APPENDIX AVAILABLE ON REQUEST

Research Report 153

Improved Source Apportionment and Speciation of Low-Volume Particulate Matter Samples

Schauer et al.

Appendix D. Determination of Elemental Composition by HR–ICP–MS

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Determination of Elemental Composition of Aqueous Solutions Using Sector-Field, High Resolution, Inductively Coupled Plasma Mass Spectrometry (HR–ICP–MS)

Thermo Finnigan ELEMENT 2 ICP-MS

Version 01/08

University of Wisconsin-Madison

State Laboratory of Hygiene

Trace Element Laboratory

Scope and Application

1.1. This document prescribes the operation and use of the ELEMENT2 sector-field high-resolution inductively coupled plasma mass spectrometer for multi-element analysis of aqueous media.

1.2. Samples suitable for this method are in liquid phase including: natural water, drinking water, acid-digested solids, urine, or other aqueous liquid extracts. The concentration of dissolved solids in the sample must not exceed 0.2% by weight to volume.

2. Summary of Method

2.1. Thermo Finnigan Element2 is a double-focusing magnetic sector mass spectrometer capable of simultaneous analysis of most elements with a concentration range spanning nine orders of magnitude. Liquid samples aspirated with a nebulizer are ionized in an argon plasma for introduction into the mass spectrometer where elemental isotope separation and detection occurs. Magnetic and electric field mass filters separate the sample ions by their mass to charge ratio at an analyzing vacuum of 10^{-7} mbar. Only the positively charged ions are focused through the flight tube of the instrument to the detector. Ions hitting the detector create a secondary voltage that is used to measure the analyte concentration. The instrument has 3 resolution settings low, medium and high that allow increased separation of isotopes. Isobaric interferences are avoided by measuring alternative isotopes, using a higher resolution setting on the instrument, modifying the sample introduction method, or sample preparation (e.g. liquid extraction from seawater). Most common polyatomic interferences are sufficiently resolved in the medium resolution acquisition mode at $R \geq 4000$.

3. Definitions

3.1. Accurate Mass: the theoretical ion mass of an isotope or molecule as given by IUPAC. The actual scan window of acquired data will be centered around this mass (±½ Mass Window).

3.2. Atomic Mass Unit (amu): defined as taking the mass of one atom of carbon-12 as being 12 amu. It is a unit of mass when expressing masses of atoms or molecules.

3.3. Auxiliary Gas (aux gas): The argon gas which serves to generate the plasma.

3.4. B-scan: scanning a mass range utilizing the magnetic field filter for mass separation, with the electric field held constant. A B-scan is used to view the entire continuous mass range from 7 – 254 m/z. It is slower than E-scan, but does not involve intensity variations vs. mass as occurs with E-scan.

3.5. Calibration Blank: the initial blank solution for calibration baseline determination – normally 2% optima grade nitric acid.

3.6. Calibration File (*.cal): contains tables of observed intensities versus known concentrations, generated using analysis of known concentration solutions.

3.7. Continuing Calibration Blank (CCB): A blank solution analyzed in the sequence sourced from the same solution as the calibration blank

3.8. Continuing Calibration Verification (CCV): A calibration verification standard analyzed between samples in the sequence.

3.9. Cool Gas: argon gas which prevents the glass torch from melting.

3.10. Counting Mode: a detection mode in which a digital measurement is made by counting electron pulses. It is very sensitive and can be used for the detection of low signals.

3.11. ESA: the electrostatic analyzer.

3.12. E-scan: scanning a mass range utilizing the electrostatic filter for mass separation. The magnetic field is kept constant, and scanning is performed electrically by varying the accelerating voltage and ESA voltage. An E-scan is limited to a -5%/+30% m/z window by the magnet position (Magnet Mass), which is held constant. If the next required mass is beyond the range of the current E-scan, the software

determines a new Magnet Mass, and a new E-scan is made from there. This is the fastest scanning mode.

