Standard Operation Procedure

Elemental Analysis of Solution samples with Inductively Coupled Plasma Mass Spectrometry

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1. Application

This method covers the analysis of minor and trace elements in solution samples by ICP-MS (VG PlasmaQuad PQ2 Turbo Plus ICP-MS).

2. Summary of method

2.1 Principle: *An aqueous sample* is converted to aerosols via a nebulizer. The aerosols are transported to the inductively coupled plasma which is a high temperature zone (8,000–10,000ºC). The analytes are heated (excited) to the respective ions. In a quadrupole mass filter, these ions are separated based on their mass-to-charge ratios (For example, the mass-to-charge ratio is 7 for $^{7}Li^{+}$, ^{70} for $^{140}Ce^{++}$, ^{140} for $^{140}Ce^{+}$, and 238 for $^{238}U^{+}$, respectively) and the ion intensities at different masses are measured (mass spectrometry). These ion intensities are proportional to the respective concentrations of analytes in the aqueous sample. The quantification is *an external multi-point linear calibration* by comparing the ion intensity of an unknown sample with that of a standard sample. Multi-element calibration standard solutions are prepared from single- and multi-element primary and/or in-house working standard solutions. Rhodium (Rh) is used as an internal reference standard. With respect to other kinds of analysis where chemical speciation is relevant (such as the concentration of ferrous iron or ferric iron), only *total elemental concentration* is analyzed by ICP-MS.

2.2 Brief procedure: Working standard solutions are freshly prepared from primary standard solutions and in-house stock standard solutions. The sample introduction system (pump and nebulizer) is visually checked. The instrument is started and let stabilized. Unknown samples are measured along with standardization blanks, other kinds of blanks, working standard solutions, drift control samples, and quality control samples. After a batch of samples are measured, the data are downloaded to an Excel spreadsheet. The data are corrected in terms of standardization blanks, other relevant blanks, drift correction, and dilution

factor application. The results are normalized to the internal reference standard. The quantification is a multi-point external linear calibration.

3. Safety

All relevant laboratory safety procedures are followed.

4. Interference

This method covers the analysis of over 30 elements in different kinds of samples by ICP-MS. A general discussion of interferences is lengthy but not necessarily relevant to a specific element/isotope, which is especially true if the sample matrix is not specifically defined. Reading the published articles is recommended. There is an enormous amount of literature relevant to the analysis of metals and non-metals by ICP-MS.

5. Sample collection, preservation and handling

Containers (bottles, vials, etc) typically are soaked in 10% nitric acid overnight and rinsed with de-ionized water for several times before use. Solution samples typically are acidified with nitric acid at a ratio of 1 – 5 mL of concentrated nitric acid to 1 liter of sample. Extra cautions need to be exercised in preventing contamination and preserving samples for some specific analyses.

6. Apparatus and device

6.1 ICP-MS: VG PlasmaQuad PQ2 Turbo Plus ICP-MS.

6.2 Fourteen-mL polystyrene test tubes (17 mm × 100 mm. e.g. Falcon plastic tubes. Cat #14-959-8 by Fisher Scientific) for the ICP-MS autosampler are cleaned by soaking in 10% nitric acid overnight and rinsed with de-ionized water. The tubes are air-dried before use.

7. Reagents

7.1 Concentrated nitric acid (e.g. TraceMetal grade. Cat # A509-212 by Fisher Scientific).

7.2 Single-element and multi-element primary standard solutions (SPEC).

7.3 In-house ICP-OES working standard solutions (Details of the ICP-OES work standard solutions are presented in a separate document “Elemental analysis of solution samples with ICP-OES”).

8. Measurement by ICP-MS

8.1 MS working standard

8.1.1 Set 14-ml Falcon tubes in the ICP-MS autosampler rack.

8.1.2 Add 10 mL of 2 % (v/v) nitric acid to each tube and label the tubes accordingly (i.e. MS 1, MS 2, MS 3, MS 4, MS 5 and MS 6).

