Application note | 001007

Elemental analysis

Sub-ppt level automated analysis of impurities in nitric acid–hydrogen peroxide solution via HR-ICP-MS

Element 2/Element XR High Resolution ICP-MS

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Keywords

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Introduction

High purity chemicals form the basis for a large range of scientific analyses. Acids such as nitric acid (HNO_3) are used as the dilution matrix in many ICP-MS applications aimed at determining trace elemental concentrations of samples in academic and commercial analytical laboratories. For all applications, it is key that the instrument provides low backgrounds and that the sample is not contaminated during the sample preparation and analysis. The purity of mineral acids is of particular importance for the semiconductor industry, where a range of process chemicals (like sulfuric and hydrochloric acids) are employed in various stages of the silicon wafer manufacture. Seastar Chemicals is a manufacturer of high purity reagents, producing ultra-pure acids for trace elemental analysis. A Thermo Scientific™ Element™ 2 HR-ICP-MS is used at Seastar Chemicals to screen reagents for contamination. Here we demonstrate how the low Limits of Detection (LODs, i.e. the lowest concentration that can be measured with statistical significance) and Background Equivalent Concentrations (BECs) which can be achieved with the Element 2 HR-ICP-MS in a clean, dedicated environment are ideally suited for the detection of low levels of contaminants in the screening of high purity chemicals.

HR-ICP-MS is based on magnetic sector field technology which can physically separate a potential interference from the target analyte by resolving their small difference in mass. Within the same method, mass resolution (R) settings (as appropriate) of low

(LR = 300), medium (MR = 4000) and high (HR = 10000) allow interference-free analysis in most sample matrices.

For most samples LODs are measured in hot plasma conditions (HP, corresponding to high plasma power). However, for some elements and depending on the sample matrix, improved LODs can be achieved in cold plasma (CP, corresponding to low plasma power). This is due to the plasma temperature being lower in CP conditions, leading to reduced ionization of Ar and a subsequent reduction in the Ar based interferences. Cold plasma also reduces potential contamination from the torch, injector and skimmer cone (e.g. Na, K, and Fe backgrounds are typically reduced). This allows the use of lower resolution settings for isotopes that were affected by Ar based interferences in HP. For example, in HP K has to be measured in HR, but in CP it can be measured in MR due to the removal of the interfering ^{38}ArH, resulting in an increase in sensitivity.

In this study LODs and BECs were determined for a total of 68 elements. The presented dataset is representative of the typical performance which can be achieved with an Element HR-ICP-MS in a clean environment dedicated to the analysis of high purity chemicals.

Analytical set up and methods

Analysis of 2% HNO_3/ 2% H_2O_2 v/v was carried out at Seastar Chemicals using an Element 2 HR-ICP-MS equipped with a PFA sample introduction system (nebulizer and spray chamber), sapphire injector and Pt sample cone to minimize potential contamination from these instrument parts (Table 1). Additionally, such an inert introduction system is resistant to aggressive matrices. Blanks and samples were introduced automatically via an autosampler.

The choice of the 2% HNO_3/ 2% H_2O_2 v/v matrix for these experiments was based on typical analysis of reagents at Seastar Chemicals. Typically for the analysis of reagents, samples are preconcentrated (to dryness) and reconstituted in 2% HNO_3 + 2% H_2O_2. This provides a concentration factor of 40 to 50 times and a constant matrix. Volatile and refractory elements are analyzed directly or by dilution with ultra-pure water using the method of standard additions.

Table 1. Instrument set up and operating conditions for analysis of high purity 2% HNO_3/ 2% H_2O_2

Sample introduction	ESI™ 100 µL/min PFA nebulizer (self-aspirating); ESI PFA double pass spray chamber; sapphire injector
Cones	Pt standard sample cone Ni X skimmer cone
RF Power	Hot plasma: 1200 W Cold plasma: 600 W
Detection sensitivity (LR)	2.3-2.5 *10^6 cps/ppb ^{115}In

The instrument set up and operating conditions are shown in Table 1.

Before the analysis, plasma conditions were tuned to maximise sensitivity while minimizing oxide formation.