3.13. HR: the abbreviation for High Resolution. The Element2 is capable of high resolution $\geq$ 10,000.

3.14. info file (*.inf): contains all information relating to a measured sample. It contains the method and parameters used to acquire the data file, and is stored together with the data file (*.dat).

3.15. Initial Calibration Verification (ICV): A calibration verification solution prepared from a stock solution different from the calibration standards. Mass window: the mass range (amu) that the software will monitor for peak acquisition.

3.16. Integration Window: This window, expressed as a % of peak width, is the region used for the calculation of peak intensity. A value of 100% means that the intensity will be calculated in a window of $\pm$½ of the peak width of the peak center or accurate mass. As an example, if 20 samples/peak is specified, with a 60% integration window, then (20 samples/peak)x(60%)=12 samples are used for integration purposes.

3.17. Internal Standard: An element, not expected to be found naturally in a sample, which is added in known and consistent quantity to the samples in order to compensate for drift effects in response or sensitivity caused by various processes in sample introduction or ion extraction.

3.18. LR: the abbreviation for Low Resolution. The Element2 is capable of low resolution $\geq$ 400.

3.19. Mass window: the mass range (amu) that the software will monitor for peak acquisition. It is centered around the accurate mass, and specified as a %. For example, a mass window of 200% means that, starting from the accurate mass, one full peak width to each side of the peak will be scanned.

3.20. MCAL: abbreviation for mass calibration. In the Element2, a suite of 6 separate and progressively accurate mass calibration runs (LR, MR, and HR, each at a wide and narrow window) are used to define a final single mass calibration.

3.21. MR: the abbreviation for Medium Resolution. The Element2 is capable of medium resolution $\geq$ 4,000.

3.22. Resolution (R): defined as dM/M at 10% peak height, calculated by dividing the centroid peak mass (m/z) by the mass difference at 10% of the maximum peak intensity.

3.23. Runs and Passes: defined in the Method Editor, specifying the number of spectra to acquire in an analysis, and how these spectra are arranged in subsequent data evaluation.

3.24. Sample Time: the integration time for each sample.

3.25. Samples per Peak: the number of samples (data acquisition points) recorded across a peak.

3.26. Search window : the extended mass range the software will search for a peak, designated as a percentage of the peak centroid. The peak center identified by the search is used by the integration window for data evaluation.

3.27. STD: abbreviation for a standard solution.

4. Interferences

4.1. Isobaric elemental interferences: Most elements have multiple isotopes and some elements have isotopes with a nominal mass shared by another element (e.g. ^{82}Kr = 81.9134 and ^{82}Se = 81.9167). In some cases, the instrument may not have the resolution required to separate these isotopes. Isotopes free from this type of interference should be chosen when an analysis element menu is created.

4.2. Polyatomic interferences: Plasma-sourced interferences are generated when sample matrix ions combine to form a mass/charge (m/z) similar to that of the analyte. Common examples include oxides, hydrides and chlorides of argon, rare-earth element oxides, and double-charged ions of barium. Refer to Table A for a specific list of common interferences or use the ELEMENT interferences and resolution software program to determine possible interferences.

5. Safety

5.1. General safe laboratory practices should be followed. Concentrated acid must only be used in the exhausting fume hoods. A labcoat, eye protection and gloves must be worn. Refer to the cleanroom procedures and protocols SOP.

5.2. Hazards associated with this procedure

5.2.1. Exposure to toxic or carcinogenic metals and acids – prepared samples frequently contain 0.7% hydrofluoric acid. Refer to MSDS information for specific analytes.

5.2.2. Pressurized gas lines and gas cylinders – the argon line feeds the instrument at 110 psi. Gas cylinders must be fastened in a stationary position when in use and capped before moving.

5.2.3. Ultra-violet light – the light escaping from the torch assembly is not filtered, avoid direct eye contact with the plasma.

5.2.4. Radiofrequency and electro-magnetic field radiation

5.2.5. High voltage electronics – the power to the electronics must be turned off before maintenance inside the instrument. The breaker is located behind the front left panel.