8.1.3 The tube MS 1 serves as a calibration blank.

8.1.4 Prepare the MS working standard solutions in the rest 5 Falcon tubes from the in-house OES working standard solutions and from the SPEC primary standard solutions (CLMS-2, CLMS-3 and CLMS-4). Add the solutions following Table 1: Working standards for ICP-MS.

Note: this method covers over 30 elements. Since the analysis by ICP-MS is flexible and can be easily expanded to other elements, and the standards of MS2–MS6 may not cover

the concentration ranges of several elements in samples, the working standards may be made in different ways.

8.1.5 MS6 contains 20 ppb of Rh (SPEC CLMS-3 contains 10 ppm of Rh already). Spike 0.02 mL of 2 ppm Rh to MS1 – MS5 as the IRS. The nominal concentration is 4 ppb.

8.2 Preparing sample solutions for ICP-MS

8.2.1 For "routine" samples, add solution samples (10 mL) to 14-mL Falcon tubes.

8.2.2 Spike 0.02 mL of 2 ppm Rh as the IRS. The nominal concentration is 4 ppb.

8.2.3 Prepare "none-routine" samples in some other methods, depending on the requested analyses, sample matrix, analyte concentrations, etc. For example, low-volume or "over-concentrated" samples are diluted before analysis. Turbid samples are left to stand overnight so that particles settle down to the bottom, or the samples are centrifugated so that particles are separated from the samples.

8.2.4 After a given amount of sample (weight or volume) is spiked with a given amount of rhodium (Rh), the concentration ratio of (analyte/Rh) is later used for quantification. Any further dilution does not change the concentration ratio (see Appendix 1 of "Elemental analysis of solution sample with ICP-OES").

8.3 ICP-MS measurement

8.3.1 Clean the cones.

8.3.2 Set up the sample introduction system. Visually check the nebulization performance. Start the instrument. Let it stabilize. The relevant instrument conditions are listed in Table 2: ICP-MS Instrument Conditions.

8.3.3 In the instrument's software, edit the acquisition procedure. General sequence: calibration blanks (i.e. 2% nitric acid with 4 ppb of Rh), calibration standard solutions (i.e. MS2 – MS6), QC or quality control sample(s), wash sample, 10-20 samples, QC(s), 10-20 samples, QC(s), and so on.

8.3.4 In the Menu, select "spal acq" containing 30+ isotopes. Edit the menu depending on specific samples or analytical requests. The analysis by ICP-MS is flexible and is easily expanded to other elements. In combination of 8.1 (MS working standard), both of the working standard and the acquisition menu can be changed accordingly for additional elements.

8.3.5 Tune the instrument. Check and confirm the instrument's general performance such as blank level, sensitivity, and stability.

8.3.6 Condition the cones by analyzing 10–15 sample solutions.

Note: With materials being deposited to the cones during samples being analyzed, the cone's condition changes with time. The change is most significant after the cones are just cleaned. In this sense, the cones need to be "conditioned" or "aged" after being cleaned. If the cones have been "slightly" used and step 8.3.1 is skipped, the condition process may be skipped.

8.3.7 Check the instrument blank levels again, especially the blank levels of Cr, Cu, Zn, Mo and Pb.

8.3.8 Set the sample rack(s) into place. Start the whole acquisition sequence.

9. Data processing after ICP-MS analysis

9.1 Download all of the acquisition data into an in-house Microsoft Excel spreadsheet "SPAL" program. Check the intensities of: internal reference standard (IRS, Rh: drifting down with increasing time and drifting up/down accordingly with sample matrix), calibration blanks and other kinds of blanks (no significant contaminations), quality control samples (drifting in an expected manner), and other samples (the change of acquisition mode from pulse counting to analog counting, extraordinarily high/low intensities).

9.2 Back in the procedure of the ICP-MS software, select/set/change the IRS concentration for the procedure. Edit IRS concentrations for individual samples if there are differences (e.g. MS6 contains 20 ppb while most samples contain 4 ppb of Rh).

9.3 Use the calibration blank (MS1) as the blank for other working standard solutions (MS2–MS6), calculate the slopes. Inspect the calibration lines.

