

Analysis of semiconductor materials using ICP-MS

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ABSTRACT

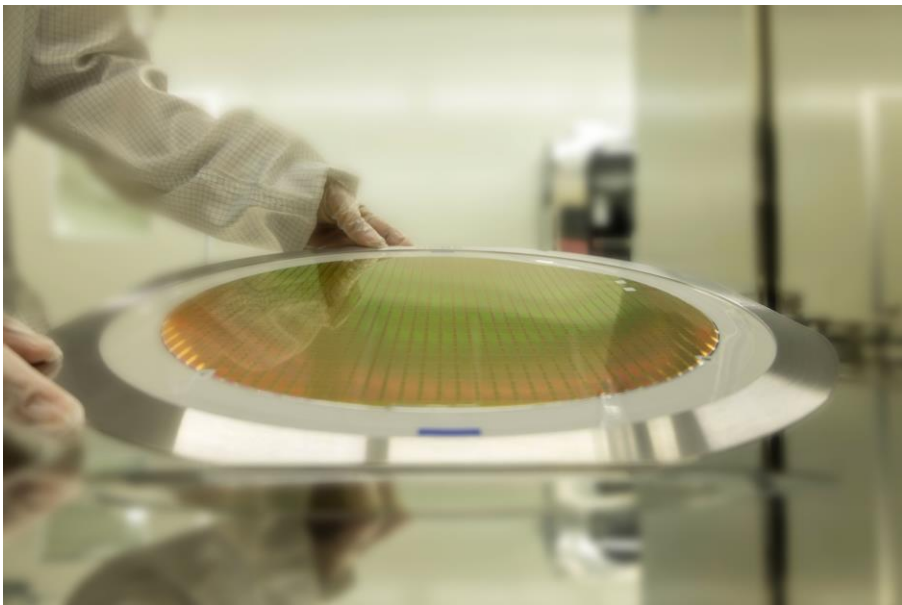
Purpose: To demonstrate the ultratrace analysis of silicon wafer VPD sample and typical semiconductor process chemicals.

Methods: The Thermo Scientific™ iCAP™ TQs ICP-MS was used to determine ultratrace metal concentrations after simple dilution.

Results: The iCAP TQs ICP-MS is shown to provide high performance, robust ultratrace metal analysis in samples typically analyzed in semiconductor manufacturing processes.

INTRODUCTION

With the continual decrease in device geometries, the maximum allowable trace metallic impurity levels in process materials, as defined by Semiconductor Equipment and Materials International (SEMI), are moving to lower levels. The most widely used semiconductor material is silicon wafer, which is required to be greater than 99.9999999% pure silicon (9N purity). Monitoring trace element contamination of the wafer surface is a routine requirement in the semiconductor industry. Vapor phase deposition (VPD) with subsequent elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) provides the required detection capability, method robustness, speed and reliability for routine and reproducible analysis and is widely applied in silicon wafer manufacturing facilities. Typical VPD samples contain high acid and silicon concentrations and the target analyte concentrations are very low. This makes the ICP-MS challenging as the sample matrix generates significant polyatomic interferences on the target elements. To obtain accurate results, elimination of these interferences using advanced technologies such as triple quadrupole ICP-MS or high resolution ICP-MS is required. This poster presents the performance achieved for analysis of synthetic VPD samples and typical semiconductor process chemicals using the iCAP TQs triple quadrupole ICP-MS with minimum sample preparation.



MATERIALS AND METHODS

Sample Preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ cm) and left to dry in a laminar flow clean hood before use. A silicon wafer was used for this study to prepare the simulated VPD sample. To digest the sample, 10 g hydrofluoric acid (50% Optima grade, Fisher Chemical) and 10 g nitric acid (68% Optima grade, Fisher Chemical) were first added gently to approximately 1.7 g of silicon wafer in a PFA sample preparation bottle. Ultrapure water (65 g) was subsequently added. The final analysis sample solution was then prepared by dilution with ultrapure water to provide a 200 mg·L⁻¹ Si matrix comparable to that produced by VPD.

