Analysis of semiconductor grade mineral acids

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Goal

To demonstrate the ideal suitability of the Thermo Scientific™ Element 2™ High Resolution ICP-MS for trace metals analysis in high purity samples, related to the manufacture of semiconductors.

Introduction

With the continual decrease of geometries used in modern IC (integrated circuit) devices, the trace metal content of process chemicals (high purity water, mineral acids, organic solvents, etc.) used in their manufacture is moving to increasingly lower levels.

Mineral acids are employed in various stages of IC device manufacture; for example, sulfuric and hydrochloric acids are used to remove organic and metal contaminants from silicon wafers. Very often the largest source of trace metal contamination in this cleaning process is the chemicals themselves. The trace metal content of these chemicals is therefore critical as high levels of contamination will decrease yields.

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Example 1. Detection Limits (LoD) & Background Equivalent Concentrations (BEC) obtained on the Thermo Scientific Element 2. (Units: pg/g).

	Cold plasma			Hot plasma	
	LoD	BEC		LoD	BEC
^{23}Na	0.03	0.4	^{115}In	0.06	0.4
^{208}Pb	0.09	0.12	^{44}Ca	0.4	1.7
^{39}K	0.14	0.14	^{48}Ti	0.11	0.12
^{56}Fe	0.22	0.08	^{51}V	0.10	0.18
^{60}Ni	0.8	3.3	^{66}Zn	0.6	1.1

Example 2. Spike Recoveries in high purity water.

Isotope	Blank (pg g^{-1})	Spike (pg g^{-1})	% Recovery
^{7}Li	0.01	4.5	91
^{23}Na	3.2	7.8	93
^{24}Mg	0.20	4.9	95
^{27}Al	2.6	7.5	97
^{39}K	0.6	5.9	105
^{52}Cr	4.6	10.1	110
^{55}Mn	0.03	4.7	94
^{56}Fe	0.4	5.0	91
^{59}Co	0.02	4.9	99
^{63}Cu	0.4	5.4	101
^{88}Sr	0.01	4.6	91
^{208}Pb	0.10	5.4	107

Analytical requirements for an ICP-MS method for the analysis of semiconductor grade mineral acids:

1. Low detection limits

For these to be achieved the following requirements are necessary:

- High Sensitivity: Thermo Scientific Element 2 HR-ICP-MS specified sensitivity is >1Mcps/ng/g In, however higher sensitivities are routinely achievable.

- Low and uniform backgrounds: the Thermo Scientific Element 2 HR-ICP-MS specification for dark noise is <0.2cps: independent of mass range or resolution mode.

- Clean sampling: With such high sensitivity and low instrument backgrounds, the measured elemental background is limited by contamination in the analyzed sample: therefore a clean, inert sample introduction system is required:

  – PFA µ-flow self-aspirating nebulizer

  – PFA spray chamber with PFA O-ring free spray chamber endcap with port for make up gas

  – Sapphire or Platinum injectors

  – Quartz torch

  – Pt tipped sample and skimmer cones

With this combination of high sensitivity, low and mass independent background in conjunction with a clean sample introduction system, sub 50 fg g^{-1} detection limits for many elements are achievable not only in relatively easy-to-measure samples such as high purity water and hydrogen peroxide (H_2O_2), but also in more complex samples such as H_2SO_4, H_3PO_4 and HCl.

2. Absolute multi-elemental accuracy: How to avoid spectral interferences

For more complicated matrices however, care has to be taken to avoid matrix induced interferences. Various instrumental methods are now available to remove these interferences.

Mass resolution
- Separates interferences from the target isotope by their small difference in mass:

  – Independent of the source of the interference:

    • Plasma gas (Ar)

    • Sample major matrix ion (S, P, Cl, etc.)

– Can be used with hot or cold plasma

– Direct analysis of the target isotope

– No previous knowledge of the sample matrix required

– No delay from changes in plasma parameters

– Delay from switching resolutions <1s

– No deterioration in random noise background

– True multi-element approach fg g^{-1} detection power maintained

Cold plasma

• Reducing the plasma power reduces Ar based interferences. However, this is not the ideal solution for all elements in all matrices:

– Reduced elemental coverage as elements with relatively high ionization potentials are not ionized

– Non-spectroscopic interferences are increased leading to increased matrix suppression