6. Apparatus and Equipment

6.1. Element2 inductively coupled plasma – mass spectrometer

6.1.1. Argon gas supply (110 psi)

6.1.2. Cyclonic spray chamber (quartz)

6.1.3. Semi demountable torch with 1.5 mm injector (quartz)

6.1.4. APEX desolvator (optional)

6.1.5. Nickel or platinum sampler and skimmer cones

6.1.6. Peristaltic pump

6.2. Labware

6.2.1. metal-free polypropylene auto-sampler tubes (17x100mm)

6.2.2. calibrated pipettes, 2-100 µL, 100-1000µL, 0.5-10.0 ml

6.2.3. metal-free pipette tips

6.2.4. Teflon or low-density polyethylene bottles

6.2.5. polyethylene or powder-free nitrile gloves

6.2.6. top-loading analytical balance, calibrated, accurate to 0.1mg

7. Reagents and Consumable Materials

7.1. Water (18.2 MΩ resistivity)

7.2. Nitric Acid (Fisher Optima grade)

7.3. Hydrochloric Acid (Fisher Optima grade)

7.4. High-purity metal stock solutions

7.5. Certified reference material: SLRS-4 (NRC Canada)

7.6. Element Tune solution: a multi-element standard in 2% HNO3 that contains the following elements at 1.0 µg/L:

Li, B, Na, Sc, Co, Fe, Zn, Y, Rh, In, Ba, Lu, Tl, U

7.7. Peristaltic pump tubing for 0.10 – 1.00 ml/min flow rates

8. Sample preservation and storage

8.1. Samples submitted for ICP-MS are normally at low level concentrations. To avoid possible contamination, trace metal clean sample handling procedures must be followed. Samples must be opened only in the laminar flow HEPA hood area. Clean gloves must be worn when directly handling samples and analytical apparatus.

8.2. The majority of analyses performed on this instrument are acidified aqueous matrix. Samples to be analyzed for trace metals must be acidified to pH <2, normally with HNO3 (Fisher Optima grade) to a final concentration of 2% w/v. Filters and other media digested with the microwave procedure contain a combination of HNO3, HCl and HF at a final total acid concentration up to 9% w/v.

8.3. All samples must be stored in Teflon or low-density polyethylene containers.

9. Instrument Setup, Tuning and Calibration

9.1. Initial conditions must be met prior to lighting the plasma.

9.1.1. Inspect the torchbox area. The cones must be clean and free of scratches or dents. The torch must be clean and the guard electrode intact. Verify there is a tight seal between

the torch glassware and spraychamber. If the torch or bonnet are dirty, or if an air leak is present, arcing may occur that can damage the guard electrode during the ignition process. Wipe any corrosion from the grounding straps with a cleanroom wiper or green scouring cloth.

9.1.2. Inspect the peristaltic pump tubing and lock the tensioners in place. Tubing must be replaced after it has been stressed beyond its elastic limit and remains flat.

9.1.3. Supply the autosampler rinse carboy with fresh 3% HNO3 (trace metal grade) and verify the waste carboy has sufficient capacity.

9.2. Tuning the ELEMENT2

9.2.1. Use the Instrument page of the ELEMENT software to start and stop the instrument.

9.2.2. Verify the peristaltic pump is rotating and the spraychamber is draining correctly. Inspect the tubing connections for leaks. Allow the instrument to warm up for 20 minutes after lighting the plasma before attempting to tune.

9.2.3. Move the autosampler probe to a vial containing the 1 µg/L Element tuning solution. Perform a B scan from 7 – 254 amu for 5 minutes to warm-up the magnet.

9.2.4. ACF update: The SEM calibration between analog and counting detection modes is automatically updated by the software provided a segment is scanned in "both" detector mode for at least 10 acquisitions. The calibration "fit" can be verified visually by viewing a scan in SHOW. In the Show window, select View, detector mode, then check the boxes for analog and counting mode. The scan will appear in the window with the analog peak in red and counting peak in blue. Where the peak intensity is less than 5.0×10^6 counts per second, the blue peak should appear without any red at the maximum.