9.4 Calculate the concentrations of other samples (conc. = intensity/slope). No blank correction yet for other samples at this step.

9.5 Download all of the concentration data into the in-house Microsoft Excel spreadsheet "SPAL" program.

9.6 Use the result of the quality control (QC) sample to correct for drift (with time). It is assumed that the drift is linear between two bracketing QC samples.

9.7 Use the calibration blank (MS-1) as the blank for the samples, carry out blank subtraction.

9.8 If relevant, use the digestion blank to correct the digest blank for digested samples, or use the appropriate blank for some other kind of blank correction.

9.9 Check the results against their respective detection limits.

9.10 Apply dilution factors if appropriate.

9.11 Generate out-going reports.

10. Quality assurance (QA) and quality control (QC)

An ICP-MS instrument is used for broad applications in unlimited situations. A general discussion about QA/QC practice is not specific to a particular application, yet detailed discussions about various applications become too lengthy and are beyond the scope of this procedure. It should be reminded that the QA/QC for any specific isotope/element has to be evaluated under certain specifications/conditions. The time in setting the QA/QC criteria is well spent only when the sample matrix is defined, the instrument and its condition are defined, and the target isotope/element is defined. Presented here are some basic operations.

10.1 The calibration standards are made from primary standards and in-house ICP-OES working standards. The in-house ICP-OES working standards are made from primary standards of several independent sources and confirmed by using some other independent primary solutions (The details of the in-house ICP-OES working standards are presented in Appendix 3 – Strategies and

implementation of quality assurance (QA) and quality control (QC) in the elemental analysis of solution samples with ICP-MS). In this way, the quality of the calibration standard is assured.

10.2 Samples are diluted to different ratios and measured. The results are used to evaluate matrix effects and dynamic ranges (calibration ranges).

10.3 Samples are analyzed by the calibration of internal standard addition.

10.4 Samples are analyzed by using ICP-OES.

10.5 Some basic performance or data are listed in Table 3: The analysis by ICP-MS. An in-house quality control water (msQC) is diluted by five times and is analyzed each time for a batch of unknown samples. The results of the msQC water are confirmed against the expected values.

10.6 The in-house quality control water (msQC) was made in 1998. The expected values are compiled from the side-by-side analysis of this msQC water with NIST 1643d water, the historical results of this msQC water by the ICP-MS analysis, and the historical results of this msQC water by the ICP-OES analysis. The results are presented in Table 4: In-house msQC value.

10.6.1 The historical results of this msQC water by ICP-OES and some limited discussion are given in Appendix 3 – Strategies and implementation of quality assurance (QA) and quality control (QC) in the elemental analysis of solution samples with ICP-OES.

10.6.2 As presented in Table 4, the values obtained in 1998 by ICP-MS and the values obtained in 2005 are in an excellent agreement for most isotopes/elements.

10.6.3 The concentrations of those elements in red color in Table 4 apparently increased with time. As discussed in Appendix 3 of "Solution samples by ICP-OES," this is due to the release of these elements from the container – glass bottle (Platinum is the exception).

10.6.4 The ICP-MS results of magnesium and vanadium might be interfered and less reliable than the results by ICP-OES. The analysis of selenium by ICP-MS might be better than that by ICP-OES.

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Table 1: Working standards for ICP-MS

The ICP-MS working standards (MSn, n = 2 - 6) are made from the in-house ICP-OES working standards (OESn, n = 1 - 5) and SPEC primary standards (CLMSn, n = 2 - 4).
MS1 = OES1 = 2 % nitric acid. OES5 actually is reserved for future use.
Elements of black color in CLMS 2&4 are from CLMS2.
Elements of red color in CLMS 2&4 are from CLMS4.