Sixty-one elements were measured in HP and fifteen in CP, of which some repeated. The total analysis time per sample was about 6 minutes to analyse 68 elements ranging from ^{9}Be to ^{238}U (Table 2). Five repeat blank measurements (HP-CP) were carried out over the course of an 8 hour run (with unknown samples measured in the interim).

A major advantage of HR-ICP-MS over TQ-ICP-MS technologies is the speed and simplicity of analysis. The high resolution of the Element HR-ICP-MS enables to measure and resolve analytes without the requirement for reaction gases. The HR-ICP-MS measurement is automatic and does not require any user intervention.

Importantly, for sample-limited customers, the total timing can be further reduced.

Table 2. Take-up, wash-out and analysis time of a single sample with automatic switching between hot and cold plasma

	Take-up time [m:ss]	Analysis time [m:ss]	Wash-out time [m:ss]
Hot Plasma	0:25	2:51	0:30
Cold Plasma	0:00	1:56	0:00

Results

Here we report the LODs and BECs determined on the 2% HNO_3/ 2% H_2O_2 blank analyses.

LOD and BEC are defined as follows:

$$LOD = \frac{(3\text{*stdev of blank intensities})\text{*(concentration of standard)}}{\text{(intensity standard-average intensity of blank)}}$$

$$BEC = \frac{\text{(blank intensities)*(concentration of standard)}}{\text{(intensity standard – average intensity of blank)}}$$

Full results are show in the Appendix (Table A1).

For the majority of elements, it was possible to achieve a LOD < 1 ppt (pg·g^{-1}) with the Element 2 HR-ICP-MS in HP (Figure 1; Table 3). For certain elements, cold plasma conditions prevent the formation of molecular interferences, thereby enabling a lower LOD to be achieved. In cold plasma conditions when Sr is introduced with the multi-element standard solution (as in this study) the doubly-charged ion $^{88}Sr^{++}$ does not form, hence does not interfere on ^{44}Ca. For ^{44}Ca measured in CP, LR a LOD of 5 ppt can thus be achieved, three times better than ^{44}Ca measured in HP, MR. The LOD of ^{63}Cu improved from 0.09 to 0.05 ppt. ^{75}As, which in HP, LR gives a LOD of ca. 6 ppt, can be measured in HP, HR with a LOD which is almost one order of magnitude better. Remarkably the LOD of ^{39}K, ^{56}Fe and ^{58}Ni measured in CP, MR are all ≤ 1 ppt.

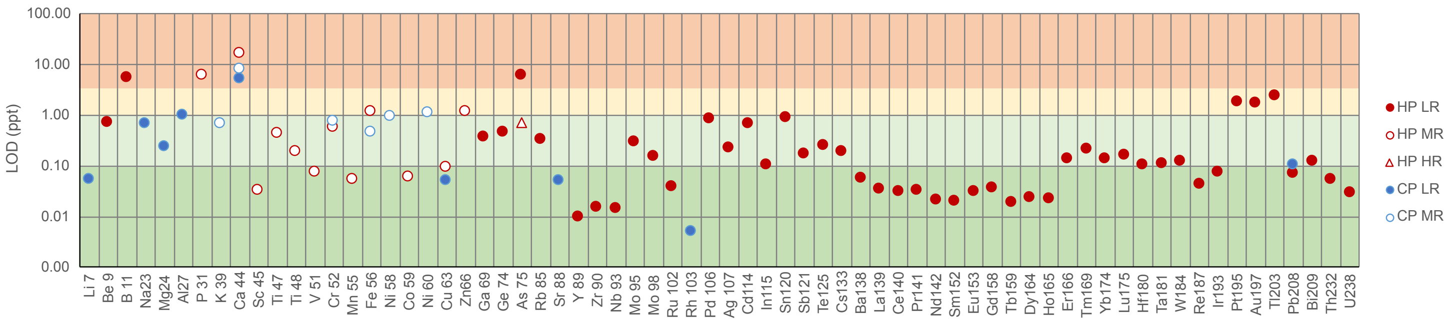

Figure 1. Limit of detection for all 68 elements, showing the difference in LOD between hot (HP; red) and cold (CP; blue) plasma. LR = low resolution (filled circles), MR = medium resolution (open circles), HR = High resolution (triangles).

