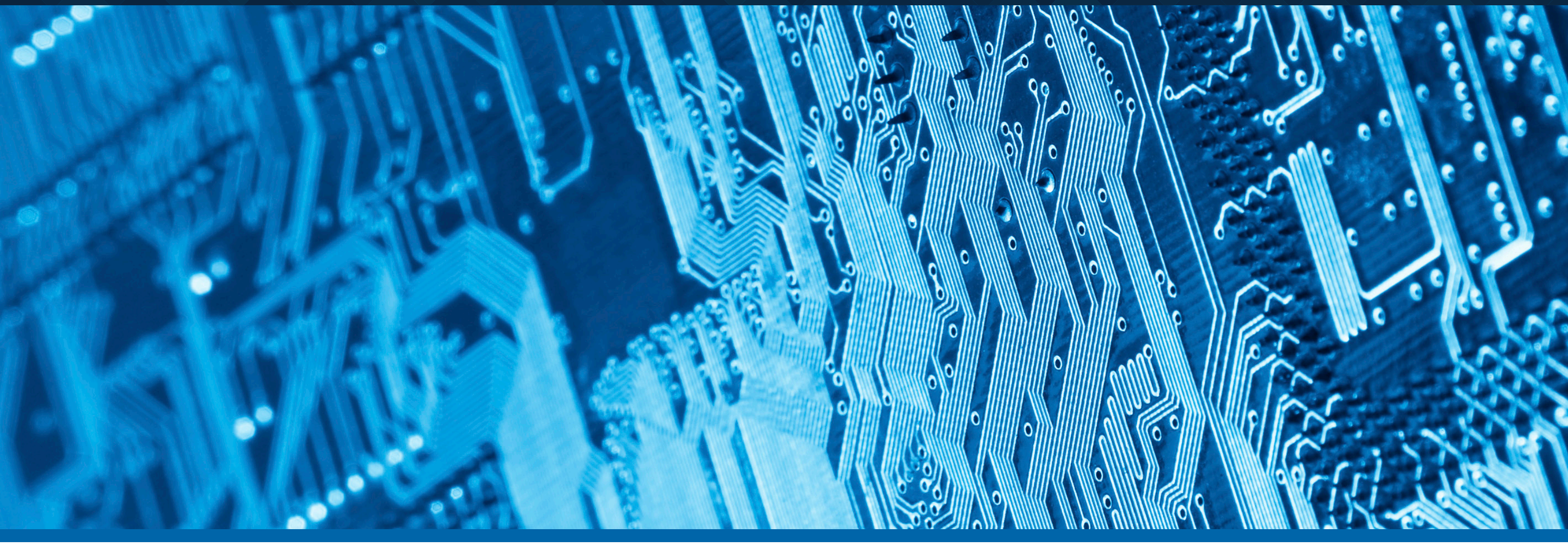

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Analysis of Semiconductor IPA (Isopropyl Alcohol) for Trace Organic Contaminants from HDPE (High-Density Polyethylene) Leachates via prep*FAST* CARBON

Brief

Organic contaminants in solvents affect semiconductor yields. prep*FAST* CARBON offers a solution to this. Semiconductor grade IPA conforms to the SEMI specifications focused on quantifying trace metals (low ppt), anions (low ppb), and assay (>99.9%). The specifications do not include trace organics, of which contamination levels can vary based upon the manufacturing process and the storage material used. The organic fingerprint of semiconductor grade IPA can differ between manufacturers, which impacts wafer processing.

Figure 1. prep*FAST* CARBON with an Agilent 6530 QTOF

Introduction

IPA is widely used in the semiconductor industry for surface preparation, cleaning, and drying. It is also the solvent typically used in the final drying step of the cleaning process. The specifications for IPA purity are very stringent. Any trace contamination left behind on the wafer surface during the final drying step has an adverse effect on processing. SEMI specifications predominantly target trace metals and anions. However, the IRDS has recognized the importance of detecting trace-level high molecular weight organic (>10 carbon atoms) contaminants in IPA, as their low volatility results in remnants on a wafer post-processing. The projected requirements for organic contaminant levels will decrease from 50 ppb in 2023 to 10 ppb in 2027.