– Other unexpected interferences may be preferentially formed at such conditions, still requiring high resolution for interference free analysis. Example: determination of ^{55}Mn in 2.5% TMAH (tetramethyl-ammonium hydroxide, $C_4H_{13}NO$).
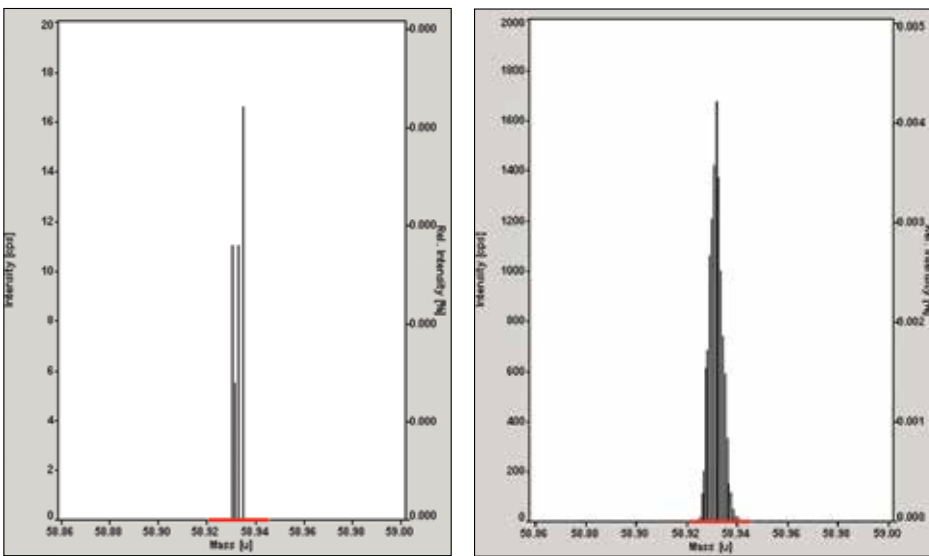

Figure 1. Comparison of spectra for ^{59}Co in blank 10% HCl and for 10 pg g^{-1} ^{59}Co in 10% HCl (R=4000, Hot Plasma).

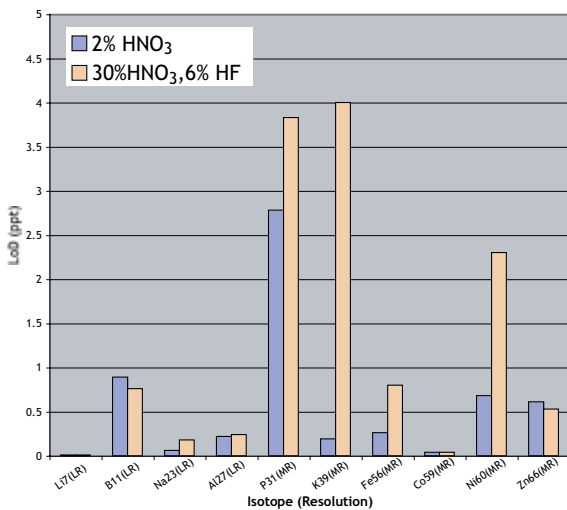## 3. The highest performance independent of sample matrix

Figure 2. Comparison of detection limits (LoD, units: pg g^{-1}) determined in 2% HNO$_3$ and 30% HNO$_3$, 6% HF.
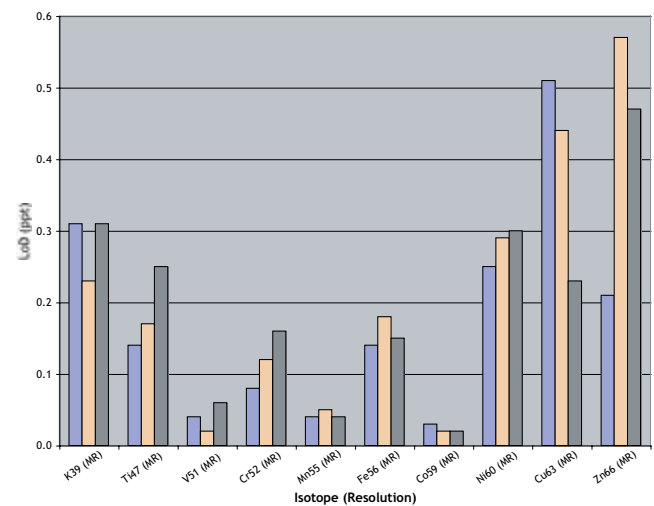
4. Reproducibility of analyses

Figure 3. Reproducibility of detection limits (LoD, units: pg g^{-1}) determined in 6% HNO$_3$, 1.2 %HF. Three separate measurements made over 6 hours.

Results

Method for the analysis of semiconductor grade HCl:

• Sample Preparation:

   – 1:10 m/m dilution (with high purity water) into precleaned PFA bottle

   – No addition of internal standard (to reduce contamination)

• Analysis:

   – Thermo Scientific Element 2 HR-ICP-MS

   – Inert sample introduction system

   – Hot plasma (removal of matrix effects, full elemental coverage, single analysis)

   – High mass resolution to provide unequivocal elemental accuracy

   – Quantification by standard addition (spike concentrations at 5 and 10 pg g^{-1})

