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Ultrapure Fluids

Identifying organic contaminants in ultrapure water at sub-parts-per-billion levels

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Unlike existing methods, a combination TD-GC-MS technique can identify semivolatile compounds, such as phthalates and siloxanes, which can affect wafer and disk-media processing.

Organic contamination deposited on wafer surfaces from ultrapure water (UPW) can seriously undermine wafer-cleaning efficiency, which leads to nonuniform etching.¹⁴ In addition, carbon-rich hydrophobic wafer surfaces are known to affect gate-oxide growth rates and reliability.⁵⁷ In the semiconductor and disk-drive industries, organic compounds in UPW are usually monitored as total oxidizable carbon (TOC) using instruments that provide excellent sensitivity but do not identify the contaminants.⁸ The identity of some organics can be established using methods developed by the Environmental Protection Agency (EPA). Purge and trap methods such as EPA 502.2 and 524.2 can be used to identify volatile organic contaminants (for example, chloroform and other trihalomethanes, as well as low-boiling organic solvents), while EPA 506 and 525.2 offer procedures for determining a variety of organic compounds using liquid-solid extraction and elution with organic solvents.⁹¹² However, none of those methods can identify and quantitate <1-ppbw levels of some semivolatile organic compounds, such as siloxanes, and plasticizers, such as dioctyl phthalate (DOP) and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate).

Because even trace amounts of these semivolatile organics can have a deleterious effect on wafer and disk-media processing, the goal of the method development project described in this article was to be able to extract these compounds from UPW and identify them. In this new method, water samples are passed through an adsorbent tube, the water is removed, and the compounds are analyzed by thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Unlike existing techniques, this process does not use any organic solvents for extraction, which eliminates the problem of interference from contaminants in the solvents and thereby increases sensitivity.



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Recovery Studies

Water removal is necessary prior to TD-GC-MS analysis because of potential detector overload or column flooding. In the initial experiments discussed in this article, carbotraps were used as adsorbents, but it was impractical to completely remove the UPW from these materials without losing some compounds of interest. Thus, a proprietary hydrophobic adsorbent, which does not retain water, was adopted.

Two types of organic standards were used in the recovery studies performed with the new adsorbent: hydrocarbons (C_6C_{28} alkanes) and other organic compounds (plasticizers, siloxanes, esters, amides, alcohols, and organophosphates). The organic compounds were spiked into 1-L bottles of UPW at 0.2 ppbw and the first four samples were passed through adsorbent-containing, stainless-steel sampling tubes at flow rates of 10, 20, 30, and 40 ml/min. The best recoveries were obtained at 30 ml/min, which was used as the standard for all further studies.

The TD-GC-MS analyses were performed using an ATD-400 automated thermal desorption system from Perkin-Elmer (Norwalk, CT) connected to an HP 6890 gas chromatograph with an HP 5972 or 5973 quadrupole mass selective detector (MSD) from Hewlett-Packard (Palo Alto, CA). The sampling tubes were heated in the ATD-400. As the organic compounds were thermally desorbed from each tube, they were swept by a helium carrier gas onto a cold trap containing the adsorbent. The organic compounds were then desorbed from the trap and passed into the GC-MS system, where each compound flowed down the column at its characteristic rate. As each compound exited the chromatograph, it entered the MSD, where it was ionized using electron impact ionization at 70 eV. The MSD collected a full mass spectrum (10700 amu) approximately once per second. The identification of each compound detected was first attempted by searching a Wiley library of 275,000 mass spectra. In cases where no match was found, the analyst provided an estimate of the most probable compound or class of compounds.

The amounts of organic contaminants in the UPW samples were estimated using the response of an n-decane external standard (unless otherwise specified). The tubes used for the standard contained the same type of adsorbent and were desorbed in the same manner as the sample tubes.

