.[3] It follows that the abundance sensitivity in dry plasma is symmetrical on both sides of the 238 peak.

Without using the filter lens, the abundance sensitivity in dry plasma measured as 237/238 and 239/238 was respectively 16 and 17 ppm. The application of voltage to the filter lens improved the abundance sensitivity to 6 and 8 ppm (11 V) and 5 and 7 ppm (13 V), respectively. The filter lens, acting as an energy filter, tends to reduce the measured signal intensity.

As an example, the ^{238}U sensitivity dropped to 44% and 21% at 11 V and 13 V, respectively, compared to the sensitivity at 0 V (Table 3). Nevertheless, the Element XR HR-ICP-MS equipped with the Jet Interface in dry plasma conditions ensured a sensitivity (with filter lens set at 13 V) in excess of 5.7×10^6 cps/ppb U.

Table 3. Abundance sensitivity measurements (experiment DP5)

Filter lens (V)	0	11	13
234 (cps)	1,593	706	342
235 (cps)	221,767	100,526	47,768
236 (cps)	1,870	810	388
237 (cps)	447	76	28
238 (cps)	27,738,991	12,215,789	5,740,202
239 (cps)	478	98	40
237/238 (ppm)	16	6	5
239/238 (ppm)	17	8	7

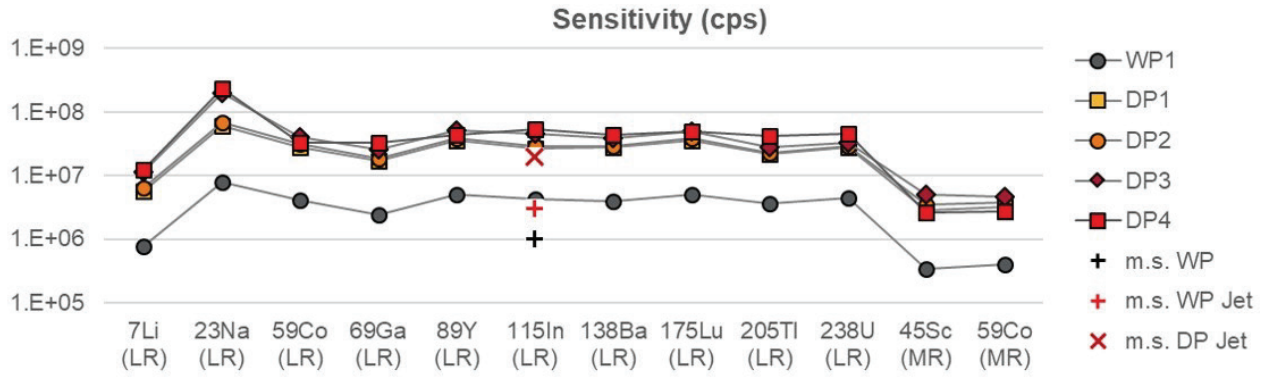

Figure 3. Sensitivity data for experiments WP1 and DP1–DP4. Specified minimum sensitivity per 1 ppb ^{115}In with standard interface in wet plasma conditions (m.s. WP) and with Jet Interface in wet and dry plasma conditions (m.s. WP Jet and m.s. DP Jet) are plotted for comparison. Note the logarithmic scale for the y-axis.

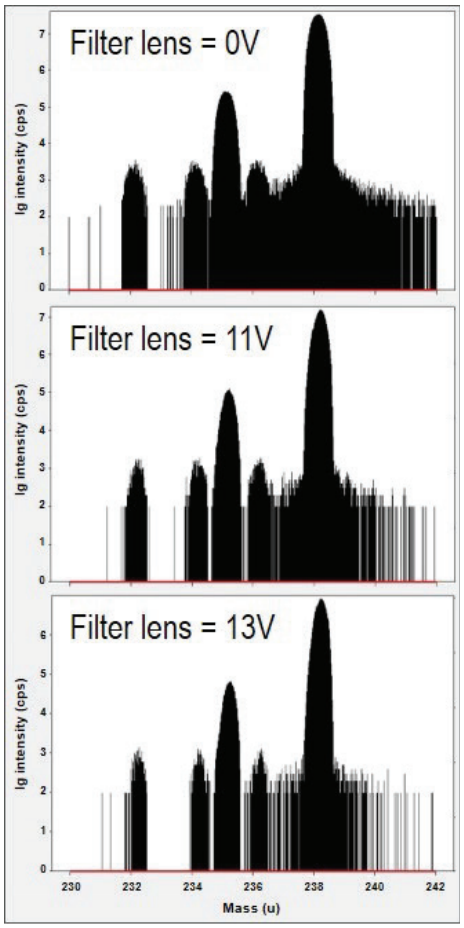

Figure 4. Mass scan across the 230–242 mass range at different filter lens voltages in dry plasma (experiment DP5). Note the logarithmic scale for the y-axis.

The lack of uranium hydride formation in dry plasma conditions was previously reported by Zheng[5] who showed the benefits of using an Element XR HR-ICP-MS equipped with Jet Interface in dry plasma to remove the peak tailing effects and ^{238}U hydride to measure ultra-trace levels of ^{239}Pu in environmental samples. Similarly, Igarashi et al.[6] used an Element XR HR-ICP-MS in dry plasma conditions to detect Pu isotopes in radioactive particles released in the environment.

Remarkably, Zheng reported a very good sensitivity of 3.5×10^6 cps/ppb ^{239}Pu determined in wet plasma with the standard interface as well as the exceptional sensitivity of 100×10^6 cps/ppb ^{239}Pu in dry plasma (using a desolvating unit with membrane) with the Jet Interface.

Conclusions

- In dry plasma, the Element HR-ICP-MS Series equipped with the Jet Interface can typically achieve a sensitivity ~30–50 times higher (i.e., ~3–5 × 10^7 cps/ppb ^{115}In) than in wet plasma without the Jet Interface (i.e., the specified 1×10^6 cps/ppb ^{115}In).
- The actual sample flow rate and the joint tuning of the operating parameters are critical in determining the ultimate sensitivity.
- An abundance sensitivity better than 7 ppm at both the low and the high mass side of the 238 peak can be achieved with an Element XR HR-ICP-MS equipped with the Jet Interface in dry plasma.
- With its >10^{12} cps dynamic range, the Element XR HR-ICP-MS can measure exceptionally high intensity signals resulting from sensitivity enhancement with the Jet Interface in dry plasma.

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