Test Method

Standards at concentrations of 25, 50 and 100 ng·L⁻¹ were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (SPEXCertiPrep™) directly to aliquots of the 200 mg·L⁻¹ Si matrix samples. Semiconductor grade 0.5% (m/m) hydrofluoric acid and 0.1% (m/m) nitric acid were used for the rinse solutions. Recovery tests were performed using 50 ng·L⁻¹ spikes.

Mass Spectrometry

A Thermo Scientific™ iCAP™ TQs ICP-MS was used for all analyses. The typical operating parameters are summarized in Table 1.

Table 1. iCAP TQs ICP-MS operating parameters.

Parameter	Value		
Nebulizer	PFA concentric nebulizer 100 µL·min ⁻¹ (self-aspirating)		
Spraychamber	High sensitivity PFA double pass spraychamber		
Injector	2.0 mm i.d., sapphire		
Interface	Pt sampler and Pt skimmer high sensitivity type		
Extraction lens	Cold plasma lens		
Measurement mode	Single quad mode		Triple quad mode
	SQ-CP-NH ₃	SQ-KED	TQ-O ₂
Forward power	520 W	1550 W	1550 W
Nebulizer gas	0.965 mL·min ⁻¹	0.999 mL·min ⁻¹	0.999 mL·min ⁻¹
CRC gas	Pure NH ₃ 0.28 mL·min ⁻¹	Pure He 4.2 mL·min ⁻¹	Pure O ₂ 0.3 mL·min ⁻¹
Dwell time	100 to 300 ms per analyte, 5 sweeps		

RESULTS

iCAP TQ Analysis of Silicon Wafer

Using the TQ-O₂ mass shift mode (shown in Figure 3), Si, N, O and F based polyatomic interferences are efficiently removed providing accurate analysis of. In TQ-O₂ mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (IMS) to reject unwanted ions. The second quadrupole (Q2) is used to selectively shift the Ti target analytes to the TiO⁺ product ions using O₂ as the reaction gas, while the potential interference do not react with O₂. The third quadrupole (Q3) then isolates the TiO⁺ product ions and removes any remaining interferences through a second stage of mass filtration allowing completely interference free analysis of the analyte to be achieved.

As can be seen in the measurement results (Table 2), LoD values (calculated from three times the standard deviation of ten replicate measurements of the calibration blank), spike recovery and reproducibility of Si matrix samples (100 ng·L⁻¹ spiked, n=5) were determined for 26 elements in the VPD sample. Accurate spike recoveries (90% to 104%) were obtained for all elements at 50 ng·L⁻¹. Although the sample contains 200 mg·L⁻¹ silicon matrix, excellent reproducibility and reliability was achieved, with ±2.2% RSD for 5 replicates, demonstrating the robustness of the iCAP TQs ICP-MS in mixed hot and cold plasma analyses.

Figure 1. ³⁹K calibration.