Recovery of n-Alkanes and Other Test Compounds. In the recovery studies for hydrocarbons, three glass bottles were each filled with 1 L of UPW. Then each bottle was spiked with 200 ng of C_6C_{28} n-alkane standards, which had been prepared in pentane. After being mixed thoroughly, the bottles yielded 0.2 ppbw of each standard in each sample. One sample was analyzed on the same day, the others were left on the bench and analyzed on the fourth and seventh days after the spike. The chromatogram for the day-1 analysis is shown in Figure 1. The amount of each n-alkane was calculated using the response factor of the corresponding external n-alkane standard. The percent recovery

data are summarized in Table I and plotted in Figure 2. Figure 3 presents a chromatogram of 200 ng of the C₆C₂₈ n-alkanes spiked directly onto an adsorbent tube, which corresponds to 0.2 ppbw if added to 1 L of UPW. After spiking, this tube was purged with 1 L of UPW.

n-Alkane	Recovery (%)		
	Day 1	Day 4	Day 7
C ₆	9	9	11
C ₇	6	6	7
C ₈	6	6	7
C ₉	4	3	4
C ₁₀	4	2	3
C ₁₁	3	2	3
C ₁₂	4	2	3
C ₁₃	5	3	4
C ₁₄	8	6	7
C ₁₆	44	26	24
C ₁₈	87	57	50
C ₂₀	87	56	49
C ₂₄	87	51	48
C ₂₈	94	45	46

Table I: Percentage of n-alkanes recovered from UPW samples containing 0.2 ppbw of each n-alkane and analyzed on different days.

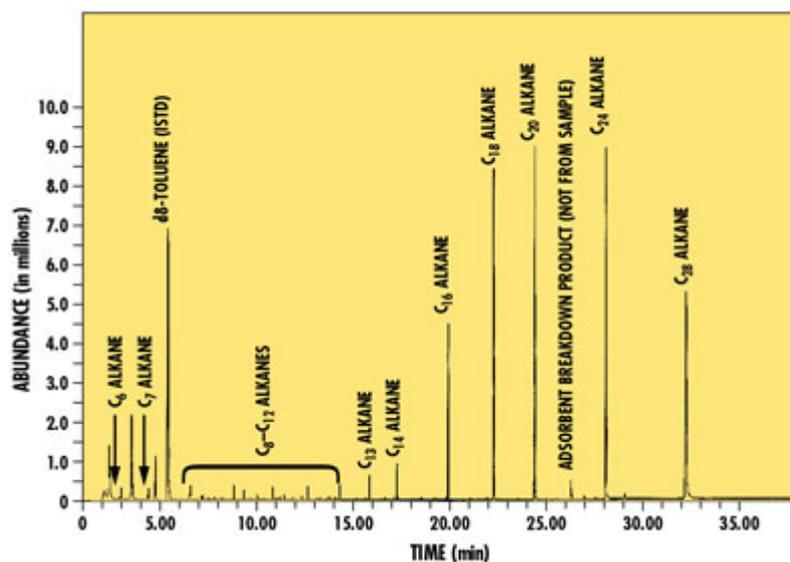


Figure 1: GC-MS chromatogram of 0.2-ppbw levels of C₆-C₂₈ n-alkane standards recovered from a UPW sample on the day of spiking (d₈-toluene was used as an internal standard).

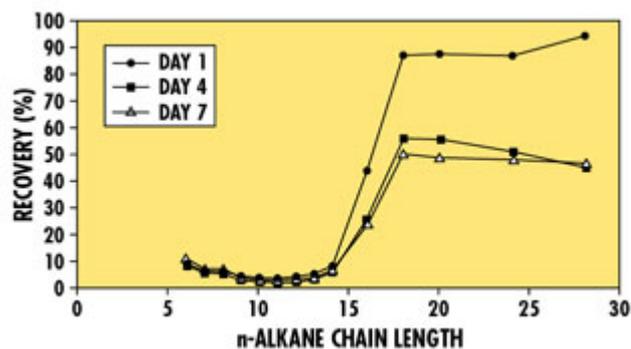


Figure 2: Plots of percent recoveries of 0.2-ppbw levels of C-6C₂₈ n-alkanes versus n-alkane chain length for samples analyzed on days 1, 4, and 7.