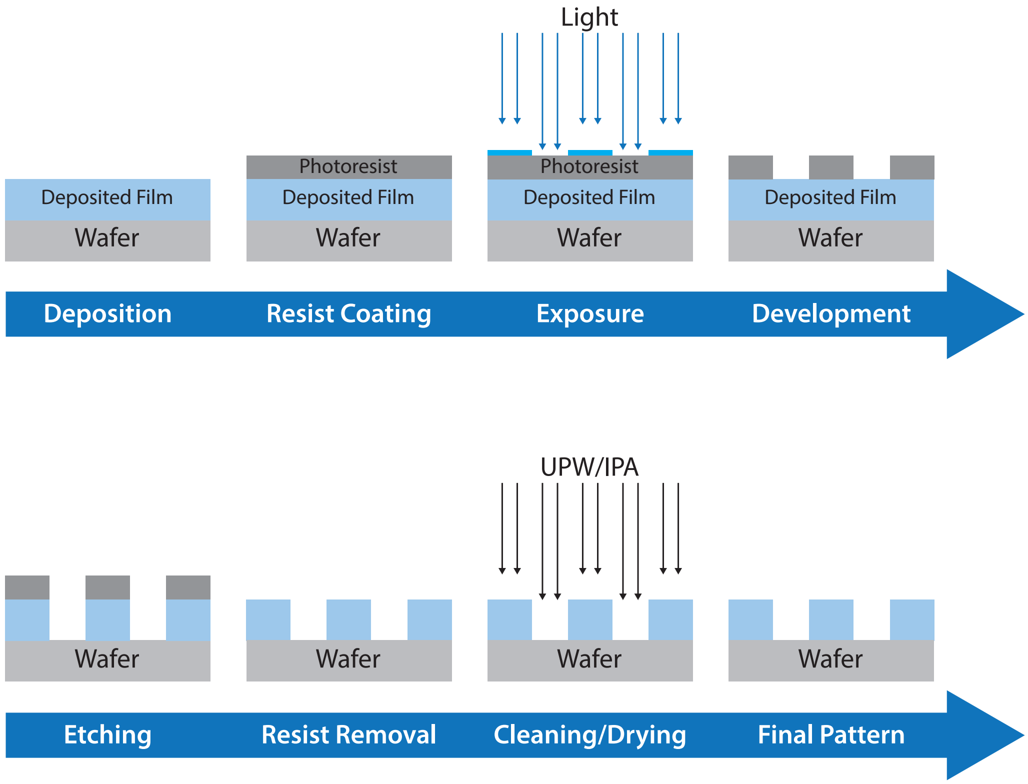

Figure 2. Illustration of semiconductor wafer production process

Table 1. Acceptable concentration limits of high molecular weight organic contaminants in IPA from 2023 IRDS YE tables

	2023	2024	2025	2026	2027
100% IPA Cleaning High Molecular Weight Organics (>10 Carbon Atoms) PPB	50	40	30	20	10
100% IPA Drying High Molecular Weight Organics (>10 Carbon Atoms) PPB	50	40	30	20	10

prep*FAST* CARBON Features

prep*FAST* CARBON is a highly automated lab system for detection and quantification of low ppt level organics and anions in a large variety of solvents, through automated sample capping, recapping, barcode reading, and more.

