Electronic supplementary information (ESI)

To shift, or not to shift: adequate selection of an internal standard in mass-shift approaches using tandem ICP-mass spectrometry (ICP-MS/MS)

Eduardo Bolea-Fernandez[a], Ana Rua-Ibarz[a], Martín Resano[b], Frank Vanhaecke[a*]

[a]Ghent University, Department of Chemistry, Atomic & Mass Spectrometry – A&MS research group, Campus Sterre, Krijgslaan 281-S12, 9000 Ghent, Belgium

[b]University of Zaragoza, Aragón Institute of Engineering Research (I3A), Department of Analytical Chemistry, Pedro Cerbuna 12, 50009 Zaragoza, Spain

*Corresponding author: Frank.Vanhaecke@UGent.be – Tel:+3292644848

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8. Table S3. ICP-MS/MS data acquisition parameters for a multi-tune method (1.0, 3.0 and 5.0 mL min^{-1} NH_3/He).

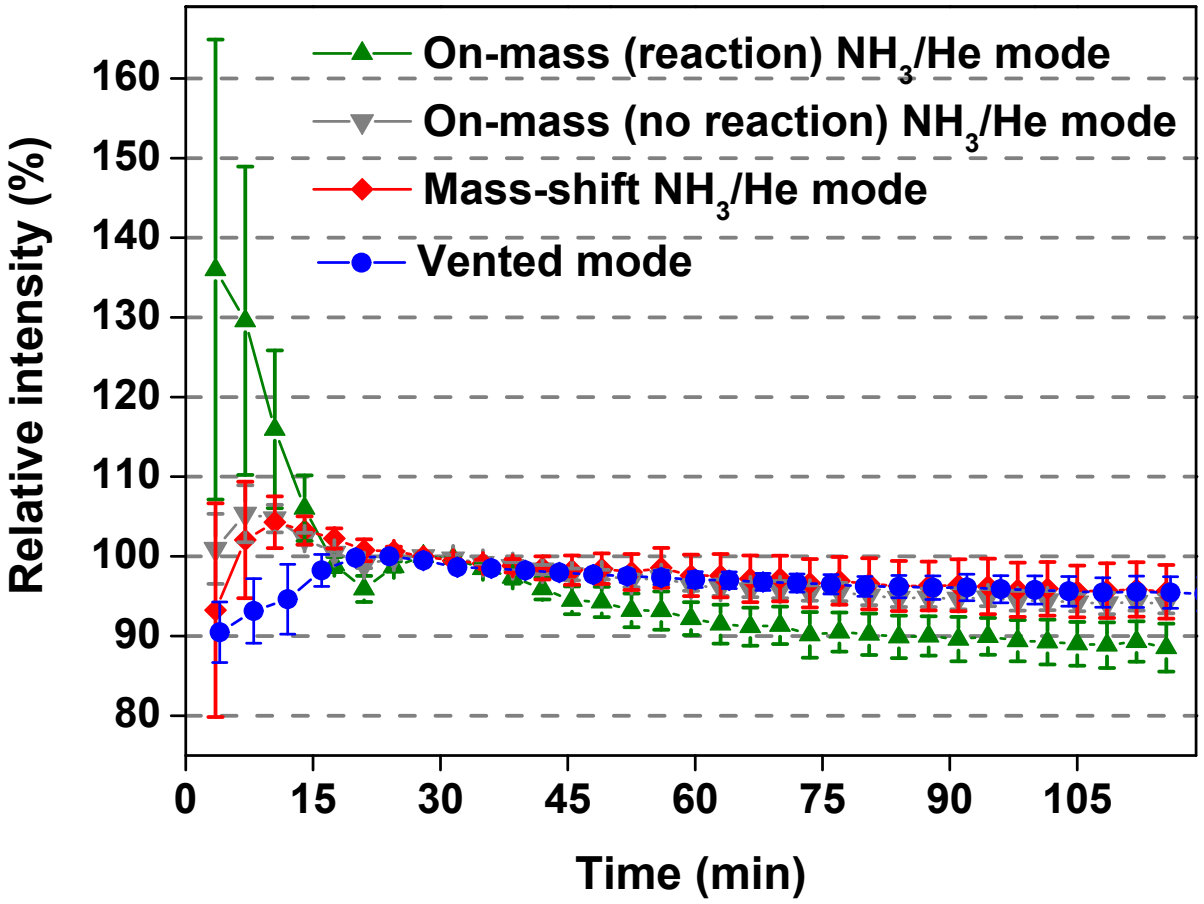


Figure S1. Evaluation of the long-term signal drift for atomic ions monitored on-mass (black squares) in NH_3/He mode, reaction product ions (mass-shift approach – red diamonds) and atomic ions monitored in vented mode (blue circles) using ICP-MS/MS. In this experiment, the instrument was drift-stabilized by running it for 4 hours with the cell pressurized with NH_3/He (3.0 mL min^{-1}) prior to signal monitoring. Uncertainties are expressed as the standard deviation of 13 and 12 relative signal intensities for atomic (both pressurized and vented modes) and reaction product ions, respectively.