   – Eighteen isotopes measured
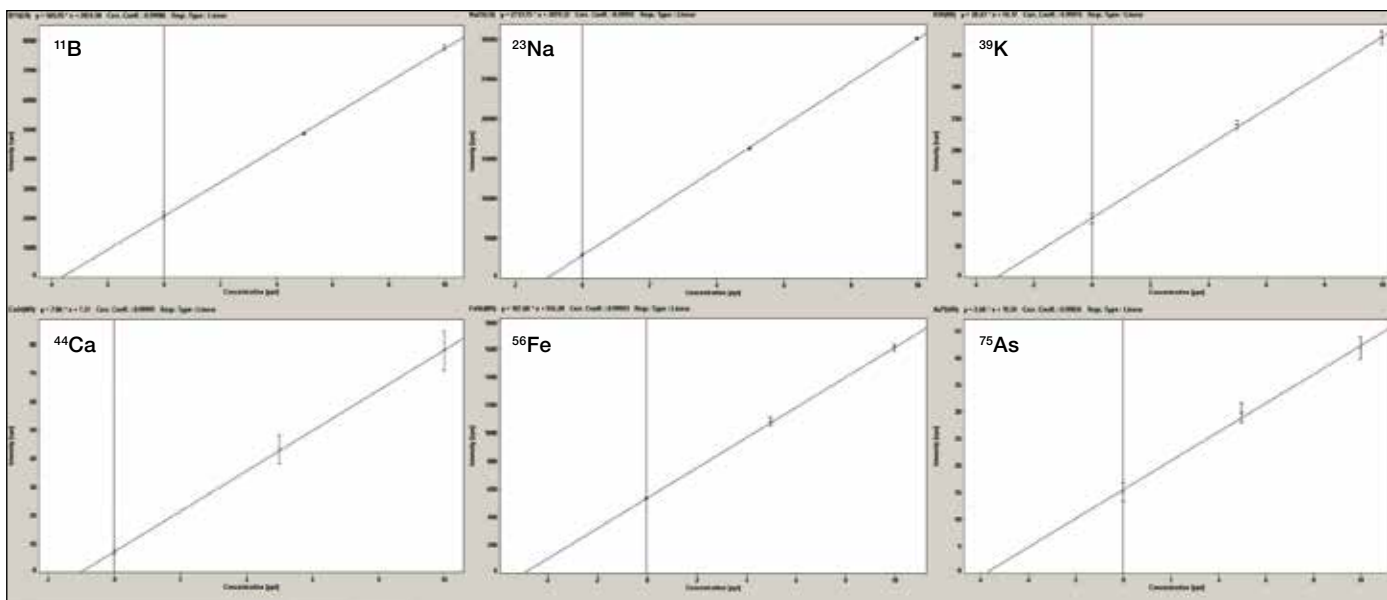
• Calibration Curves

Figure 4. Selection of calibration curves for the analysis of 10% m/m HCl using hot plasma conditions. Spikes at 5 and 10 pg g^{-1}. No blank subtraction performed.

- Background Equivalent Concentrations and Detection Limits:

Table 1. LoD & BEC values for the analysis of 10% m/m HCl in hot plasma.

	BEC [pg g^{-1}]	LoD [pg g^{-1}]
^{11}B (LR)	3.7	0.3
^{23}Na (LR)	1.1	0.1
^{118}Sn (LR)	5.8	0.7
^{121}Sb (LR)	0.07	0.13
^{138}Ba (LR)	0.07	0.02
^{207}Pb (LR)	0.5	0.2
^{24}Mg (MR)	0.6	0.3
^{27}Al (MR)	5.0	0.4
^{44}Ca (MR)	1.0	0.7
^{48}Ti (MR)	0.12	0.10
^{52}Cr (MR)	0.4	0.4
^{55}Mn (MR)	0.06	0.12
^{56}Fe (MR)	5.0	0.3
^{59}Co (MR)	0.04	0.07
^{60}Ni (MR)	1.6	0.7
^{63}Cu (MR)	1.2	0.9
^{39}K (HR)	3.3	0.1
^{75}As (HR)	5.6	3.2

All isotopes measured give BEC values well below 10 ppt in 10% m/m HCl. Three sigma detection limits in the 10% m/m HCl are below 1 pg g^{-1} for 17 of the 18 elements determined.

- Spike Recovery:

  – Results of spike recovery experiments should agree to with 75-125% of the spiked value for 10% m/m HCl.

Table 2. Measured concentrations (pg g^{-1}) and percentage recoveries in a spiked sample of 10% m/m HCl in hot plasma using the Thermo Scientific Element 2 HR-ICP-MS.

Isotope	Spike concentration	% Recovery
^{11}B (LR)	5.2	104
^{23}Na (LR)	5.4	107
^{118}Sn (LR)	5.3	106
^{121}Sb (LR)	5.2	104
^{138}Ba (LR)	5.3	106
^{207}Pb (LR)	5.3	105
^{24}Mg (MR)	5.3	107
^{27}Al (MR)	5.8	116
^{44}Ca (MR)	5.5	109
^{48}Ti (MR)	5.3	105
^{52}Cr (MR)	5.6	111
^{55}Mn (MR)	5.3	106
^{56}Fe (MR)	5.3	105
^{59}Co (MR)	5.4	108
^{60}Ni (MR)	5.4	107
^{63}Cu (MR)	5.3	106
^{39}K (HR)	4.3	87
^{75}As (HR)	4.5	90

Conclusions

An ICP-MS method for the analysis of high-purity HCl has been developed. The Thermo Scientific Element 2 HR-ICP-MS has been shown to provide the sensitivity, resistance to matrix, reliability and elemental selectivity to allow the determination of sub pg g^{-1} concentrations in process chemicals used in the semiconductor industry.

Find out more at **thermofisher.com/HR-ICP-MS**

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