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# Determination of ultratrace elements in photoresist solvents using the Thermo Scientific iCAP TQs ICP-MS

## Authors

Tomoko Vincent,
Product Specialist,
Thermo Fisher Scientific

## Keywords

Cold plasma, iCAP TQs, KED, Mass shift, NMP, PGMEA, Photoresist, Triple quadrupole, Semiconductor, Ultratrace

## Goal

To determine ultratrace metal concentrations in semiconductor grade NMP and PGMEA. To demonstrate the use of cold plasma and triple quadrupole technologies to reduce background equivalent concentrations (BEC) and detection limits (LOD). To demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS for performing reproducible, ultratrace ng·L⁻¹ (ppt) measurements with reliable switching between multiple analysis modes (hot/cold plasma, single/ triple quadrupole) within a single measurement.

## Introduction

Propylene glycol methyl ether acetate (PGMEA) and N-methyl-2-pyrrolidone (NMP) are the base organic solvents of semiconductor photoresists used in the production of sub-µm structures in microelectronic manufacturing. As photoresists come into direct contact with wafer surfaces, their components must be controlled for trace metal purity.

Because of its high elemental sensitivity, ICP-MS is widely used in quality control analyses of materials in the semiconductor industry. A simple ICP-MS analytical method for the direct analysis of photoresist solvents would provide a useful control for ultratrace (ng·L⁻¹) levels of analytes and avoid any contamination caused by any sample preparation.

PGMEA and NMP have historically been considered as difficult matrices to analyze directly by ICP-MS due to their high volatility (see Table 1) and high carbon content which can lead to significant polyatomic interferences.

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In this application note, cold plasma, kinetic energy discrimination and triple quadrupole ICP-MS technologies are combined within a single analytical method in the Thermo Scientific iCAP TQs ICP-MS to remove all polyatomic interferences. With the use of cold plasma, the ICP ion source is run at a significantly lower forward power, effectively suppressing the ionization of argon and carbon and therefore eliminating any subsequent polyatomic species that would otherwise interfere with target analyte ions. For some analytes that are more sensitive under hot plasma conditions, a triple quadrupole mass shift analysis mode was automatically selected for accurate, interference free analysis.

Table 1. Chemical properties.

|  | Vapor Pressure (mm·Hg) at 20 ˚C |
|---|---|
| $H_2O$ | 17.5 |
| PGMEA | 3.7 |
| NMP | < 0.3 |

## Sample preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MOhm cm) and left to dry in a laminar flow clean hood before use. Standards at concentrations of 200, 400 and 1000 ng·L$^{-1}$ were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (prepared from single element standards in semiconductor grade isopropyl alcohol) directly to the PGMEA and NMP samples. Semiconductor grade PGMEA was used for the rinse and blank solutions. Recovery tests were performed using 100 ng·L$^{-1}$ spikes.

## Instrumentation

A dedicated sample introduction system was used for the routine, direct analysis of organic solvents. The introduction system consisted of a 100 µL·min$^{-1}$ self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a peltier cooled quartz spraychamber (at -10 ˚C). High purity oxygen (30 mL·min$^{-1}$) was added to the nebulizer aerosol stream via a port in the spraychamber elbow to prevent carbon matrix build up on the interface. A 1.0 mm diameter quartz injector minimized carbon loading of the plasma.

Platinum tipped sample and skimmer cones were necessary because of the oxygen addition. All samples were presented for analysis using a Teledyne CETAC Autosampler ASX-112FR System (Omaha, NE, USA). The iCAP TQs ICP-MS was operated in SQ-KED (single quadrupole He KED), SQ-CP-NH$_3$ (single quadrupole, cold plasma with NH$_3$ as a reaction gas) and TQ-O$_2$ mass shift (triple quadrupole with O$_2$ as a reaction gas) modes. All parameters are presented in Table 2. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.