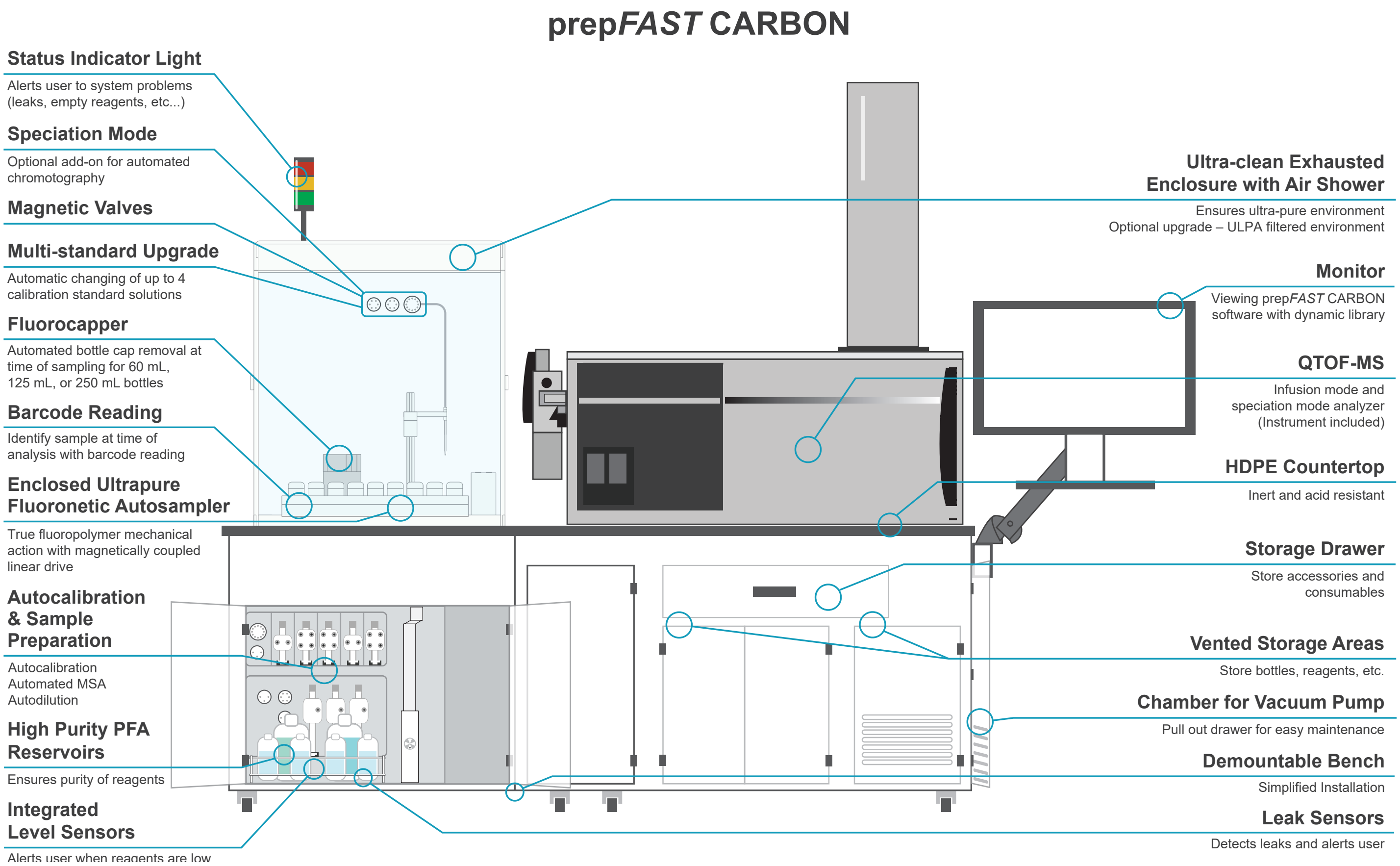

Figure 3. Features diagram of the prep*FAST* CARBON

Experimental

prep*FAST* CARBON was used to analyze semiconductor grade IPA (meeting the SEMI specifications) from three different suppliers. IPA from two of the suppliers was shipped in HDPE containers, and the other was shipped in a glass container. IPA from the source containers were aliquoted into clean PFA bottles. The capped bottles were loaded onto the autosampler of the prep*FAST* CARBON. The prep*FAST* CARBON system was set to obtain both positive and negative ion spectra and to perform MSA calibration using a 50-compound calibration standard. In-line standard additions autogenerated calibration curves used to quantify known compounds and approximate unknown compounds.

Results indicated contamination by HDPE leachates, so subsequent leaching studies were performed. These studies tested three resin beads commonly used in HDPE manufacturing and HDPE coupons manufactured from corresponding beads. The resin beads and container coupons used in the study were stored in IPA at 400C for eight weeks, to simulate approximately six months of storage at room temperature.