	In-house OES working standards				SPEC CLMS		selected	MS2	MS3	MS4	MS5	MS6
								mL from these standards, to ppb unit				
	OES2 ppm	OES3 ppm	OES4 ppm	OES5 ppm	2&4 ppm	3 ppm		OES2 0.02	OES3 0.02	OES4 0.02	2&4 0.02	3 0.02
Li	2		10		10		yes	4		20	20	
Be	1	1			10		yes	2	2		20	
B	2		10		10		yes	4		20	20	
Na		20	100		10				40	200	20	
Mg	2	20	100	300	10			4	40	200	20	
Al	2	10	100		10			4	20	200	20	
Si			5	10	10					10	20	
P	5	20	100	400	10			10	40	200	20	
S	2	20	100	400	10			4	40	200	20	
K	5	20	100	500	10			10	40	200	20	
Ca	2	20	100	400	10			4	40	200	20	
Ti	2	5			10		yes	4	10		20	
V	1	5			10		yes	2	10		20	
Cr	0.5	2			10		yes	1	4		20	
Mn	1	1	4	40	10			2	2	8	20	
Fe	2	10	100		10			4	20	200	20	
Co	1	5			10		yes	2	10		20	
Ni	2	5			10		yes	4	10		20	
Cu	2	2	20		10		yes	4	4	40	20	
Zn	1	1	20		10		yes	2	2	40	20	
Ga					10		yes				20	
Ge					10		yes				20	
As	2	5			10		yes	4	10		20	
Se	2	5			10		yes	4	10		20	
Rb					10		yes				20	
Sr	2				10		yes	4			20	
Y			5	10						10		20
Zr					10						20	
Nb					10						20	
Mo	1		10		10		yes	2		20	20	
Ru						10	yes					20
Rh						10	IRS					20

Table 1: Working standards for ICP-MS (cont'd)

	In-house OES working standards				SPEC CLMS		selected	MS2	MS3	MS4	MS5	MS6
								mL from these standards, to ppb unit				
	OES2 ppm	OES3 ppm	OES4 ppm	OES5 ppm	2&4 ppm	3 ppm		OES2 0.02	OES3 0.02	OES4 0.02	2&4 0.02	3 0.02
Pd						10	yes					20
Ag		1	2		10		yes		2	4	20	
Cd	1	1			10		yes	2	2		20	
In					10		yes				20	
Sn						10	yes					20
Sb		2	5			10	yes		4	10		20
Te						10						20
Cs					10		yes				20	
Ba	1	10			10		yes	2	20		20	
Hf						10						20
Ta					10						20	
W					10						20	
Re					10						20	
Ir						10						20
Pt						10	yes					20
Au						10	yes					20
Tl	2	5			10		yes	4	10		20	
Pb	2	5			10		yes	4	10		20	
Bi	1		2		10		yes	2		4	20	
U					10		yes				20	

Table 2: ICP-MS Instrument Conditions

ICP-MS	VG PlasmaQuad PQ2 Turbo Plus ICP-MS
Plasma forward power	1350 W
Plasma reflected power	< 5 W
Coolant gas flow rate	14 liter/min
Auxiliary gas flow rate	0.6 liter/min
Nebulizer gas flow rate	0.83 liter/min
Nebulizer	Conikal (nominal flow rate: 1 mL/min)
Spray chamber	Double-pass Scott-type
Spray chamber temperature	Water-cooled at 5C
Sampling depth	10 mm
Sample cone	1.0 mm nickel
Skimmer cone	0.7 mm nickel
Ion lenses setting	Optimized on 115In
Sample uptake rate	0.85 mL/min
Sample uptake time	50 s
Acquisition time	60 s twice
Wash time	15 s
Acquisition menu	spal acq
Detector mode	Dual
Acquisition format	Scan
Dwell PC	320 us
Dwell analog	640 us
Channels/amu	24
Start mass	5.6 amu
End mass	238.4 amu
Mass skip range	10.4 - 48.6
(Mass skip range may be	53.4 - 57.6
set to different values	78.4 - 80.6
depending on specific	88.4 - 96.6
samples)	123.4 - 132.6
	136.4 - 194.6
	210.4 - 236.6