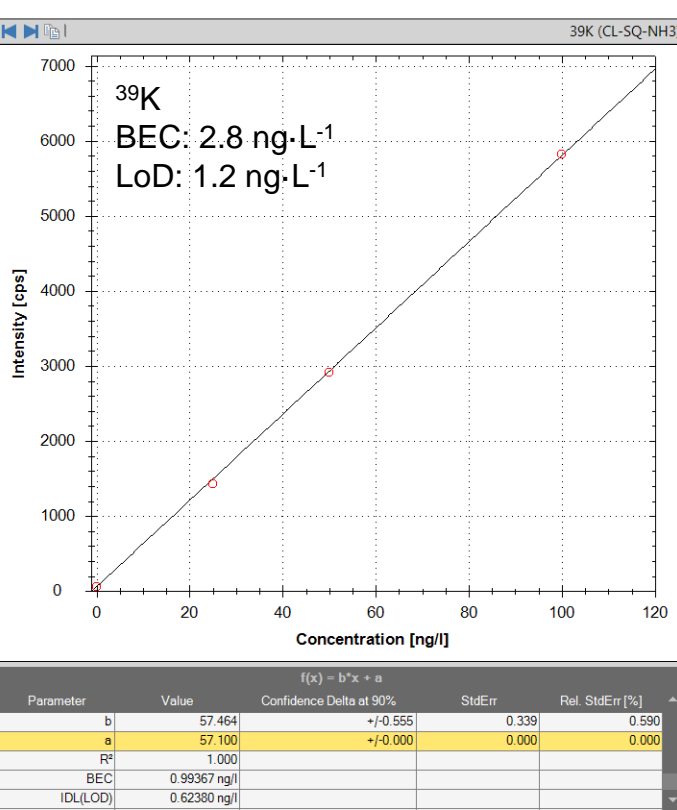
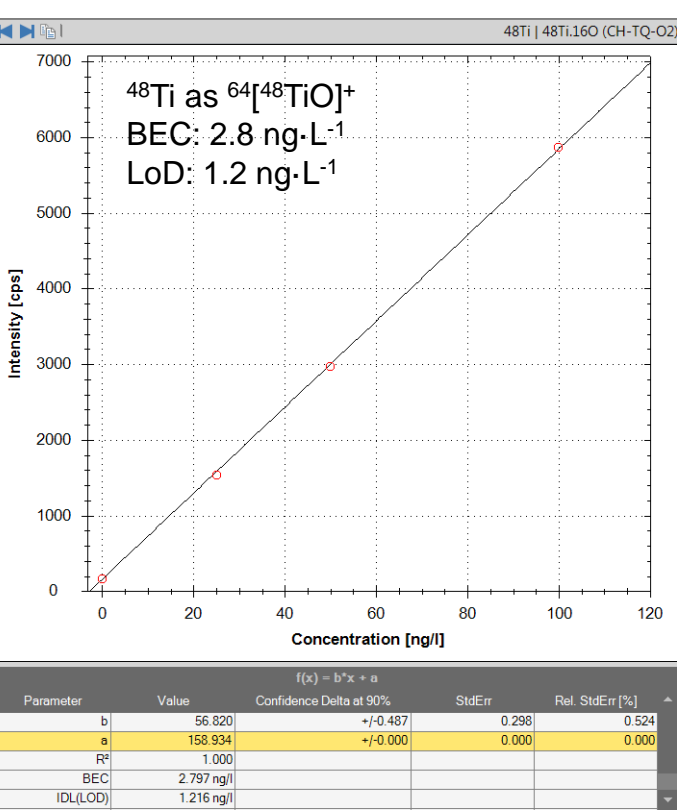


Figure 2. ⁴⁸Ti (as ⁶⁴[⁴⁸TiO]⁺) calibration.



Calibration curves for K and Ti in Si 200 mg·L⁻¹ are shown in Figures 1 and 2. The calibrations, performed with calibration standards in the ng·L⁻¹ range, showed excellent linearity and sensitivity. The low backgrounds achieved for the more challenging analytes such as ⁴⁸Ti was possible through improved interference removal with triple quadrupole modes and cold plasma operation.

Figure 3. Analysis of ⁴⁸Ti using the iCAP TQs ICP-MS with ammonia or oxygen as reactive gas.