Table 2. Instrument Parameters

Agilent 6530 QTOF	
Ion Source	Electrospray Ionization
Mode	Infusion Mode
Resolution	15,000-40,000

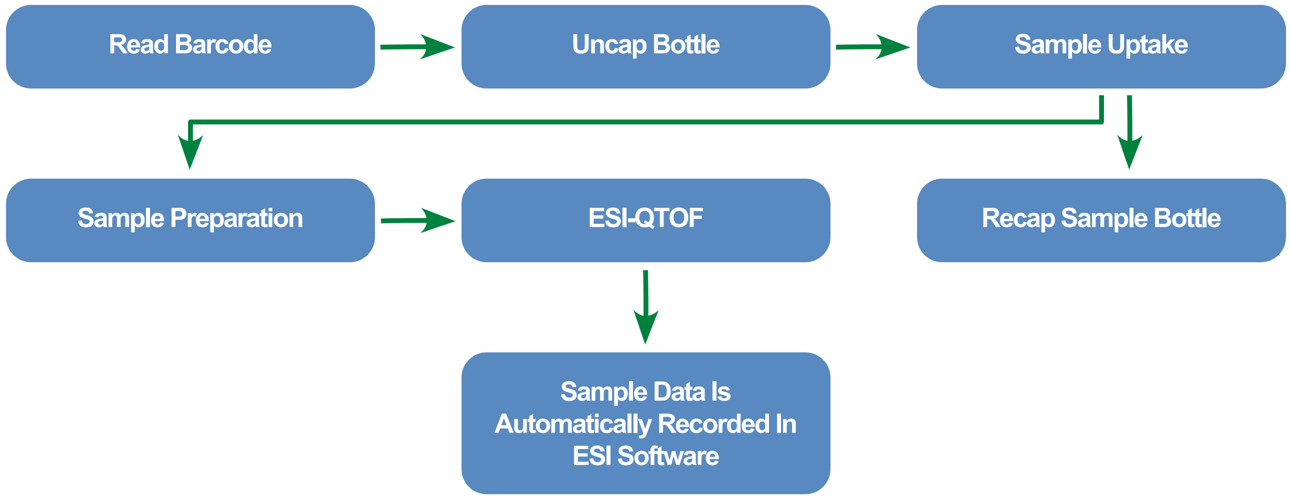

Figure 4. Workflow diagram for the prep*FAST* CARBON

Effects of Storage Vessel Material on Contamination

Supplier Variance Study

Figure 5 shows the mass spectra for IPA sourced from three different manufacturers. Comparison of the three spectra indicates that the contaminant profile of the IPA varies significantly across all three sources. These differences could be caused by the synthesis and distillation processes or from materials used during storage and transport.

