Direct Determination of Ultratrace Elements in Semiconductor Grade Hydrofluoric Acid HF (48%) using the Thermo Scientific iCAP Qs ICP-MS

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Application Brief 43197

Key Words
Hydrofluoric Acid, Semiconductor, Cold Plasma

Goal
To directly determine ultratrace metal concentrations in undiluted 48% semiconductor grade hydrofluoric acid using the Thermo Scientific iCAP Qs ICP-MS. Demonstrate the use of cold plasma to reduce background equivalent concentrations (BEC) and improve detection limits (LoD).

Introduction
Semiconductor process chemicals with ultratrace metal content are required in order to minimize production losses due to reduced performance or defects. Hydrofluoric acid (HF), for example, is routinely used as a wet chemical etchant to remove silicon dioxide layers in semiconductor devices. Routine, automated quantification of ng·L^{-1} level metal contaminants in HF is therefore required in order to maintain end product quality.

HF is an extremely corrosive acid and its vapor can cause serious harm to human health. Analytical techniques that minimize exposure to manufacturing personnel are therefore preferred. Additionally, due to the extremely low target concentration levels in semiconductor process chemicals, sample handling should be minimized in order to avoid contamination.

In this application, the Thermo Scientific™ iCAP™ Qs ICP-MS, in a single cold plasma measurement mode, was used for the direct trace metal analysis of 48% semiconductor grade HF. All samples were introduced into the iCAP Qs ICP-MS using a CETAC ASX-112FR Autosampler that offers the following features:

- Compact design for close coupling, leading to reduced uptake and washout times.
- Dual flowing rinse stations with solutions supplied via a gas displacement pump to minimize contamination.
- Metal free sample area and integrated cover to prevent airborne contamination.
- Flexible configuration of (PFA) autosampler vials.
- Fully control via Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS).

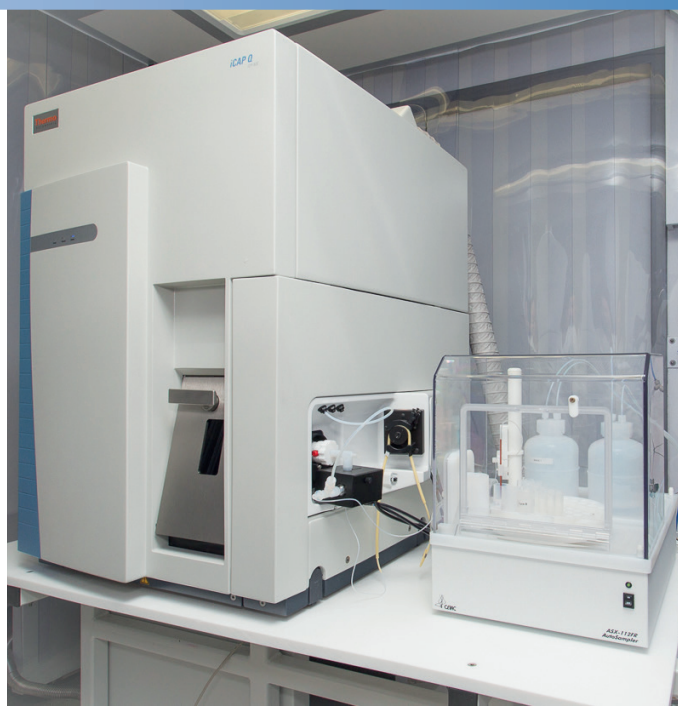

Figure 1: The Thermo Scientific iCAP Qs ICP-MS coupled with the CETAC ASX-112FR Autosampler.

Sample Preparation
Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultra pure water (18.2 MΩ) and left to dry in a laminar flow clean hood before use. Multi-element standards at concentrations of 10, 20, 50 and 200 ng·L^{-1} were prepared gravimetrically by adding the appropriate quantity of a multi-elemental SPEX Certiprep stock solution directly to the 48% HF samples. In order to assess recovery in the 48% HF, a spike recovery test at 20 ng·L^{-1} was performed.

Note: It is strongly recommended to pre-clean all sample vials and rinse bottles in an acid bath solution (3% HF, 2% HNO_3, 2% H_2O_2) for 72 hours before use.

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Instrument Configuration

The instrument configuration used is shown in Table 1. (Please note, the iCAP Qs ICP-MS is set up in non-clean room conditions.)

Table 1: Instrument configuration.

Parameter	Value
Spray Chamber	PFA 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

Results

Cold plasma (CP) inhibits the formation of the sample matrix induced $(^{1}H^{19}F)_2$ interference, allowing calcium to be measured at the most sensitive ^{40}Ca isotope. The improved performance that this allows is demonstrated in Figure 2 where BEC and LoD values of less than 5 ng·L^{-1} were achieved for calcium in 48% HF.

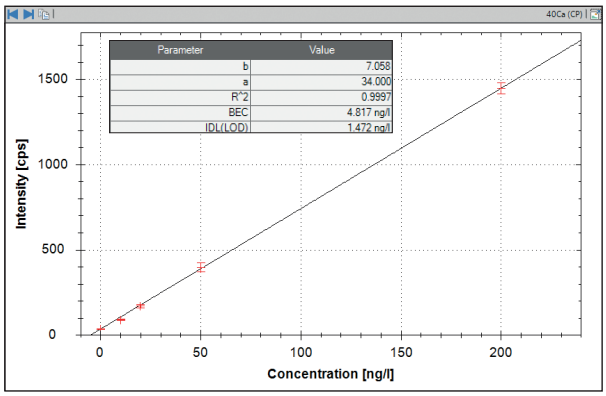

Figure 2: Cold plasma calibration curve for ^{40}Ca in 48% HF.

As can be seen in Table 2, the performance of the iCAP Qs ICP-MS for the direct analysis of 48% HF using cold plasma demonstrates:

- Excellent LoD and BEC values using a single analysis mode.
- 90% to 107% recoveries for a 20 ng·L^{-1} spike.
- Suppression of plasma and sample matrix induced interferences for accurate analysis at ultratrace concentrations.

With a single mode analysis time of 75 seconds (including uptake and wash) high throughput analyses can be achieved.

Table 2: iCAP Qs ICP-MS performance data for 48% HF. Recovery values are shown as the percentage recovery for a 20 ng·L^{-1} spike.

Analyte	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{7}Li	0.03	0.03	97
^{23}Na	0.2	1.6	100
^{24}Mg	0.5	0.6	101
^{27}Al	0.4	9.7	91
^{39}K	0.6	20.4	105
^{40}Ca	1.5	4.8	102
^{52}Cr	0.2	12.9	107
^{55}Mn	0.2	0.4	96
^{56}Fe	1.1	3.4	107
^{58}Ni	0.7	0.7	99
^{59}Co	0.5	0.7	100
^{63}Cu	1.6	4.2	91
^{66}Zn	3.5	5.0	106
^{88}Sr	0.5	0.1	99
^{107}Ag	0.6	0.7	97
^{111}Cd	0.7	0.4	90
^{115}In	0.1	0.05	96
^{205}Tl	0.1	0.03	101
^{208}Pb	0.2	0.02	93
^{209}Bi	0.5	0.1	104

Conclusion

The Thermo Scientific iCAP Qs ICP-MS has been shown to offer the high sensitivity and freedom from contamination and interference required for the direct determination of ultratrace (ng·L^{-1}) metal concentrations in semiconductor grade 48% HF. The method described is fast, simple and reliable: ideal for efficient and accurate analysis in exacting semiconductor laboratories.

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