

# Analysis of Semiconductor Grade Mineral Acids by Sector Field ICP-MS

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## Key Words

- High Resolution ICP-MS
- Semiconductor
- Mineral Acids
- Finnigan™ ELEMENT2

## 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. The organization SEMI (Semiconductor Equipment and Materials International, www.semi.org), is responsible for defining the maximum trace metal content in these process chemicals. For the manufacture of ICs with geometries of <0.2µm, SEMI guidelines (defined as ‘future chemical-purity needs’) for process chemical require maximum trace metal concentrations to be as low as 10 pg g<sup>-1</sup>.

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.

ICP-MS, with its multi-elemental capabilities and high sensitivity, has become very popular for the analysis of process chemicals in IC manufacture. For simple matrices, such as high purity water and hydrogen peroxide, direct analysis without any sample preparation is possible.

For more complicated process chemicals however, for example H<sub>2</sub>SO<sub>4</sub>, the recommended analysis methods used to meet lower grade (ng g<sup>-1</sup> level content) SEMI specifications recommend evaporation and subsequent reconstitution in dilute HNO<sub>3</sub>. This is recommended in order to remove the sample matrix that may:

- Reduce instrumental sensitivity caused by matrix suppression
- Be too aggressive a matrix for the ICP-MS sample introduction system
- Form spectroscopic interferences that degrade detection limits

However for the highest purity materials (with SEMI Grade C guideline concentrations at the pg g<sup>-1</sup> level) there are, at present, no SEMI recommended analysis methods available. For these chemicals, the methods employed for higher grades (evaporation, etc.) can not be used as the chance of contamination from the sample handling is increased and new ICP-MS methods have to be developed.

## Analytical requirements for a new 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: Finnigan™ ELEMENT2 specified sensitivity is >1Mcps/ng/g In, however higher sensitivities are routinely achievable.
- Low and uniform backgrounds: the Finnigan ELEMENT2 specification for dark noise is <0.2cps: independent of mass range or resolution mode.
- Clean sampling: With such high sensitivity and low instrument backgrounds, any measured elemental background is only limited by contamination in the analyzed sample: therefore a clean, inert sample introduction system is required:
  - PFA µflow 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

	COLD PLASMA		HOT PLASMA	
	LoD	BEC	LoD	BEC
<sup>23</sup> Na	0.03	0.38	<sup>115</sup> In	0.06 0.40
<sup>208</sup> Pb	0.09	0.12	<sup>44</sup> Ca	0.39 1.74
<sup>39</sup> K	0.14	0.14	<sup>48</sup> Ti	0.11 0.12
<sup>56</sup> Fe	0.22	0.08	<sup>51</sup> V	0.10 0.18
<sup>60</sup> Ni	0.79	3.30	<sup>66</sup> Zn	0.61 1.08

Example 1: Detection Limits (LoD) & Background Equivalent Concentrations (BEC) obtained on the Finnigan ELEMENT2. (Units: pg/g)

ISOTOPE	BLANK (pg g <sup>-1</sup> )	SPIKE (pg g <sup>-1</sup> )	% RECOVERY
<sup>7</sup> Li	0.01	4.5	91
<sup>23</sup> Na	3.20	7.8	93
<sup>24</sup> Mg	0.20	4.9	95
<sup>27</sup> Al	2.60	7.5	97
<sup>39</sup> K	0.60	5.9	105
<sup>52</sup> Cr	4.60	10.1	110
<sup>55</sup> Mn	0.03	4.7	94
<sup>56</sup> Fe	0.40	5.0	91
<sup>58</sup> Co	0.02	4.9	99
<sup>63</sup> Cu	0.40	5.4	101
<sup>88</sup> Sr	0.01	4.6	91
<sup>208</sup> Pb	0.10	5.4	107

Example 2: Spike Recoveries in high purity water.

With this combination of high sensitivity, low and mass independent background in conjunction with a clean sample introduction system, sub 50 fg g<sup>-1</sup> detection limits are achievable not only in relatively easy-to-measure samples such as high purity water and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), but also in more complex samples such as H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> 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.