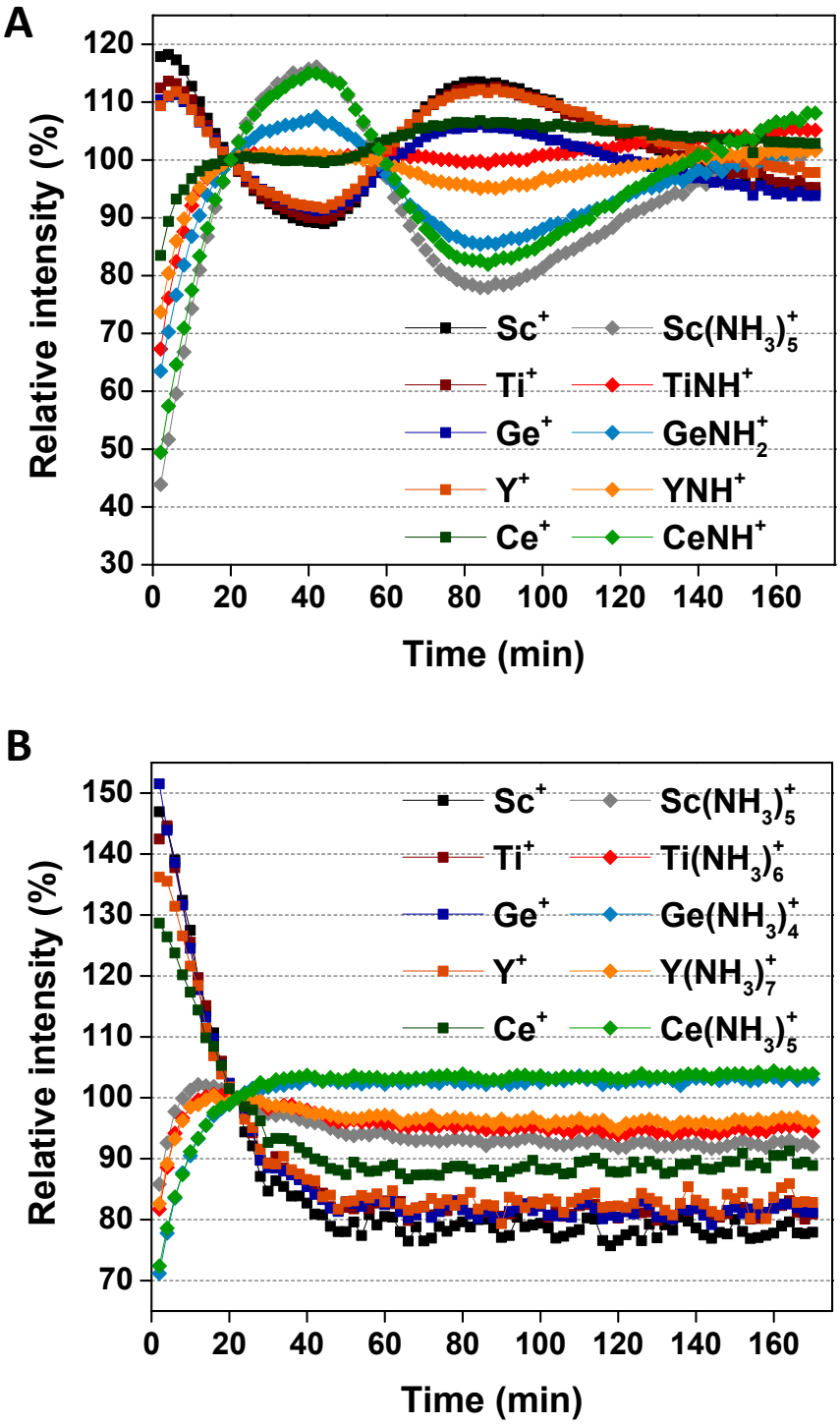
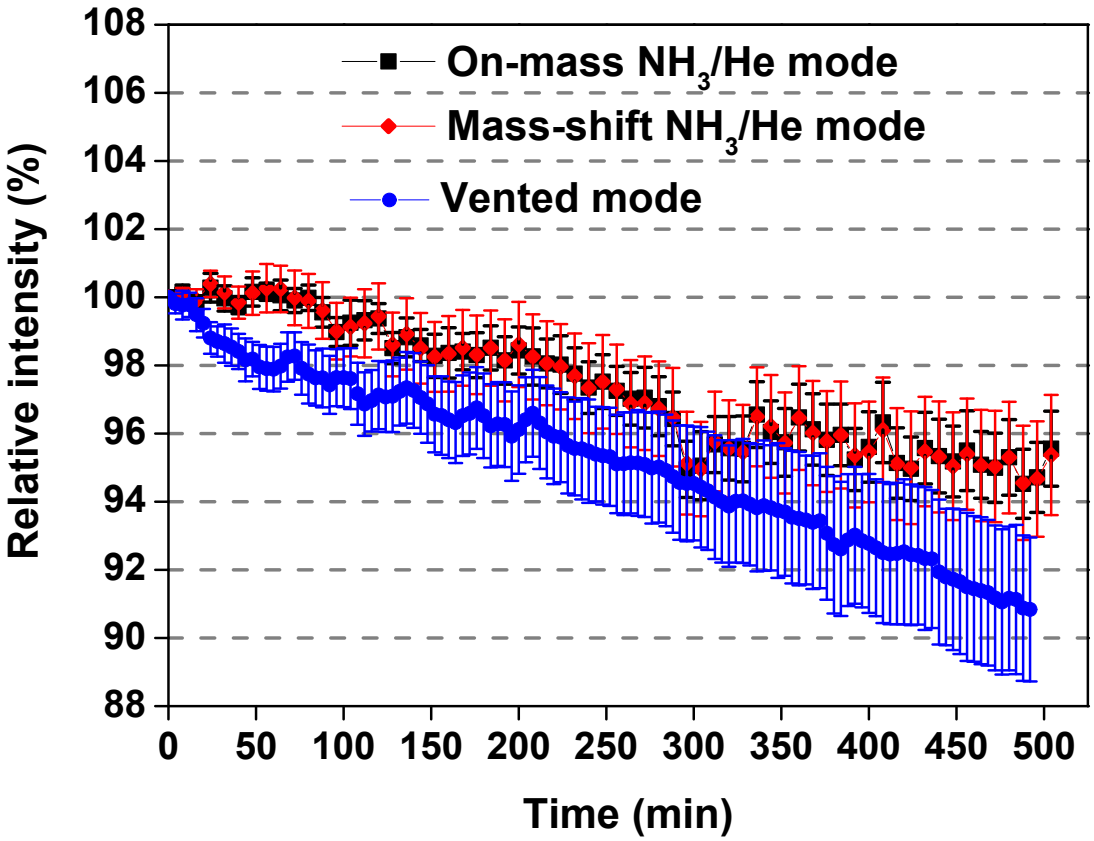


Figure S2. Short-term signal stability/drift for atomic ions and their corresponding optimum reaction product ions at 1.0 mL min^{-1} of NH_3/He (A) and at 3.0 mL min^{-1} of NH_3/He (B) for Sc, Ti, Ge, Y and Ce. In this experiment, the instrument was not previously stabilized with the NH_3/He gas mixture.



