

Determination of ultratrace elements in semiconductor grade hydrochloric acid using the Thermo Scientific iCAP RQ ICP-MS

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Keywords

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Goal

To develop a method for the ultratrace determination of metals in semiconductor grade hydrochloric acid (HCl) using the Thermo Scientific™ iCAP™ RQ 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, ³⁹K, ⁵¹V, ⁵²Cr, ⁷⁴Ge and ⁷⁵As 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™ RQ ICP-MS was not installed in a clean room.

Table 1. Instrument configuration and operation parameters.

| Parameter | Value |
|------------------------|--|
| Spraychamber | Quartz cyclonic |
| Nebulizer | Microflow PFA-100 (self-aspirating) |
| Injector | 2.0 mm I.D., sapphire |
| Interface | Cold plasma platinum sampler and high sensitivity platinum skimmer |
| Extraction Lens System | Cold plasma |

| 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 RQ 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).

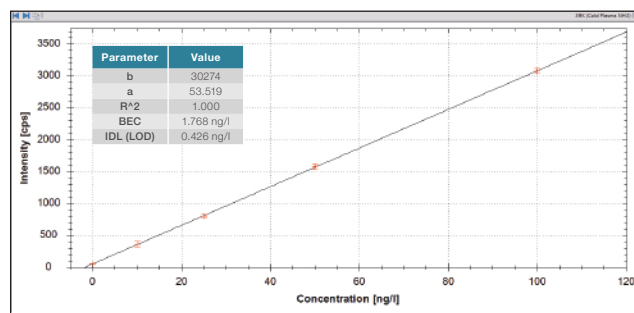


Figure 1. Calibration curve for ³⁹K in 20% HCl (interference ¹H₂³⁷Cl⁺).

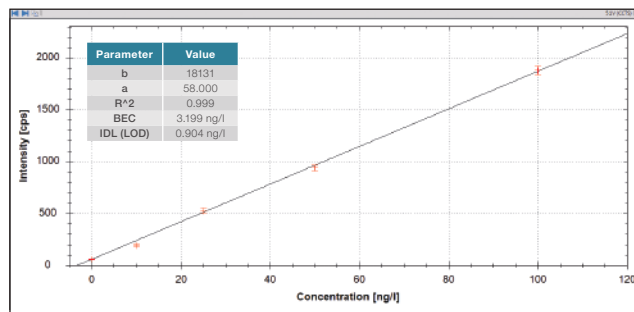


Figure 2. Calibration curve for ⁵¹V in 20% HCl (interference ³⁵Cl¹⁶O⁺).

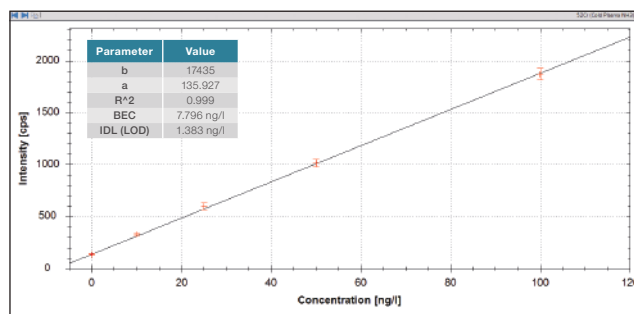


Figure 3. Calibration curve for ⁵²Cr in 20% HCl (interference ³⁵Cl¹⁶O¹H⁺).

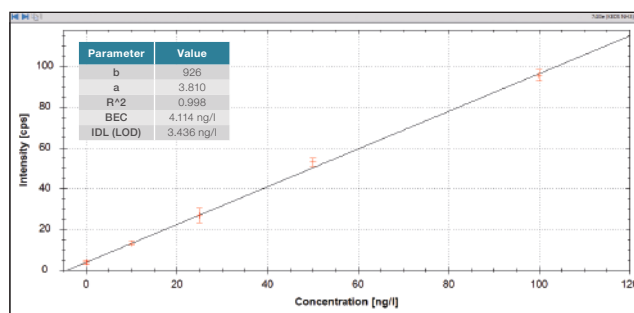


Figure 4. Calibration curve for ⁷⁴Ge in 20% HCl (interference ³⁷Cl₂⁺).

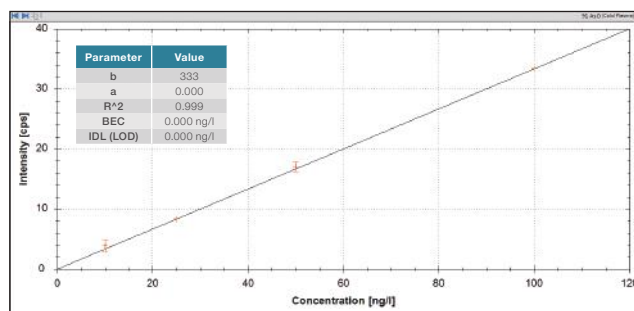


Figure 5. Calibration curve for ⁷⁵As (as ⁷⁵As¹⁶O⁺) in 20% HCl (interference ⁴⁰Ar³⁵Cl⁺).

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

Table 2. Thermo Scientific iCAP RQ ICP-MS performance for 20% HCl. A detection limit of <0.001 ng·L⁻¹ was recorded for ⁷⁵As (as ⁷⁵As¹⁶O⁺ in cold plasma operation) since all repeats 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 iCAP RQ 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.

Find out more at thermofisher.com/SQ-ICP-MS