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

[1]Tomoko Vincent, [2]Tokutaka Ikemoto, [2]Tomoko Aoki, [2]Makiko Shimura
[1]Thermo Fisher Scientific, Bremen, Germany, [2]Thermo Fisher Scientific, Yokohama, Japan

Key Words

Hydrochloric Acid, Semiconductor, Cold Plasma, KED, CCT

Goal

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

Introduction

The organization SEMI (Semiconductor Equipment and Materials International, ***www.semi.org***) has announced a guideline (defined as "Future Chemical – Purity Needs") for maximum trace metal concentrations to be as low as 10 ng·L^{-1} in process chemicals. For example SEMI specification C27-0708 defines maximum metal contamination levels in concentrated hydrochloric acid (HCl).

HCl is used in silicon wafer cleaning processes to remove dust, organic contamination and any thin oxide layer. This cleaning process, called SC-2 (Standard Clean, 2nd step) is performed with a 1-15% HCl solution.

Due to a series of complex Cl and Ar based polyatomic interferences, ^{39}K, ^{51}V, ^{52}Cr, ^{74}Ge and ^{75}As are often difficult to analyze at ultratrace concentrations in HCl.

Sample preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. Standards at concentrations of 10, 25, 50 and 100 ng·L^{-1} were prepared gravimetrically by adding the appropriate quantity of a multi-elemental SPEX CertiPrep™ stock solution directly to concentrated HCl (32-35% HCl Optima™ grade from Fisher Chemical), and diluted with ultrapure water to make 20% HCl. 20% HCl solutions for analysis was used for the rinse and blank solutions. Spike tests were performed at 10 ng·L^{-1}.

Method

The instrument configuration and operation parameters are shown in Table 1. Please note that the Thermo Scientific™ iCAP™ Qs ICP-MS was not installed in a clean room.

Table 1: 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	No Gas
CP-NH_3	580 W	1% NH_3 in 99% He, 7.0 mL•min^{-1}
CCT-NH_3	1550 W	50% NH_3 in 50% He, 0.8 mL•min^{-1}
CCT-O_2	1550 W	50% O_2 in 50% He, 2.0 mL•min^{-1}
KED-He	1550 W	100% He, 5.0 mL•min^{-1}
KED-NH_3	1550 W	1% NH_3 in 99% He, 4.0 mL•min^{-1}

Results

As can be seen in Figures 1 to 5, the powerful collision cell capabilities of the QCell in the iCAP Qs ICP-MS provide the advanced performance required for the sensitive and accurate determination of difficult elements, such as K, V, Cr, Ge, As in 20% HCl.

- Cold plasma inhibits the formation of Cl and Ar based interferences (on K and Cr).
- Cold plasma promotes the formation of AsO^+ (shifting the target analyte to an interference free mass range).
- The combination of automatic low mass cut off with different QCell modes (CCT, KED) effectively suppress Cl based interferences (on V and Ge).

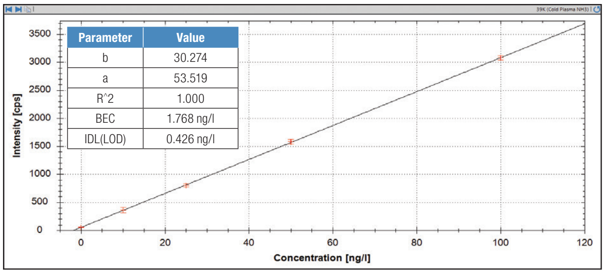

Figure 1: Calibration curve for ^{39}K in 20% HCl (interference $^{1}H_2{}^{37}Cl^+$).

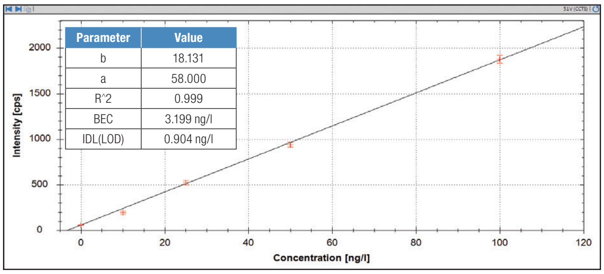

Figure 2: Calibration curve for ^{51}V in 20% HCl (interference $^{35}Cl^{16}O^+$).

