Determination of Ultratrace Elements in Semiconductor Grade Sulfuric Acid using the Thermo Scientific iCAP Qs ICP-MS

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Application Brief 43205

Key Words
Sulfuric Acid, Semiconductor, Cold Plasma, KED, CCT

Goal

To develop a method for the ultratrace determination of metals in semiconductor grade sulfuric acid using the Thermo Scientific iCAP Qs ICP-MS.

Introduction

Concentrated sulfuric acid (H_2SO_4) is used in the semiconductor industry to remove organic substances from the surface of silicon wafers. Since H_2SO_4 comes into contact with wafer surfaces, it is necessary to monitor its trace elemental impurities.

High sulfur matrices are problematic in ICP-MS analysis due to the formation of spectral interferences that are preferentially created due to their low ionization energies in the ICP ion source. The most challenging elements in the trace determination of sulfuric acid are Ti, V, Cr, Zn and Ge. All major isotopes of these metals are severely interfered by polyatomic species generated by the sample matrix (see Table 1).

Table 1: Typical target isotopes with commonly observed interferences.

Isotope	Abundance	Matrix-Based Interferences
^{47}Ti	7.3%	$^{33}S^{14}N^+$, $^{32}S^{15}N^+$, $^{32}S^{14}N^1H^+$
^{48}Ti	73.8%	$^{32}S^{16}O^+$
^{51}V	100%	$^{33}S^{18}O^+$, $^{34}S^{16}O^1H^+$, $^{32}S^{18}O^1H^+$
^{52}Cr	83.8%	$^{34}S^{18}O^+$, $^{33}S^{18}O^1H^+$
^{53}Cr	9.5%	$^{34}S^{18}O^1H^+$
^{64}Zn	48.6%	$^{32}S_2^+$, $^{32}S^{16}O_2^+$
^{66}Zn	27.9%	$^{32}S^{34}S^+$, $^{33}S_2^+$, $^{34}S^{16}O_2^+$, $^{36}S^{16}O^{14}N^+$
^{68}Zn	18.8%	$^{34}S_2^+$, $^{32}S^{36}S^+$, $^{34}S^{16}O^{18}O^+$
^{72}Ge	27.7%	$^{40}Ar^{32}S^+$
^{74}Ge	35.5%	$^{40}Ar^{34}S^+$

Sample Preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. Concentrated H_2SO_4 (98% Optima grade H_2SO_4, from Fisher Chemical) was 10-fold diluted with ultrapure water before analysis. Standards at concentrations of 10, 25, 50 and 100 $ng{\cdot}L^{-1}$ were prepared gravimetrically by adding the appropriate quantity of a multi-elemental SPEX CertiPrep™ stock. 9.8% H_2SO_4 was used for the rinse and blank solutions. Spike tests were performed at 10 $ng{\cdot}L^{-1}$.

Method

The instrument configuration and operation parameters are shown in Table 2. Please note, the Thermo Scientific™ iCAP™ Qs ICP-MS was not installed in a clean room.

Table 2: Instrument configuration and operation parameters.

Parameter	Value
Spray Chamber	Quartz cyclonic
Nebulizer	MicroFlow PFA-100 (self-aspirating)
Injector	2.0 mm I.D., Sapphire
Interface	Cold plasma platinum sampler and skimmer
Extraction Lens	Cold plasma lens kit

Mode	RF Power	QCell Technique
CP	580 W	-
CP-NH_3	580 W	1% NH_3 in He, 7.0 $mL{\cdot}min^{-1}$
CCT-Cluster	1550 W	50% NH_3 in He, 0.8 $mL{\cdot}min^{-1}$
CCT-NH_3	1550 W	1% NH_3 in He, 10.0 $mL{\cdot}min^{-1}$
KED-He	1550 W	100% He, 5.0 $mL{\cdot}min^{-1}$
KED-NH_3	1550 W	1% NH_3 in He, 4.0 $mL{\cdot}min^{-1}$

Results

Table 3 shows the performance of the analysis of 9.8% H_2SO_4 with the iCAP Qs ICP-MS:

- Excellent semiconductor level LoD and BEC were produced for all analytes through a combination of different measurement modes.
- Outstanding performance was achieved for V, Cr, Zn and Ge indicating the effective suppression of all matrix induced interferences (see Figure 1 for V).
- CCT-Cluster mode (50% NH_3 in He) effectively shifts the target analyte to an interference free region enabling ultratrace Ti quantification (see Figure 2).
- Accurate spike recoveries from 92% to 108% were obtained for 27 elements at 10 ng·L^{-1}.
- Cold plasma is suitable for the analysis of mineral acid samples such as 9.8% sulfuric acid.