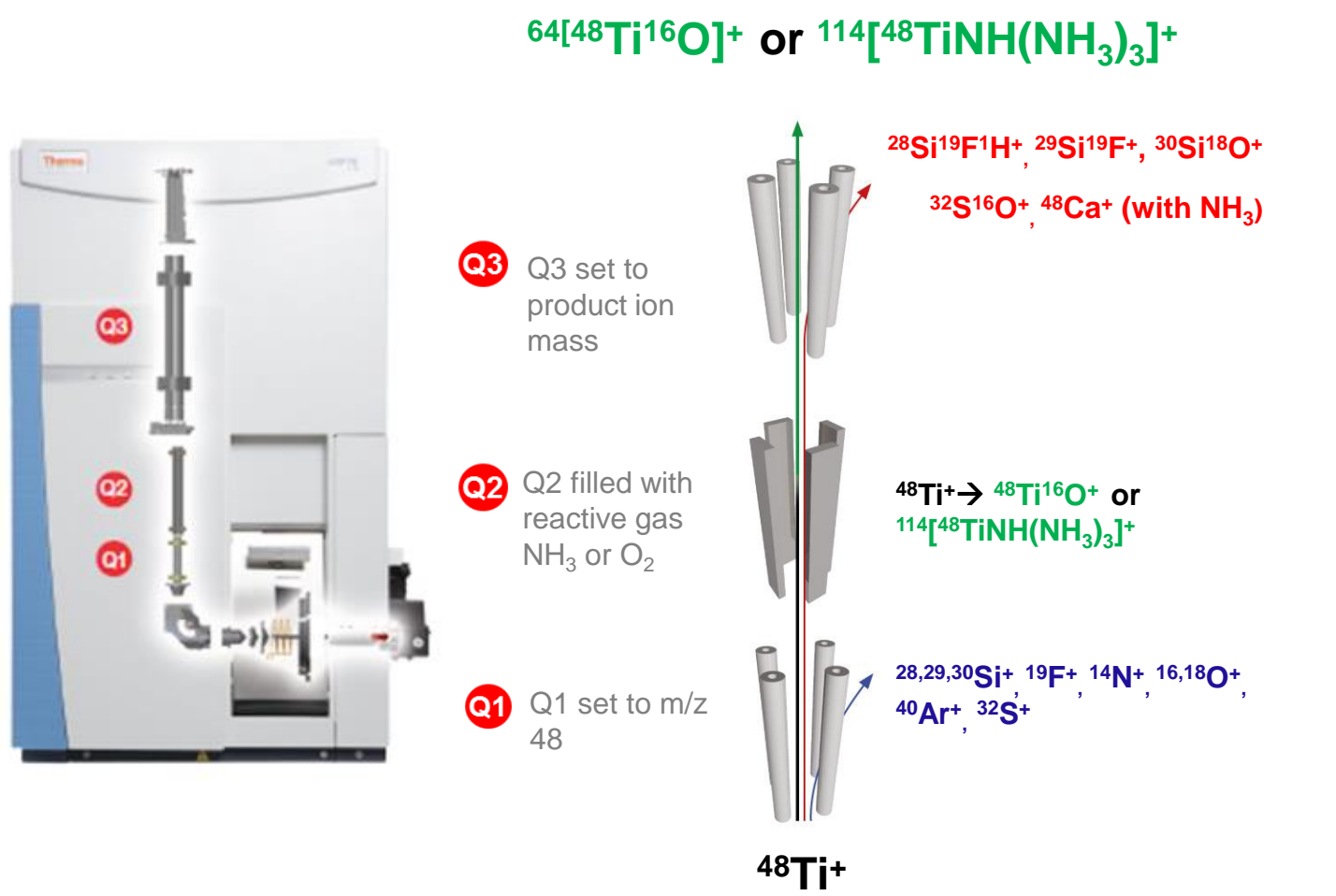


Table 2. LoD, results, recovery and reproducibility (n=5) for the analysis of a silicon matrix sample. Please note that LoD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible..

	Analysis mode	LoD (ng·L ⁻¹)	Results (ng·L ⁻¹)	50 ng·L ⁻¹ recovery (%)	Reproducibility (n=5) (%)
⁷ Li	SQ-CP-NH ₃	0.1	0.02	98%	95.2±3.7
²³ Na	SQ-CP-NH ₃	0.6	2.3	100%	100.2±1.5
²⁴ Mg	SQ-CP-NH ₃	0.3	0.4	99%	98.3±2.2
²⁷ Al	SQ-CP-NH ₃	1.3	6.0	104%	105.2±3.1
³⁹ K	SQ-CP-NH ₃	0.6	1.0	98%	101.0±1.5
⁴⁰ Ca	SQ-CP-NH ₃	1.0	4.1	103%	101.4±4.1
⁴⁸ Ti at 64 m/z	TQ-O ₂	1.2	2.8	99%	105.7±1.5
⁵¹ V at 67 m/z	TQ-O ₂	0.2	0.8	98%	103.1±1.6
⁵⁵ Mn	SQ-CP-NH ₃	2.3	3.5	97%	103.8±1.9
⁵⁶ Fe	SQ-CP-NH ₃	1.6	3.4	98%	102.2±3.3
⁵⁹ Co	SQ-CP-NH ₃	0.9	2.2	97%	99.0±2.3
⁶³ Cu	SQ-CP-NH ₃	0.9	1.7	98%	99.5±1.2
⁶⁶ Zn	SQ-KED	1.9	7.7	90%	111.1±3.4
⁷¹ Ga	SQ-KED	1.2	2.3	91%	106.9±4.4
⁷⁴ Ge at 91 m/z	TQ-O ₂	1.0	2.7	100%	104.1±1.2
⁷⁵ As at 91 m/z	TQ-O ₂	0.4	0.7	101%	106.0±2.5
⁸⁸ Sr	SQ-KED	0.2	0.1	98%	105.2±2.8
⁹⁰ Zr	SQ-KED	0.1	0.1	96%	105.7±2.6
⁹⁸ Mo	SQ-KED	0.5	1.1	93%	107.0±3.8
¹⁰⁷ Ag	SQ-KED	0.3	1.0	95%	107.0±4.0
¹¹¹ Cd	SQ-KED	0.4	0.6	95%	111.1±4.5
¹¹⁸ Sn	SQ-KED	0.3	0.6	93%	107.9±4.0
¹²¹ Sb	SQ-KED	0.1	0.1	93%	105.3±2.0
¹³⁸ Ba	SQ-KED	0.1	0.1	93%	105.7±4.5
¹⁸⁴ W	SQ-KED	0.1	0.2	93%	103.6±3.8
²⁰⁸ Pb	SQ-KED	0.3	1.2	91%	107.2±4.1