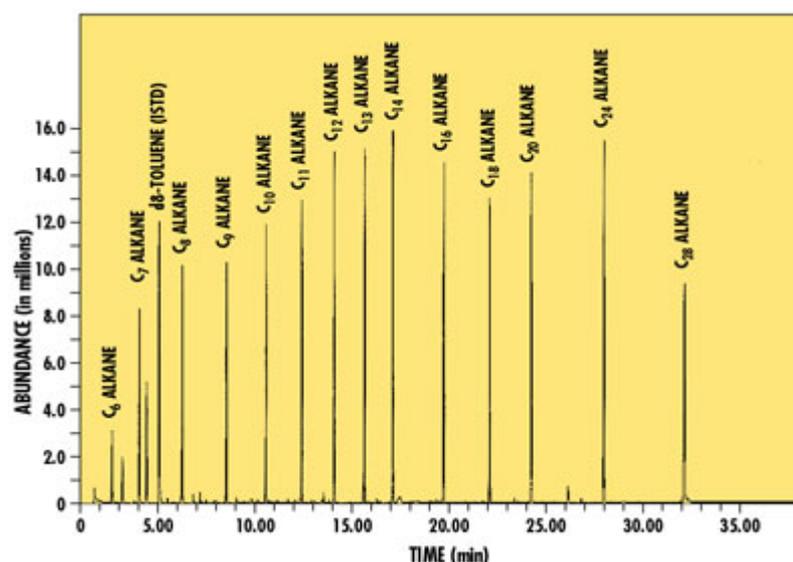


Figure 3: GC-MS chromatogram of 200 mg of C6-C28 n-alkane standards spiked onto a dry adsorbent sampling tube, which was then purged with 1 L of UPW. (This corresponds to 0.2-ppbw levels if the standards were added to 1 L of UPW.)

Similar recovery studies were performed using a number of organic compounds, including plasticizers and siloxanes. Each compound was spiked in 1 L of UPW at a 0.2-ppbw level (200 ng/L). The stock solutions of the standards were prepared in acetone. The resulting chromatogram is shown in Figure 4 and the percent recovery data are listed in Table II.

Compound	Recovery (%)	Compound	Recovery (%)
Plasticizers		Amides	
Diethyl phthalate	43	Dibutyl formamide	18
2,2,4-trimethyl-1,3-pentanediol diisobutyrate	74	N-methyl-2-pyrrolidinone	0
(TXIB)	97	Caprolactam	0
Dibutyl phthalate	56		
Diocetyl adipate	54		
Diocetyl phthalate			
Siloxanes		Alcohol/Aldehydes	
Cyclo(Me ₂ SiO) ₅	73	2-ethylhexanol	54
Cyclo(Me ₂ SiO) ₄	44	Benzaldehyde	59
Cyclo(Me ₂ SiO) ₃	21	2-butoxyethanol	0
Hexamethyldisiloxane	16	Benzyl alcohol	2
Esters (low boiling)		Phosphates	
Ethyl acetate	0	Triphenyl phosphate	116
Butyl acetate	81	Triethyl phosphate	10
Propylene glycol	6		

methyl ether acetate	Tributyl phosphate Tris(chloropropyl) phosphate	2
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Table II: Percentage of a variety of organic compounds recovered from UPW samples containing 0.2 ppbw of each organic compound.

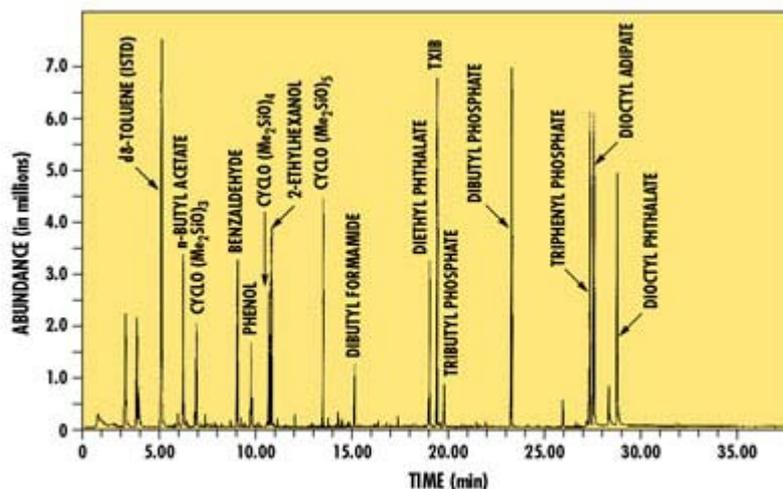


Figure 4: GC-MS chromatogram of 0.2-ppbw levels of various organic compounds recovered from a UPW sample.

Experimental Results. The results for the day-1 n-alkane sample (presented in Table I and Figure 2) show that the recovery rates of the C_6C_{14} n-alkanes were between 2 and 10%, while the recovery rate of the C_{16} n-alkane was 44% and the $C_{18}C_{28}$ n-alkanes were >85%. For the day-4 and day-7 samples, the recovery rates of the C_6C_{10} n-alkanes remained approximately the same as for the day-1 sample (2-11%). The C_{16} recovery level fell from 44% on day 1 to approximately 25%, with similar results for both the day-4 and day-7 samples. The recovery levels for $C_{18}C_{28}$ n-alkanes also decreased to between 45 and 57% for the day-4 and day-7 samples. Clearly, storage of the samples for 47 days reduced the recovery levels of $\geq C_{16}$ n-alkanes. This result is most likely due to adsorption of high-boiling n-alkanes to the walls of the glass bottles, indicating that such samples should be analyzed as soon as possible after collection. The alternative is collecting organic contaminants from UPW samples onto adsorbent-containing sampling tubes. Experiments involving on-line sampling techniques are in progress.

