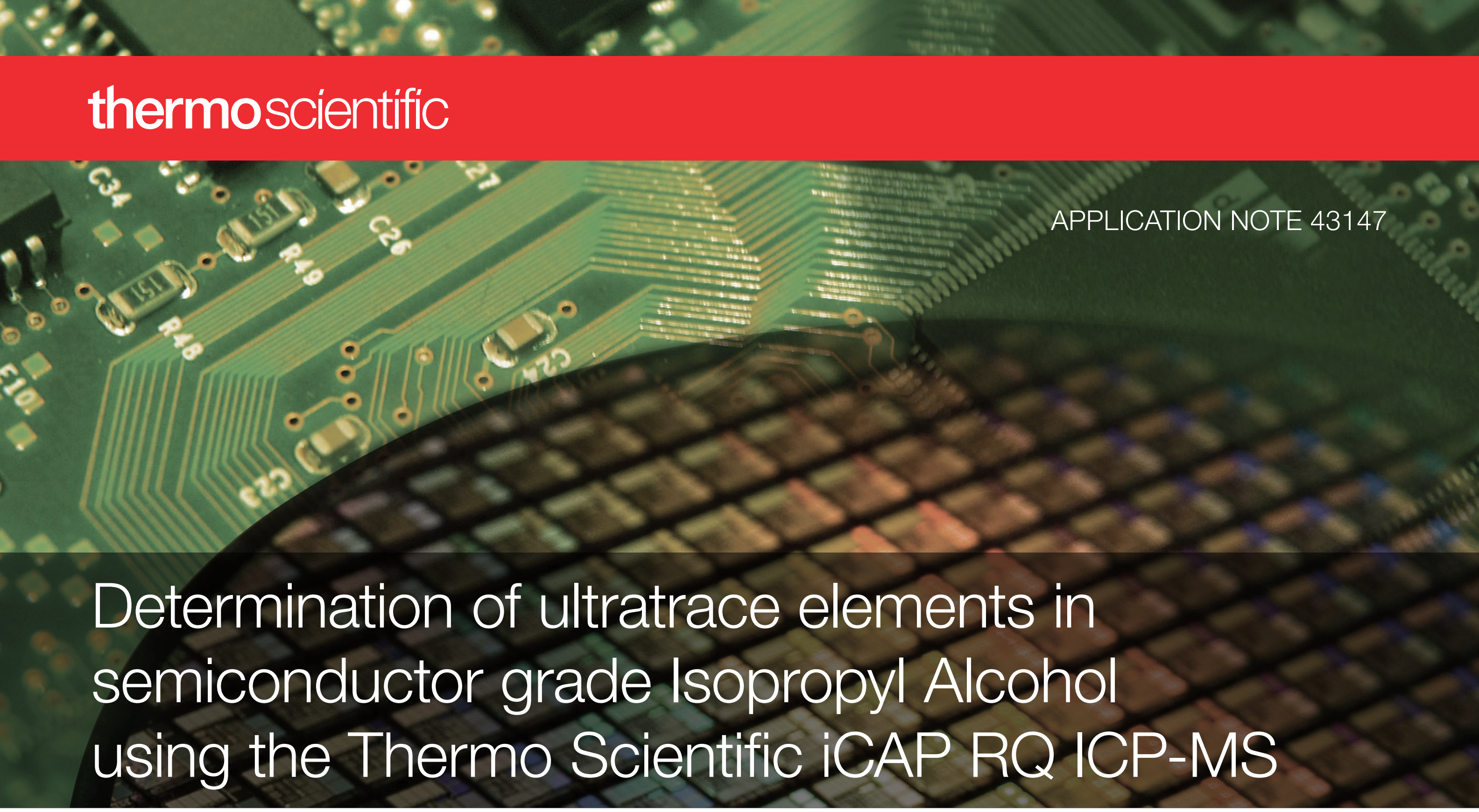
thermoscientific



APPLICATION NOTE 43147

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

Authors

Tomoko Vincent[1], Vicki Wu[2], Julian D. Wills[1], Lothar Rottmann[1], [1]Thermo Fisher Scientific, Germany, [2]Joy Allied Technology, Taiwan.

Keywords

Cold plasma, iCAP RQ, ICP-MS, IPA, organics, semiconductor

Goal

To determine ultratrace metal concentrations in semiconductor grade isopropyl alcohol (IPA). Use cold plasma to reduce background equivalent concentrations (BEC) and detection limits (LoD) to demonstrate reproducible ultratrace (ng·L^{-1}) measurements. Demonstrate the reliable switching between hot and cold plasma within a single measurement to maximize sample throughput.