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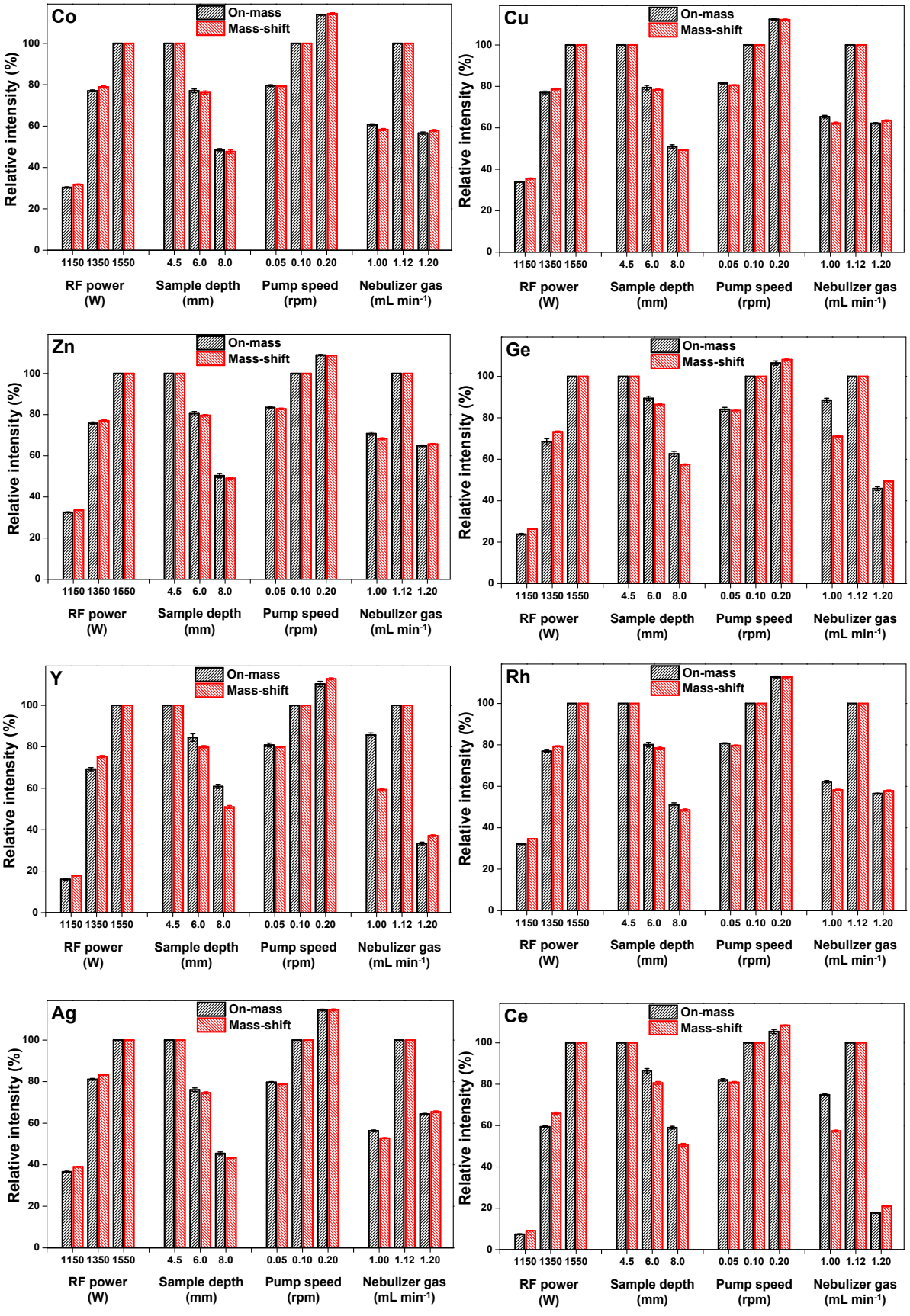
Co
Cu
Zn
Ge
Y
Rh
Ag
Ce
On-mass
Mass-shift
Relative intensity (%)
0
20
40
60
80
100
1150 1350 1550
4.5 6.0 8.0
0.05 0.10 0.20
1.00 1.12 1.20
RF power (W)
Sample depth (mm)
Pump speed (rpm)
Nebulizer gas (mL min-1)