The most significant question posed by these results is why the C_6C_{14} n-alkanes were lost. A comparison of Figures 1 and 3 shows that the dry adsorbent material retains all C_6C_{28} n-alkanes very well, including those with shorter chain lengths. It seems that the low-boiling alkanes are either lost to ambient atmosphere as the UPW passes through the adsorbent-containing sampling tube or disappear because of their

relatively high solubility in water.¹³ Because small n-alkanes are well below their saturation limits in water, phaseout is not expected to occur. For example, the solubility of n-octane is about 400 ppb at 20° C.¹³

As shown in Table II, 0.2-ppbw levels of a variety of plasticizers and siloxanes of interest to the semiconductor and disk-media industries could be detected by this method. However, most of the low-boiling polar compounds tested, such as ethyl acetate, propylene glycol methyl ether acetate, n-methyl-2-pyrrolidone, caprolactam, 2-butoxyethanol, and benzyl alcohol, exhibited poor or no recovery (0%). It is probable that these compounds were not trapped by the adsorbent because they are very water soluble. The poor recovery rates ($\leq 10\%$) of three of the alkyl phosphates--triethyl, tributyl, and tris(chloropropyl)--may be due to their hydrolysis, poor partitioning from UPW onto the adsorbent, or decomposition during thermal desorption. Triphenyl phosphate, the least likely of the phosphate compounds tested to hydrolyze in water, had a recovery level $>100\%$.

EPA Method 525.2 describes the analysis of a number of organic compounds, including plasticizers, by liquid-solid extraction (LSE) and capillary column GC-MS.¹² In this method, organic compounds are extracted by passing 1 L of water through a cartridge or disk containing a solid matrix with a chemically bonded C₁₈ organic phase. The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate and methylene chloride solvents, used consecutively, and this extract is concentrated further by the evaporation of some of the solvents. The detection limits for diethyl phthalate and dioctyl adipate are approximately 0.1 to 0.2 ppbw. The TD-GC-MS method has two main advantages over this EPA method:

- Dioctyl and dibutyl phthalates, TXIB, and siloxanes can be analyzed at <0.2 -ppbw levels, whereas EPA 525.2 does not provide recovery data for these compounds.
- Because compounds are thermally desorbed from the adsorbent directly into the GC instrument, the problems posed by the presence of contaminants in an eluting solvent and by sample dilution are eliminated. Thus, the signal-to-background ratio and sensitivity are high, providing excellent detection limits.

Analysis of Real Samples

When UPW at selected semiconductor and disk-drive locations was tested by the TD-GC-MS method, the most common contaminants found were dioctyl or higher alkyl phthalates at 0.1 ppbw or less.¹⁴ These contaminants probably would not be detected at these trace levels by TOC monitoring or other currently available methods.

Manufacturer A. At one facility, samples were taken from reverse osmosis (RO) reject water and at the final filter. The chromatograms of these samples are given in Figures 5 and 6. The RO-reject-water sample (Figure 5) had significant amounts of a variety of organic

compounds, such as various methanes, ethyl p-ethoxybenzoate, alkylphenoxyethanol isomers, oleic acid, nonylphenylamine isomers, and squalene. None of these compounds were present in the water sampled at the final filter (Figure 6), which indicates that the RO process was working efficiently. A few compounds, including dioctyl adipate (at 0.01 ppbw) and didecyl phthalate (at 0.12 ppbw) were detected in the final-filter sample but not in the RO-reject sample. This result indicates that these contaminants were added to the UPW somewhere downstream of the RO system.