9.2.5. Low resolution tuning: Open the Tune window of the software. Load the Li_In_U.scn file and begin scanning in low resolution. Adjust the plasma group parameters to obtain a signal of 1.0×10^6 cps at ^{115}In, 1.8×10^6 cps at ^{238}U, and 7.0×10^5 cps at ^{7}Li for a 1 µg/L concentration. Refer to Table (B) for normal settings of each tuning parameter. Copy the plasma group parameters to all resolutions. Save the tune

file as the date+nebulizer (e.g. 020107cyc for February 1, 2007, cyclonic nebulizer). Adjust the lens settings to obtain a stable signal. Copy the lens group parameters to all resolutions and save the tune file again.

9.2.6. Medium resolution tuning: Load the '**Thermo_Fe_ArO**' group file and begin scanning in medium resolution to tune the high-resolution lenses. The target resolution in MR mode is 4200. Copy the high resolution lens settings to all resolutions. Save the tune file.

9.2.7. High resolution tuning: Aspirate a solution containing potassium. Load the '**Thermo_K_ArH**' group file and begin scanning in high resolution. Verify that the resolution is above 10000, providing sufficient separation between K and ArH. Adjust the HR lens settings as necessary. Copy the high resolution lens settings to all resolutions. Save the tune file.

9.2.8. Perform a method scan to verify the mass calibration is valid and that the mass windows are sufficiently wide in the sequence method to acquire complete peaks in all resolutions. Use the Show window for visual inspection of the acquired data. If the medium or high resolution data show incomplete peaks, adjust the mass windows or update the mass calibration (Section 9.3) as necessary.

9.2.9. Enter the saved instrument tune settings into the Instrument Tuning Log book. Verify that the sensitivity and peak resolution are within acceptable range (Refer to Table C).

9.3. Mass Calibration Procedure:

9.3.1. Place the auto sampler arm to a vial containing the 1 µg/L Element Tune solution. (Note: the instrument must be tuned before performing a mass calibration). Open the METHOD tab on the acquisition pane of the Instrument page. Select '**LRMC'** for the file ID, Select '**Thermo_masscalibration_LR_wide'** for the Method ID, select '**Mass Calibration'** as the data type. Begin the scanning to acquire data for the Low resolution mass calibration. After the scan is complete, open the '**Mass Calibration**' window and load the '**LRMC**' file. Update the mass calibration by selecting the automatic update option. Return to the method acquisition window and repeat the procedure using the '**Thermo_masscalibration_LR_Narrow**' method. After the low resolution mass calibration is updated, the procedure must be repeated using the wide and narrow skip region settings for the medium resolution and high resolution acquisition modes. The manufacturer's operating manual should be consulted in case of uncertainty regarding this procedure.

9.4. Sequence Pre-Qualification Parameters

9.4.1. Monitor the sample take-up time and verify that the sample time in the sequence is sufficient.

9.4.2. Monitor the rinse-out time for analytes such as Zn or Rh and verify that the sample wash time in the sequence is sufficient for elements in the method.

9.4.3. Move the auto sampler probe to the rinse position or to a vial with blank solution to aspirate while setting up the sample vials for the sequence.

9.5. Method Set-up

9.5.1. The Method file designates the isotopes to be monitored at each resolution and parameters such as the mass widow, scan type, integration time, and detector mode. It also defines the number of acquisition scans at each resolution. The method used for a sequence is determined by the type of samples to be analyzed and requested elements. Specific methods have been constructed for on-going projects.

9.5.2. It is recommended to create a low resolution method based on the analysis method used to run at the end of a sequence. This will allow the sequence to finish and remain with the slit

position at the low resolution setting and shield the entrance slits from excess wear from the ion beam.

9.6. Analytical Sequence Set-up

9.6.1. Data acquisition on the ELEMENT consists of a sequence file with a list of samples. The sample information includes the name, method used, calibration, and auto sampler uptake and wash times, Use the SEQUENCE window to enter the sample information into a unique sequence file. Save the sequence with the proper date code or batch ID.