iCAP TQs Analysis of 9.8% H₂SO₄

Sulfuric acid (H₂SO₄) is one of the common semiconductor process chemicals. The challenges for the ultratrace elemental analysis of sulfuric acid by ICP-MS are:

- > Minimizing sample preparation to avoid any contamination
- > The aggressive nature and high viscosity of the sample
- > S based spectral interferences

In this study 98% H₂SO₄ was simply diluted with high purity water (1:10 m/m) before analysis so avoiding any contamination. By using a inert, acid resistant sample introduction system including a PFA nebulizer, the aggressive acid sample could be reliably aspirated into the ICP ion source. In this sample matrix, titanium is severely affected by S based species at all isotopes.

Table 3. Titanium isotopes with commonly observed interferences in H₂SO₄.

Isotope	Abundance	H ₂ SO ₄ Interferences
⁴⁶ Ti	8%	³² S ¹⁴ N ⁺
⁴⁷ Ti	7.3%	³³ S ¹⁴ N ⁺
⁴⁸ Ti	73.8%	³² S ¹⁶ O ⁺
⁴⁹ Ti	5.5%	³³ S ¹⁶ O ⁺
⁵⁰ Ti	5.4%	³⁴ S ¹⁶ O ⁺

Using the TQ-NH₃ mass shift mode (shown in Figure 3), S, N and O based polyatomic interferences are efficiently removed providing accurate analysis of. In TQ-NH₃ mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (IMS) to reject unwanted ions. The second quadrupole (Q2) is used to selectively shift the Ti target analytes to the product ions using NH₃ as the reaction gas, while the potential interference do not react with NH₃. The third quadrupole (Q3) then isolates the Ti(NH₃)⁺ product ions and removes any remaining interferences through a second stage of mass filtration allowing completely interference free analysis of the analyte to be achieved.

A comparison of the analytical performance for the iCAP TQs for the determination of the major titanium isotope (⁴⁸Ti) in 9.8% H₂SO₄ using both single quadrupole (SQ) and triple quadrupole (TQ) NH₃ mass shift analysis modes on the iCAP TQs is shown in Figures 5 and 6. While SQ-NH₃ can provide a single digit ng·L⁻¹ LoD (Figure 5), it's only by using the TQ-NH₃ mode that all polyatomic interferences from 9.8% H₂SO₄ matrix are sufficiently removed to provide sub ng·L⁻¹ detection (Figure 6). This clearly shows that, for the very lowest detection capabilities in semiconductor process chemicals such as 98% H₂SO₄, the powerful interference suppression capabilities provided by the iCAP TQs ICP-MS are required.

Figure 5. Calibration curve for ⁴⁸Ti in 9.8% H₂SO₄ with SQ NH₃ mass shift mode.