### 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. Example: determination of <sup>55</sup>Mn in 2.5% TMAH (tetramethyl-ammonium hydroxide, C<sub>4</sub>H<sub>13</sub>NO) using both **HOT** and **COLD** plasma:

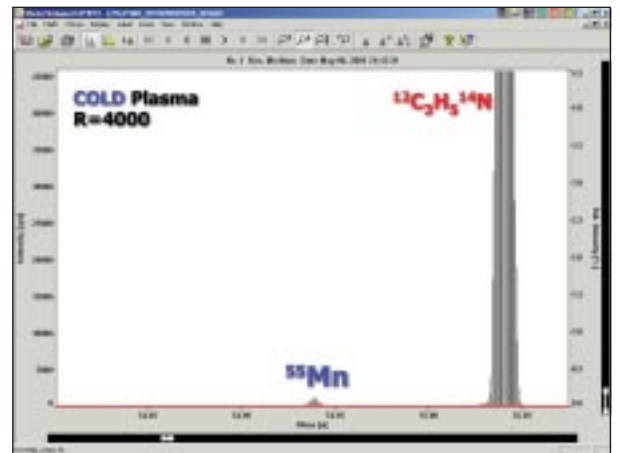
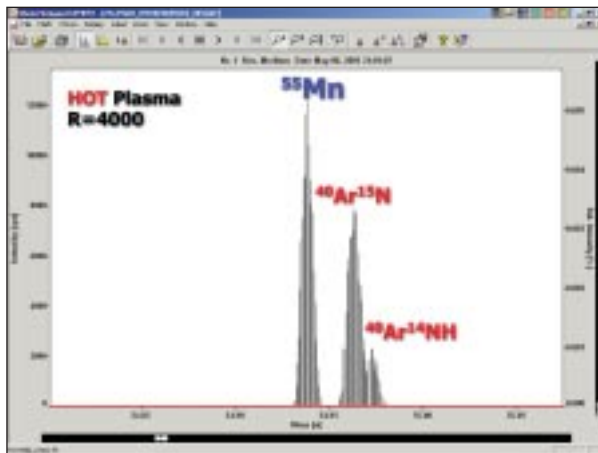
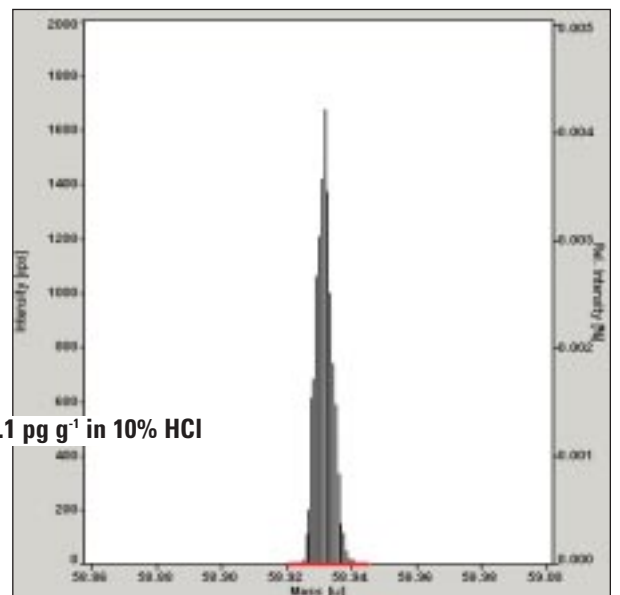
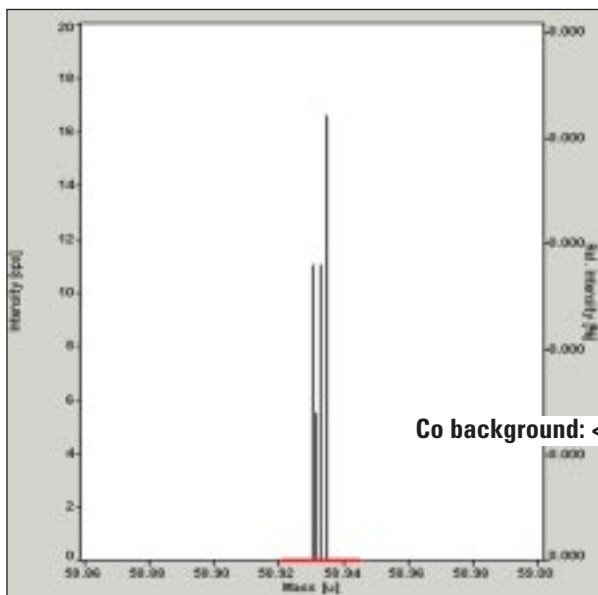


Figure 1: Spectra for <sup>55</sup>Mn in 2.5% TMAH using **HOT** and **COLD** plasma parameters.