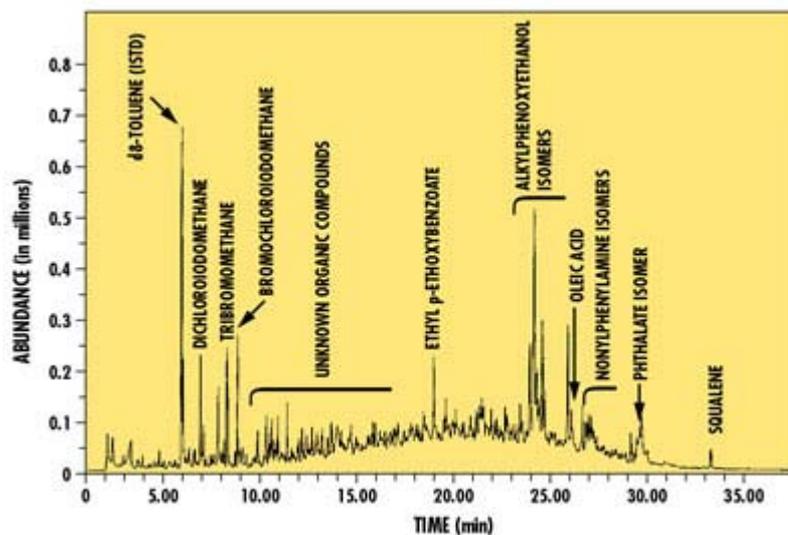


Figure 5: GC-MS chromatogram of an RO-reject-water sample collected at manufacturer A.

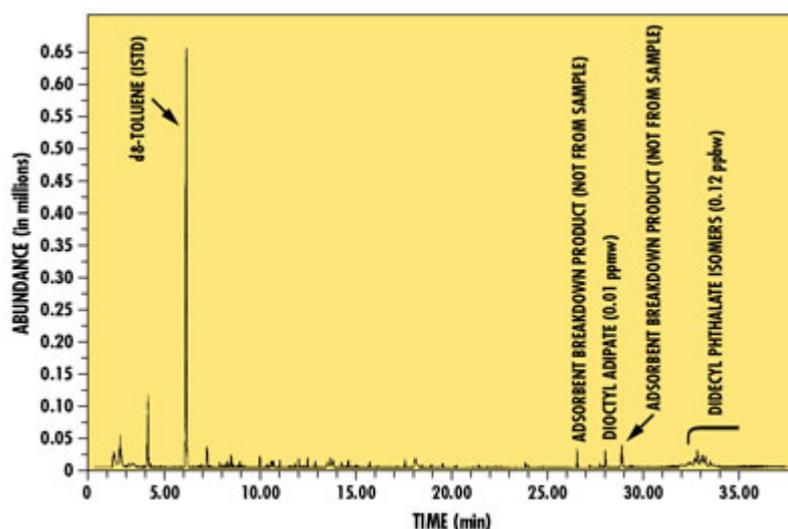


Figure 6: GC-MS chromatogram of a final-filter UPW sample collected at manufacturer A.

Manufacturer B. At another manufacturing facility, UPW samples

were collected at the final filter and from the return stream. As shown in Figure 7, an analysis of the final-filter sample indicated the presence of butyl benzyl phthalate, butylated hydroxytoluene (BHT), acetophenone, 2-ethylhexanol, and benzaldehyde. Similar levels of all these compounds were also detected in the return water.

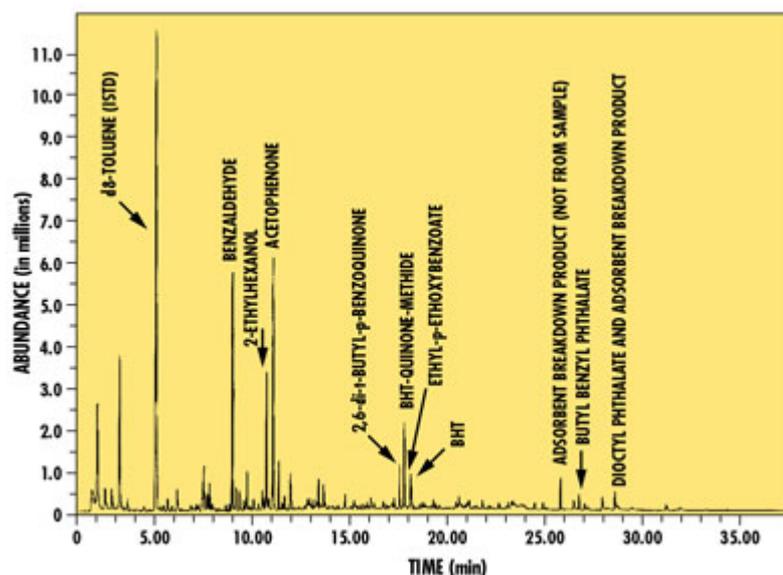


Figure 7: GC-MS chromatogram of a final-filter UPW sample collected at manufacturer B.