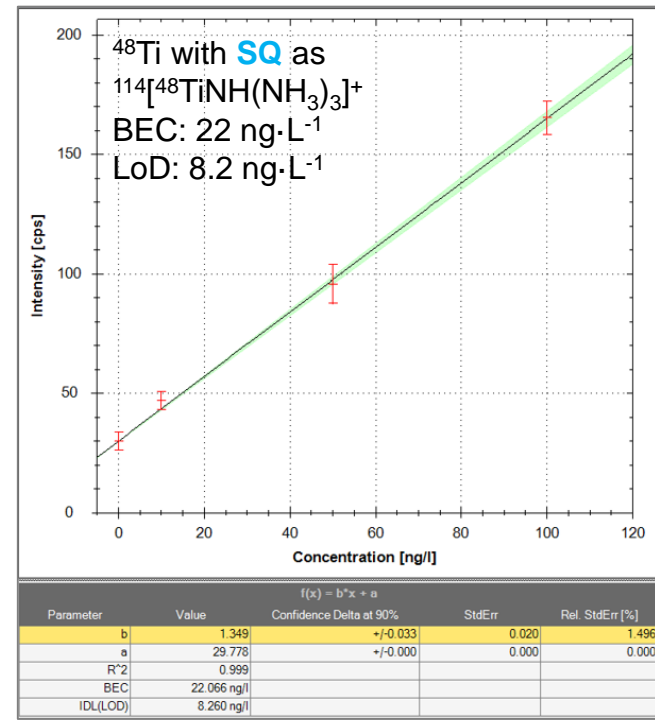
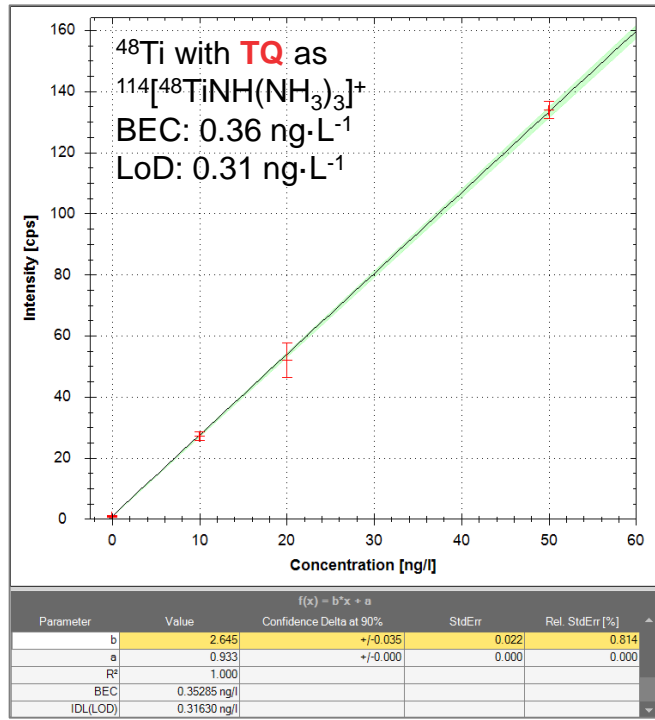


Figure 6. Calibration curve for ⁴⁸Ti in 9.8% H₂SO₄ with TQ NH₃ mas shift mode.



iCAP TQs Analysis of IPA

Isopropyl alcohol (IPA) is used to clean wafers during production in the semiconductor industry. As IPA comes into direct contact with wafer surfaces, it must be controlled for its trace metal purity. An ICP-MS technique for the direct analysis of IPA provides a useful control for ultratrace (ng·L⁻¹) levels of analytes in IPA and avoids any contamination caused by sample preparation.

IPA has historically been considered a difficult matrix to analyze directly by ICP-MS due to its high volatility, low viscosity and high carbon content (Table 4).

Calibration curves for the analysis of ³⁹K and ⁷⁵As in IPA by the iCAP TQs are shown in Figures 7 and 8. The use of TQ-O₂ mode for the analysis of ⁷⁵As as ⁹¹[⁷⁵AsO]⁺ both eliminates polyatomic interferences and increases absolute sensitivity. With the robust RF generator in the iCAP TQs the advantages from the use of cold plasma (minimized formation of argon based polyatomic interferences and reduced backgrounds for low ionization potential (IP) elements such as K) can be leveraged for organic solvents with detection at the single digit ng·L⁻¹ level. As can be seen in the images from the iCAP TQs torch box camera, cold plasma analysis at 600 W provides a strong, robust plasma, even for the direct analysis of organic solvents such as IPA,

Table 4. Chemical properties.