### 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<sup>-1</sup> detection power maintained



Co background: < 0.1 pg g<sup>-1</sup> in 10% HCl

Figure 2: Comparison of spectra for <sup>59</sup>Co in blank 10% HCl and for 10 pg g<sup>-1</sup> <sup>59</sup>Co in 10% HCl (R=4000, Hot Plasma).

### 3. The highest performance independent of sample matrix

### 4. Reproducibility of analyses

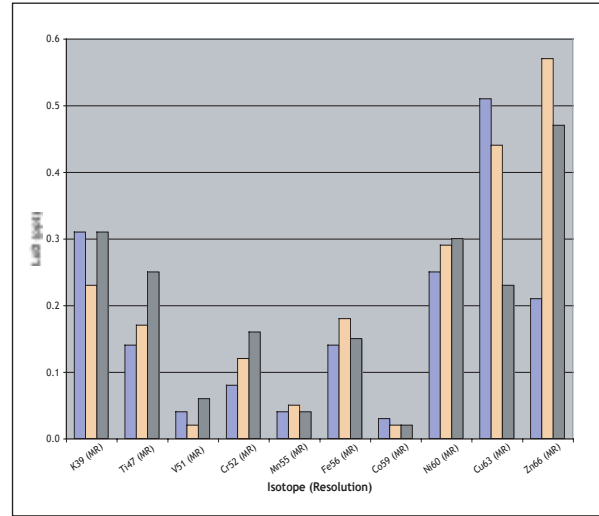
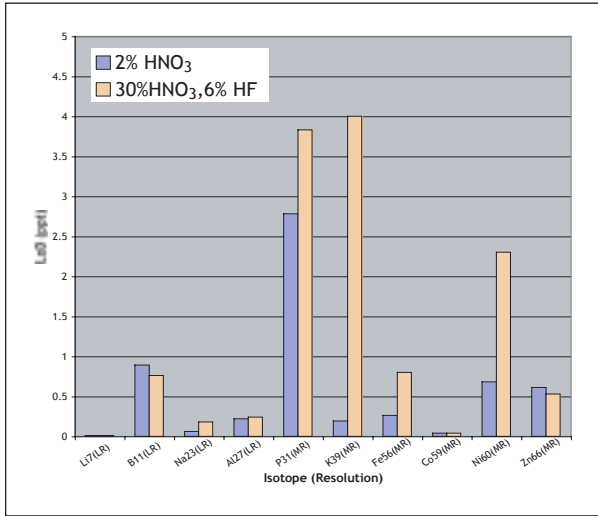


Figure 3: Comparison of detection limits (LoD, units: pg g<sup>-1</sup>) determined in 2% HNO<sub>3</sub> and 30% HNO<sub>3</sub>, 6% HF.

Figure 4: Reproducibility of detection limits (LoD, units: pg g<sup>-1</sup>) determined in 6% HNO<sub>3</sub>, 1.2 %HF. Three separate measurements made over 6 hours.

## Results

Method for the analysis of semiconductor grade HCl to meet SEMI Tier C requirements (100 pg g<sup>-1</sup> max.).

- Sample Preparation:

- 1:10 m/m dilution (with high purity water) into precleaned PFA bottle
- No addition of internal standard (to reduce contamination)

- Analysis:

- Finnigan ELEMENT2 Sector Field 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<sup>-1</sup>)
- Eighteen isotopes measured
- Calibration Curves