Table 3. Limit of detection (ppt) for all elements. Note the different LOD between hot and cold plasma for the elements acquired in both modes

LODs (ppt)	Hot plasma			Cold plasma	
	LR	MR	HR	LR	MR
^{7}Li				0.05	
^{9}Be	0.7				
^{11}B	5				
^{23}Na				0.7	
^{24}Mg				0.2	
^{27}Al				1.0	
^{31}P		6			
^{39}K					0.7
^{44}Ca		16		5	8
^{45}Sc		0.03			
^{47}Ti		0.4			
^{48}Ti		0.2			
^{51}V		0.07			
^{52}Cr		0.6			0.7
^{55}Mn		0.05			
^{56}Fe		1.2			0.5
^{58}Ni					1.0
^{59}Co		0.06			
^{60}Ni					1.1
^{63}Cu		0.09		0.05	
^{66}Zn		1.2			
^{69}Ga	0.4				
^{74}Ge	0.5				
^{75}As	6		0.7		
^{85}Rb	0.4				
^{88}Sr				0.05	
^{89}Y	0.01				
^{90}Zr	0.01				
^{93}Nb	0.01				
^{95}Mo	0.3				
^{98}Mo	0.2				
^{102}Ru	0.04				
^{103}Rh				< 0.005	
^{106}Pd	0.9				

LODs (ppt)	Hot plasma			Cold plasma	
	LR	MR	HR	LR	MR
^{107}Ag	0.2				
^{114}Cd	0.7				
^{115}In	0.1				
^{120}Sn	0.9				
^{121}Sb	0.2				
^{125}Te	0.3				
^{133}Cs	0.2				
^{138}Ba	0.06				
^{139}La	0.03				
^{140}Ce	0.03				
^{141}Pr	0.03				
^{142}Nd	0.02				
^{152}Sm	0.02				
^{153}Eu	0.03				
^{158}Gd	0.04				
^{159}Tb	0.02				
^{164}Dy	0.02				
^{165}Ho	0.02				
^{166}Er	0.1				
^{169}Tm	0.2				
^{174}Yb	0.1				
^{175}Lu	0.2				
^{180}Hf	0.1				
^{181}Ta	0.1				
^{184}W	0.1				
^{187}Re	0.04				
^{193}Ir	0.08				
^{195}Pt	2				
^{197}Au	2				
^{203}Tl	2				
^{208}Pb	0.07			0.1	
^{209}Bi	0.1				
^{232}Th	0.05				
^{238}U	0.03				

Conclusions

- The high resolution of the Element Series HR-ICP-MS allows high purity chemicals to be automatically analyzed for a large range of trace elemental concentrations by means of a simple method (employing LR, MR, HR as appropriate and without the need for reaction gases) with a total measurement time of a few minutes.
- As required, cold plasma conditions can be employed to achieve better LODs for some elements (e.g. a typical LOD <1 ppt can be achieved for ^{39}K, ^{56}Fe and ^{58}Ni measured in CP, MR).
- Overall, the low instrument background, the high signal stability and detection sensitivity of the instrument, a clean sample introduction system and the combination of hot and cold plasma power settings (and appropriate tune settings) typically allow to achieve LODs of <1 ppt for most elements in a 2% HNO_3/ 2% H_2O_2 matrix.

Appendix

Table A1. Repeat measurements of 2% HNO_3/ 2% H_2O_2 matrix (blank); the limit of detection and background equivalent concentration were calculated for each isotope using the formula presented in the Results section. The detection sensitivity was determined based on the analysis of a 1 ppb multielement standard solution