Table 3: The analysis by ICP-MS

		Mass	Slope	LOD	cBlk	msQC/5
			cps/ppb	ppb	ppb	ppb
1	Li	7	19775	0.02	1.15	6.2
2	Be	9	3893	0.06	0.01	4.1
3	B	10	506	0.20	0.83	35.3
4	Ti	49	346	0.20	0.30	5.4
5	V	51	5582	0.03	0.27	7.4
6	Cr	52	4949	0.10	0.44	8.5
7	Co	59	6492	0.01	0.01	3.4
8	Ni	60	1521	0.10	0.36	3.7
9	Cu	65	1699	0.10	0.04	18.8
10	Zn	66	553	0.30	1.63	10.1
11	Ga	71	4455	0.02	0.01	0.4
12	Ge	74	837	0.20	0.07	11.8
13	As	75	673	0.10	0.15	11.6
14	Se	82	61	2.00	1.42	14.6
15	Rb	85	4823	0.02	0.01	36.4
16	Sr	86	702	0.01	0.13	8.8
17	Mo	98	1506	0.05	0.02	4.8
18	Ru	101	1116	0.02	0.01	3.8
19	Pd	108	1793	0.06	0.02	6.1
20	Ag	109	3071	0.02	0.01	3.2
21	Cd	111	602	0.06	0.03	22.5
22	In	115	6789	0.01	0.002	0.04
23	Sn	118	1463	0.03	0.02	9.7
24	Sb	121	1536	0.02	0.01	7.8
25	Cs	133	5520	0.01	0.004	8.5
26	Ba	135	390	0.10	0.06	9.2
27	Pt	195	1553	0.05	0.01	3.7
28	Au	197	1952	0.03	0.01	0.4
29	Tl	205	4822	0.02	0.003	5.8
30	Pb	208	3313	0.03	0.04	13.1
31	Bi	209	3964	0.02	0.02	5.8
32	U	238	6461	0.02	0.003	7.2

Table 4: In-house msQC value

Si, P, S and Cl: ppm. Others: ppb

	1998	2005 ICP-MS		2005 ICP-OES			1998	2005 ICP-MS		2005 ICP-OES	
	avg	avg	sd	avg	sd		avg	avg	sd	avg	sd
Li 7	31	31	2	30	1	Ag 109	15.8	16.3	0.4		
Be 9	20	20	1			Cd 111	113	112	7	112	2
B 10	178	176	9	175	2	In 115	0.2	0.2	0.1		
Na 23	135			306	5	Sn118	48	49	1		
Mg 26	287	282	17	265	13	Sb 121	38	40	2		
Al 27	32	63	9	82	9	Te 125	120				
Si 28	1.4			2.9	0.0	I 127	8				
P 31	2.9			3.1	0.1	Cs 133	42	43	1		
S 34	4.6			4.6	0.1	Ba 138	46	46	2	46	1
Cl 35	25.0					La 139	54				
K 39				135	10	Ce 140	54				
Ca 44	418			831	26	Pr 141	31				
Sc 45	57					Nd 146	55				
Ti 49	27	29	2	26	1	Sm 147	55				
V 51	43	43	2	37	2	Eu 153	0.02				
Cr 52	43	43	3	42	1	Gd 157	52				
Mn 55	46	49	2	51	0	Tb 159	19				
Fe 56	166	221	4	228	3	Dy 163	32				
Co 59	17	17	1	16	2	Ho 165	31				
Ni 60	18	18	1	19	2	Er 167	31				
Cu 65	93	95	5	95	3	Tm 169	31				
Zn 66	49	51	3	52	3	Yb 172	31				
Ga 69	2.1	1.9	0.2			Lu 175	31				
Ge 74	57	61	5			Hf 178	32				
As 75	55	59	5	61	13	Ta 181	28				
Br 81						W 184	24				
Se 82	74	72	3	56	10	Os 189	12				
Rb 85	173	182	3			Ir 193	31				
Sr 88	43	45	1	44	1	Pt 195	30	19	2		
Y 89	28	26	1	29	3	Au 197	2.2	2.1	0.6		
Zr 90	70					Tl 205	29	29	1		
Nb 93	31					Pb 208	64	64	2	69	6
Mo 98	25	25	1	22	3	Bi 209	29	29	1		
Ru 99	19	19	2			Th 232	36				
Pd 105	30	31	1			U 238	36	36	1		