Other Manufacturing Facilities. UPW samples were analyzed using the TD-GC-MS technique at five other plants. Of the five final-filter samples tested, three were relatively clean. A representative chromatogram, shown in Figure 8, shows the absence of peaks from semivolatile organic compounds. The fourth site in this group had a 0.08-ppbw level of dioctyl phthalate, a plasticizer added to plastics or elastomers, as depicted in Figure 9, and the fifth site had low levels of 2-methylthiobenzothiazole (which may be used as a fungicide), styrene, and benzaldehyde. Return-water samples were tested at three of the five additional sites. In all cases, the types and levels of organic compounds detected in return water were similar to those found in the final-filter samples. These results indicate that the TD-GC-MS method works very well to trap <0.2-ppbw levels of semivolatile organic compounds from UPW.

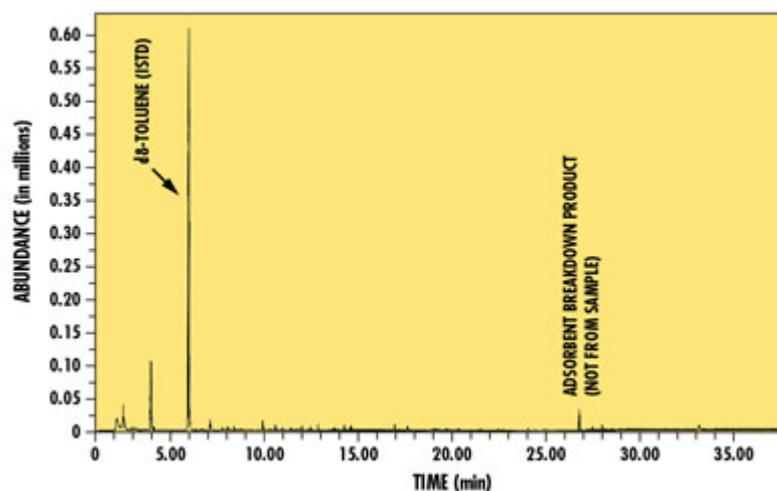


Figure 8: Representative GC-MS chromatogram of final-filter UPW samples collected at five additional manufacturers.

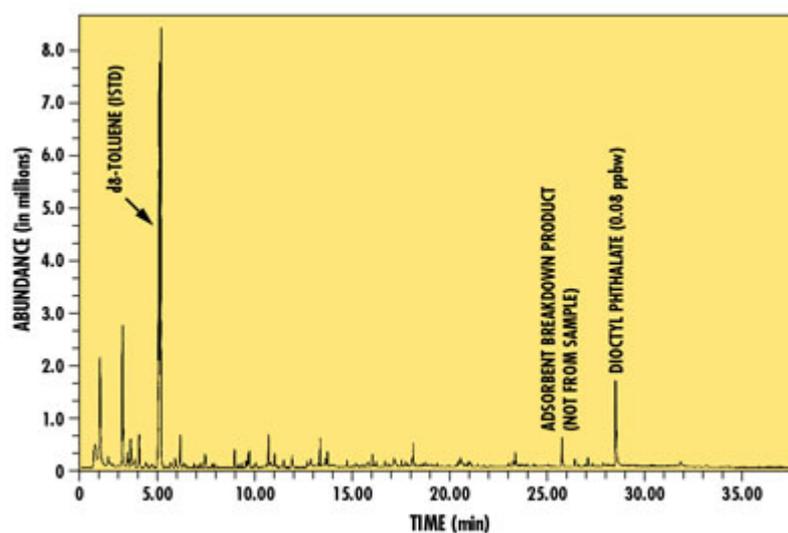


Figure 9: GC-MS chromatogram of a final-filter UPW sample collected at the fourth of the additional five sites under investigation.

A Case Study

Because UPW systems can become contaminated during modifications or system failures, process engineers benefit from having a baseline for semivolatile organics. Then, when contaminant excursions occur, the off-baseline compounds can be identified by the TD-GC-MS method and their sources sought. In the case study presented here, a semiconductor-grade UPW system had a TOC excursion of 3900 ppb from a baseline of <5 ppb after system modifications had been made. One modification involved welding in a new segment of PVDF pipe, the edges of which were wiped with isopropanol (IPA) before welding. As shown in Figure 10, when the UPW was analyzed to identify the contaminant responsible for the increase in TOC, a large peak identified as 3-hexanone was detected along with peaks representing 3-hexanol and a variety of ketones, alkyl esters, and n-alkanes. The

new pipe was tested for organic outgassing, but nothing was detected. An examination of several other potential sources of the contaminant also were negative.