Figure S4. Relative intensities for all nuclides measured as atomic or reaction product ion under different instrument settings. The relative intensities were normalized relative to those obtained under optimum conditions (see Table 1). Uncertainties are expressed as the standard deviation of 5 measurement replicates.

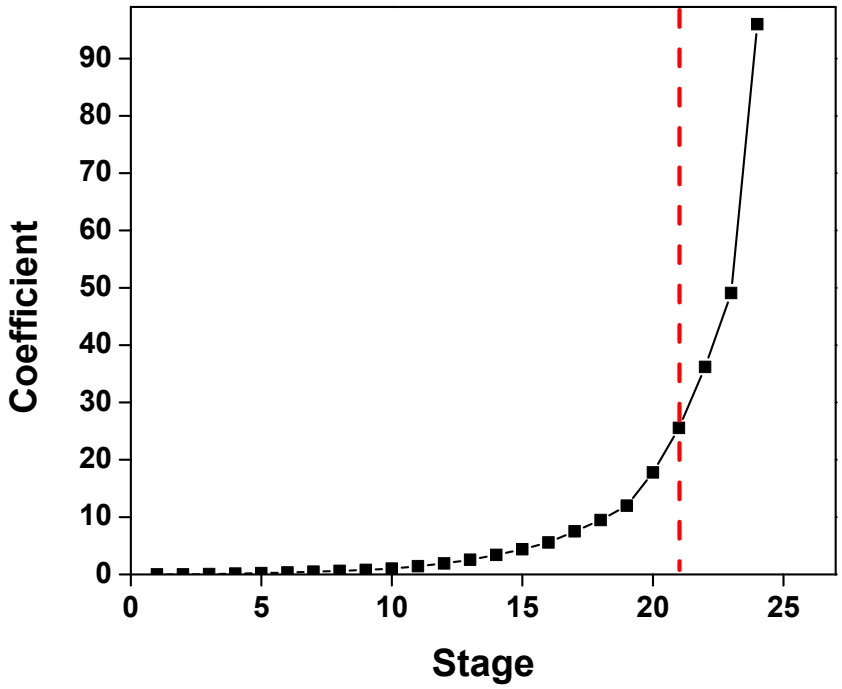

Figure S5. Scree plot of coefficients obtained after hierarchical cluster analysis by stage (the red dotted line represents the stop of the cluster analysis).

Table S1. Best suited reaction product ion under compromise conditions for multi-element determination (3.0 mL min^{-1} of NH_3/He) and the reaction product ion providing the highest signal intensity and the corresponding gas flow rate for all of the target elements.