	Blank 1 (cps)	Blank 2 (cps)	Blank 3 (cps)	Blank 4 (cps)	Blank 5 (cps)	Average (cps)	St. dev. (cps)	Detection sensitivity (cps/ppb)	LOD (ppt)	BEC (ppt)
Hot plasma										
Be9(LR)	411	354	321	363	388	367	34	$1.4\cdot10^5$	0.7	3
B11(LR)	6474	6174	5315	5479	5529	5794	501	$2.8\cdot10^5$	5	21
Ga69(LR)	951	917	1238	859	962	985	147	$1.2\cdot10^6$	0.4	0.8
Ge74(LR)	4598	4599	4686	4666	4534	4617	61	$4.0\cdot10^5$	0.5	12
As75(LR)	1480	1524	1342	1317	2116	1556	325	$1.6\cdot10^5$	6	10
Rb85(LR)	3633	3610	3197	3339	3647	3485	205	$1.8\cdot10^6$	0.4	2
Y89(LR)	42	32	33	50	47	41	8	$2.5\cdot10^6$	0.01	0.02
Zr90(LR)	45	32	42	45	40	41	5	$1.1\cdot10^6$	0.01	0.04
Nb93(LR)	32	13	35	32	22	27	9	$1.9\cdot10^6$	0.01	0.01
Mo95(LR)	98	63	37	30	27	51	30	$3.0\cdot10^5$	0.3	0.2
Mo98(LR)	446	474	526	493	489	486	29	$5.8\cdot10^5$	0.2	0.8
Ru102(LR)	172	152	155	159	175	162	10	$8.0\cdot10^5$	0.04	0.2
Pd106(LR)	134	90	57	93	490	173	179	$6.2\cdot10^5$	0.9	0.3
Ag107(LR)	561	456	466	489	346	463	78	$1.0\cdot10^6$	0.2	0.4
Cd114(LR)	483	449	546	431	638	509	84	$3.7\cdot10^5$	0.7	1
In115(LR)	269	427	242	249	287	295	76	$2.2\cdot10^6$	0.1	0.1
Sn120(LR)	6044	6108	6330	5740	5992	6043	213	$7.1\cdot10^5$	0.9	9
Sb121(LR)	73	107	53	92	62	77	22	$3.9\cdot10^5$	0.2	0.2
Te125(LR)	11	8	6	10	12	9	2	$2.7\cdot10^4$	0.3	0.3
Cs133(LR)	2139	2157	1796	1950	2104	2029	154	$2.5\cdot10^6$	0.2	0.8
Ba138(LR)	179	252	217	197	260	221	35	$1.9\cdot10^6$	0.06	0.1
La139(LR)	78	85	40	33	43	56	24	$2.1\cdot10^6$	0.03	0.03
Ce140(LR)	12	40	18	20	60	30	20	$1.9\cdot10^6$	0.03	0.02
Pr141(LR)	33	75	23	14	62	41	26	$2.5\cdot10^6$	0.03	0.02
Nd142(LR)	15	13	18	10	27	17	7	$9.4\cdot10^5$	0.02	0.02
Sm152(LR)	22	27	23	23	33	26	4	$6.7\cdot10^5$	0.02	0.04
Eu153(LR)	47	45	40	25	65	44	14	$1.4\cdot10^6$	0.03	0.03
Gd158(LR)	37	40	30	27	48	36	9	$6.9\cdot10^5$	0.04	0.05
Tb159(LR)	18	35	7	8	40	22	15	$2.4\cdot10^6$	0.02	0.009
Dy164(LR)	10	17	8	15	22	14	6	$7.1\cdot10^5$	0.02	0.02
Ho165(LR)	7	45	16	5	34	21	17	$2.4\cdot10^6$	0.02	0.009
Er166(LR)	12	23	90	8	17	30	34	$7.6\cdot10^5$	0.1	0.04
Tm169(LR)	32	37	393	16	45	105	161	$2.3\cdot10^6$	0.2	0.05
Yb174(LR)	10	3	82	2	7	21	34	$7.6\cdot10^5$	0.1	0.03
Lu175(LR)	12	19	266	14	35	69	110	$2.1\cdot10^6$	0.2	0.03
Hf180(LR)	20	8	67	5	7	21	26	$7.6\cdot10^5$	0.1	0.03
Ta181(LR)	52	37	202	45	45	76	71	$2.0\cdot10^6$	0.1	0.04
W184(LR)	32	20	72	18	20	32	23	$5.6\cdot10^5$	0.1	0.06
Re187(LR)	62	40	72	27	38	48	18	$1.3\cdot10^6$	0.04	0.04