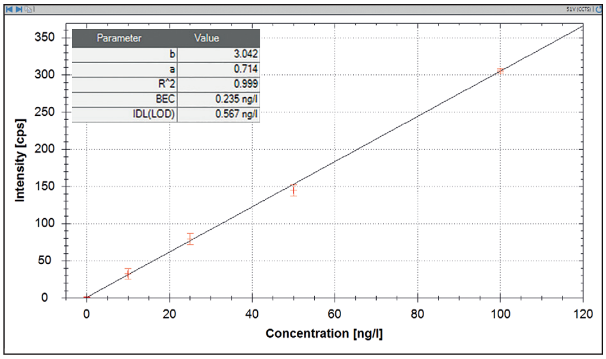

Figure 1: Calibration curve for ^{51}V in 9.8% H_2SO_4.

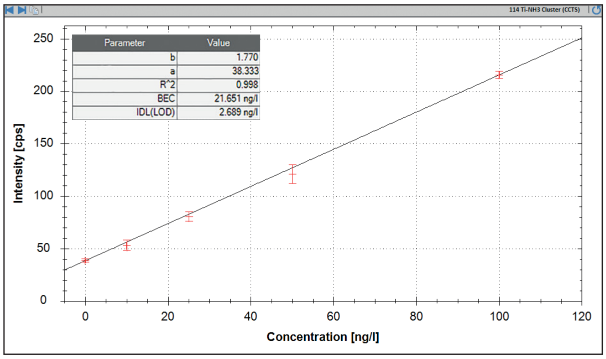

Figure 2: Calibration curve for $^{48}Ti^{14}N^1H(^{14}N^1H_3)_3^+$ in 9.8% H_2SO_4.

Table 3: iCAP Qs ICP-MS performance for the analysis of 9.8% H_2SO_4.

Analyte	Mode	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{7}Li	CP	0.3	0.9	99
^{23}Na	CP	0.7	2.6	107
^{24}Mg	CP-NH_3	0.9	0.8	102
^{27}Al	CP	0.9	1.1	99
^{39}K	CP	2.2	8.5	102
^{40}Ca	CP	5.9	17.0	103
$^{48}TiNH(NH_3)_3$	CCT-Cluster	2.7	21.7	97
^{51}V	CCT-NH_3	0.6	0.2	100
^{53}Cr	CP-NH_3	2.7	1.7	103
^{55}Mn	CP	0.3	0.2	102
^{56}Fe	CP	1.0	1.8	100
^{58}Ni	CP	1.5	2.1	98
^{59}Co	CP	0.3	0.1	99
^{65}Cu	CP	1.9	1.1	103
^{68}Zn	KED-NH_3	1.9	2.9	99
^{71}Ga	CP	0.5	0.1	101
^{74}Ge	KED-He	0.1	0.1	108
^{75}As	KED-NH_3	0.7	0.8	100
^{85}Rb	KED-He	1.0	0.6	105
^{88}Sr	KED-NH_3	0.5	0.4	107
^{111}Cd	KED-He	1.2	0.5	107
^{115}In	KED-He	0.3	0.1	96
^{138}Ba	KED-NH_3	1.1	0.5	92
^{205}Tl	KED-He	0.6	1.4	97
^{208}Pb	KED-He	1.5	3.1	98
^{209}Bi	KED-He	0.5	0.4	101
^{238}U	KED-He	0.4	0.3	105

Conclusion

The Thermo Scientific iCAP Qs ICP-MS provides excellent performance for the ultratrace determination of metals in semiconductor grade H_2SO_4. The flexible combination of different analysis modes has been shown to be ideally suited for the ultratrace metal determination in advanced semiconductor applications.

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