Table 2. Instrument configuration and operating parameters.

| Parameter | Value | | |
|---|---|---|---|
| Nebulizer | PFA concentric nebulizer 100 µL·min$^{-1}$ (self-aspirating) | | |
| Spraychamber | Quartz cyclonic spraychamber cooled at -10 ˚C | | |
| Additional Gas | Pure O$_2$ gas, 30 mL·min$^{-1}$ | | |
| Injector | 1.0 mm I.D., Quartz | | |
| Interface | Pt sampler and Pt (high sensitivity) skimmer | | |
| Extraction Lens | Cold plasma lens | | |
| Measurement Mode | Single quadrupole | | Triple quadrupole |
|  | SQ-KED | SQ-CP-NH$_3$ | TQ-O$_2$ |
| Forward Power | 1550 W | 540 W | 1550 W |
| Nebulizer Gas | 1.17 L·min$^{-1}$ | 0.68 L·min$^{-1}$ | 1.17 L·min$^{-1}$ |
| CRC Gas | Pure He, 4.2 mL·min$^{-1}$ | Pure NH$_3$, 0.28 mL·min$^{-1}$ | Pure O$_2$, 0.3 mL·min$^{-1}$ |
| Dwell Time | 100 to 300 ms per analyte, 5 sweeps | | |
| Lens Setting | Optimized using autotune | | |

Identical instrument parameters were used for the analysis of both the NMP and PGMEA solvents for improved sample throughput without any sacrifice in performance.

## Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for multi-element analysis in a range of routine applications. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination and triple quadrupole analysis modes), the ultimate performance can be achieved, specifically tailored for each application. Through the implementation of Reaction Finder in the Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, the choice of isotope and analysis mode for each target element is made automatically, making triple quadrupole ICP-MS as easy to use as single quadrupole systems.

For example, using the TQ-$O_2$ mass shift mode (schematically shown in Figure 2), the C, N, O and Ar based polyatomic interferences are efficiently removed leading to accurate analysis of As. In TQ-$O_2$ mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (the Q2 collision/reaction cell) is used to selectively shift the As target analytes to the $AsO^+$ product ions using $O_2$ as the reaction gas, while any remaining carbon based polyatomic interference will not react with $O_2$. The third quadrupole (Q3) then isolates the $AsO^+$ product ions = and removes any remaining interferences through a second stage of mass filtration allowing completely interference free quantification.
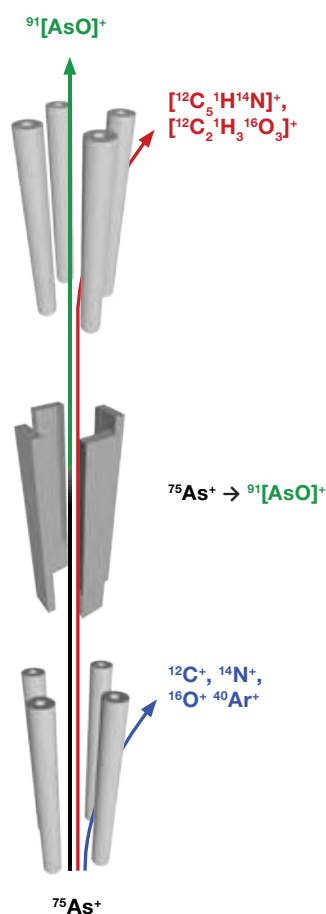


Figure 1. iCAP TQs ICP-MS. In TQ-$O_2$ triple quadrupole mode, Q2 (collision/reaction cell) is pressurized with oxygen as a reaction gas, Q1 is set to the analyte mass ($M^+$) and Q3 is set to the product ion mass ($MO^+$) or ($M^+$).



Figure 2. Schematic showing TQ-$O_2$ mass shift mode for the analysis of arsenic ($^{75}As$ as $^{91}[AsO]^+$).

Figure 3. Sample list from Qtegra ISDS Software. NMP and PGMEA solvents were analyzed with identical instrument and method parameters within a single LabBook.

A summary of the results from the trace elemental analysis of semiconductor grade PGMEA and NMP is shown in Table 3. For each of the twenty one analytes, the analysis mode, detection limits (LOD), calculated from three times the standard deviation of ten replicate measurements of the calibration blank and spike recovery are provided.