	Vapor Pressure (mm·Hg) at 20° C	Viscosity (mPa·s) at 25° C
H ₂ O	17.5	0.89
IPA	30.8	2.37

Figure 7. Calibration curve for ⁷⁵As in IPA with TQ-O₂ mass shift mode.

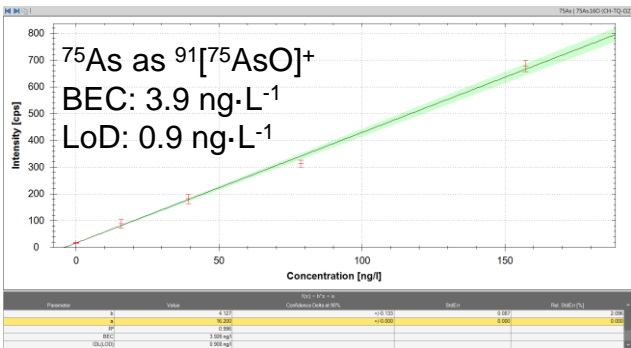
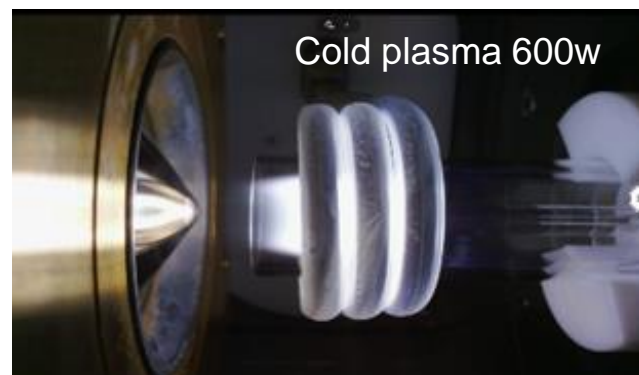
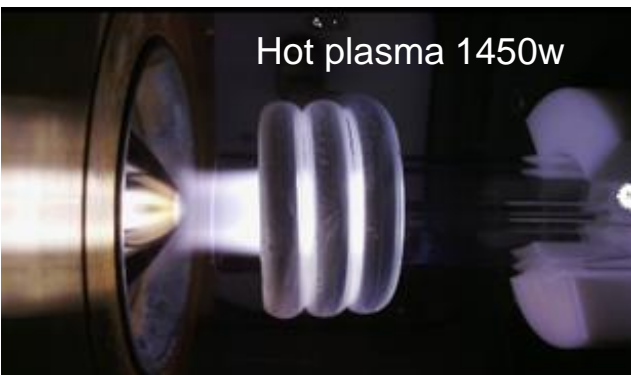
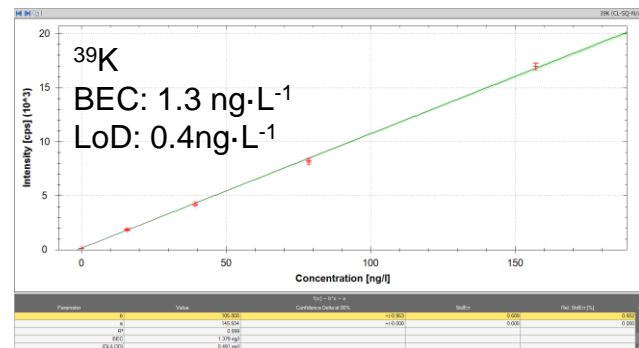


Figure 8. Calibration curve for ³⁹K in IPA with cold plasma (600 W).



CONCLUSIONS

- The Thermo Scientific iCAP TQs ICP-MS provided the highest sensitivity and the freedom from interferences required for the measurement of ultratrace (sub ng·L⁻¹) concentration levels in semiconductor samples.
- Switching between hot and cold plasma conditions is achievable with the robust RF generator in the iCAP TQs, resulting in improved analysis of organic solvents.

TRADEMARKS/LICENSING

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