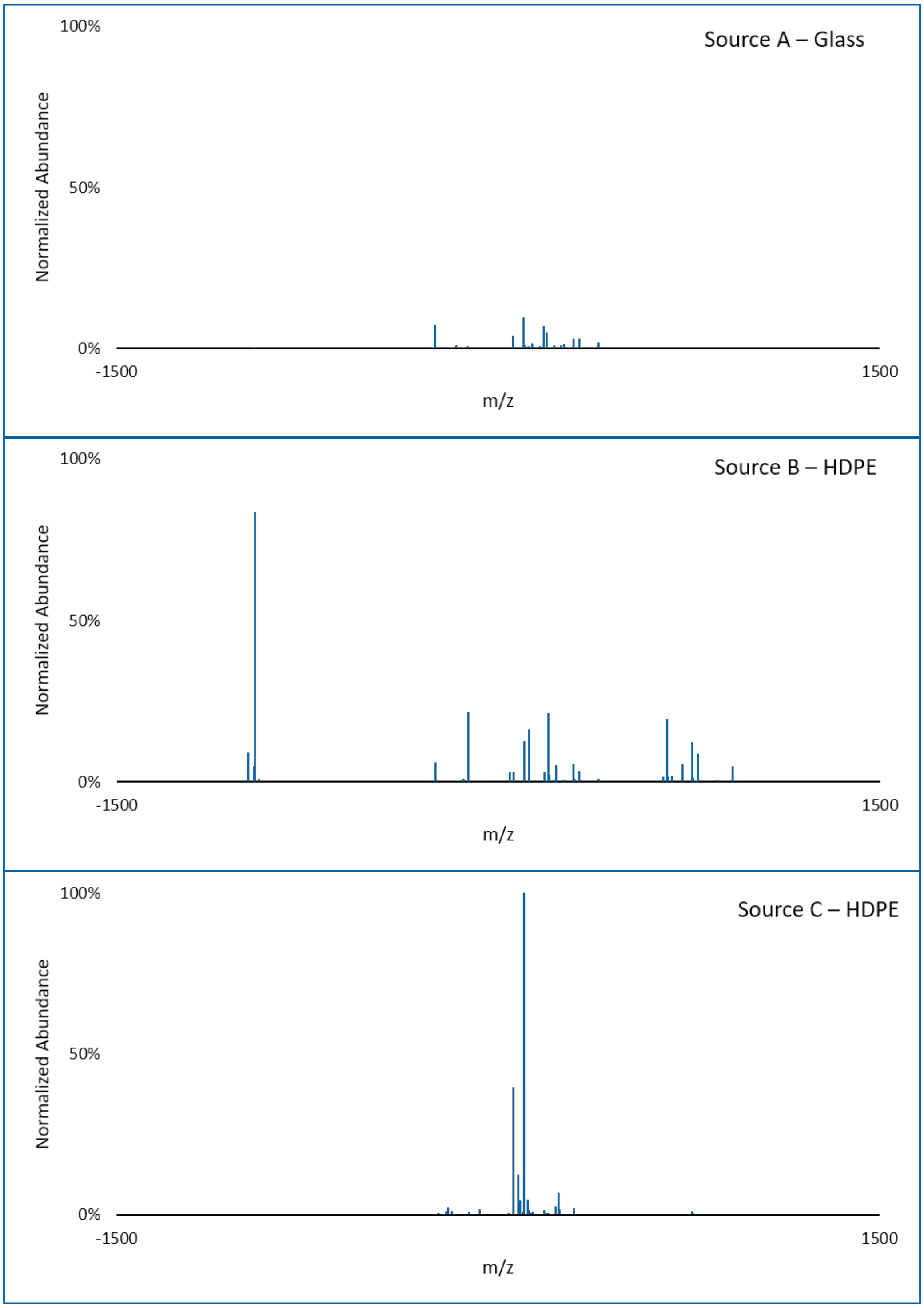

Figure 5. Mass spectra for IPA sourced from three different manufacturers.

Effects of Storage Vessel Material on Contamination *(Continued)*

prep*FAST* CARBON's NearQuant, an algorithm which accurately approximates organic compound concentrations, quantified contamination levels in each supplier's IPA.

IPA from supplier A, supplied in a glass vessel, had the lowest levels of organic contamination. IPA supplied in HDPE containers have significantly higher levels of contamination. The likely cause of the high contamination is leaching from the containers, assuming like manufacturing processes. The differences between supplier B and C are likely from differences in resins used to manufacture the HDPE containers.

Table 3. NearQuant calculation of contaminants, sorted by class. All values are in ppb.

Semiconductor Grade IPA	Container	N Class	P Class	CHO Class
Supplier A	Glass	2.2	ND	2.0
Supplier B	HDPE	19.9	14.2	4.2
Supplier C	HDPE	911.4	10.4	72.1

*ND = No Data

Table 4. NearQuant calculation of contaminants, carbon-binned. All values are in ppb.

Semiconductor Grade IPA	<C5	C5-C7	C8-C9	C10-C11	C12-C17	C18-C25	C26-C51
Supplier A (Glass Container)	0.6	1.8	0.2	0.4	0.9	0.3	ND
Supplier B (HDPE Container)	0.1	4.9	0.5	1.0	1.9	2.0	27.8
Supplier C (HDPE Container)	53.6	797.2	6.4	2.6	109.2	ND	21.0

Container Resin Bead Leaching

All three resin beads, commonly used to manufacture HDPE containers, were subjected to leaching studies. The resin beads were submerged in IPA and stored at 40 °C for eight weeks to simulate an approximately six months of room temperature storage. prep*FAST* CARBON analyzed the leachates at the end of the eight-week period.