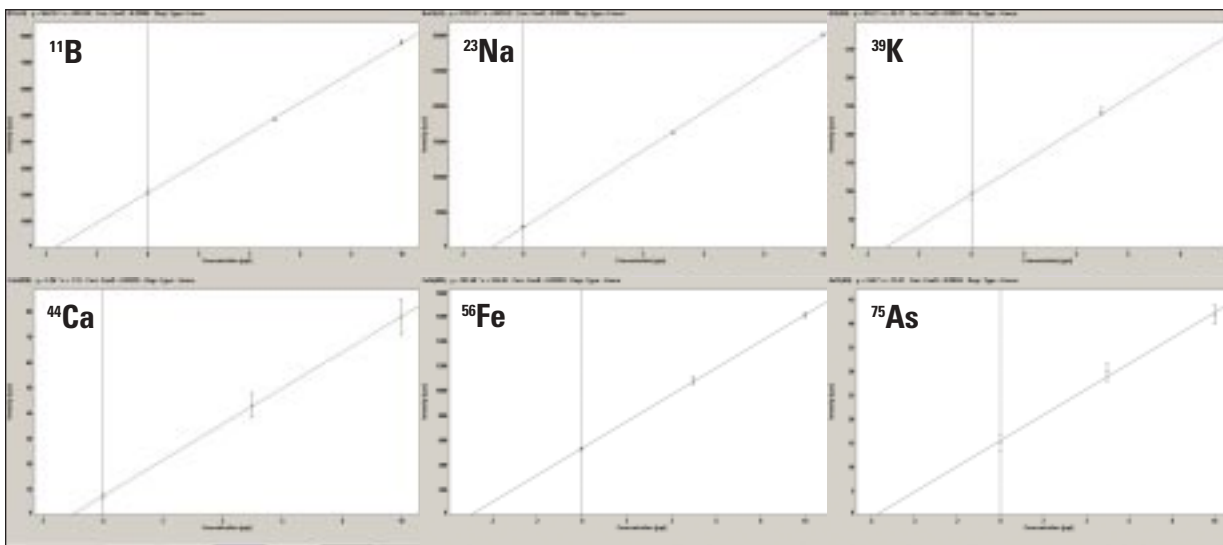


Figure 5: Selection of calibration curves for the analysis of 10% m/m HCl using hot plasma conditions. Spikes at 5 and 10 pg g<sup>-1</sup>. No blank subtraction performed.

- Background Equivalent Concentrations/Detection Limits:

	BEC: BACKGROUND EQUIVALENT CONCENTRATION	LoD: DETECTION LIMIT
<sup>11</sup> B (LR)	3.72	0.31
<sup>23</sup> Na (LR)	1.06	0.11
<sup>118</sup> Sn (LR)	5.84	0.66
<sup>121</sup> Sb (LR)	0.07	0.13
<sup>138</sup> Ba (LR)	0.07	0.02
<sup>207</sup> Pb (LR)	0.47	0.23
<sup>24</sup> Mg (MR)	0.59	0.33
<sup>27</sup> Al (MR)	4.97	0.36
<sup>44</sup> Ca (MR)	1.03	0.73
<sup>48</sup> Ti (MR)	0.12	0.10
<sup>52</sup> Cr (MR)	0.38	0.44
<sup>55</sup> Mn (MR)	0.06	0.12
<sup>56</sup> Fe (MR)	4.93	0.26
<sup>59</sup> Co (MR)	0.04	0.07
<sup>60</sup> Ni (MR)	1.58	0.66
<sup>63</sup> Cu (MR)	1.23	0.88
<sup>39</sup> K (HR)	3.31	0.12
<sup>75</sup> As (HR)	5.63	3.16

Table 1: LoD & BEC (units: pg g<sup>-1</sup>) values for the analysis of 10% m/m HCl in hot plasma. No blank subtraction performed.

All isotopes measured give BEC values well below 10 ppt in 10% m/m HCl, therefore meeting the 100 pg g<sup>-1</sup> SEMI Tier C requirement in concentrated HCl. Three sigma detection limits in the 10% m/m HCl are below 1 pg g<sup>-1</sup> for 17 of the 18 elements determined.

- Spike Recovery:

– For methods to be accepted as valid by SEMI, results of spike recovery experiments should agree to within 75-125% of the spiked value. The spike concentration should be at 50% of the specified concentration and is therefore 5 pg g<sup>-1</sup> for the analysis of TIER C grade 10% m/m HCl.

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

Table 2: Measured concentrations (pg g<sup>-1</sup>) and percentage recoveries in a spiked sample of 10% m/m HCl in hot plasma using the Finnigan ELEMENT2.

## Conclusions

An ICP-MS method for the analysis of SEMI Tier C HCl has been developed. The Finnigan ELEMENT2 Sector Field ICP-MS has been shown to provide the sensitivity, resistance to matrix, reliability and elemental selectivity to allow the determination of sub pg g<sup>-1</sup> concentrations in process chemicals used in the semiconductor industry.

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