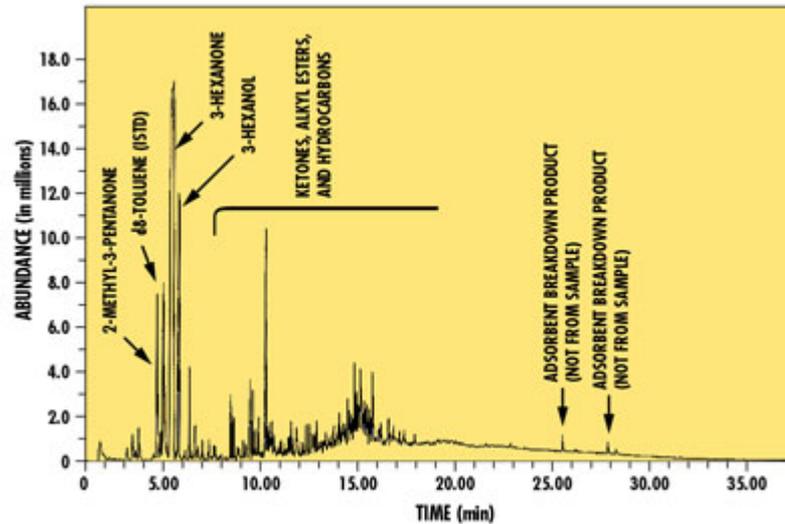


Figure 10: GC-MS chromatogram of a semiconductor-grade UPW sample collected at the final filter during a 3900-ppb TOC excursion.

The bottle of organic solvent labeled IPA was no longer available, but the maintenance personnel who had used it declared it had smelled like IPA. However, two operators stated that a paintlike odor had emanated from the UPW system, even though no painting had been done. Unfortunately, the source of the contaminant was never identified. The system TOC level returned to normal in about a week, presumably as a result of use, dilution, and the action of TOC-removal UV lamps. As illustrated in Figure 11, another UPW sample was analyzed a few weeks later and all the contaminants that had been detected had disappeared.

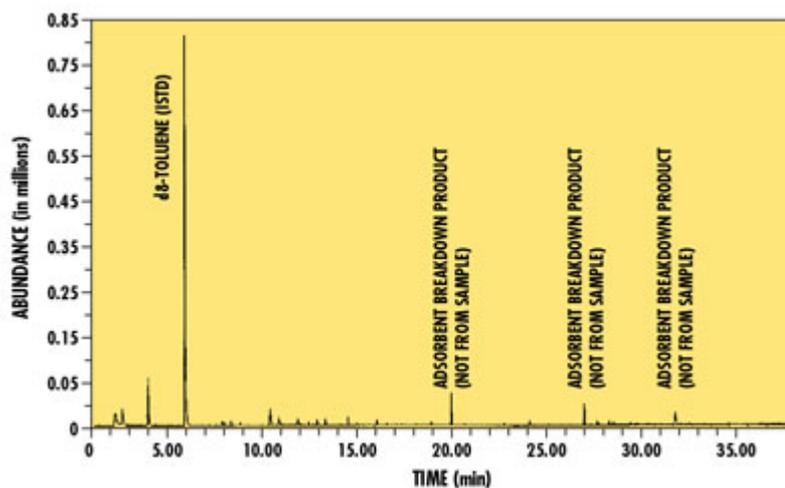


Figure 11: GC-MS chromatogram of a semiconductor-grade UPW sample collected at the final filter a few weeks after the TOC excursion graphed in Figure 10. The TOC had returned to its baseline of <5 ppb.

For the purposes of comparison, the 3900-ppb-TOC-level sample also was analyzed by the EPA 502.2 purge and trap GC method using an electrolytic conductivity detector (ELCD) and a photoionization detector (PID). An unknown peak at 27 minutes appeared on the PID chromatogram only, suggesting that the contaminant was an organic compound with a double bond and that it did not have halogenated functional groups. Neither the ELCD nor PID analysis could positively identify the compound. When a UPW sample taken after the TOC level had returned to normal also was analyzed using EPA 502.2, the unknown peak was gone.