Table 3. LOD, recovery data for the analysis of PGMEA and NMP. Please note that LOD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible.

| Analyte | Analysis Mode | LOD (ng·L$^{-1}$) | | Spike Recovery (100 ng·L$^{-1}$) | |
|---------|---------------|-------|------|--------|------|
|         |               | PGMEA | NMP  | PGMEA  | NMP  |
| $^{7}$Li | SQ-CP-NH$_3$ | 0.2 | 0.9 | 97% | 98% |
| $^{23}$Na | SQ-CP-NH$_3$ | 1.3 | 10.2 | 98% | 97% |
| $^{24}$Mg | SQ-CP-NH$_3$ | 0.4 | 5.0 | 97% | 91% |
| $^{27}$Al | SQ-CP-NH$_3$ | 1.1 | 3.8 | 97% | 100% |
| $^{39}$K | SQ-CP-NH$_3$ | 1.3 | 6.4 | 102% | 106% |
| $^{40}$Ca | SQ-CP-NH$_3$ | 1.2 | 8.1 | 96% | 94% |
| $^{52}$Cr | SQ-CP-NH$_3$ | 2.0 | 3.3 | 97% | 92% |
| $^{55}$Mn | SQ-CP-NH$_3$ | 0.3 | 8.4 | 93% | 99% |
| $^{56}$Fe | SQ-CP-NH$_3$ | 3.1 | 2.0 | 104% | 103% |
| $^{59}$Co | SQ-CP-NH$_3$ | 0.4 | 0.7 | 95% | 100% |
| $^{63}$Cu | SQ-CP-NH$_3$ | 1.2 | 3.4 | 98% | 96% |
| $^{51}$V | SQ-KED | 2.6 | 2.8 | 105% | 96% |
| $^{66}$Zn | SQ-KED | 14.3 | 18.8 | 94% | 100% |
| $^{98}$Mo | SQ-KED | 1.6 | 2.1 | 97% | 111% |
| $^{107}$Ag | SQ-KED | 1.5 | 1.8 | 97% | 111% |
| $^{111}$Cd | SQ-KED | 3.7 | 2.6 | 85% | 107% |
| $^{138}$Ba | SQ-KED | 0.1 | 0.0 | 94% | 101% |
| $^{208}$Pb | SQ-KED | 0.8 | 1.4 | 97% | 108% |
| $^{48}$Ti at 64 *m/z* | TQ-O$_2$ | 1.9 | 3.7 | 88% | 106% |
| $^{75}$As at 91 *m/z* | TQ-O$_2$ | 2.0 | 2.4 | 99% | 106% |
| $^{80}$Se at 96 *m/z* | TQ-O$_2$ | 1.9 | 4.6 | 95% | 109% |

Spike recoveries of between 88% and 111% were obtained for all twenty-one elements in NMP and PGMEA.

The low detection limits achieved for the more challenging analytes in NMP and PGMEA organic solvents showcase the powerful interference removal capabilities from the combination of cold plasma and triple quadrupole technologies on the iCAP TQs ICP-MS.

## Calibration curves

Calibration curves for Mg, Ti, As and Ag in PGMEA are shown in Figure 4. The calibrations, performed with calibration points at 100, 200 and 1000 ng·L$^{-1}$, demonstrate the excellent sensitivity and linearity achieved with different types of organic solvent using common instrument parameters.
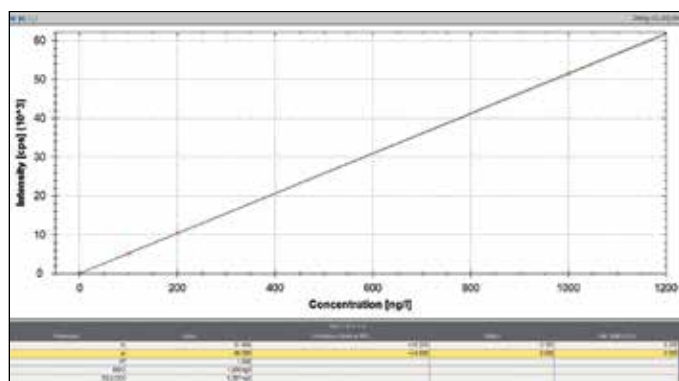