9.6.2. The standard analytical sequence on the ELEMENT includes an initial blank, a 3 - 5 level standard calibration, a second source calibration verification solution, continuing check blanks and continuing calibration verification samples. The primary calibration standard must be prepared from certified stock solutions and entered into the Trace Metal Standards log. The primary standard may be diluted at the sequence set-up time for the mid-range and low calibration level standards. Additional calibration standards with high concentrations of cations or metals may be added to the calibration to increase the calibration range. The default matrix for blanks and standards is 2% HNO3. This matrix may be changed as required by a specific project, however, samples, blanks and standards should be analyzed in the same matrix

9.6.3. Analytical precision is monitored by duplicate analysis for 10% of the samples in the sequence.

9.6.4. Analytical accuracy is monitored by a second source mid-range calibration standard, matrix spike samples and matrix spike duplicate samples on 10% of the samples in the sequence.

9.6.5. The certified reference material SLRS-4 should be analyzed at least once during a sequence or at a frequency determined by the project supervisor.

9.6.6. Sample Dilution: Many samples processed by microwave digestion require dilution. The typical dilution rate is 1:10, where 0.5 ml of sample is added to an auto sampler tube followed by 4.5 ml of blank.

9.6.7. Internal Standard Addition: An internal standard is used for post acquisition correction of drift in the sensitivity. Indium, and bismuth should be added directly to the auto sampler tube prior to dispensing the sample. If not quantified as an

analyte, gallium is also added as an internal standard. Alternately, a mixing coil and peristaltic pump are utilized for on-line addition. The internal standard is added to yield a concentration between 2 and 10 µg/L.

10. Data handling

10.1. Data Export

10.1.1. The completed sequence should be reported in ascii format with the file name as the sequence name. Data in the ascii report file must include the isotope number, measured intensity, standard deviation, relative standard deviation, and centroid mass.

10.1.2. The software program EXCEL is used to processes and calculate the final values for data reporting. Refer to the Data Analysis SOP for details.

11. References

EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry

Analysis of Surface Waters for Trace. Elements By ICP-MS.
Lake Michigan Mass Balance Study Methods Compendium; USEPA,1996; Vol. 3, pp 3-96.

[y]Common molecular ion interferences in ICP-MS.
Michael Plantz, Varian, ICP-MS-6, June, 1996.

[z]A Table of Polyatomic Interferences in ICP-MS.
T.W. May and R.H. Wiedmeyer, U.S. Geological Survey. Atomic Spectroscopy, Vol. 19(5), Sept/Oct 1998.

Appendix I ICP-MS Batch Analysis QA Outline

Sample Type	Frequency
24-36 Samples per Batch	
ICP-MS Qualification	
-Blank Level Check	Before each sample batch
-Stability Check	Before each sample batch
-Sensitivity Check	Before each sample batch
-Resolution Check	Before each sample batch
-Interference Check	Before each new method
Blanks Levels During Run	
Calibration Blank	One per batch
Check Blanks	One for every 12 samples
Recovery	
Blank Matrix Spike	One per batch
Matrix Spike, (MS, MSD)	Four per batch
Internal Standards, (^{115}In,^{209}Bi)	All Samples
Precision	
Replicate Sample Acquisitions	Four per resolution
Lab Duplicates (within batch)	Two per batch
Calibration Check (CCV)	One every 12 samples
Accuracy	
Initial Calibration Verification standard	One per batch
Standard Reference Material (SLRS-4)	One per batch

Table A: Core Analytes, Resolutions Scanned, and Potential Interferences (relative abundances (%) in parentheses):