Conclusion

Typically, levels of organic contaminants in UPW that are deleterious to wafer and disk-media processing are monitored using on-line TOC analyzers. This practice provides information on real-time changes in water quality and is effective in the early detection of trouble in UPW production systems. However, TOC analyzers do not identify the organic compounds. The TD-GC-MS method described in this article was developed to provide that capability.

When a problem occurs that correlates to high TOC levels, the identification of the responsible contaminant can be useful in tracing the source of the excursion. For example, if a contaminant is detected in UPW, its possible sources could be determined by outgassing the materials used in the piping system. A correlation could be made between what was detected in the UPW and what outgassed from the various component materials. Since TOC levels at semiconductor plants are often <5 ppb and few previously available methods identify compounds in UPW at trace levels, the TD-GC-MS method should prove valuable for baselining what contaminants are present in UPW systems and troubleshooting contaminant sources when failures occur.

Although the TD-GC-MS method has several benefits, it also has limitations. Polar organic compounds with low boiling points are not trapped effectively by this method. Specifically, n-alkanes with boiling points significantly lower than those of C₁₄ may not be recovered. In addition, thermally unstable compounds may decompose to other compounds, and some reactive compounds, such as amines and acidic components, can interact to form new compounds. Finally, ionic compounds with high molecular weights and polymeric materials, which cannot be volatilized by GC, cannot be analyzed by this technique.

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References

1. M Kogure et al., "Ozonized Ultrapure Water Treatment of Organic Contamination on Si-Wafer Surface," in *Proceedings of the Annual Technical Meeting of the Institute of Environmental Sciences* (Mount Prospect, IL: Institute of Environmental Sciences, 1993), 380385.
2. J Ruzylo, G Duranko, and AM Hoff, "Preoxidation UV Treatment of Silicon Wafers," *Journal of the Electrochemical Society* 134, no. 8 (1987): 20522055.
3. MK Balazs, "Ultrapure Water: Friend or Foe," *Solid State Technology* 36, no. 10 (1993): 7581.
4. T Chu and MK Balazs, "Ultrapure Water Testing at the Point of Use" (Sunnyvale, CA: Balazs Analytical Laboratory, 1992).
5. Y Shiramizu and H Kitajima, "Effect of Organic Compounds on Gate Oxide Reliability," in *Extended Abstracts of the International Conference on Solid State Devices and Materials* (Osaka, Japan: International Conference on Solid State Devices and Materials, 1995), 273275.
6. S De Gendt et al., "Impact of Organic Contamination on Gate Oxide Integrity," in *Proceedings of the 14th International Symposium on Contamination Control of the Institute of Environmental Sciences and Technology* (Mount Prospect, IL: Institute of Environmental Sciences and Technology, 1998), 87-93.
7. T Ohmi et al., "Native Oxide Growth and Organic Impurity Removal on Si Surface with Ozone-Injection Ultrapure Water," *Journal of the Electrochemical Society* 140, no. 3 (1993): 804-810.
8. T Mizuniwa, "TOC Removal Technology," in *Ultraclean Technology Handbook*, vol. 1 (New York: Marcel Dekker, 1993), 363377.
9. "Volatile Organic Compounds in Water by Purge and Trap Capillary Column GC with PID and ELCD Detectors in Series," EPA Method 502.2, rev. 2.1 (Washington, DC: EPA, 1995).
10. "Measurement of Purgeable Organic Contaminants in Water by Capillary Column GC-MS," EPA Method 524.2, rev. 4.1 (Washington, DC: EPA, 1992); JW Munch, ed. (Washington, DC: EPA, 1995).
11. "Determination of Phthalate and Adipate Esters in Drinking Water by Liquid-Liquid or Liquid-Solid Extraction and Gas Chromatography with Photoionization Detection," EPA Method 506, rev. 1.1 (Washington, DC: EPA, 1995).
12. "Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry," EPA Method 525.2, rev.

2 (Washington, DC: EPA, 1995).

13. CL Yaws, "Hydrocarbons: Water Solubility Data," *Chemical Engineering* (April 1990): 177180.
14. MJ Camenzind, CJ Chargin, and A Kumar, "Method for Identification and Quantitation of Sub-Parts-Per-Billion Levels of Semivolatile Organic Contaminants in UPW," in *Proceedings of the Semiconductor Pure Water and Chemicals Conference* (Santa Clara, CA: Semiconductor Pure Water and Chemicals Conference, 1999), 5168.



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