Introduction

Isopropyl alcohol (IPA) is used to solvent 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. Because of its high elemental sensitivity, ICP-MS is widely used in quality control analyses of materials used in the semiconductor industry. A direct ICP-MS technique for the analysis of IPA would provide a useful control for ultratrace (ng·L^{-1}) levels of analytes in IPA and avoid 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. In this study instead of using kinetic energy discrimination (KED) to remove carbon based interferences from the sample matrix and argon based interferences from the ICP, cold plasma was employed. With this approach the ICP ion source is run at a significantly lower power, effectively suppressing the ionization of argon and carbon and therefore eliminating interfering polyatomic species that would otherwise interfere with target analyte ions. This approach is particularly effective for the alkali metals and permits their direct analysis at the ultratrace concentration levels required by the semiconductor industry.

ThermoFisher SCIENTIFIC

Sample and calibration solution preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ) and left to dry in a laminar flow clean hood before use. Standards at concentrations of 20, 50, 100 and 200 ng·L^{-1} were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (prepared from single element standards) directly to the IPA samples. Semiconductor grade IPA was used for the rinse and blank solutions. In order to assess recovery in the IPA matrix, an IPA sample was spiked with 100 ng·L^{-1} and compared with the unspiked sample.

Instrument configuration

The Thermo Scientific™ iCAP™ RQ ICP-MS was used for all analyses. Due its high transmission interface and proprietary 90 degree ion optics for the removal of neutral species, the iCAP RQ ICP-MS provides the high elemental sensitivity and low backgrounds – in both hot and cold plasma – for the ultratrace determination of trace elements in semiconductor samples.

A dedicated organic matrix sample introduction system was used for the routine, direct analysis of IPA. The introduction system consisted of a 100 µL·min^{-1} self aspirating PFA micro flow nebulizer (Elemental Scientific, Omaha, NE, USA) and a peltier cooled quartz spraychamber (at -10 °C). Oxygen, precisely regulated by a low flow MFC controlled by the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was added to the aerosol stream via a port in the spraychamber elbow to prevent carbon matrix build up on the interface region. A 1.0 mm diameter quartz injector minimized carbon loading of the plasma. Platinum tipped sampler and skimmer cones were necessary because of the oxygen addition.

Operating parameters

The operating parameters used for iCAP RQ ICP-MS used in this work are shown in Table 1.

Table 1. Instrument Parameters.

Parameter	Value
Hot Plasma Power	1350 W
Cold Plasma Power	800 W
Spraychamber	Quartz cyclonic
Peltier Temperature	-10 °C
Hot Plasma Nebulizer Gas Flow	0.7 L·min^{-1}
Cold Plasma Nebulizer Gas Flow	1.0 L·min^{-1}
Oxygen Gas Flow	50 mL·min^{-1}
Nebulizer	MicroFlow PFA-100 (self-aspirating)
Injector	1.0 mm I.D., quartz
Interface	Platinum sampler and high sensitivity platinum skimmer
Dwell Time	100 ms per peak, 10 sweeps

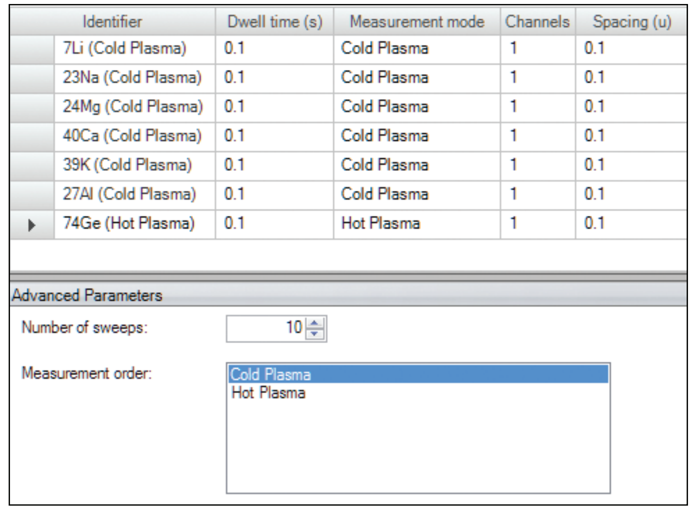
In this application, the measurement of 26 elements at ultratrace concentrations in IPA was achieved in less than 5 minutes. This includes sample uptake, analysis and washout as well as the switching time between hot and cold plasma within each measurement.