Figure 4a. Mg in PGMEA using SQ-CP-NH$_3$ mode.
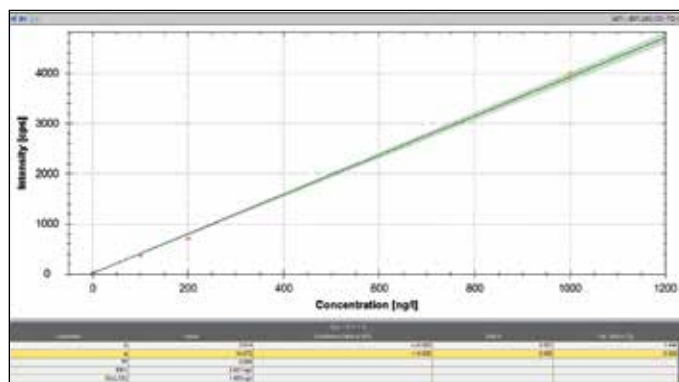


Figure 4b. Ti in PGMEA using TQ-O$_2$ mass shift mode.
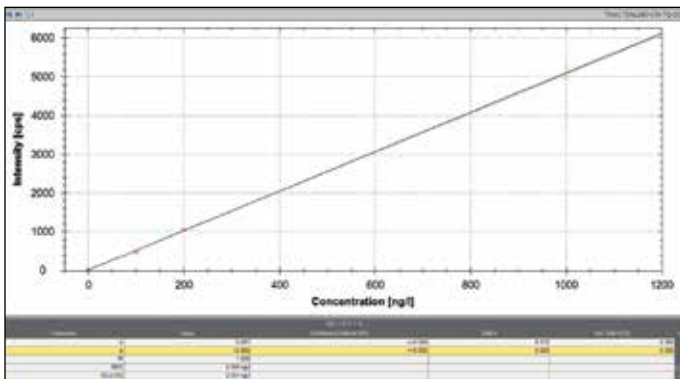
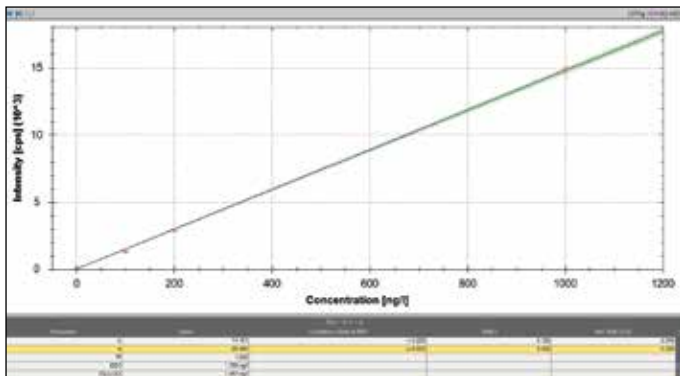**Figure 4c. As in PGMEA using TQ-O$_2$ mass shift mode.**



**Figure 4d. Ag in PGMEA using CP-SQ-KED.**

## Conclusion

The Thermo Scientific iCAP TQs ICP-MS has been shown to provide sensitive and accurate multielemental analysis of NMP and PGMEA photoresist solvents at ultratrace (ng·L$^{-1}$) concentration levels. The combination of single and triple quadrupole technologies with hot and cold plasma modes – even in volatile organic solvents – provides the analytical flexibility and instrumental performance to deliver the detection limits required for semiconductor level analyses.

Although NMP and PGMEA have different chemical formulae and properties, the iCAP TQs ICP-MS allows the use of a single analytical method for both solvents, simplifying the analytical procedure and improving productivity.

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