Nuclide	Gas flow rate (mL min^{-1})	Q2	Reaction product ion	Intensity (cps L μg^{-1})
^{24}Mg	3.0	75	$Mg(NH_3)_3^+$	1000
^{45}Sc	1.0	130	$Sc(NH_3)_5^+$	25000
	3.0			12000
^{48}Ti	1.0	63	$TiNH^+$	29000
	3.0	150	$Ti(NH_3)_6^+$	19000
^{56}Fe	3.0	90	$Fe(NH_3)_2^+$	38000
^{59}Co	2.0	93	$Co(NH_3)_2^+$	47000
	3.0			36000
^{65}Cu	3.0	99	$Cu(NH_3)_2^+$	38000
^{66}Zn	3.0	100	$Zn(NH_3)_2^+$	1800
^{74}Ge	1.0	90	$GeNH_2^+$	9100
	3.0	125	$Ge(NH_3)_3^+$	7000
^{89}Y	1.0	104	YNH^+	58000
	3.0	191	$Y(NH_3)_6^+$	43000
^{103}Rh	4.0	171	$Rh(NH_3)_4^+$	67000
	3.0			63000
^{107}Ag	4.0	141	$Ag(NH_3)_2^+$	9700
	3.0			7500
^{140}Ce	1.0	155	$CeNH^+$	34000
	3.0	225	$Ce(NH_3)_5^+$	17000

Table S2. ICP-MS/MS data acquisition parameters for a multi-tune method (no gas, 3.0 mL min^{-1} NH_3/He).

	No gas		3.0 mL min^{-1} NH_3/He	
Element	**Q1 → Q2**	**Int. time/mass (s)**	**Q1 → Q2**	**Int. time/mass (s)**
Mg	---	---	24 → 75	1
Sc	---	---	45 → 130	1
Ti	---	---	48 → 150	1
Fe	---	---	56 → 90	1
Co	---	---	59 → 59	1
Co	---	---	59 → 93	1
Cu	---	---	65 → 65	1
Cu	---	---	65 → 99	1
Zn	---	---	66 → 66	1
Zn	---	---	66 → 100	1
Ga	---	---	71 → 71	1
Ge	---	---	74 → 74	1
Ge	---	---	74 → 125	1
Y	---	---	89 → 89	1
Y	---	---	89 → 191	1
Rh	---	---	103 → 103	1
Rh	---	---	103 →171	1
Ag	---	---	107 → 107	1
Ag	---	---	107 → 141	1
Cd	---	---	111 → 111	1
In	---	---	115 → 115	1
Cs	---	---	133 → 133	1
Ce	---	---	140 → 140	1
Ce	---	---	140 → 225	1
Tl	---	---	205 → 205	1
U	235 → 235	30	---	---
Stabilization time (s)	0	10	30	
Replicates	5	5	5	
Total analysis time/sample (s)	378	398	438	

Table S3. ICP-MS/MS data acquisition parameters for a multi-tune method (1.0, 3.0 and 5.0 mL min^{-1} NH_3/He).

	1.0 mL min^{-1} NH_3/He		3.0 mL min^{-1} NH_3/He		5.0 mL min^{-1} NH_3/He	
Element	**Q1 → Q2**	**Int.time/mass (s)**	**Q1 → Q2**	**Int.time/mass (s)**	**Q1 → Q2**	**Int.time/mass (s)**
Mg	---	---	24→75	1	---	---
Sc	---	---	45→130	1	---	---
Ti	---	---	48→150	1	---	---
Fe	---	---	56→90	1	---	---
Co	---	---	59→59	1	---	---
Co	---	---	59→93	1	---	---
Cu	---	---	65→65	1	---	---
Cu	---	---	65→99	1	---	---
Zn	---	---	66→66	1	---	---
Zn	---	---	66→100	1	---	---
Ga	---	---	71→71	1	---	---
Ge	---	---	74→74	1	---	---
Ge	---	---	74→125	1	---	---
Y	---	---	89→89	1	---	---
Y	---	---	89→191	1	---	---
Rh	---	---	103→103	1	---	---
Rh	---	---	103→171	1	---	---
Ag	---	---	107→107	1	---	---
Ag	---	---	107→141	1	---	---
Cd	---	---	111→111	1	---	---
In	---	---	115→115	1	---	---
Cs	---	---	133→133	1	---	---
Ce	---	---	140→140	1	---	---
Ce	---	---	140→225	1	---	---
Tl	---	---	205→205	1	---	---
U	235→235	30	---	---	235→235	30
Stabilization time (s)	0		10		30	
Replicates	5		5		5	
Total analysis time/sample (s)	539		569		629	