Result and discussion

The dynamic frequency RF generator used in the iCAP RQ ICP-MS is lightning fast in comparison to older designs that rely on mechanical matching network to adjust to impedance changes caused by sample matrices and doesn't require a grounded shield to achieve cold plasma. By virtue of this design, the iCAP RQ ICP-MS ion source is significantly more robust so that pure organic solvents can be routinely analyzed at higher sample flow rates than would be possible with older RF generator designs. Running at higher sample flow rates offers improved sensitivity – especially important with semiconductor applications that continually challenge ICP-MS detection limits. The iCAP RQ ICP-MS RF generator maintains a stable analyte signal over extended measurement periods even when switching between hot and cold plasma in every analysis.

Assigning different analysis modes per isotope is easily performed in the Qtegra ISDS Software (Figure 2). Low ionization potential (IP) elements (e.g. alkali metals such as Li, Na, Mg, K, Ca as well as first row transition metals such as Cr, Fe etc.) are measured with low backgrounds and high sensitivities in cold plasma and higher IP elements are analyzed in hot plasma. For example, the analysis of magnesium (*m/z* 24) in IPA under hot plasma conditions is complicated by a carbon dimer species ($^{12}C_2$). As can been seen in Figure 3 and Table 2 however, by using cold plasma the interference at *m/z* 24 is removed and the sub ng·L^{-1} detection limit (LoD) and background equivalent concentration (BEC) values meet the requirements for ultratrace analyses in semiconductor relevant materials such as IPA.

Figure 1. Thermo Scientific iCAP RQ ICP-MS.



Identifier	Dwell time (s)	Measurement mode	Channels	Spacing (u)
7Li (Cold Plasma)	0.1	Cold Plasma	1	0.1
23Na (Cold Plasma)	0.1	Cold Plasma	1	0.1
24Mg (Cold Plasma)	0.1	Cold Plasma	1	0.1
40Ca (Cold Plasma)	0.1	Cold Plasma	1	0.1
39K (Cold Plasma)	0.1	Cold Plasma	1	0.1
27Al (Cold Plasma)	0.1	Cold Plasma	1	0.1
74Ge (Hot Plasma)	0.1	Hot Plasma	1	0.1

Advanced Parameters

Number of sweeps: 10

Measurement order: Cold Plasma, Hot Plasma

Figure 2. Screenshot from Qtegra ISDS Software showing the definition of Hot and Cold plasma per isotope and how to choose the order of the measurement modes used in an analysis.