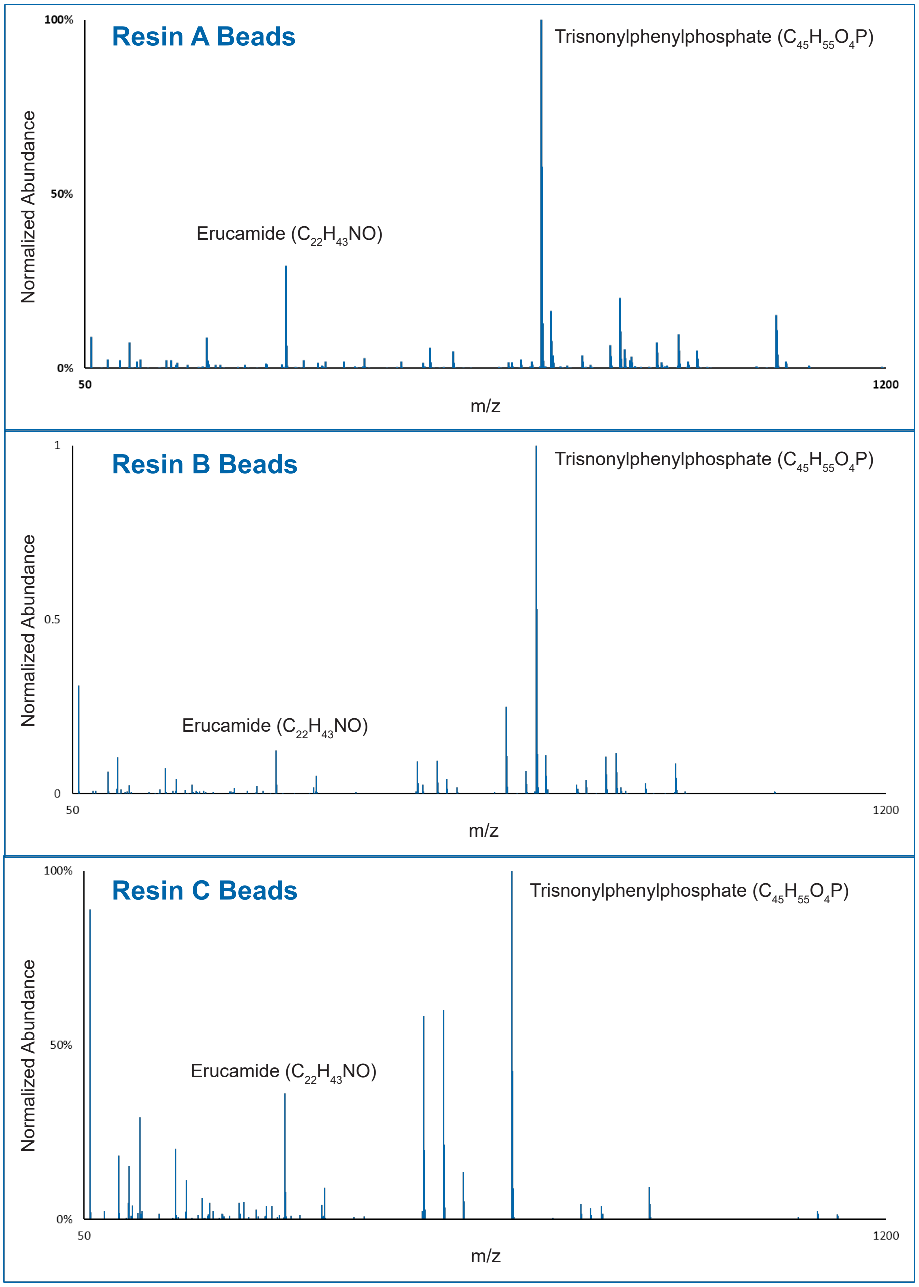

Figure 6. Three mass spectra of resin bead leach tests from all three sources.

High molecular weight leachates are worrisome in semiconductor fabrication. With high boiling points, these leachates cannot be removed from wafers as efficiently, leading to lower semiconductor yields. All resins leached Erucamide, a slip agent in the manufacturing process. Resins A & B leached high Trisnonylphenylphosphate, a commonly used antioxidant. Resin C leached high Trisditertbutylphenylphosphate, a processing stabilizer. See Figure 8 for NearQuant quantitation of high molecular weight leachates for each resin.

HDPE Coupon Leaching Study

Coupons, small pieces of HDPE storage drum lining, manufactured from the previously studied resins, were also submerged in IPA and stored at 40 °C for eight weeks to replicate six months of storage at room temperature. Coupons used had approximately 1 in 2 of surface area per tablet.