		Resolutions Scanned:				
Analyte	***Mass***	***LR***	***MR***	***HR***	**Polyatomic Interferences[y,z]**	**Isobaric Interferences**
Ag	107 (51.84)	x			$^{91}Zr^{16}O^+$	
	109 (48.16)	x			$^{92}Zr^{16}OH^+$	
Al	27 (100)		x	x	$^{12}C^{15}N^+$, $^{13}C^{14}N^+$, $H^{12}C^{14}N^+$	
As	75 (100)		x	x	$^{40}Ar^{35}Cl^+$, $^{59}Co^{16}O^+$, $^{36}Ar^{38}ArH^+$, $^{38}Ar^{37}Cl^+$, $^{36}Ar^{39}K^+$, $^{43}Ca^{16}O_2^+$, $^{23}Na^{12}C^{40}Ar^+$, $^{12}C^{31}P^{16}O_2^+$	
Ba	138 (71.70)		x			Ce (0.25), La (0.09)
Be	9 (100)	x				
Ca	43 (0.135)		x	x	$^{27}Al^{16}O^+$	
	44 (2.086)		x	x	$^{12}C^{16}O_2^+$, $^{14}N_2{}^{16}O^+$, $^{28}Si^{16}O^+$	
Cd	111 (12.80)	x			$^{95}Mo^{16}O^+$, $^{94}Zr^{16}OH^+$, $^{39}K_2{}^{16}O_2H^+$	
	114 (28.73)	x			$^{98}Mo^{16}O^+$, $^{98}Ru^{16}O^+$	Sn (0.65)
Ce	140 (88.48)	x	x			
Co	59 (100)		x		$^{43}Ca^{16}O^+$, $^{42}Ca^{16}OH^+$, $^{24}Mg^{35}Cl^+$, $^{36}Ar^{23}Na^+$, $^{40}Ar^{18}OH^+$, $^{40}Ar^{19}F^+$	
Cr	52 (83.79)		x		$^{35}Cl^{16}OH^+$, $^{40}Ar^{12}C^+$, $^{36}Ar^{16}O^+$, $^{37}Cl^{15}N^+$, $^{34}S^{18}O^+$, $^{36}S^{16}O^+$, $^{38}Ar^{14}N^+$, $^{36}Ar^{15}NH^+$, $^{35}Cl^{17}O^+$	
	53 (9.50)		x		$^{37}Cl^{16}O^+$, $^{38}Ar^{15}N^+$, $^{38}Ar^{14}NH^+$, $^{36}Ar^{17}O^+$, $^{36}Ar^{16}OH^+$, $^{35}Cl^{17}OH^+$, $^{35}Cl^{18}O^+$, $^{36}S^{17}O^+$, $^{40}Ar^{13}C^+$	
Cs	133 (100)	x			$^{101}Ru^{16}O_2^+$	
Cu	63 (69.17)		x		$^{31}P^{16}O_2^+$, $^{40}Ar^{23}Na^+$, $^{47}Ti^{16}O^+$, $^{23}Na^{40}Ca^+$, $^{46}Ca^{16}OH^+$, $^{36}Ar^{12}C^{14}NH^+$, $^{14}N^{12}C^{37}Cl^+$, $^{16}O^{12}C^{35}Cl^+$	
Dy	163 (24.9)	x	x		$^{147}Sm^{16}O^+$	
	164 (28.2)	x	x			Er (1.61)
Eu	153 (52.2)	x	x		$^{137}Ba^{16}O^+$	
Fe	56 (91.72)		x	x	$^{40}Ar^{16}O^+$, $^{40}Ca^{16}O^+$, $^{40}Ar^{15}NH^+$, $^{38}Ar^{18}O^+$, $^{38}Ar^{17}OH^+$, $^{37}Cl^{18}OH^+$	
	57 (2.2)		x	x	$^{40}Ar^{16}OH^+$, $^{40}Ca^{16}OH^+$, $^{40}Ar^{17}O^+$, $^{38}Ar^{18}OH^+$, $^{38}Ar^{19}F^+$	
Ga	69 (60.11)	x	x	x	$^{35}Cl^{16}O^{18}O^+$, $^{35}Cl^{17}O_2^+$, $^{37}Cl^{16}O_2^+$, $^{36}Ar^{33}S^+$, $^{33}S^{18}O_2^+$, $^{34}S^{17}O^{18}O^+$, $^{36}S^{16}O^{17}O^+$, $^{33}S^{36}S^+$	
	71 (39.89)	x	x	x	$^{35}Cl^{18}O_2^+$, $^{37}Cl^{16}O^{18}O^+$, $^{37}Cl^{17}O_2^+$, $^{36}Ar^{35}Cl^+$, $^{36}S^{17}O^{18}O^+$, $^{38}Ar^{33}S^+$	
Hf	178 (27.30)	x	x			
Ho	165 (100)	x	x	x	$^{149}Sm^{16}O^+$	
K	39 (93.26)		x	x	$^{38}ArH^+$	
La	139 (99.91)	x	x			
Li	7 (92.5)	x				
Lu	175 (97.41)	x	x		$^{159}Tb^{16}O^+$	
Mg	25 (10.00)		x	x	$^{12}C_2H^+$, $^{12}C^{13}C^+$	
Mn	55 (100)		x	x	$^{40}Ar^{14}NH^+$, $^{39}K^{16}O^+$, $^{37}Cl^{18}O^+$, $^{40}Ar^{15}N^+$, $^{38}Ar^{17}O^+$, $^{36}Ar^{18}OH^+$, $^{38}Ar^{16}OH^+$, $^{37}Cl^{17}OH^+$, $^{23}Na^{32}S^+$, $^{36}Ar^{19}F^+$	
Mo	95 (15.92)		x		$^{40}Ar^{39}K^{16}O^+$, $^{79}Br^{16}O^+$	
Na	23 (100)		x	x		
Nb	93 (100)	x				