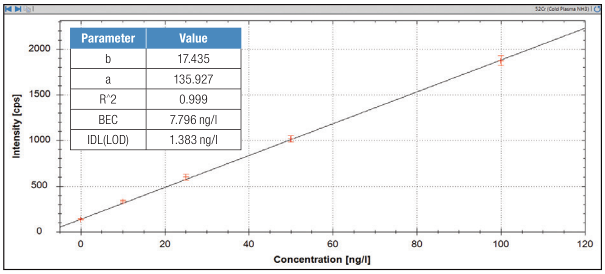

Figure 3: Calibration curve for ^{52}Cr in 20% HCl (interference $^{35}Cl^{16}O^{1}H^+$).

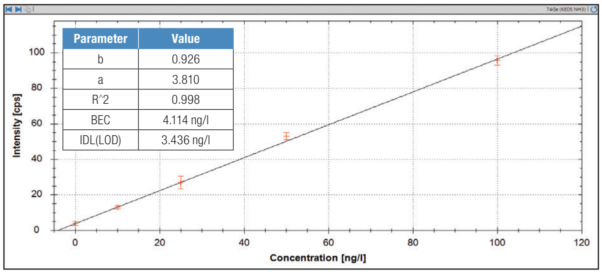

Figure 4: Calibration curve for ^{74}Ge in 20% HCl (interference $^{37}Cl_2{}^+$).

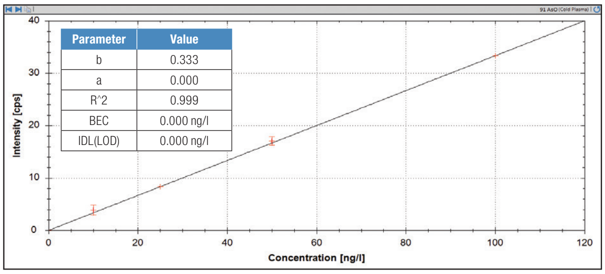

Figure 5: Calibration curve for ^{75}As (as $^{75}As^{16}O^+$) in 20% HCl (interference $^{40}Ar^{35}Cl^+$).

The capability of the iCAP Qs ICP-MS to reliably analyze 20% HCl is demonstrated by the excellent LoD and BEC value shown in Table 2. Spike recoveries (for only 10 ng·L^{-1}) of between 91% to 115% for 29 elements in 20% HCl demonstrate the excellent interference removal and accuracy achieved by the iCAP Qs ICP-MS using the method described.

Table 2: iCAP Qs ICP-MS performance for 20% HCl. As ($^{75}As^{16}O^+$) A detection limit of ‹0.001 ng·L^{-1} was recorded for ^{75}As since all repeats at $^{75}As^{16}O^+$ in the blank gave the same intensities "0".

Analyte	Mode	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{7}Li	CP	0.07	0.05	108
^{23}Na	CP	0.2	0.4	105
^{24}Mg	CP	0.3	0.2	110
^{27}Al	CP	0.7	0.8	115
^{39}K	CP-NH_3	0.4	1.8	102
^{40}Ca	CP	1.4	9.5	104
^{51}V	CCT-NH_3	0.9	3.2	93
^{52}Cr	CP-NH_3	1.4	7.8	111
^{55}Mn	CP-NH_3	0.5	0.4	105
^{57}Fe	CP	1.0	3.1	100
^{59}Co	CP	0.5	0.3	94
^{60}Ni	CP	2.6	4.7	95
^{63}Cu	CP	1.8	3.1	104
^{66}Zn	KED-NH_3	3.0	9.6	96
^{71}Ga	KED-He	1.3	0.8	96
^{74}Ge	KED-NH_3	3.4	4.1	99
^{75}As (AsO^+)	CP	<0.001	<0.001	99
^{80}Se	CCT- O_2	0.3	15	93
^{85}Rb	CP	0.2	0.06	108
^{88}Sr	KED-He	0.2	0.02	105
^{111}Cd	KED-He	0.6	0.1	92
^{115}In	KED-He	0.2	0.3	93
^{133}Cs	KED-He	0.01	0.01	93
^{138}Ba	KED-He	0.01	0.01	98
^{202}Hg	KED-He	0.6	1.3	91
^{205}Tl	KED-He	0.2	0.3	92
^{208}Pb	KED-He	0.2	1.2	94
^{209}Bi	KED-He	0.4	1.6	93
^{238}U	KED-He	0.03	0.03	93

Conclusion

The Thermo Scientific iCAP Qs ICP-MS has been shown to offer the high sensitivity and freedom from interferences required for the measurement of ultratrace (ng·L^{-1}) concentration levels in semiconductor grade HCl. Flexible operation combined with the high performance of the QCell provide significant improvements ideally suited for the requirements of advanced semiconductor applications.

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