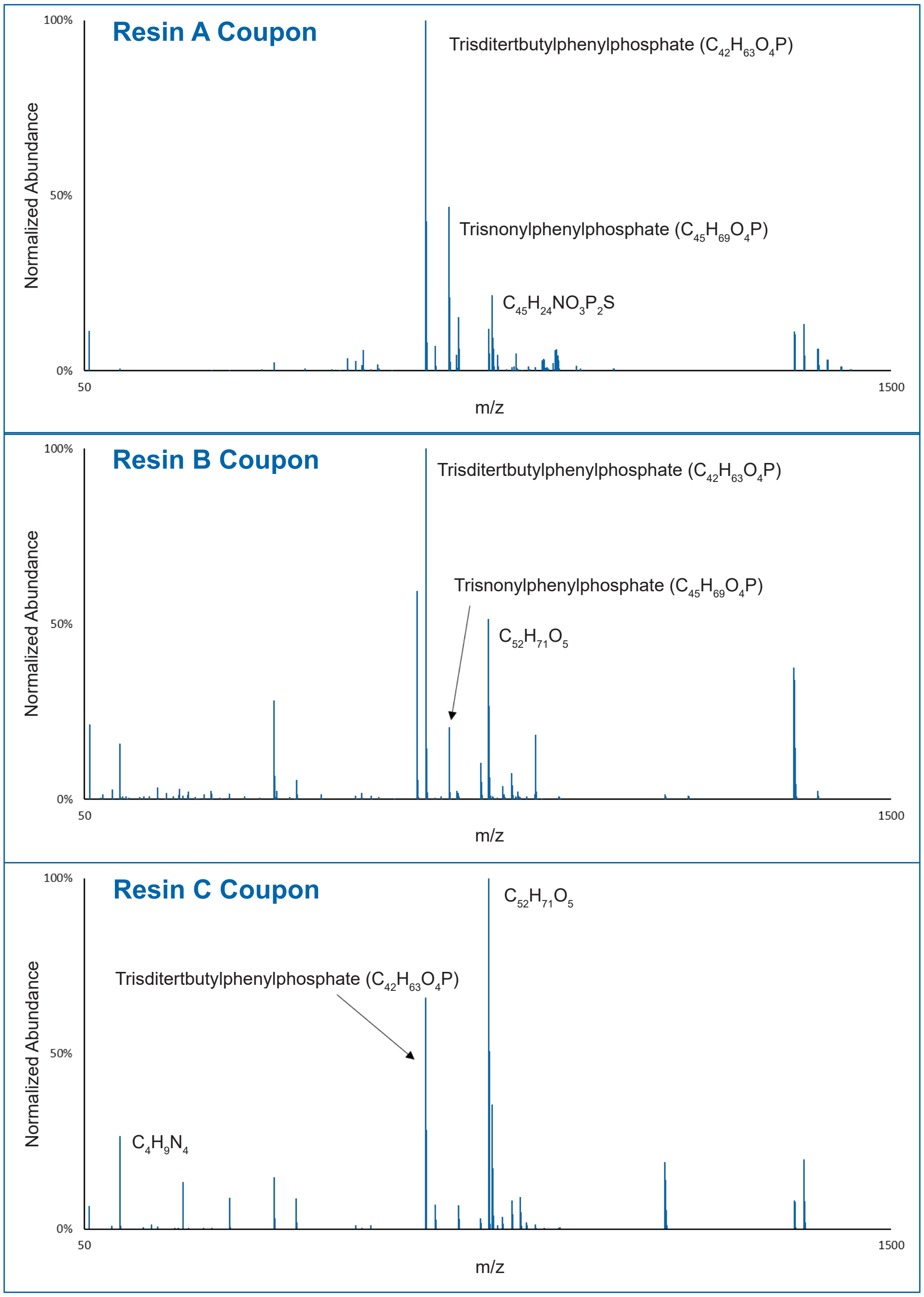

Figure 7. Three mass spectra of resin coupon leach tests from all three sources.

Coupons from containers fabricated from different resins have varying leaching profiles. The profile of the coupon is different from the profile for the corresponding resin beads. New contaminants are seen in the leaching profile for all coupons and are likely the result of the container manufacturing process and additives used during the manufacturing process. See Figure 8 for NearQuant quantitation of high molecular weight leachates for each coupon.