Nd	143 (12.18)	x	x			
	146 (17.19)	x	x		$^{98}Ru^{16}O_3^+$	
Ni	60 (26.22)		x		$^{44}Ca^{16}O^+$, $^{23}Na^{37}Cl^+$, $^{43}Ca^{16}OH^+$	
P	31 (100)		x		$^{14}N^{16}OH^+$, $^{15}N_2H^+$, $^{15}N^{16}O^+$, $^{14}N^{17}O^+$, $^{13}C^{18}O^+$, $^{12}C^{18}OH^+$	
Pb	208 (52.4)	x			$^{192}Pt^{16}O^+$	
Pd	106 (27.33)	x				Cd (1.25)
	108 (26.46)	x				Cd (0.89)
Pr	141 (100)	x	x			
Pt	195 (33.8)	x	x			
Rb	85 (72.16)	x	x			
Rh	103 (100)	x	x			
Ru	101 (17.0)	x	x		$^{40}Ar^{61}Ni^+$, $^{64}Ni^{37}Cl^+$	
	102 (31.6)	x	x			Pd (1.02)
S	32 (95.02)		x	x	$^{16}O_2^+$, $^{14}N^{18}O^+$, $^{15}N^{17}O^+$, $^{14}N^{17}OH^+$, $^{15}N^{16}OH^+$, $^{14}N^{16}OH_2^+$	
Sb	121 (57.36)	x			$^{105}Pd^{16}O^+$	
Sc	45 (100)		x		$^{12}C^{16}O_2H^+$, $^{13}C^{16}O_2^+$, $^{28}Si^{16}OH^+$, $^{29}Si^{16}O^+$, $^{14}N_2{}^{16}OH^+$	
Se	77 (7.63)	x	x		$^{40}Ar^{37}Cl^+$, $^{36}Ar^{40}ArH^+$, $^{38}Ar_2H^+$, $^{12}C^{19}F^{14}N^{16}O_2^+$	
	82 (8.73)	x	x		$^{12}C^{35}Cl_2^+$, $^{34}S^{16}O_3^+$, $^{40}Ar_2H_2^+$	Kr (11.6)
Sm	152 (26.7)	x	x		$^{104}Ru^{16}O_3^+$	Gd (0.20)
Sn	118 (24.23)	x	x		$^{102}Ru^{16}O^+$, $^{102}Pd^{16}O^+$	
	120 (32.59)	x	x		$^{104}Ru^{16}O^+$, $^{104}Pd^{16}O^+$	Te (0.10)
Sr	88 (82.58)		x			
Te	126 (18.95)	x	x		$^{110}Pd^{16}O^+$	Xe (0.09)
	128 (31.69)	x	x		$^{96}Ru^{16}O_2^+$	Xe (1.91)
Th	232 (100)	x				
Ti	48 (73.8)		x		$^{31}P^{16}OH^+$, $^{32}S^{16}O^+$, $^{34}S^{14}N^+$, $^{33}S^{15}N^+$, $^{14}N^{16}O^{18}O^+$, $^{14}N^{17}N_2^+$, $^{12}C_4^+$, $^{36}Ar^{12}C^+$	Ca (0.19)
	49 (5.5)		x		$^{32}S^{16}OH^+$, $^{32}S^{17}O^+$, $^{35}Cl^{14}N^+$, $^{34}S^{15}N^+$, $^{33}S^{16}O^+$, $^{14}N^{17}O_2H^+$, $^{14}N^{35}Cl^+$, $^{36}Ar^{13}C^+$, $^{36}Ar^{12}CH^+$, $^{12}C^{37}Cl^+$, $^{31}P^{18}O^+$	
Tl	205 (70.48)	x				
U	238 (99.27)	x				
V	51 (99.75)	x			$^{35}Cl^{16}O^+$, $^{34}S^{16}OH^+$, $^{38}Ar^{13}C^+$, $^{36}Ar^{15}N^+$, $^{36}Ar^{14}NH^+$, $^{37}Cl^{14}N^+$, $^{36}S^{15}N^+$, $^{33}S^{18}O^+$, $^{34}S^{17}O^+$	
W	182 (26.3)	x	x		$^{166}Er^{16}O^+$	
	184 (30.67)	x	x			Os (0.02)
Y	89 (100)	x	x			
Yb	174 (31.8)	x	x			Hf (0.16)
Zn	66 (27.9)		x		$^{50}Ti^{16}O^+$, $^{34}S^{16}O_2^+$, $^{33}S^{16}O_2H^+$, $^{32}S^{16}O^{18}O^+$, $^{32}S^{17}O_2^+$, $^{33}S^{16}O^{17}O^+$, $^{32}S^{34}S^+$, $^{33}S_2^+$	