Calibration data

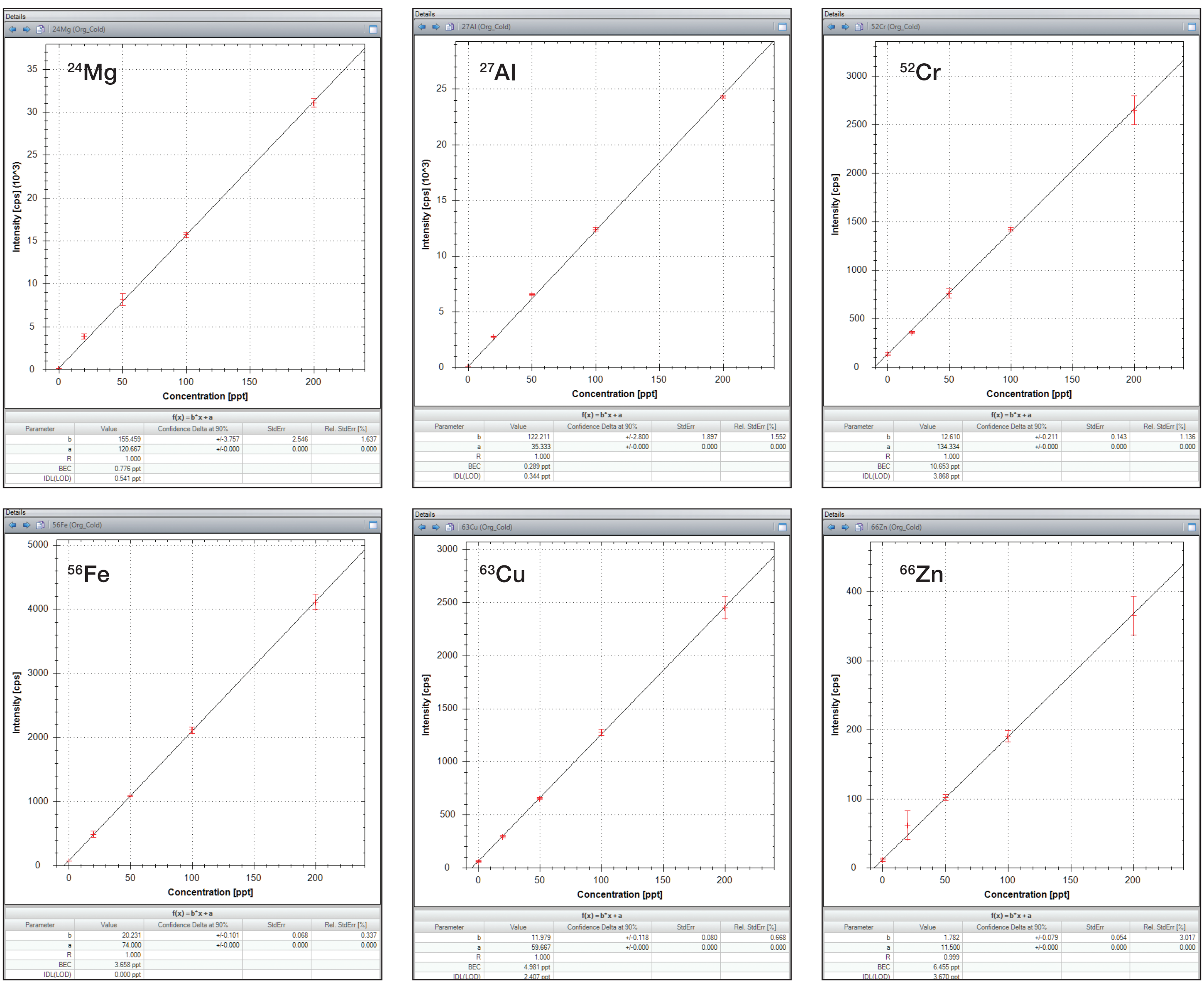


Figure 3. Cold plasma calibration curves with points 20, 50, 100 and 200 (ng·L^{-1}).

Table 2. BEC, LoD and recovery data for the analysis of semiconductor grade IPA. Please note that BEC and LoD values are dependent on the sample measured. Recovery values are shown as the percentage recovery for a 100 $ng \cdot L^{-1}$ spike in IPA. An ^{56}Fe LoD of < 0.001 $ng \cdot L^{-1}$ was recorded since all three repeats at ^{56}Fe in the IPA blank gave the same count rate.

	Analysis Mode	BEC ($ng \cdot L^{-1}$)	LoD ($ng \cdot L^{-1}$)	Recovery (%)
^{7}Li	Cold	0.031	0.007	99%
^{11}B	Hot	107	29	89%
^{23}Na	Cold	10	0.8	101%
^{24}Mg	Cold	0.78	0.54	101%
^{27}Al	Cold	0.29	0.34	97%
^{39}K	Cold	14	0.31	97%
^{40}Ca	Cold	7.4	3.1	118%
^{51}V	Hot	4.0	1.4	100%
^{52}Cr	Cold	11	3.9	97%
^{55}Mn	Cold	7.3	1.6	97%
^{56}Fe	Cold	3.7	< 0.001	98%
^{58}Ni	Cold	0.40	0.52	97%
^{59}Co	Cold	1.9	1.2	103%
^{63}Cu	Cold	5.0	2.4	106%
^{66}Zn	Cold	6.5	3.7	109%
^{74}Ge	Hot	5.1	3.9	90%
^{75}As	Hot	7.6	11	107%
^{107}Ag	Cold	0.41	0.42	116%
^{111}Cd	Hot	0.26	0.39	104%
^{115}In	Cold	0.01	0.04	100%
^{120}Sn	Hot	0.10	0.001	103%
^{138}Ba	Hot	0.014	0.014	102%
^{197}Au	Hot	1.0	1.4	86%
^{205}Tl	Cold	0.07	0.22	100%
^{208}Pb	Cold	0.13	0.39	99%
^{209}Bi	Cold	0.001	0.001	98%

Conclusion

The Thermo Scientific iCAP RQ ICP-MS has been shown to offer the high sensitivity and freedom from contamination and interference required for the measurement of ultratrace ($ng \cdot L^{-1}$) concentration levels in semiconductor grade IPA. Fast, reliable, in measurement switching between hot and cold plasma even for volatile organic solvents such as IPA is made possible with the dynamic frequency RF generator used in the iCAP RQ ICP-MS, improving sample throughput.

Products and Reagents used in this Application Note	
Organic Matrix Kit	1324711
250 $mL \cdot min^{-1}$ Additional Gas MFC	1322530
100 $\mu L \cdot min^{-1}$ PFA Nebulizer	1600342
Platinum Tipped Sample Cone	3601289
Platinum Tipped Skimmer Cone	1341430

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

ThermoFisher SCIENTIFIC