Details of High Molecular Weight Contaminants in Semiconductor-Grade IPA

High molecular weight phosphates have high boiling points, which makes them particularly difficult to remove during wafer production. Contaminants which exceed the level required for processing 2 nm and 3 nm semiconductor nodes are present in the IPA stored in HDPE containers for approximately 6 months.

Table 5. A list of common, high mass IPA contaminants with corresponding boiling points.

Contaminant	Boiling Point
Erucamide	461 °C
Dinoctylphthalate	384 °C
Trisditertbutylphenylphosphite	>400 °C
Trisditertbutylphenylphosphate	~610 °C
Trisnonylphenylphosphate	~708 °C

Effects of High Molecular Weight Contaminants in Semiconductor-Grade IPA

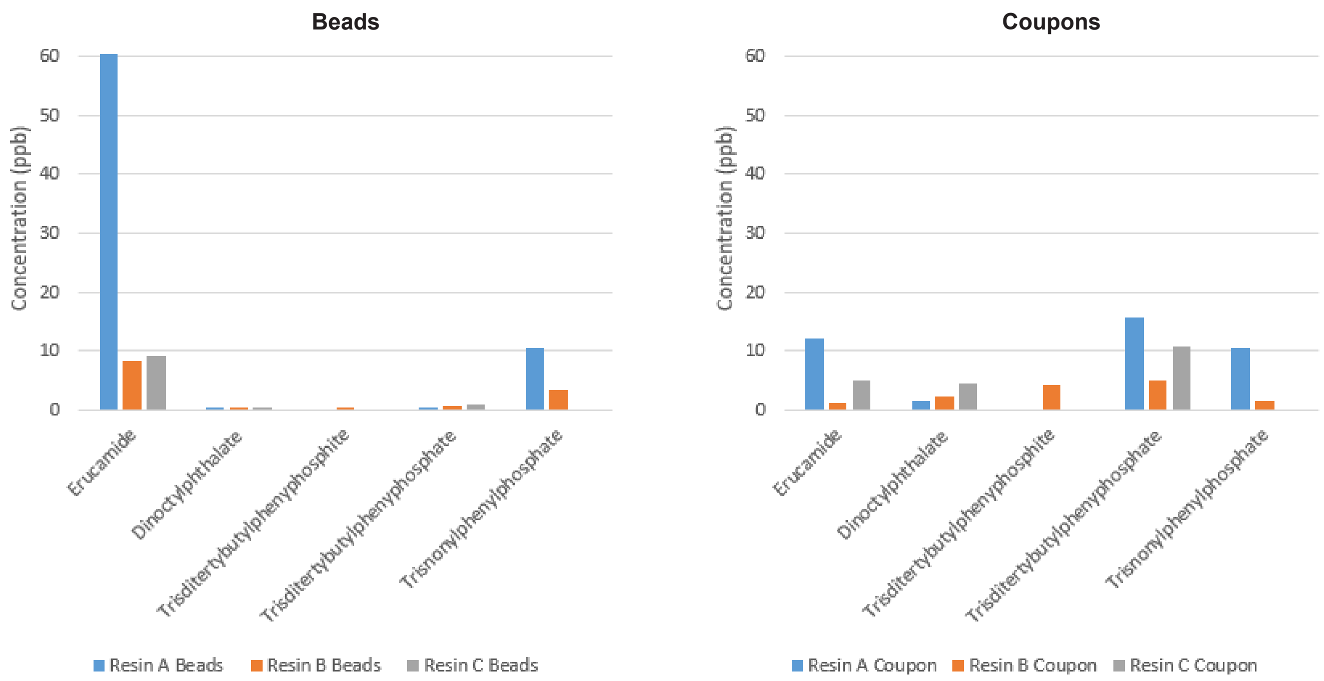

Figure 8. Quantification of high molecular weight contaminants in the leaching profile of both the beads (Left) and the coupons (Right), utilizing response factors obtained through MSA calibrations.

Conclusion

prep*FAST* CARBON found that HDPE storage containers led to increased contamination of semiconductor grade IPA by high molecular weight contaminants. The prep*FAST* CARBON system was used to measure these contaminants at trace levels, proving it to be an essential tool in chemical analysis laboratories to ensure that IPA meets industry requirements, at both semiconductor fabrication facilities and supplier quality control laboratories.

Notes