Ir193(LR)	93	55	60	32	25	53	27	$1.1\cdot10^6$	0.08	0.05
Pt195(LR)	178	185	710	600	432	421	240	$3.9\cdot10^5$	2	1
Au197(LR)	62	70	65	43	58	60	10	$1.7\cdot10^4$	2	3
Tl203(LR)	1069	553	127	82	118	390	426	$5.4\cdot10^5$	2	0.7
Pb208(LR)	55	53	105	57	85	71	23	$9.9\cdot10^5$	0.07	0.07
Bi209(LR)	105	222	205	65	132	146	67	$1.6\cdot10^6$	0.1	0.09
Th232(LR)	2	5	50	0	3	12	21	$1.2\cdot10^6$	0.05	0.01
U238(LR)	2	6	38	0	4	10	16	$1.6\cdot10^6$	0.03	0.006
P31(MR)	222	261	247	228	212	234	20	$1.0\cdot10^4$	6	23
Ca44(MR)	324	339	392	354	427	367	42	$8.2\cdot10^3$	16	46
Sc45(MR)	17	17	18	23	18	19	2	$2.2\cdot10^5$	0.03	0.09
Ti47(MR)	4	4	3	4	8	4	2	$1.4\cdot10^4$	0.4	0.3
Ti48(MR)	52	39	49	44	63	49	9	$1.5\cdot10^5$	0.2	0.3
V51(MR)	14	19	20	17	27	19	5	$1.9\cdot10^5$	0.07	0.1
Cr52(MR)	283	231	240	222	194	234	32	$1.7\cdot10^5$	0.6	1
Mn55(MR)	30	28	22	29	23	26	4	$2.0\cdot10^5$	0.05	0.1
Fe56(MR)	1795	1599	1690	1733	1663	1696	74	$1.9\cdot10^5$	1.2	9
Co59(MR)	12	12	16	9	20	14	4	$2.2\cdot10^5$	0.06	0.06
Cu63(MR)	32	36	37	37	41	37	3	$1.0\cdot10^5$	0.09	0.4
Zn66(MR)	44	42	43	43	31	41	5	$1.3\cdot10^4$	1.2	3
As75(HR)	2	2	0	0	1	1	1	$3.8\cdot10^3$	0.7	0.3
Cold Plasma										
Li7(LR)	2	6	4	4	9	5	3	$1.6\cdot10^5$	0.05	0.03
Na23(LR)	1104	1250	1341	1194	1180	1214	88	$3.8\cdot10^5$	0.7	3
Mg24(LR)	104	133	140	137	134	130	15	$1.8\cdot10^5$	0.2	0.7
Al27(LR)	312	320	361	382	440	363	52	$1.6\cdot10^5$	1.0	2
Ca44(LR)	156	187	196	176	167	176	16	$9.6\cdot10^3$	5	19
Cu63(LR)	21	19	24	20	18	20	2	$1.4\cdot10^5$	1.2	0.1
Sr88(LR)	2	20	2	6	16	9	8	$4.8\cdot10^5$	0.05	0.02
Rh103(LR)	0	0	0	0	0	0	0	$2.2\cdot10^5$	<0.005	<0.005
Pb208(LR)	0	0	4	2	6	2	3	$7.4\cdot10^4$	0.1	0.03
K39(MR)	27	27	38	32	67	38	17	$7.4\cdot10^4$	0.7	0.5
Ca44(MR)	11	12	13	13	17	13	2	$8.0\cdot10^2$	8	17
Cr52(MR)	27	20	17	16	18	20	4	$1.8\cdot10^4$	0.7	1
Fe56(MR)	17	23	22	19	21	20	2	$1.5\cdot10^4$	0.5	1
Ni58(MR)	15	16	24	16	18	18	4	$1.1\cdot10^4$	1.0	2
Ni60(MR)	5	6	6	8	9	7	2	$4.8\cdot10^3$	1.1	1

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