Secondary analytes which can also be analyzed:						
Au	197 (100)		x	x	$^{181}Ta^{16}O^{+}$	
B	11 (80.1)	x				
Er	166 (33.6)	x	x		$^{150}Nd^{16}O^{+}$, $^{150}Sm^{16}O^{+}$	
	167 (22.95)	x	x		$^{151}Eu^{16}O^{+}$	
Gd	157 (15.65)		x	x	$^{138}Ba^{19}F^{+}$, $^{141}Pr^{16}O^{+}$	
Ge	72 (27.66)			x	$^{40}Ar^{32}S^{+}$, $^{38}Ar^{34}S^{+}$, $^{36}Ar_2^{+}$, $^{37}Cl^{17}O^{18}O^{+}$, $^{35}Cl^{37}Cl^{+}$, $^{36}S^{18}O_2^{+}$, $^{36}S_2^{+}$, $^{36}Ar^{36}S^{+}$, $^{56}Fe^{16}O^{+}$, $^{40}Ar^{16}O_2^{+}$, $^{40}Ca^{16}O_2^{+}$	
Ir	193 (62.7)		x	x		
Os	189 (16.1)		x	x		
Re	185 (37.40)		x	x		
Si	28 (92.23)		x	x	$^{14}N_2^{+}$, $^{12}C^{16}O^{+}$	
Ta	181 (99.99)	x	x		$^{165}Ho^{16}O^{+}$	
Tb	159 (100)	x	x		$^{143}Nd^{16}O^{+}$	
Tm	169 (100)	x	x		$^{153}Eu^{16}O^{+}$	
Zr	90 (51.45)		x	x		